ORGANOMETALLICS

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PNP-Ligated Heterometallic Rare-Earth/Ruthenium Hydride Complexes Bearing Phosphinophenyl and Phosphinomethyl Bridging Ligands

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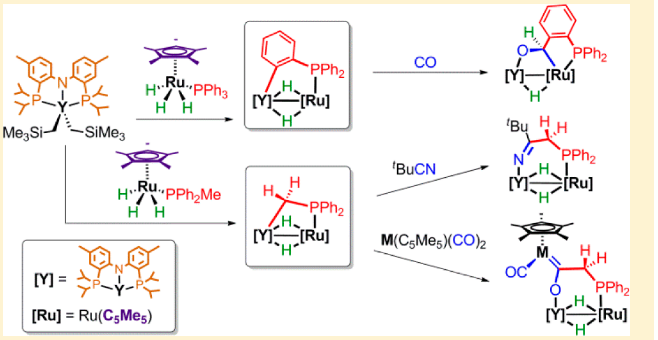
Supporting Information

ABSTRACT: The reaction of rare-earth bis(alkyl) complexes containing a bis(phosphinophenyl)amido pincer (PNP), $\mathrm{LnPNP_{iPr}(CH_2SiMe_3)_2}$ (**1-Ln**, Ln = Y, Ho, Dy), with ruthenium trihydride phosphine complexes, $\mathrm{Ru(C_5Me_5)H_3PPh_3}$ and $\mathrm{Ru(C_5Me_5)H_3PPh_2Me}$, gave the corresponding bimetallic Ln/Ru complexes bearing two hydride ligands and a bridging phosphinophenyl (μ-$\mathrm{C_6H_4PPh_2}$-κP:κC^1, **2a-Ln**) or a bridging phosphinomethyl ligand (μ-$\mathrm{CH_2PPh_2}$-κP:κC, **2b-Ln**), respectively. Reaction of **2a-Y** with CO gas at 1 atm and at 20 °C in toluene-d_8 afforded the complex **3a-Y**, which bears a bridging pseudo-oxymethylene ligand (μ-OCH(o-$\mathrm{C_6H_4}$)$\mathrm{PPh_2}$-κP:κO) and a bridging hydride ligand on the Y/Ru centers. Computational studies by the DFT method suggested that **3a-Y** was formed in two steps: first the coordination of CO (ΔG(B3PW91) = 22.9; ΔG(M06) = 14.9 kcal/mol) and migratory insertion of the $\mathrm{Y{-}C_6H_4}$ group ($\Delta G^{\ddagger}$(B3PW91) = 13.3; $\Delta G^{\ddagger}$(M06) = 16.7 kcal/mol), followed by a rapid intramolecular hydride migration to the resulting acyl group. Complex **2b-Y** reacted with organic nitriles (tBuCN, $\mathrm{CH_3CN}$, PhCN), an aldimine (PhNCHPh), an isonitrile (tBuNC), and group IX transition-metal carbonyls ($\mathrm{M(C_5Me_5)(CO)_2}$, M = Rh, Ir) via insertion of the reactive $\mathrm{Y{-}CH_2}$ group into the unsaturated bond. These reactions afforded complexes with new ligand scaffolds, including a bridging alkylideneamidophosphine (**4b-Y**), an amidophosphine (**7b-Y**), an η^2-iminoacylphosphine (**8b-Y**), and oxycarbenephosphine (**9b-Y** and **10b-Y**) ligands at the binuclear Y/Ru core. All of these reaction products were structurally characterized by X-ray crystallography, NMR spectroscopy, and elemental analyses.



■ INTRODUCTION

Heteromultimetallic polyhydride complexes containing both rare-earth (Ln) and transition metals (M) are an important class of organometallic compounds. The potential synergistic effect of the electronically different metal centers may lead to unique reactivity, which otherwise is not accessible by their homomultinuclear counterparts.[1] Most of the heteromultimetallic polyhydride complexes, however, were constructed using cyclopentadienyl rare-earth units as building blocks,[2−4] and the reaction chemistry of these polyhydride complexes remained limited, despite recent progress.

We have recently synthesized a series of Ln/M heteromultimetallic polyhydrides (Ln = Y, Dy, Ho, Lu; M = Mo, W, Ru, Os, Ir) by using rare-earth alkyl and hydride complexes containing a mono(cyclopentadienyl) ligand as building blocks.[3] Some of these heteromultimetallic polyhydrides such as $\mathrm{[(YCp')_4(\mu\text{-}H)_{11}Mo(C_5Me_5)]}$ ($\mathrm{Cp' = C_5Me_4SiMe_3}$) showed unique hydrogen uptake and release properties in both solution and the solid state.[3d,e] On the other hand, from our recent studies on rare-earth-metal-based polymerization catalysts[5] and polyhydride complexes,[1b,5c,d,6] we found that the replacement of the coordinated cyclopentadienyl ligand with a bis(phosphinophenyl)amido pincer (PNP)[5c,d,7] or an amidinate ligand[5c,d,8] could have a significant influence on the reactivity and selectivity in isoprene polymerization and on the structures of the resulting rare-earth-metal complexes. These results prompted us to study Ln/M heteromultimetallic polyhydride complexes containing noncyclopentadienyl rare-earth units. Herein, we report the synthesis and the reactivity of a new family of heterometallic Ln/Ru polyhydride complexes containing a bis(phosphinophenyl)amido pincer on the rare-earth metal.

■ RESULTS AND DISCUSSION

Synthesis of Bimetallic Ln/Ru Complexes 2a and 2b.

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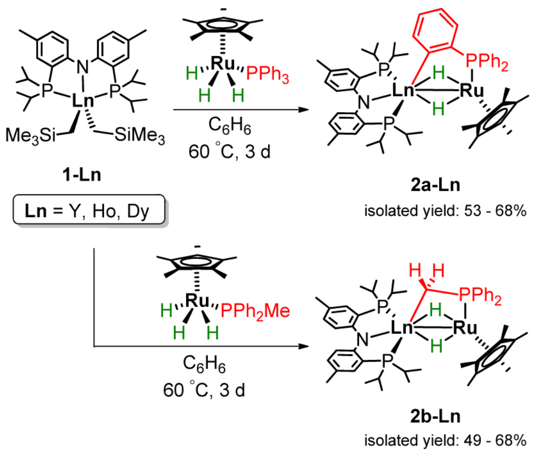
Received: December 20, 2013
Published: February 6, 2014

Ln/M heteromultimetallic polyhydride complexes.[2b,c,e,f,3a,b,4b] The reaction of rare-earth bis(alkyl) complexes Ln(PNP$_{iPr}$)(CH$_2$SiMe$_3$)$_2$, (**1-Ln**, Ln = Y, Ho, Dy)[7b] with 1 equiv of the ruthenium trihydride phosphine complex Ru(C$_5$Me$_5$)H$_3$PPh$_3$[9] for 3 days at 60 °C in C$_6$D$_6$ furnished the bimetallic Ln/Ru complexes **2a-Ln**, accompanied by the elimination of tetramethylsilane (Scheme 1). One of the trihydrides on ruthenium was formally deprotonated by an alkyl group, and this was followed by activation of a C–H bond at the ortho position of the phenyl ring of coordinated PPh$_3$ on the rare-earth metal. The resulting bimetallic complexes, **2a-Ln**, contain two bridging hydride ligands and an ortho-metalated phenyl ring of PPh$_3$ at Ln. This is structurally analogous to heterometallic Lu/Ru complexes containing a "Lu(C$_5$Me$_5$)" unit.[3a]

Scheme 1. Synthesis of Bimetallic Ln/Ru Complexes 2a-Ln and 2b-Ln (Ln = Y, Ho, Dy)



Reaction of **1-Ln** and 1 equiv of Ru(C$_5$Me$_5$)H$_3$PPh$_2$Me[9] under similar reaction conditions gave the dihydride complex **2b-Ln**, bearing a bridging phosphinomethyl ligand (Scheme 1). Selective C–H bond activation took place at the methyl group of PPh$_2$Me over the more acidic C–H group at the ortho position of the phenyl ring, likely owing to steric reasons.[3a] No intermediates were observed by ^{1}H and ^{31}P NMR during the course of all of these reactions at 60 °C or at lower temperatures. On the other hand, we attempted to prepare analogous bimetallic Lu/Ru complexes that contain a "Lu(C$_5$Me$_5$)" unit,[3a] by heating **1-Lu**[7b] with Ru(C$_5$Me$_5$)H$_3$PPh$_3$ or Ru(C$_5$Me$_5$)H$_3$PPh$_2$Me in C$_6$D$_6$ at 60 °C. These reactions spanned over weeks and gave minimal conversion to the desired Lu/Ru complexes **2a-Lu** and **2b-Lu**. We therefore did not pursue these complexes further.

In solution, complexes **2a-Y** and **2b-Y** gave characteristic features pertaining to two bridging hydrides and the bridging phosphine ligand on the binuclear Y/Ru centers in their ^{31}P, ^{1}H, and ^{13}C NMR spectra (see the Experimental Section). In particular, the ortho-metalated carbon of the phenyl ring in **2a-Y** was observed as a triplet at 200.9 ppm (J = 51.8 Hz), while the methylene carbon of **2b-Y** was observed as a triplet at 44.1 ppm (J = 24.0 Hz). The solid-state structures of **2a-Ln** and **2b-Ln** further confirm the spectroscopic assignment by NMR (Figures 1 and 2). The Ln–Ru distances in **2a** are slightly shorter than those of **2b**, while the variation in distances between the binuclear Ln/Ru centers within each class of complexes is small, given the similar effective ionic radii of Y^{3+} (0.900 Å), Ho^{3+} (0.901 Å), and Dy^{3+} (0.912 Å). The Ru-P(1) bond distances of **2a-Ln** and **2b-Ln** are in the expected range for analogous bimetallic Lu/Ru complexes.[3a] The Ln–C(1) distances are slightly longer in comparison to its Lu/Ru congener, as expected, as a result of a smaller effective ionic radius (Lu^{3+} 0.861 Å). All of the bridging hydrides were located by an electron density map during Fourier synthesis and were further refined. The Ru–H and Ln–H bond distances are summarized in Table 1. It is noteworthy that the bimetallic complexes **2-Ho** and **2-Dy** represent the first examples of structurally characterized heterometallic Ho/Ru and Dy/Ru compounds (see the Supporting Information for full details).

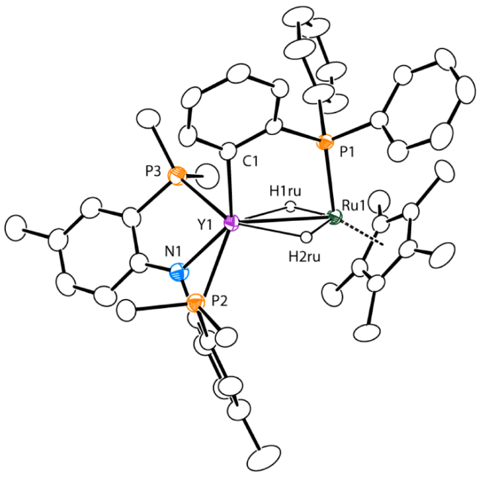


Figure 1. ORTEP representation of **2a-Y** depicted with thermal ellipsoids at 50% probability. The methyl groups of the isopropyl substituents and most of the hydrogens are omitted for clarity. Selected bond distances and bond angles are given in Table 1.

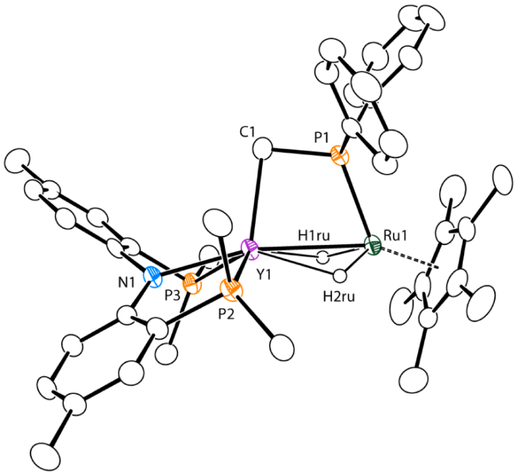


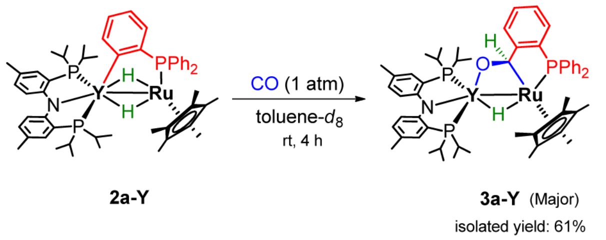
Figure 2. ORTEP representation of **2b-Y** depicted with thermal ellipsoids at 50% probability. The methyl groups of the isopropyl substituents, the solvent molecule, and most of the hydrogens are omitted for clarity. Selected bond distances and bond angles are given in Table 1.

Reaction of Bimetallic Complexes 2-Y with Carbon Monoxide. We were interested in studying the reaction of complexes **2-Y** with molecules containing unsaturated bonds. Complex **2b-Y** reacted with 1 atm of carbon monoxide at 40 or 60 °C for a prolonged period (up to 4 days) to give an intractable mixture, along with about 30% of the starting complex. To our delight, complex **2a-Y** reacted smoothly with 1 atm of carbon monoxide gas at 20 °C in 4 h to give **3a-Y** as the major

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for Complexes 2a-Ln and 2b-Ln (Ln = Y, Ho, Dy)

	2a-Y	2a-Ho	2a-Dy	2b-Y	2b-Ho	2b-Dy
Ln(1)−Ru(1)	2.9062(5)	2.8912(5)	2.9095(4)	2.9151(5)	2.9101(6)	2.9206(5)
Ln(1)−C(1)	2.396(3)	2.372(4)	2.395(4)	2.367(3)	2.358(4)	2.383(4)
Ln(1)−N(1)	2.312(3)	2.305(3)	2.320(3)	2.347(3)	2.335(3)	2.347(4)
Ln(1)−P(2)	2.9067(10)	2.9037(12)	2.9173(10)	2.8912(9)	2.8696(11)	2.8837(12)
Ln(1)−P(3)	2.9173(11)	2.9004(12)	2.9195(11)	2.8698(9)	2.8893(11)	2.9004(12)
Ru(1)−P(1)	2.2883(9)	2.2851(12)	2.2886(10)	2.2856(10)	2.2937(11)	2.2959(12)
Ln(1)−H(1ru)	2.24(4)	2.13(4)	2.10(3)	2.27(3)	2.19(3)	2.16(4)
Ln(1)−H(2ru)	2.24(4)	2.14(4)	2.19(4)	2.21(3)	2.22(4)	2.20(6)
Ru(1)−H(1ru)	1.59(4)	1.57(3)	1.62(4)	1.50(5)	1.58(5)	1.57(8)
Ru(1)−H(2ru)	1.62(3)	1.61(4)	1.58(4)	1.53(2)	1.66(3)	1.56(4)
Ln(1)−Ru(1)−P(1)	81.81(3)	81.92(3)	82.41(3)	69.19(2)	69.12(3)	69.24(3)
Ru(1)−Ln(1)−C(1)	94.54(9)	94.60(9)	93.40(8)	80.32(8)	80.57(9)	80.13(11)
Ln(1)−C(1)−P(1)				91.04(14)	91.22(15)	91.05(19)

Scheme 2. Reaction of Bimetallic Y/Ru Complex 2a-Y with Carbon Monoxide



product (Scheme 2). Complex **3a-Y** was formed in two steps: first the migratory insertion of the Y−C_6H_4 unit of **2a-Y** into the CO triple bond, followed by hydride migration to the electrophilic acyl group, giving a pseudo(2-(diphenylphosphino)-phenyl)oxomethylene ligand that bridges the binuclear Y/Ru centers. We did not observe any intermediates, including the first insertion product, by NMR spectroscopy during the course of the reaction. In a related context, migratory insertions of coordinated hydrides or alkyl ligands of group IV and V complexes into carbon monoxide were described in the literature.[10] Double migratory insertion of hydride ligands into carbon monoxide led to the formation of an oxymethylene unit, [M−CH_2−O−M].[6c,11] On the other hand, heterometallic Zr/Ru[12] and Zr/Mo[13] complexes containing hydride or methyl ligands reacted with carbon monoxide to give bridging formyl and acetyl ligands, respectively. Similar insertion reactions involving hydride ligands of heteromultimetallic complexes and carbon dioxide were also reported.[14]

The solid-state structure of **3a-Y** reveals a single-bond character of C−O in the Y−OC group (C(1)−O(1) = 1.443(3) Å, Figure 3). The carbon (C(1)) that originated from carbon monoxide becomes tetrahedral (Ru(1)−C(1)−O(1) = 118.97(18)°; Ru(1)−C(1)−C(12) = 114.62(19)°; O(1)−C(1)−C(12) = 109.7(2)°; O(1)−C(1)−H(1) = 103.8°). At the same time, the ruthenium center (Ru(1)) forms the fourth apex of such a distorted tetrahedron along with O(1), C(12), and H(1), with a Ru(1)−C(1) bond distance of 2.231(3) Å. The Y(1)−O(1) distance (2.057(2) Å) lies in the expected range of analogous alkoxide complexes of yttrium.[6a,c,15] In addition, only one bridging hydride was located by Fourier synthesis, with Y(1)−H(ru) and Ru(1)−H(ru) distances at 2.24(3) and 1.67(3) Å, respectively. The geometry-optimized structure of **3a-Y** with complete internal coordinates by a DFT study (B3PW91/6-31G* at 1 atm, 298 K) reveals a similarity in geometric parameters (selected bond lengths (Å) Y−O = 2.05, C−O = 1.43, Ru-C = 2.25, Y−H = 2.34, Ru-H = 1.66; see the Supporting Information).

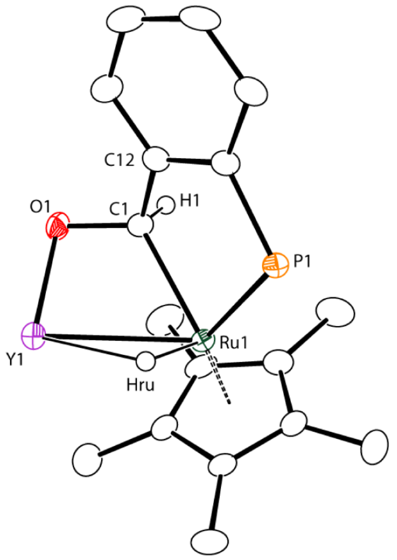


Figure 3. ORTEP representation of **3a-Y** depicted with thermal ellipsoids at 50% probability. The PNP_{iPr} pincer, the diphenyl rings on phosphorus, and most of the hydrogens are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Y(1)−Ru(1), 2.8207(4); Y(1)−O(1), 2.057(2); Ru(1)−C(1), 2.231(3); Ru(1)−P(1), 2.2392(8); Y(1)−H(ru), 2.24(3); Ru(1)−H(ru), 1.67(3); C(1)−O(1), 1.443(3); Y(1)−Ru(1)−C(1), 60.97(7); Y(1)−O(1)−C(1), 94.93(15); Ru(1)−C(1)−O(1), 118.97(18); Ru(1)−C(1)−C(12), 114.62(19); O(1)−C(1)−C(12), 109.7(2).

On the other hand, the carbon resonance that originated from carbon monoxide was observed at 74.6 ppm as a singlet in toluene-d_8 at −40 °C in its $^{13}C\{^1H\}$ NMR spectrum.[16] Labeling studies using enriched ^{13}CO gas afforded the complex **3a-Y-^{13}C**. The $^{13}C\{^1H\}$ NMR spectrum established the identity of the bridging pseudo(2-(diphenylphosphino)phenyl)-oxomethylene ligand (μ-O-^{13}CH-(*o*-C_6H_4)PPh_2-κP:κO), giving exclusively an enhanced signal at 74.6 ppm. This provides evidence for an insertion reaction. Further, the *ipso*-CH proton of such a bridging group was resolved and observed at −40 °C in toluene-d_8 at 7.36 ppm (dd, J_{HP} = 3.7, 4.8, 8.0 Hz) in its ^1H NMR spectrum. A doublet of triplets (dt) at −12.23 ppm was assigned to the bridging metal hydride, which integrates to one proton with regard to all other peaks in the ^1H NMR spectrum.

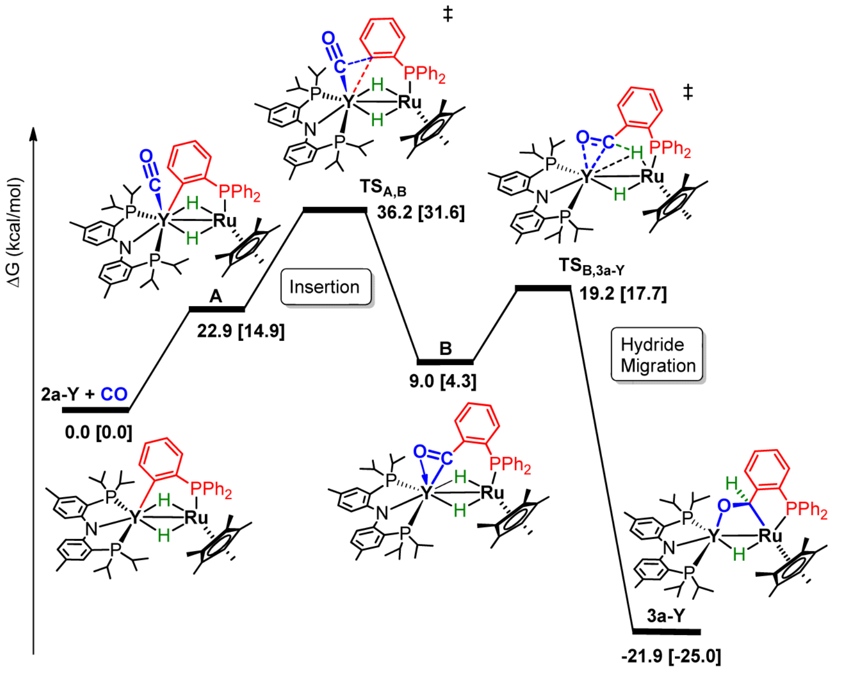


Figure 4. Computed energy profile (B3PW91/6-31G*, at 1 atm, 298 K) for the reaction of complex **2a-Y** with CO to form complex **3a-Y**, starting from the left and moving to the right. All of the free energies (Δ*G*) are reported relative to **2a-Y** and CO, in kcal/mol. The free energies calculated by single-point calculations using the M06 functional (M06/6-31G*, 1 atm, 298 K) are given in parentheses in kcal/mol.

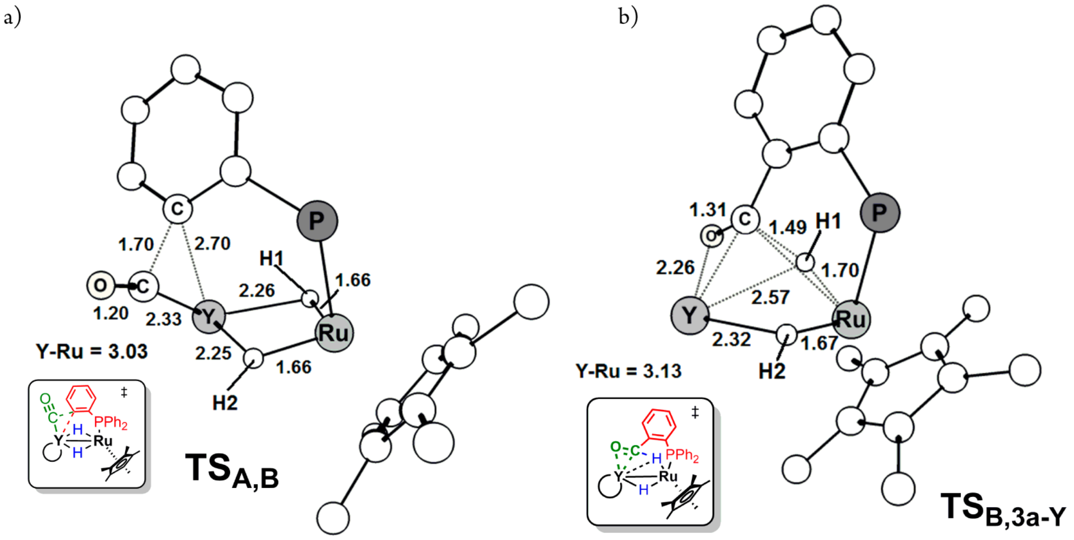


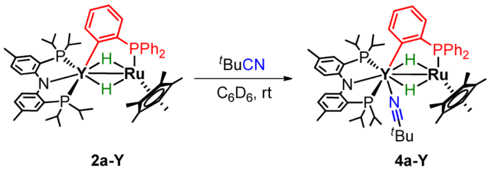
Figure 5. Calculated transition state structures (B3PW91/6-31G*, at 1 atm, 298 K) for (a) the insertion of a Y−C_6H_4 group into CO (**TS$_{A,B}$**) and (b) hydride migration into the bridging (2-(dimethylphosphino)phenyl)oxomethanide ligand (**TS$_{B,3a-Y}$**), with selected distances for both in Å. The PNP$_{iPr}$ pincer and the phenyl rings on phosphorus are omitted for clarity.

We therefore propose that complex **2a-Y** first reacts with 1 equiv of carbon monoxide via insertion of the Y−C_6H_4 group into the CO triple bond. Our DFT calculations (B3PW91/6-31G*, at 1 atm, 298 K, and single-point calculations with M06/6-31G*, 1 atm, 298 K[17]) suggest that the first step of the reaction is the coordination of carbon monoxide to **2a-Y** to form **A**, which is 22.9 kcal/mol uphill (Δ*G*(M06) = 14.9 kcal/mol). The insertion reaction then takes place with a free energy barrier ($\Delta G^{\ddagger}$) of 13.3 kcal/mol ($\Delta G^{\ddagger}$(M06) = 16.7 kcal/mol). The η^2-acyl intermediate **B** (Y−O = 2.33 Å, Y−C = 2.29 Å, C−O = 1.26 Å; see Figure 4 and the Supporting Information)[10b,18] is 9.0 kcal/mol less stable in comparison to **2a-Y** and CO (Δ*G*(M06) = +4.3 kcal/mol) and could rapidly convert to **3a-Y** through intramolecular hydride migration. Overall, the formation of **3a-Y** from **2a-Y** and carbon monoxide is exergonic by 21.9 kcal/mol (Δ*G*(M06) = −25.0 kcal/mol).

Of interest, the transition state structure depicted in Figure 5a for the insertion of the Y−C_6H_4 group into CO in **2a-Y** (structure **TS$_{A,B}$** in Figure 4) represents an early transition state. It has a long C_{CO}−C_{Ph} bond (1.70 Å) and a short C−O bond (1.20 Å). This was further confirmed by intrinsic reaction coordinate (IRC) calculations.[19] In addition, an early transition state for the hydride migration step (structure **TS$_{B,3a-Y}$**; see Figures 4 and 5b) was identified by IRC calculations. The Ru−H bond in **TS$_{B,3a-Y}$** remains almost intact (1.70 Å), while a C−H bond that originated from the acyl carbon barely forms (C−H = 1.49 Å).

Reaction of Bimetallic Complexes 2-Y with Molecules Containing Unsaturated C−N Bonds. We extended our investigation to the reactivity of complexes **2a-Y** and **2b-Y** toward molecules containing unsaturated C−N bonds. Complex **2a-Y** reacted with 1 equiv of pivalonitrile, giving the coordination complex **4a-Y** (Scheme 3). In sharp contrast, reaction of **2b-Y** and pivalonitrile in a 1:1 stoichiometric ratio afforded the insertion product **4b-Y** via a 1,3-shift of the coordinated methylene group on Y (Scheme 4).[20] The presence of a sterically demanding phosphinophenyl bridging group in **2a-Y** and the more nucleophilic phosphinomethyl bridging group in **2b-Y** clearly marks the difference in reactivity of these two bimetallic Y/Ru complexes toward the nitrile group.

Scheme 3. Reaction of Bimetallic Y/Ru Complex 2a-Y with Pivalonitrile



The solid-state structure of **4b-Y** shows an alkylideneamidophosphine ligand that bridges the binuclear Y/Ru centers (Figure 6a). The short C(2)−N(1) bond distances in the two asymmetric units of **4b-Y** (1.257(4) and 1.254(4) Å, Table 2) are consistent with those of a typical imine linkage, and they are in the expected range for similar samarium[21] and zirconium[22] complexes containing an alkylideneamido ligand. In fact, this is longer than that of the coordinated nitrile in **4a-Y** (1.139(3) Å; see the complete structure for **4a-Y** in the Supporting Information). In addition, the short Y−N bond distance in **4b-Y** (2.152(3) Å) in comparison to that of **4a-Y** (2.546(2) Å) is indicative of its formally anionic character.

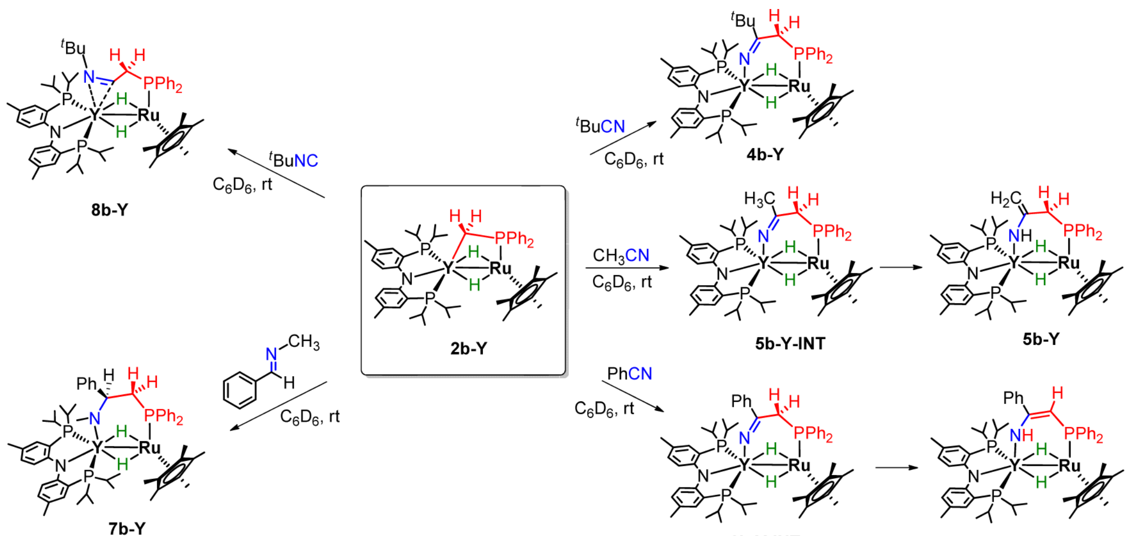
Complex **2b-Y** reacted with a stoichiometric amount of acetonitrile in C_6D_6 solution to give the formal insertion product **5b-Y-INT** in quantitative NMR yield. This slowly tautomerized to **5b-Y** at 20 °C in 2 days via a 1,3-proton shift from the methyl group to the nitrile nitrogen (Scheme 4).[20b−d] The characteristic doublet at 81.0 ppm (J_{CP} = 3.8 Hz) in its $^{13}C\{^1H\}$ NMR spectrum and the singlet at 3.59 ppm in its ^1H NMR spectrum established the presence of a vinylic CH_2 group in **5b-Y**. In addition, complex **2b-Y** reacted with a stoichiometric amount of benzonitrile in C_6D_6, affording first the insertion product **6b-Y-INT**. This was characterized in solution by NMR spectroscopy. Enolization of the alkylideneamidophosphine ligand then took place via a 1,3-proton shift from the methylene linker to the nitrile nitrogen, giving **6b-Y** in 67% isolated yield (Scheme 4).[23] On the other hand, complex **2a-Y** reacted with acetonitrile and benzonitrile to give multiple products, which were believed to be a mixture of coordination compound, insertion, and enolization products. These were not further isolated or characterized, however.

Complex **6b-Y** contains a bridging enamidophosphine ligand. The solid-state structure reveals a short C(1)−C(2) bond (1.393(5) Å) in comparison to that in **4b-Y** (1.524(4) Å) and a longer C(2)−N(1) bond (1.338(5) Å) in comparison to that in **4b-Y** (1.257(4) Å), which are typical of a coordinated enamido ligand (Figure 6b).[20d] The presence of an NH proton at 5.11 ppm and an olefinic proton at 4.88 ppm in its ^1H NMR spectrum in C_6D_6 further supports the identity of **6b-Y**.

Reaction of **2a-Y** with *N*-benzylidenemethylamine did not occur at 20 or 60 °C. In contrast, complex **2b-Y** reacted with the same substrate at 20 °C instantaneously to furnish complex **7b-Y** in quantitative NMR yield. This was formed via a 1,3-shift of the methylene group on yttrium to the C═N functional group (Scheme 4). The C(2)−N(1) bond (1.495(4) Å) is the longest in comparison to those in complexes **4b-Y** and **6b-Y**, which lies in the single C−N bond regime. In addition, the short Y(1)−N(1) bond (2.159(2) Å) is indicative of a strong anionic σ donor from the amidophosphine bridging ligand (Figure 6c).

Complex **2b-Y** reacted with 1 equiv of *tert*-butyl isocyanide, giving **8b-Y** upon instant mixing at 20 °C in C_6D_6 (Scheme 4). The $^{13}C\{^1H\}$ NMR spectrum of the reaction mixture containing **8b-Y** revealed a doublet at 271.8 ppm (J_{CP} = 40.5 Hz), which corresponds to the isonitrile carbon in the Y−η^2-CN*t*Bu linkage.[20b,24] The solid-state structure of **8b-Y** confirms its spectroscopic assignment (Figure 6d). This complex was formed via insertion of the methylene bridge of **2b-Y** to the isonitrile

Scheme 4. Reaction of Bimetallic Y/Ru Complex 2b-Y with Molecules Containing Unsaturated C−N Bonds



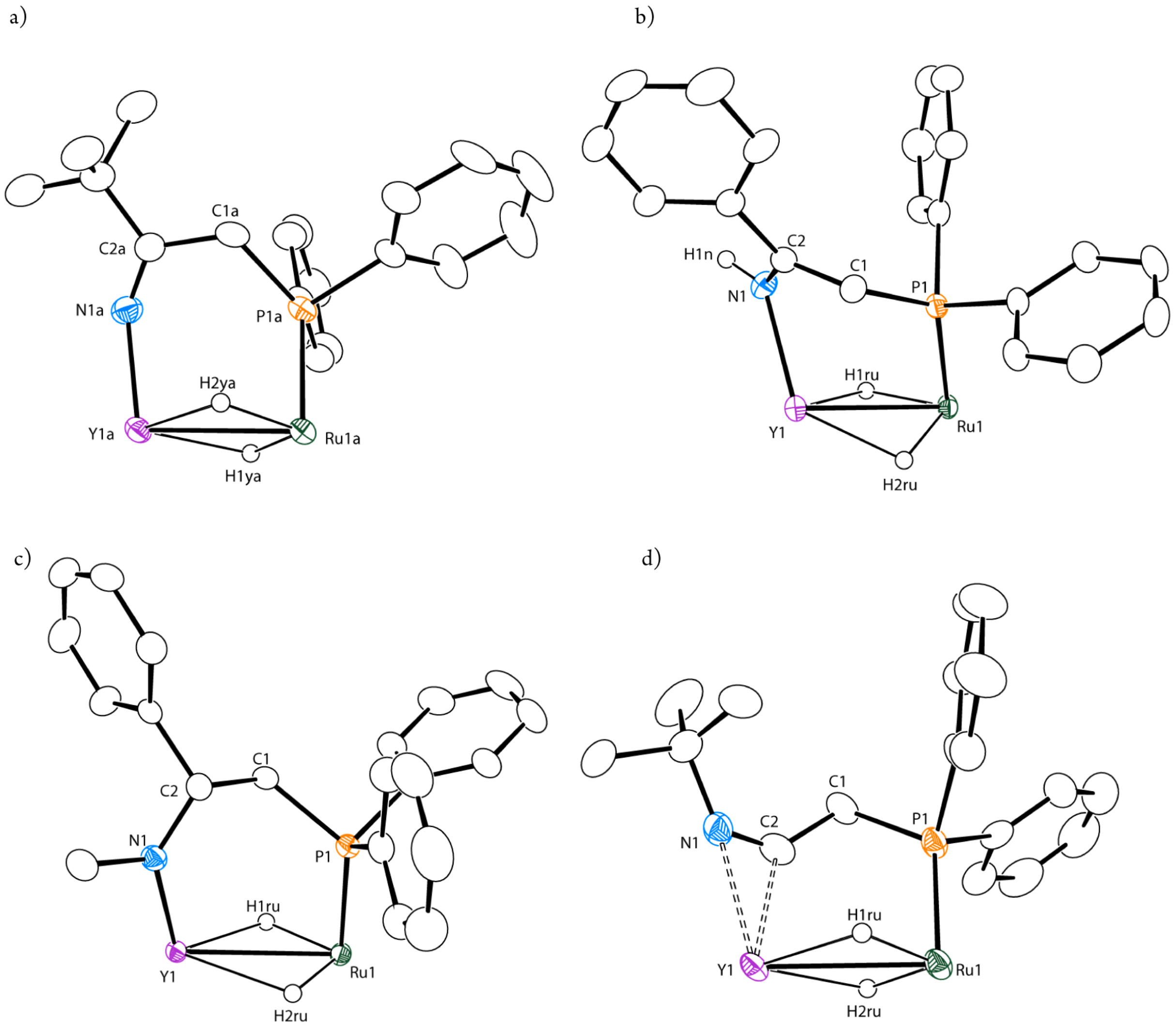


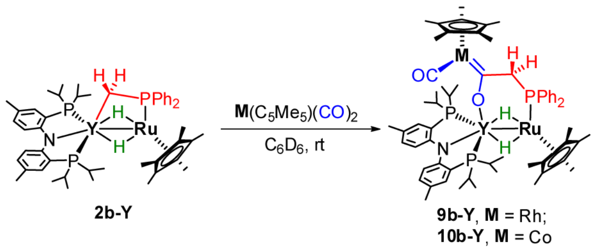
Figure 6. ORTEP representations of (a) **4b-Y**, (b) **6b-Y**, (c) **7b-Y**, and (d) **8b-Y** depicted with thermal ellipsoids at 50% probability. The $\mathrm{PNP}_{i\mathrm{Pr}}$ pincer and the C_5Me_5 ligand, most of the hydrogens, the disordered *tert*-butyl group in **4b-Y**, and the solvent molecule in **7b-Y** are omitted for clarity. Only one of the asymmetric units of **4b-Y** is shown. Selected bond distances and bond angles are given in Table 2.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Complexes 4b-Y, 6b-Y, 7b-Y, and 8b-Y

4b-Y		6b-Y, 7b-Y, 8b-Y			
			6b-Y	7b-Y	8b-Y
Y(1a)−Ru(1a)	2.9671(4)	Y(1)−Ru(1)	2.9626(6)	3.0096(4)	3.0370(8)
Y(1a)−N(1a)	2.152(3)	Y(1)−N(1)	2.300(3)	2.159(2)	2.395(5)
		Y(1)−C(2)			2.268(6)
Ru(1a)−P(1a)	2.2768(8)	Ru(1)−P(1)	2.2654(10)	2.2562(8)	2.2680(16)
Y(1a)−H(1ya)	2.08(3)	Y(1)−H(1ru)	2.26(4)	2.16(3)	2.13(7)
Y(1a)−H(2ya)	2.16(2)	Y(1)−H(2ru)	2.12(4)	2.23(3)	2.18(7)
Ru(1a)−H(1ya)	1.64(2)	Ru(1)−H(1ru)	1.67(3)	1.64(3)	1.66(7)
Ru(1a)−H(2ya)	1.68(3)	Ru(1)−H(2ru)	1.58(4)	1.57(3)	1.68(7)
C(2a)−N(1a)	1.257(4)	C(2)−N(1)	1.338(5)	1.459(4)	1.266(8)
C(1a)−C(2a)	1.524(4)	C(1)−C(2)	1.393(5)	1.536(4)	1.489(8)
Y(1a)−Ru(1a)−P(1a)	84.71(2)	Y(1)−Ru(1)−P(1)	70.34(3)	84.53(2)	89.36(5)
Y(1a)−N(1a)−C(2a)	138.3(2)	Y(1)−N(1)−C(2)	92.1(2)	132.02(18)	68.9(3)
		Y(1)−C(2)−C(1)			138.5(5)
Ru(1a)−P(1a)−C(1a)	122.06(10)	Ru(1)−P(1)−C(1)	123.69(13)	122.87(10)	120.1(2)
N(1a)−C(2a)−C(1a)	122.3(3)	N(1)−C(2)−C(1)	117.8(3)	111.6(2)	135.4(6)

functional group, forming an η^2-iminoacyl phosphine ligand across the Y/Ru binuclear centers. The C(2)−N(1) bond distance is typical of a double bond (1.266(8) Å), with Y(1)−N(1) and Y(1)−C(2) bond distances at 2.393(5) and 2.268(6)

Scheme 5. Reaction of Bimetallic Y/Ru Complex 2b-Y with Group IX Transition Metal Carbonyls



Å, respectively.[24] The reactivity of **2b-Y** toward isocyanide is similar to that of an yttrium alkyl complex, $Y(C_5Me_5)_2CH_2(3,5\text{-}(CH_3)_2\text{-}C_6H_3)$, reported by Teuben and co-workers[20b] and with that of an yttrium anilido hydride complex reported by Chen and co-workers.[24c]

Reaction of Bimetallic Complex 2-Y with Transition Metal Carbonyls. Complex **2a-Y** did not react with the coordinated carbonyl ligand in $M(C_5Me_5)(CO)_2$ (M = Rh, Co). On the other hand, the reaction of these complexes with **2b-Y** afforded the insertion products **9b-Y** (M = Rh) and **10b-Y** (M = Co) (Scheme 5), respectively. These were formed via nucleophilic attack of the methylene group at one of the coordinated carbonyl ligands on Rh or Co. Bercaw and co-workers reported a similar reaction starting with $Sc(C_5Me_5)_2CH_3$ and $Co(C_5H_5)(CO)_2$, giving an insertion product formulated as $(C_5H_5)Co(CO)(\mu\text{-}C(CH_3)O\text{-}\kappa C{:}\kappa O)Sc(C_5Me_5)_2$.[25] Chen and co-workers reported a similar reaction, starting with a yttrium anilido hydride complex and $Mo(CO)_6$. The reaction product, which contains a $Y{-}OCHMo(CO)_5$ linkage, was formed by a nucleophilic attack of a Y−H group at one of the coordinated carbonyl ligands.[24c] We previously reported the reaction of the tetranuclear yttrium polyhydride $[\{Cp'Y(\mu\text{-}H)_2\}_4(THF)]$ ($Cp' = C_5Me_4SiMe_3$) with $M(C_5Me_5)(CO)_2$ (M = Rh, Ir). The C−O bonds of the resulting oxymethylene groups were cleaved, giving bis(methylcarbene) dioxo dihydride complexes.[26]

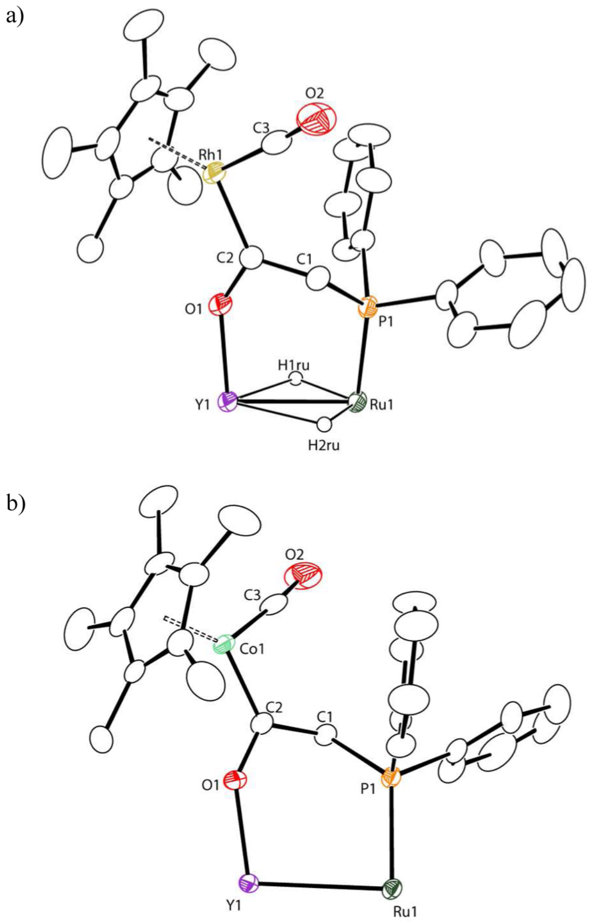


Figure 7. ORTEP representations of (a) **9b-Y** and (b) **10b-Y** depicted with thermal ellipsoids at 50% probability. The PNP_{iPr} pincer and the C_5Me_5 ligand and most of the hydrogens are omitted for clarity. The hydride ligand in **10b-Y** was omitted. Selected bond distances and bond angles are given in Table 3.

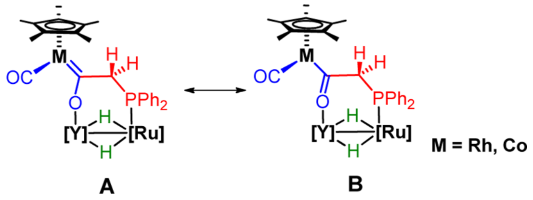


Figure 8. The two resonance forms, **A** and **B**, of complexes **9b-Y** and **10b-Y**.

Complexes **9b-Y** and **10b-Y** were structurally characterized (Figure 7) by an X-ray diffraction study. The complexes were notable for the presence of a bridging oxycarbenephosphine ligand ($M{=}C(O)CH_2PPh_2$). Bond lengths and angles of **9b-Y** and **10b-Y** are summarized in Table 3. One of the bridging hydrides in **10b-Y** was not located from the electron density map during Fourier synthesis. The short Rh(1)−C(2) and Co(1)−C(2) distances (1.925(3) and 1.820(5) Å) is characteristic of a Fischer carbene. These lie in a similar range for a series of heterometallic Zr/Rh and Zr/Co alkoxy-Fischer carbene complexes reported by Erker and co-workers ($Rh{-}C_{av}$ = 1.93 Å; $Co{-}C_{av}$ = 1.83 Å).[27] The C(2) carbon derived from the carbonyl group, along with Rh(1), C(1), and O1(1), are coplanar, with a sum of bond angles around such a carbon equal to 360°. The C(2)−O(1) distances (**9b-Y**, 1.305(3) Å; **10b-Y**, 1.318(6) Å) are longer than those of the unreacted carbonyl ligand (C(3)−O(2) distances: **9b-Y**, 1.150(4) Å; **10b-Y**, 1.160(6) Å), and they are typical in those of a oxycarbene group. The C(2)−O(1) distances of **9b-Y** and **10b-Y** are also longer than those of yttrium ketone complexes with a $Y{-}\eta^1{-}O{=}CR_2$ linkage ($C{=}O_{av}$ = 1.23 Å).[28] In addition, the Y−O bond distances are much shorter than those in this family of complexes ($Y{-}O_{av}$ = 2.31 Å). These are suggestive of the presence of a highly charged oxygen group of the oxycarbenephosphine ligand. On the other hand, the carbene carbons ($Y{-}OC{=}M$) on Rh and Co were observed at 280.1 (**9b-Y**, d, J_{RhC} = 56.9 Hz) and 284.8 ppm (**10b-Y**, s) in their corresponding $^{13}C\{^1H\}$ NMR spectra measured in C_6D_6. The coordinated carbonyl ligands were observed at 199.8 (**9b-Y**, d, J_{RhC} = 104.6 Hz) and 213.5 ppm (**10b-Y**, s), respectively. The spectroscopic data and the structural parameters obtained for complexes **9b-Y** and **10b-Y** are indicative of the resonance form **A** depicted in Figure 8.[25,27]

The reaction of complex **2b-Y** with coordinated carbonyls took place via insertion of $Y{-}CH_2$ into the carbonyl group without participation of the metal hydrides. This is in sharp contrast to the case where both the bridging phosphinophenyl group and the hydride ligand of **2a-Y** are involved in the insertion reaction with carbon monoxide. No further reaction

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for Complexes **9b-Y** and **10b-Y**

9b-Y		**10b-Y**	
Y(1)−Ru(1)	2.9272(4)	Y(1)−Ru(1)	2.9254(7)
Y(1)−O(1)	2.132(2)	Y(1)−O(1)	2.119(3)
Ru(1)−P(1)	2.2715(8)	Ru(1)−P(1)	2.2766(12)
Y(1)−H(1ru)	2.23(3)	Y(1)−H(1ru)	2.31(5)
Y(1)−H(2ru)	2.16(4)	Y(1)−H(2ru)	*a*
Ru(1)−H(1ru)	1.62(3)	Ru(1)−H(1ru)	1.37(5)
Ru(1)−H(2ru)	1.60(4)	Ru(1)−H(2ru)	*a*
C(2)−O(1)	1.305(3)	C(2)−O(1)	1.318(6)
C(3)−O(2)	1.150(4)	C(3)−O(2)	1.160(6)
Rh(1)−C(2)	1.925(3)	Co(1)−C(2)	1.820(5)
Rh(1)−C(3)	1.824(3)	Co(1)−C(3)	1,710(6)
C(1)−C(2)	1.513(4)	C(1)−C(2)	1.523(7)
Y(1)−Ru(1)−P(1)	87.18(2)	Y(1)−Ru(1)−P(1)	87.17(4)
Y(1)−O(1)−C(2)	142.25(19)	Y(1)−O(1)−C(2)	143.9(3)
O(1)−C(2)−C(1)	111.4(6)	O(1)−C(2)−C(1)	109.7(4)
Rh(1)−C(2)−O(1)	121.1(2)	Co(1)−C(2)−O(1)	123.7(4)
Rh(1)−C(2)−C(1)	127.5(2)	Co(1)−C(2)−C(1)	126.5(3)

[a] This hydride was not located during Fourier synthesis.

involving hydride ligands was observed in attempts to heat solutions containing **9b-Y** or **10b-Y**.

■ CONCLUSIONS

A new family of heterometallic Ln/Ru dihydride complexes containing a “Ln(PNP$_{iPr}$)” unit were synthesized and structurally characterized. These complexes bear bridging phosphinophenyl (μ-$C_6H_4PPh_2$-κP:κC^1, **2a-Ln**) and bridging phosphinomethyl ligands (μ-CH_2PPh_2-κP:κC, **2b-Ln**) on the binuclear Ln/Ru core. The bimetallic Y/Ru complex **2a-Y** with a phosphinophenyl bridging ligand reacted with carbon monoxide via two steps, with first the migratory insertion of the Y−C_6H_4 group into the CO triple bond, followed by a nucleophilic attack of a bridging hydride at an η^2-acyl group, affording complex **3a-Y** bearing a pseudo(2-(diphenylphosphino)-phenyl)oxomethylene ligand and a hydride ligand on the Y/Ru centers. In contrast, the reaction of complex **2b-Y** containing a phosphinomethyl bridging ligand with various unsaturated molecules took place via insertion of the Y−CH_2 group into the unsaturated bond without participation of the metal hydride. This afforded heterometallic Y/Ru complexes with new ligand scaffolds, such as alkylideneamidophosphine (**4b-Y**), amidophosphine (**7b-Y**), η^2-iminoacylphosphine (**8b-Y**) and oxycarbenephosphine (**9b-Y** and **10b-Y**) bridging ligands.

■ EXPERIMENTAL SECTION

Synthesis. All of the preparations and manipulations were carried out under a nitrogen atmosphere using standard Schlenk-line and glovebox techniques. Nitrogen gas was purified by passing through a Dryclean column packed with 4 Å molecular sieves (Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.), whereas nitrogen gas for an MBRAUN glovebox was constantly circulated through a catalyst unit loaded with copper and 4 Å molecular sieves. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer (MBRAUN) to ensure both were always below 0.1 ppm. All of the solvents were purchased from Kanato Kagaku Co., purified by use of a MBRAUN SPS-800 solvent purification system, and dried over fresh sodium chips prior to use. All of the substrates that were used for reactivity studies were purchased from commercial sources and degassed prior to use. Carbon monoxide gas was purchased from Suzuki Shokan Co., purified by passing through a Dryclean column packed with 4 Å molecular sieves (Nikka Seiko Co.) prior to use.

Deuterated benzene (C_6D_6), toluene (C_7D_8), and tetrahydrofuran (C_4D_8O) were purchased from Sigma Aldrich and were distilled from sodium benzophenone ketyl under a nitrogen atmosphere, dried over fresh sodium chips prior to use. All of the samples for NMR spectroscopic measurements were prepared in a glovebox by use of NMR tubes equipped with a J. Young valve. NMR spectra were recorded on a JEOL-AL400 spectrometer operating at 400 MHz for ^1H, 100 MHz for ^{13}C, and 161 MHz for ^{31}P. Chemical shifts (δ) are reported in ppm. ^1H and $^{13}C\{^1H\}$ NMR spectra were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane (TMS). All ^{31}P chemical shifts were measured relative to 85% phosphoric acid as an external reference. All infrared spectra were recorded on a Shimadzu IR Prestige-21 spectrometer. Elemental analyses were performed on a MICRO CORDER JM10 (J-Science Lab. Co.) elemental analyzer.

The synthesis of Y(PNP$_{iPr}$)(CH_2SiMe_3)$_2$ (**1-Y**) was previously reported.[7b] The syntheses of Ho(PNP$_{iPr}$)(CH_2SiMe_3)$_2$ (**1-Ho**) and Dy(PNP$_{iPr}$)(CH_2SiMe_3)$_2$ (**1-Dy**) were similar to those of **1-Y**. Results of elemental analysis pertaining to **1-Ho**, **2-Ho**, **1-Dy**, and **2-Dy** are given in the Supporting Information. The preparations of Ru(C_5Me_5)-H_3PPh_3, Ru(C_5Me_5)H_3PPh_2Me,[9] and Co(C_5Me_5)(CO)$_2$[29] were reported in the literature. The rhodium(I) complex Rh(C_5Me_5)(CO)$_2$ was purchased from Sigma Aldrich and was used as received.

X-ray Crystallographic Studies. Suitable crystals for an X-ray diffraction study were obtained as described below. These were manipulated under a microscope in a glovebox filled with nitrogen. X-ray diffraction data collections were performed on a Bruker D8 QUEST diffractometer equipped with a CMOS area detector, using a IμS (Incoatec Microfocus Source) microfocus sealed tube with Mo Kα radiation (λ = 0.71073 Å) at 167 K. The Bravais lattice and the unit cell parameters were determined by the Bruker APEX2[30] software package. The raw frame data were processed, and absorption corrections were done using SAINT[30] and SADABS[30] embedded in Bruker APEX2 to yield the reflection data (*hkl*) file. All of the structures were solved using SHELXS-97[31] or SUPERFLIP.[32] Structural refinement was performed using the SHELXL-97 option in the WINGX system,[33] on F^2 anisotropically for all of the non-hydrogen atoms by the full-matrix least-squares method. Analytical scattering factors for neutral atoms were used throughout the analysis. The SQUEEZE[34] option in PLATON[35] was performed to remove electron density from the observed data contributed by disordered hexane molecules in **2a-Y**, **2a-Ho**, **2a-Dy**, **3a-Y**, and **4b-Y**. The phenyl group of the cyclometalated PPh_3

ligand (C(13)−C(18)) on **4a-Y** was modeled as disordered over two positions at 53% and 47% occupancies. These carbon atoms were further confined as coplanar. In addition, the *tert*-butyl group of the nitrile (C(31)−C(33)) was modeled over two positions at 57% and 43% occupancies. The disordered *tert*-butyl group of the nitrile (C(4A)−C(6A)) of one of the asymmetric units of **4b-Y** was modeled over two positions at 54% and 46% occupancies, as were the methyl groups of the isopropyl substituent of the PNP$_{iPr}$ ligand of another asymmetric unit, at 52% and 48% occupancies (C(43B) and C(44B)) and at 54% and 46% occupancies (C(46B) and C(47B)), respectively. The same anisotropic displacement parameters were used for all of these disordered carbon atoms. On the other hand, the same anisotropic displacement parameters were used for carbon atoms of phenyl or isopropyl groups in the following complexes: the phenyl group of the cyclometalated PPh$_3$ ligand (C(13)−C(18)) and methyl groups of the isopropyl substituent of the PNP$_{iPr}$ ligand (C(49), C(50); C(52), C(53)) of **2a-Y**; the phenyl group of the cyclometalated PPh$_3$ ligand (C(7)−C(12)) of **2a-Ho**; the phenyl group of the cyclometalated PPh$_3$ ligand (C(13)−C(18)) of **2a-Dy**; the aryl ring of the C$_5$Me$_5$ ligand (C(14)−C(18)) of **2b-Dy**; the phenyl groups (C(29)−C(34); C(36)−C(41)) and the methyl groups of the isopropyl substituent of the PNP$_{iPr}$ ligand (C(49), C(50)) of **7b-Y**. The bridging metal hydrides in all of the structures were located by an electron density map during Fourier synthesis, and their positions were refined isotropically. All other hydrogen atoms were placed at geometrically calculated positions and refined using a riding model. The residual electron densities in all of the structures were of no chemical significance. Selected crystal data and data collection and refinement parameters are summarized in Tables S2 and S3 in the Supporting Information. Crystallographic data are available from the CCDC under file numbers 970680 (**2a-Y**), 970681 (**2a-Ho**), 970682 (**2a-Dy**), 970683 (**2b-Y**·0.5 C$_6$H$_{14}$), 970684 (**2b-Ho**·0.5 C$_6$H$_{14}$), 970685 (**2b-Dy**·0.5 C$_6$H$_{14}$), 970686 (**3a-Y**), 970688 (**4a-Y**), 970689 (**4b-Y**), 970690 (**6b-Y**), 970691 (**7b-Y**), 970692 (**8b-Y**·0.5 C$_4$H$_{10}$O), 970693 (**9b-Y**), and 970694 (**10b-Y**).

[(PNP$_{iPr}$)Y(μ-H)$_2$(μ-C$_6$H$_4$PPh$_2$-κP:κC^1)Ru(C$_5$Me$_5$)] (2a-Y). A Schlenk tube was charged with **1-Y** (279 mg, 0.403 mmol), Ru(C$_5$Me$_5$)H$_3$PPh$_3$ (202 mg, 0.403 mmol), and benzene (14 mL). The reaction mixture was heated at 60 °C for 3 days. After the reaction had gone to completion, the solvent was removed under reduced pressure. The solid residue was suspended in hexanes (2 mL) and chilled at −30 °C for several hours. The yellow solid that separated from the mother liquid was collected on a glass frit, washed with cold hexanes (2 × 1 mL), and dried in vacuo. Yield: 280 mg, 68%. Suitable crystals for an X-ray diffraction study were obtained by slow diffusion of hexanes into a saturated solution of **2a-Y** in benzene at 20 °C under a nitrogen atmosphere. ^{1}H NMR (C$_6$D$_6$, 293 K, δ): 8.09 (t, J_{HH} = 8.7 Hz, CH of PPh$_2$C$_6$H$_4$, 2H), 7.81 (t, J_{HH} = 8.7 Hz, CH of PPh$_2$C$_6$H$_4$, 2H), 7.68 (d, J_{HH} = 6.1 Hz, CH of PPh$_2$C$_6$H$_4$, 1H), 7.54 (t, J_{HH} = 7.3 Hz, CH of PPh$_2$C$_6$H$_4$, 1H), 7.40 (m, Ar-CH of PNP$_{iPr}$, 1H), 7.22 (m, CH of PPh$_2$C$_6$H$_4$, 4H), 7.07 (m, CH of PPh$_2$C$_6$H$_4$, Ar-CH of PNP$_{iPr}$, 5H), 6.98 (m, Ar-CH of PNP$_{iPr}$, 2H), 6.91 (m, CH of PPh$_2$C$_6$H$_4$, 1H), 6.84 (m, Ar-CH of PNP$_{iPr}$, 1H), 2.23 (s, Me of PNP$_{iPr}$, 3H), 2.14 (s, Me of PNP$_{iPr}$, 3H), 2.04 (m, CH of *i*Pr, 2H), 1.84 (m, CH of *i*Pr, 1H), 1.73 (m, CH of *i*Pr, 1H), 1.69 (s, Me of C$_5$Me$_5$, 15H), 1.44 (dd, J_{HH} = 6.1 Hz, J_{HP} = 15.9 Hz, Me of *i*Pr, 3H), 1.36 (dd, J_{HH} = 6.1 Hz, J_{HP} = 16.5 Hz, Me of *i*Pr, 3H), 1.08 (dd, J_{HH} = 7.3 Hz, J_{HP} = 9.8 Hz, Me of *i*Pr, 3H), 1.00 (dd, J_{HH} = 7.3 Hz, J_{HP} = 14.7 Hz, Me of *i*Pr, 3H), 0.87 (m, Me of *i*Pr, 9H), 0.66 (dd, J_{HH} = 6.1 Hz, J_{HP} = 15.9 Hz, Me of *i*Pr, 3H), −12.35 (t, J_{HP} = 24.5 Hz, Ru-H, 1H), −12.66 (t, J_{HP} = 24.5 Hz, Ru-H, 1H). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K, δ): 200.9 (t, J = 51.8 Hz, Y-C$_{Ar}$). 162.6 (d, J_{CP} = 21.1 Hz, C$_{Ar}$), 160.1 (d, J_{CP} = 55.6 Hz, C$_{Ar}$), 157.2 (d, J_{CP} = 19.2 Hz, C$_{Ar}$), 143.6 (d, J_{CP} = 40.3 Hz, C$_{Ar}$), 143.4 (d, J_{CP} = 51.8 Hz, C$_{Ar}$), 135.8 (d, J_{CP} = 11.5 Hz, C$_{Ar}$), 135.9 (C$_{Ar}$), 134.2 (d, J_{CP} = 11.5 Hz, C$_{Ar}$), 133.8 (d, J_{CP} = 11.5 Hz, C$_{Ar}$), 133.5 (C$_{Ar}$), 133.2 (C$_{Ar}$), 133.1 (C$_{Ar}$), 131.5 (d, J_{CP} = 6.7 Hz, C$_{Ar}$), 129.2 (C$_{Ar}$), 128.9 (C$_{Ar}$), 127.6 (C$_{Ar}$), 127.4 (d, J_{CP} = 8.6 Hz, C$_{Ar}$), 127.1 (d, J_{CP} = 8.6 Hz, C$_{Ar}$), 125.8 (C$_{Ar}$), 125.0 (C$_{Ar}$), 124.7 (d, J_{CP} = 6.7 Hz, C$_{Ar}$), 124.5 (d, J_{CP} = 4.8 Hz, C$_{Ar}$), 119.4 (d, J_{CP} = 15.3 Hz, C$_{Ar}$), 117.6 (d, J_{CP} = 26.8 Hz, C$_{Ar}$), 117.0 (d, J_{CP} = 5.8 Hz, C$_{Ar}$), 88.0 (C$_{Ar}$ of C$_5$Me$_5$), 24.9 (*i*Pr), 24.6 (*i*Pr), 21.4 (d, J_{CP} = 11.5 Hz, *i*Pr), 21.0 (*i*Pr), 20.7 (Me of PNP$_{iPr}$), 20.5 (d, J_{CP} = 10.5 Hz, *i*Pr), 20.0 (m, Me of PNP$_{iPr}$, *i*Pr), 19.8 (d, J_{CP} = 6.7 Hz, *i*Pr), 19.2 (m, *i*Pr), 18.6 (*i*Pr), 18.5 (*i*Pr), 17.1 (*i*Pr), 11.9 (Me of C$_5$Me$_5$). ^{31}P NMR (C$_6$D$_6$, 293 K, δ): 52.64 (s, PPh$_2$C$_6$H$_4$), 10.57 (dd, J_{PP} = 12.4 Hz, J_{YP} = 64.4 Hz, PNP$_{iPr}$), 4.87 (dd, J_{PP} = 12.4 Hz, J_{YP} = 61.9 Hz, PNP$_{iPr}$). Anal. Calcd for C$_{54}$H$_{71}$NP$_3$RuY: C, 63.77; H, 7.04; N, 1.38. Found: C, 63.40; H, 7.27; N, 1.60.

[(PNP$_{iPr}$)Y(μ-H)$_2$(μ-CH$_2$PPh$_2$-κP:κC)Ru(C$_5$Me$_5$)] (2b-Y). A Schlenk tube was charged with **1-Y** (300 mg, 0.433 mmol), Ru(C$_5$Me$_5$)H$_3$PPh$_2$Me (190 mg, 0.432 mmol), and benzene (14 mL). The reaction mixture was heated at 60 °C for 3 days. After the reaction had gone to completion, the solvent was removed under reduced pressure. The solid residue was suspended in hexanes (10 mL) and the suspension stirred at 20 °C for 0.5 h. The yellow solid that separated from the mother liquid was collected on a glass frit, washed with cold hexanes (2 × 1 mL), and dried in vacuo. Yield: 233 mg, 68%. Suitable crystals for an X-ray diffraction study were obtained as a hexane solvate by slow diffusion of hexanes into a saturated solution of **2b-Y** in benzene at 20 °C under a nitrogen atmosphere. ^{1}H NMR (THF-d_8, 293 K, δ): 7.79 (t, J_{HH} = 7.3 Hz, CH of PPh$_2$CH$_2$, 2H), 7.55 (t, J_{HH} = 7.4 Hz, CH of PPh$_2$CH$_2$, 2H), 7.18 (m, CH of PPh$_2$CH$_2$, 2H), 7.12 (m, CH of PPh$_2$CH$_2$, Ar-CH of PNP$_{iPr}$, 3H), 7.07 (m, Ar-CH of PNP$_{iPr}$, 1H), 6.84 (d, J_{HH} = 2.5 Hz, Ar-CH of PNP$_{iPr}$, 2H), 6.71 (m, CH of PPh$_2$CH$_2$, Ar-CH of PNP$_{iPr}$, 4H), 2.37 (m, CH of *i*Pr, 2H), 2.13 (s, Me of PNP$_{iPr}$, 6H), 1.60 (s, Me of C$_5$Me$_5$, 15H), 1.56 (m, CH of *i*Pr, 2H), 1.35 (dd, J_{HH} = 6.1 Hz, J_{HP} = 14.4 Hz, Me of *i*Pr, 6H), 1.11 (dd, J_{HH} = 6.1 Hz, J_{HP} = 14.7 Hz, Me of *i*Pr, 6H), 1.00 (m, Me of *i*Pr, 12H), 0.81 (t, J_{HP} = 12.2 Hz, CH of Y−CH$_2$, 1H), 0.00 (t, J_{HP} = 12.2 Hz, CH of Y-CH$_2$, 1H), −13.10 (dd, J_{HP} = 19.6, 22.0 Hz, Ru−H, 2H). ^{13}C{^{1}H} NMR (THF-d_8, 293 K, δ): 162.7 (d, J_{CP} = 20.1 Hz, C$_{Ar}$), 149.0 (d, J_{CP} = 16.3 Hz, C$_{Ar}$), 147.8 (d, J_{CP} = 27.8 Hz, C$_{Ar}$), 135.0 (d, J_{CP} = 11.5 Hz, C$_{Ar}$), 134.1 (d, J_{CP} = 11.5 Hz, C$_{Ar}$), 127.2 (C$_{Ar}$), 127.0 (C$_{Ar}$), 126.9 (C$_{Ar}$), 125.7 (C$_{Ar}$), 121.2 (d, J_{CP} = 4.8 Hz, C$_{Ar}$), 119.5 (m, C$_{Ar}$), 85.4 (C$_{Ar}$ of C$_5$Me$_5$), 44.1 (t, J = 24.0 Hz, Y-CH$_2$), 25.8 (*i*Pr), 25.6 (*i*Pr), 25.4 (*i*Pr), 20.7 (Me of PNP$_{iPr}$), 20.5 (m, *i*Pr), 20.4 (m, *i*Pr), 19.9 (d, J_{CP} = 9.6 Hz, *i*Pr), 19.2 (*i*Pr), 18.0 (m, *i*Pr), 12.4 (Me of C$_5$Me$_5$). ^{31}P NMR (THF-d_8, 293 K, δ): 46.78 (d, J_{PP} = 17.3 Hz, PPh$_2$CH$_2$), 5.39 (m, br, PNP$_{iPr}$); (C$_6$D$_6$, 293 K, δ): 48.62 (d, J_{PP} = 12.4 Hz, PPh$_2$CH$_2$), 11.33 (dd, J_{PP} = 9.9, 14.9 Hz, J_{YP} = 69.4 Hz, PNP$_{iPr}$), 5.67 (dd, J_{PP} = 9.9, 14.9 Hz, J_{YP} = 71.8 Hz, PNP$_{iPr}$). Anal. Calcd for C$_{49}$H$_{69}$NP$_3$RuY: C, 61.63; H, 7.28; N, 1.47. Found: C, 61.77; H, 7.29; N, 1.38.

[(PNP$_{iPr}$)Y(μ-H)(μ-CHO(o-C$_6$H$_4$)PPh$_2$-κP:κO)Ru(C$_5$Me$_5$)] (3a-Y). An NMR tube fitted with a J. Young valve was charged with **2a-Y** (180 mg, 0.177 mmol) and toluene-d_8 (0.8 mL). The reaction mixture was degassed by freeze−pump−thaw cycles at least three times, and the tube was back-filled with CO gas (1 atm) at 20 °C. The reaction progress was monitored by ^{1}H and ^{31}P NMR at 20 °C. After the reaction had gone to completion, the toluene-d_8 solution was diluted with toluene (2 mL) under a nitrogen atmosphere. The solution was then filtered, and the solvent was removed under reduced pressure. The residue that was obtained was recrystallized in hexanes (1 mL) at −30 °C overnight. The yellow solid that separated from the mother liquid was isolated, washed with cold hexanes (2 × 1 mL), and dried in vacuo to give a yellow powder. Yield: 113 mg, 61%. Complex **3a-Y** crystallized as fine yellow plates by cooling a saturated solution of **3a-Y** in hexanes at −30 °C for 1 week. These were used for an X-ray diffraction study. ^{1}H NMR (toluene-d_8, 233 K, δ): 8.54 (s, CH of PPh$_2$C$_6$H$_4$, 1H), 8.19 (m, CH of PPh$_2$C$_6$H$_4$, 3H), 7.59 (s, CH of PPh$_2$C$_6$H$_4$, 2H), 7.57 (m, CH of PPh$_2$C$_6$H$_4$, 1H), 7.36 (dd, J_{HP} = 3.7, 4.8, 8.0 Hz, CH of Y-OCH−Ru, 1H), 7.14 (m, CH of PPh$_2$C$_6$H$_4$, Ar-CH of PNP$_{iPr}$, 3H), 7.05 (m, Ar-CH of PNP$_{iPr}$, 2H), 6.98 (m, Ar-CH of PNP$_{iPr}$, 2H), 6.91 (d, J_{HH} = 8.6 Hz, CH of PPh$_2$C$_6$H$_4$, 2H), 2.55 (m, CH of *i*Pr, 1H), 2.35 (s, Me of PNP$_{iPr}$, 3H), 2.23 (s, Me of PNP$_{iPr}$, 3H), 2.16 (m, CH of *i*Pr, 3H), 1.58 (s, Me of C$_5$Me$_5$, 15H), 1.39 (dd, J_{HH} = 6.1 Hz, J_{HP} = 15.9 Hz, Me of *i*Pr, 3H), 1.24 (dd, J_{HH} = 6.1 Hz, J_{HP} = 15.3 Hz, Me of *i*Pr, 3H), 1.19 (m, Me of *i*Pr, 3H), 1.04 (dd, J_{HH} = 7.3 Hz, J_{HP} = 14.5 Hz, Me of *i*Pr, 3H), 0.70 (m, Me of *i*Pr, 9H), −0.25 (dd, J_{HH} = 6.1, 7.9 Hz, J_{HP} = 18.7 Hz, Me of *i*Pr, 3H),

−12.23 (dt, J_{HH} = 6.1 Hz, J_{HP} = 26.3 Hz, Ru-H, 1H). $^{13}C\{^{1}H\}$ NMR (toluene-d_8, 233 K, δ): 171.9 (d, J_{CP} = 32.3 Hz, Y-OCH-C_{PPh}). 160.8 (d, J_{CP} = 21.5 Hz, C_{Ar}), 150.4 (d, J_{CP} = 15.4 Hz, C_{Ar}), 143.8 (d, J_{CP} = 33.8 Hz, C_{Ar}), 139.1 (d, J_{CP} = 38.5 Hz, C_{Ar}), 138.1 (C_{Ar}), 137.7 (d, J_{CP} = 10.8 Hz, C_{Ar}), 133.4 (d, J_{CP} = 24.6 Hz, C_{Ar}), 132.7 (d, J_{CP} = 29.2 Hz, C_{Ar}), 130.3 (C_{Ar}), 127.0 (m, C_{Ar}), 126.6 (d, J_{CP} = 16.9 Hz, C_{Ar}), 126.4 (m, C_{Ar}), 124.4 (C_{Ar}), 123.7 (d, J_{CP} = 15.4 Hz, C_{Ar}), 123.2 (m, C_{Ar}), 116.1 (d, J_{CP} = 16.9 Hz, C_{Ar}), 113.8 (d, J_{CP} = 6.2 Hz, C_{Ar}), 85.7 (C_{Ar} of C_5Me_5), 74.6 (Y-OCH−Ru), 24.8 (*i*Pr), 24.2 (*i*Pr), 22.8 (d, J_{CP} = 6.2 Hz, *i*Pr), 21.3 (*i*Pr), 21.1 (m, *i*Pr), 20.9 (Me of PNP_{iPr}), 20.7 (m, Me of PNP_{iPr}, *i*Pr), 20.2 (*i*Pr), 19.7 (m, *i*Pr), 19.6 (m, *i*Pr), 19.5 (m, *i*Pr), 19.4 (*i*Pr), 19.3 (*i*Pr), 19.2 (m, *i*Pr), 17.4 (*i*Pr), 10.1 (Me of C_5Me_5). ^{31}P NMR (toluene-d_8, 233 K, δ): 75.11 (d, J_{PP} = 19.8 Hz, $PPh_2C_6H_4$), 11.73 (dd, J_{PP} = 9.9 Hz, J_{YP} = 86.7 Hz, PNP_{iPr}), −7.68 (d, J_{YP} = 61.9 Hz, PNP_{iPr}). IR (Nujol, cm^{-1}): 1920 (w, Ru−H stretch), 897 (m, C−O stretch). Anal. Calcd for $C_{55}H_{71}NOP_3RuY\cdot0.5\ C_6H_{14}$: C, 64.02; H, 7.23; N, 1.29. Found: C, 64.27; H, 7.24; N, 1.52.

[(PNP_{iPr})Y(μ-H)(μ-^{13}CHO(o-C_6H_4)PPh_2-κP:κO)Ru(C_5Me_5)] (3a-Y-^{13}C). The reaction was performed similarly to the preparation of **3a-Y**, starting with **2a-Y** (180 mg, 0.177 mmol), toluene-d_8 (0.8 mL), and ^{13}CO gas (1 atm) at 20 °C. Yield: 117 mg, 63%. The ^{13}C NMR spectrum of **3a-Y-^{13}C** measured at 233 K in toluene-d_8 showed an enhancement in peak intensity at δ 74.6 ppm as a result of the presence of a μ-^{13}CHO(o-C_6H_4)PPh_2-κP:κO group, otherwise its ^{1}H, ^{31}P, and ^{13}C NMR spectral information were identical with those of **3a-Y** measured at 233 K in toluene-d_8. IR (Nujol, cm^{-1}): 1875 (w, Ru−H stretch), 882, (m, C−O stretch).

[(PNP_{iPr})Y(NC*t*Bu)(μ-H)$_2$(μ-$C_6H_4PPh_2$-κP:κC^1)Ru(C_5Me_5)] (4a-Y). An NMR tube fitted with a J. Young valve was charged with **2a-Y** (85 mg, 0.084 mmol), pivalonitrile (*t*BuCN, 7 mg, 0.084 mmol), and C_6D_6 (0.8 mL). The reaction mixture was mixed thoroughly at 20 °C. ^{1}H and ^{31}P NMR spectra of the reaction mixture showed full conversion to **4a-Y** in 1 h. The solvent was then removed under reduced pressure. The residue that was obtained was recrystallized in hexanes (1 mL) at −30 °C overnight. An orange solid was isolated; this was further washed with cold hexanes (2 × 1 mL) and dried in vacuo, affording the title complex as an orange-yellow solid. Yield: 62 mg, 67%. Yellow blocks were obtained for an X-ray diffraction study by slow diffusion of diethyl ether into a saturated solution of **4a-Y** in tetrahydrofuran at −30 °C under a nitrogen atmosphere. ^{1}H NMR (C_6D_6, 293 K, δ): 8.10 (t, J_{HH} = 8.6 Hz, CH of $PPh_2C_6H_4$, 2H), 7.88 (t, J_{HH} = 8.6 Hz, CH of $PPh_2C_6H_4$, 2H), 7.44 (m, CH of $PPh_2C_6H_4$, Ar-CH of PNP_{iPr}, 2H), 7.24 (m, CH of $PPh_2C_6H_4$, 4H), 7.14 (m, CH of $PPh_2C_6H_4$, 2H), 7.09 (m, Ar-CH of PNP_{iPr}, 2H), 6.96 (d, J_{HH} = 8.6 Hz, Ar-CH of PNP_{iPr}, 2H), 6.91 (m, CH of $PPh_2C_6H_4$, 2H), 6.87 (m, CH of $PPh_2C_6H_4$, 1H), 6.83 (m, d, J_{HH} = 8.6 Hz, Ar-CH of PNP_{iPr}, 1H), 2.18 (m, Me of PNP_{iPr}, CH of *i*Pr, 7H), 2.07 (m, CH of *i*Pr, 1H), 2.00 (m, CH of *i*Pr, 1H), 1.91 (s, Me of C_5Me_5, 15H), 1.75 (m, CH of *i*Pr), 1.32 − 1.20 (m, Me of *i*Pr, 12H), 1.07 (dd, J_{HH} = 7.3 Hz, J_{HP} = 15.53 Hz, Me of *i*Pr, 3H), 0.91 (dd, J_{HH} = 7.3 Hz, J_{HP} = 14.7 Hz, Me of *i*Pr, 3H), 0.74 (s, Me of *t*Bu, 9H), 0.71 (dd, J_{HH} = 6.1 Hz, J_{HP} = 14.1 Hz, Me of *i*Pr, 3H), 0.61 (dd, J_{HH} = 7.3 Hz, J_{HP} = 15.9 Hz, Me of *i*Pr, 3H), −12.91 (m, Ru-H, 2H). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 293 K, δ): 199.1 (dd, J_{CP} = 49.2, 58.5 Hz, Y-C_{Ar}). 162.6 (d, J_{CP} = 21.5 Hz, C_{Ar}), 162.4 (d, J_{CP} = 20.0 Hz, C_{Ar}), 159.8 (d, J_{CP} = 58.5 Hz, C_{Ar}), 145.0 (d, J_{CP} = 29.2 Hz, C_{Ar}), 144.1 (d, J_{CP} = 29.2 Hz, C_{Ar}), 137.6 (d, J_{CP} = 27.7 Hz, C_{Ar}), 135.7 (d, J_{CP} = 12.3 Hz, C_{Ar}), 134.3 (d, J_{CP} = 10.8 Hz, C_{Ar}), 132.8 (d, J_{CP} = 12.3 Hz, C_{Ar}), 132.3 (d, J_{CP} = 30.8 Hz, C_{Ar}), 131.1 (d, J_{CP} = 7.7 Hz, C_{Ar}), 128.4 (C_{Ar}), 127.4 (C_{Ar}), 127.3 (C_{Ar}), 127.2 (d, J_{CP} = 7.7 Hz, C_{Ar}), 127.0 (d, J_{CP} = 7.7 Hz, C_{Ar}), 126.7 (C_{Ar}), 126.0 (C_{Ar}), 125.5 (d, J_{CP} = 3.1 Hz, C_{Ar}), 125.1 (Y-NC), 124.1 (d, J_{CP} = 6.2 Hz, C_{Ar}), 121.5 (d, J_{CP} = 16.9 Hz, C_{Ar}), 121.2 (d, J_{CP} = 6.2 Hz, C_{Ar}), 120.8 (d, J_{CP} = 7.7 Hz, C_{Ar}), 120.2 (d, J_{CP} = 18.5 Hz, C_{Ar}), 87.0 (C_{Ar} of C_5Me_5), 28.1 (CMe_3), 27.2 (CMe_3), 25.7 (d, J_{CP} = 27.7 Hz, *i*Pr), 21.0 (d, J_{CP} = 9.2 Hz, *i*Pr), 20.9 (Me of PNP_{iPr}), 20.8 (m, *i*Pr), 20.2 (d, J_{CP} = 7.7 Hz, *i*Pr), 19.7 (*i*Pr), 19.5 (*i*Pr), 19.4 (m, *i*Pr), 19.3 (*i*Pr), 18.8 (m, *i*Pr), 12.4 (Me of C_5Me_5). ^{31}P NMR (C_6D_6, 293 K, δ): 61.99 (s, $PPh_2C_6H_4$), 7.81 (dd, J_{PP} = 19.8 Hz, J_{YP} = 61.9 Hz, PNP_{iPr}), 6.15 (dd, J_{PP} = 19.8 Hz, J_{YP} = 61.9 Hz, PNP_{iPr}). Anal. Calcd for $C_{59}H_{80}N_2P_3RuY\cdot C_6H_{14}$: C, 65.81; H, 7.99; N, 2.36. Found: C, 65.77; H, 7.64; N, 2.73.

[(PNP_{iPr})Y(μ-H)$_2$(μ-NC*t*BuCH_2PPh_2-κP:κN)Ru(C_5Me_5)] (4b-Y). An NMR tube fitted with a J. Young valve was charged with **2b-Y** (100 mg, 0.105 mmol), pivalonitrile (*t*BuCN, 9 mg, 0.108 mmol), and C_6D_6 (0.8 mL). The reaction mixture was mixed thoroughly at 20 °C. ^{1}H and ^{31}P NMR spectra of the reaction mixture showed full conversion to **4b-Y** in 1 h. The solvent was then removed under reduced pressure. The residue that was obtained was recrystallized in hexanes (1 mL) at −30 °C overnight. A yellow solid was isolated; this was further washed with cold hexanes (2 × 0.5 mL) and dried in vacuo, affording the title complex as a yellow solid. Yield: 59 mg, 54%. Yellow blocks were obtained for an X-ray diffraction study by cooling a saturated solution of **4b-Y** in hexanes at −30 °C under a nitrogen atmosphere. ^{1}H NMR (C_6D_6, 293 K, δ): 8.04 (t, J_{HH} = 7.3 Hz, CH of PPh_2CH_2, 2H), 7.79 (t, J_{HH} = 8.6 Hz, CH of PPh_2CH_2, 2H), 7.45 (m, CH of PPh_2CH_2, 1H), 7.25 (t, J_{HH} = 7.3 Hz, CH of PPh_2CH_2, 2H), 7.21 (t, J_{HH} = 7.3 Hz, Ar-CH of PNP_{iPr}, 2H), 7.11 (t, J_{HH} = 6.1 Hz, CH of PPh_2CH_2, 2H), 7.05 (m, Ar-CH of PNP_{iPr}, 2H), 6.99 (m, Ar-CH of PNP_{iPr}, 1H), 6.92 (d, J_{HH} = 4.9 Hz, CH of PPh_2CH_2, 1H), 6.86 (d, J_{HH} = 7.3 Hz, Ar-CH of PNP_{iPr}, 1H), 3.83 (m, P-CH_2), 2.28 (s, Me of PNP_{iPr}, 3H), 2.15 (s, Me of PNP_{iPr}, 3H), 2.11 (m, CH of *i*Pr, 2H), 1.96 (m, CH of *i*Pr, 1H), 1.84 (m, CH of *i*Pr, 1H), 1.60 (s, Me of C_5Me_5, 15H), 1.60 − 1.47 (m, Me of *i*Pr, 12H), 1.23 (m, Me of *i*Pr, 6H), 1.09 (dd, J_{HH} = 6.1 Hz, J_{HP} = 17.1 Hz, Me of *i*Pr, 6H), 0.98 (s, Me of *t*Bu, 9H), −13.78 (m, Ru-H, 2H). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 293 K, δ): 169.9 (d, J_{CP} = 6.2 Hz, Y-NC), 163.7 (d, J_{CP} = 21.5 Hz, C_{Ar}), 158.2 (d, J_{CP} = 21.5 Hz, C_{Ar}), 143.0 (d, J_{CP} = 15.4 Hz, C_{Ar}), 142.7 (d, J_{CP} = 12.3 Hz, C_{Ar}), 134.3 (d, J_{CP} = 10.8 Hz, C_{Ar}), 134.1 (d, J_{CP} = 10.8 Hz, C_{Ar}), 133.4 (C_{Ar}), 132.7 (d, J_{CP} = 10.8 Hz, C_{Ar}), 132.5 (C_{Ar}), 129.2 (C_{Ar}), 128.0 (C_{Ar}), 127.3 (d, J_{CP} = 7.7 Hz, C_{Ar}), 125.8 (C_{Ar}), 123.7 (C_{Ar}), 121.4 (d, J_{CP} = 16.9 Hz, C_{Ar}), 117.9 (d, J_{CP} = 18.5 Hz, C_{Ar}), 115.9 (d, J_{CP} = 7.7 Hz, C_{Ar}), 87.7 (C_{Ar} of C_5Me_5), 51.0 (d, J_{CP} = 33.8 Hz, P-CH_2), 41.5 (CMe_3), 29.1 (CMe_3), 27.7 (*i*Pr), 25.2 (*i*Pr), 24.9 (*i*Pr), 22.5 (d, J_{CP} = 9.2 Hz, *i*Pr), 21.2 (*i*Pr), 21.1 (Me of PNP_{iPr}), 20.7 (Me of PNP_{iPr}), 20.3 (d, J_{CP} = 9.2 Hz, *i*Pr), 19.9 (d, J_{CP} = 10.8 Hz, *i*Pr), 19.6 (d, J_{CP} = 6.2 Hz, *i*Pr), 19.4 (m, *i*Pr), 19.2 (*i*Pr), 18.7 (d, J_{CP} = 13.8 Hz, *i*Pr), 17.8 (*i*Pr), 13.9 (*i*Pr), 11.9 (Me of C_5Me_5). ^{31}P NMR (C_6D_6, 293 K, δ): 66.61 (s, PPh_2CH_2), 11.34 (dd, J_{PP} = 14.9 Hz, J_{YP} = 75.6 Hz, PNP_{iPr}), 3.04 (dd, J_{PP} = 12.4 Hz, J_{YP} = 69.4 Hz, PNP_{iPr}). Anal. Calcd for $C_{54}H_{78}N_2P_3RuY$: C, 62.48; H, 7.57; N, 2.70. Found: C, 62.31; H, 7.69; N, 2.53.

[(PNP_{iPr})Y(μ-H)$_2$(μ-NC$CH_3CH_2PPh_2$-κP:κN)Ru(C_5Me_5)] (5b-Y-INT). An NMR tube fitted with a J. Young valve was charged with **2b-Y** (20 mg, 0.021 mmol) and acetonitrile (1.1 mL from a 0.019 M solution in C_6D_6, 0.021 mmol). The title complex was observed instantaneously by ^{1}H and ^{31}P NMR upon mixing at 20 °C. Complex **5b-Y-INT** slowly converted to **5b-Y** upon standing at 20 °C in C_6D_6 solution over 2 days. ^{1}H NMR (C_6D_6, 293 K, δ): 7.99 (t, J_{HH} = 8.6 Hz, CH of PPh_2CH_2, 2H), 7.81 (t, J_{HH} = 7.3 Hz, CH of PPh_2CH_2, 2H), 7.46 (m, CH of PPh_2CH_2, 1H), 7.28 (t, J_{HH} = 7.3 Hz, CH of PPh_2CH_2, 2H), 7.22 (t, J_{HH} = 8.6 Hz, Ar-CH of PNP_{iPr}, 2H), 7.07 (m, CH of PPh_2CH_2, Ar-CH of PNP_{iPr}, 4H), 6.99 (m, Ar-CH of PNP_{iPr}, 1H), 6.94 (d, J_{HH} = 3.4 Hz, CH of PPh_2CH_2, 1H), 6.88 (d, J_{HH} = 8.6 Hz, Ar-CH of PNP_{iPr}, 1H), 3.96 (t, J_{HP} = 11.0 Hz, P−CH_2, 1H), 3.61 (t, J_{HP} = 11.0 Hz, P-CH_2, 1H), 2.28 (s, Me of PNP_{iPr}, 3H), 2.17 (s, Me of PNP_{iPr}, 3H), 2.13 (m, CH of *i*Pr, 2H), 1.98 (m, CH of *i*Pr, 1H), 1.84 (m, CH of *i*Pr, 1H), 1.60 (s, Me of C_5Me_5, 15H), 1.56 (s, Me of CH_3CN, 3H), 1.35 (dd, J_{HH} = 6.1 Hz, J_{HP} = 15.9 Hz, Me of *i*Pr, 3H), 1.24 (m, Me of *i*Pr, 6H), 1.17 (dd, J_{HH} = 7.3 Hz, J_{HP} = 12.3 Hz, Me of *i*Pr, 6H), 1.10 (dd, J_{HH} = 6.1 Hz, J_{HP} = 12.8 Hz, Me of *i*Pr, 3H), 1.07 (dd, J_{HH} = 7.3 Hz, J_{HP} = 13.5 Hz, Me of *i*Pr, 3H), 0.98 (dd, J_{HH} = 7.3 Hz, J_{HP} = 12.2 Hz, Me of *i*Pr, 3H), −13.52 (t, J_{HP} = 25.7 Hz, Ru-H, 1H), −13.72 (t, J_{HP} = 26.9 Hz, Ru-H, 1H). ^{31}P NMR (C_6D_6, 293 K, δ): 66.92 (t, J_{PP} = 19.8 Hz, PPh_2CH_2), 12.18 (dd, J_{PP} = 17.3 Hz, J_{YP} = 76.8 Hz, PNP_{iPr}), 3.63 (dd, J_{PP} = 14.9 Hz, J_{YP} = 69.4 Hz, PNP_{iPr}).

[(PNP_{iPr})Y(μ-H)$_2$(μ-HNC(CH_2)CH_2PPh_2-κP:κN)Ru(C_5Me_5)] (5b-Y). An NMR tube fitted with a J. Young valve was charged with **2b-Y** (70 mg, 0.073 mmol), acetonitrile (3 mg, 0.073 mmol), and C_6D_6 (0.6 mL). The title complex was observed by ^{1}H and ^{31}P NMR upon instant mixing of the reaction solution at 20 °C. The solvent was then removed under reduced pressure. A yellow-brown solid was isolated and dried in vacuo. Yield: 73 mg, 99%. ^{1}H NMR (C_6D_6, 293 K, δ): 7.91 (t, J_{HH} = 9.8 Hz, CH of PPh_2CH_2, 2H), 7.86 (t, J_{HH} = 9.8 Hz, CH of PPh_2CH_2, 2H), 7.81 (m, CH of PPh_2CH_2, 1H), 7.39 (m, Ar-CH of PNP_{iPr}, 1H), 7.26 (m, CH of PPh_2CH_2, Ar-CH of PNP_{iPr}, 4H), 7.14 (m, CH_2 of PPh_2CH_2, 1H), 7.05 (m, Ar-CH of PNP_{iPr}, 1H), 7.03 (m, CH of PPh_2CH_2, 1H), 6.93 (m, Ar-CH of PNP_{iPr}, 1H), 6.85 (m, CH of PPh_2CH_2, Ar-CH of PNP_{iPr}, 2H), 5.44 (s, NH, 1H), 3.98 (d, J_{HP} = 7.3 Hz, P-CH_2, 2H), 3.59 (s, $NC{=}CH_2$, 1H), 3.45 (s, $HNC{=}CH_2$, 1H), 2.25 (s, Me of PNP_{iPr}, 3H), 2.22 (m, CH of *i*Pr, 1H), 2.13 (s, Me of PNP_{iPr}, 3H), 2.09 (m, CH of *i*Pr, 2H), 1.98 (m, CH of *i*Pr, 1H), 1.60 (s, Me of C_5Me_5, 15H), 1.58 (m, Me of *i*Pr, 3H), 1.51 (dd, J_{HH} = 7.3, 8.1 Hz, J_{HP} = 16.7 Hz, Me of *i*Pr, 3H), 1.23 (dd, J_{HH} = 6.1, 7.3 Hz, J_{HP} = 15.3 Hz, Me of *i*Pr, 3H), 1.18 (dd, J_{HH} = 6.1, 7.3 Hz, J_{HP} = 10.4 Hz, Me of *i*Pr, 3H), 1.10 (dd, J_{HH} = 6.1, 7.3 Hz, J_{HP} = 15.3 Hz, Me of *i*Pr, 3H), 1.00 (dd, J_{HH} = 6.1, 7.3 Hz, J_{HP} = 15.3 Hz, Me of *i*Pr, 3H), 0.92 (dd, J_{HH} = 7.3 Hz, J_{HP} = 14.7 Hz, Me of *i*Pr, 3H), 0.84 (dd, J_{HH} = 7.3, 7.8 Hz, J_{HP} = 12.0 Hz, Me of *i*Pr, 3H). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 293 K, δ): 163.6 (d, J_{CP} = 25.9 Hz, C_{Ar}), 158.6 (m, C_{Ar}) 153.8 (Y-HNC), 146.5 (C_{Ar}), 141.8 (m, C_{Ar}), 134.2 (m, C_{Ar}), 133.1 (d, J_{CP} = 8.6 Hz, C_{Ar}), 132.9 (m, C_{Ar}), 132.7 (d, J_{CP} = 10.5 Hz, C_{Ar}), 128.1 (C_{Ar}), 127.8 (C_{Ar}), 127.2 (m, C_{Ar}), 125.0 (m, C_{Ar}), 124.3 (C_{Ar}), 121.3 (d, J_{CP} = 15.3 Hz, C_{Ar}), 117.3 (C_{Ar}), 117.1 (m, C_{Ar}), 88.0 (C_{Ar} of C_5Me_5), 81.0 (d, J_{CP} = 3.8 Hz, $HNC{=}CH_2$), 55.0 (d, J_{CP} = 23.0 Hz, P-CH_2), 25.1 (d, J_{CP} = 23.0 Hz, *i*Pr), 22.1 (d, J_{CP} = 9.6 Hz, *i*Pr), 21.0 (Me of PNP_{iPr}), 20.6 (m, Me of PNP_{iPr}, *i*Pr), 20.4 (d, J_{CP} = 8.6 Hz, *i*Pr), 19.7 (d, J_{CP} = 11.5 Hz, *i*Pr), 19.5 (m, *i*Pr), 19.2 (d, J_{CP} = 6.7 Hz, *i*Pr), 19.0 (d, J_{CP} = 11.5 Hz, *i*Pr), 18.6 (*i*Pr), 17.7 (*i*Pr), 11.9 (Me of C_5Me_5). ^{31}P NMR (C_6D_6, 293 K, δ): 56.16 (d, J_{PP} = 9.9 Hz, PPh_2CH_2), 9.90 (dd, J_{PP} = 14.9, 17.3 Hz, J_{YP} = 70.6 Hz, PNP_{iPr}), 2.77 (dd, J_{PP} = 14.9, 17.3 Hz, J_{YP} = 68.1 Hz, PNP_{iPr}). Anal. Calcd for $C_{51}H_{72}N_2P_3RuY$: C, 61.50; H, 7.29; N, 2.81. Found: C, 61.85; H, 7.42; N, 2.83.

[(PNP_{iPr})Y(μ-H)$_2$(μ-$NCC_6H_5CH_2PPh_2$-κP:κN)Ru(C_5Me_5)] (6b-Y-INT) and [(PNP_{iPr})Y(μ-H)$_2$(μ-$HNC_6H_5CHPPh_2$-κP:κN)Ru(C_5Me_5)] (6b-Y). An NMR tube fitted with a J. Young valve was charged with **2b-Y** (75 mg, 0.079 mmol), benzonitrile (8.1 mg, 0.079 mmol), and C_6D_6 (0.8 mL). Formation of **6b-Y-INT** was observed by ^{1}H, ^{31}P, and ^{13}C NMR upon instant mixing of the reaction solution at 20 °C. This slowly converted to **6b-Y**, along with small quantities of unidentified byproducts, upon standing at 20 °C in C_6D_6 solution for 2 days, as observed by ^{1}H and ^{31}P NMR. The solvent was then removed under reduced pressure, and the residue that was obtained was recrystallized in hexanes (1 mL) at −30 °C. This afforded an orange crystalline solid, which was isolated, washed with cold hexanes (2 × 0.5 mL), and dried in vacuo, giving complex **6b-Y**. Yield: 56 mg, 67%. Yellow blocks of **6b-Y** were obtained for an X-ray diffraction study by slow diffusion of hexanes into a saturated solution of **6b-Y** in benzene at −30 °C under a nitrogen atmosphere.

6b-Y-INT. ^{1}H NMR (C_6D_6, 293 K, δ): 7.85 (m, CH of PPh_2CH_2, 2H), 7.78 (m, CH of PPh_2CH_2, 2H), 7.64 (m, CH of PPh_2CH_2, 2H), 7.48 (m, CH of PPh_2CH_2, 1H), 7.04 (m, CH of PPh_2CH_2, Ar-CH of PNP_{iPr}, CH of PhCN, 10H), 6.93 (m, Ar-CH of PNP_{iPr}, 1H), 6.89 (m, Ar-CH of PNP_{iPr}, 1H), 6.81 (m, Ar-CH of PNP_{iPr},1H), 6.67 (m, Ar-CH of PNP_{iPr}, 1H), 4.53 (t, J_{HP} = 8.6 Hz, P−CH_2, 1H), 4.22 (t, J_{HP} = 8.6 Hz, P−CH_2, 1H), 2.28 (s, Me of PNP_{iPr}, 3H), 2.16 (s, Me of PNP_{iPr}, 3H), 2.08 (m, CH of *i*Pr, 2H), 1.98 (m, CH of *i*Pr, 1H), 1.85 (m, CH of *i*Pr, 1H), 1.66 (s, Me of C_5Me_5, 15H), 1.59 (dd, J_{HH} = 4.9 Hz, J_{HP} = 15.9 Hz, Me of *i*Pr, 3H), 1.50 (dd, J_{HH} = 6.1 Hz, J_{HP} = 12.8 Hz, Me of *i*Pr, 3H), 1.24 (m, Me of *i*Pr, 6H), 1.14 (m, Me of *i*Pr, 3H), 1.06 (m, Me of *i*Pr, 6H), 0.97 (m, Me of *i*Pr, 3H), −13.43 (t, J_{HP} = 25.7 Hz, Ru-H, 1H), −13.63 (t, J_{HP} = 24.5 Hz, Ru-H, 1H). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 293 K, δ): 178.8 (Y-NC), 163.6 (d, J_{CP} = 22.0 Hz, C_{Ar}), 161.5 (d, J_{CP} = 4.8 Hz, C_{Ar}), 158.6 (d, J_{CP} = 20.1 Hz, C_{Ar}), 143.3 (d, J_{CP} = 29.7 Hz, C_{Ar}), 142.8 (C_{Ar}), 141.2 (d, J_{CP} = 27.8 Hz, C_{Ar}), 134.6 (d, J_{CP} = 11.5 Hz, C_{Ar}), 133.4 (d, J_{CP} = 9.6 Hz, C_{Ar}), 132.9 (C_{Ar}), 132.6 (d, J_{CP} = 5.8 Hz, C_{Ar}), 132.1 (C_{Ar}), 129.0 (d, J_{CP} = 10.5 Hz, C_{Ar}), 128.2 (C_{Ar}), 127.8 (d, J_{CP} = 13.4 Hz, C_{Ar}), 127.5 (C_{Ar}), 127.4 (d, J_{CP} = 7.7 Hz, C_{Ar}), 127.1 (d, J_{CP} = 8.6 Hz, C_{Ar}), 125.6 (m, C_{Ar}), 124.0 (C_{Ar}), 121.5 (d, J_{CP} = 16.3 Hz, C_{Ar}), 119.4 (C_{Ar}), 117.8 (d, J_{CP} = 19.2 Hz, C_{Ar}), 116.3 (d, J_{CP} = 6.7 Hz, C_{Ar}), 112.3 (C_{Ar}), 87.8 (C_{Ar} of C_5Me_5), 54.1 (d, J_{CP} = 28.8 Hz, P-CH_2), 25.2 (m, *i*Pr), 22.6 (d, J_{CP} = 15.3 Hz, *i*Pr), 21.0 (d, J_{CP} = 7.7 Hz, *i*Pr), 20.9 (m, *i*Pr), 20.7 (Me of PNP_{iPr}), 20.3 (d, J_{CP} = 8.6 Hz, *i*Pr), 19.7 (m, *i*Pr), 19.6 (m, *i*Pr), 19.3 (d, J_{CP} = 7.7 Hz, *i*Pr), 19.0 (d, J_{CP} = 9.6 Hz, *i*Pr), 17.9 (*i*Pr), 12.0 (Me of C_5Me_5). ^{31}P NMR (C_6D_6, 293 K, δ): 68.63 (s, PPh_2CH_2), 11.59 (dd, J_{PP} = 12.4 Hz, J_{YP} = 76.8 Hz, PNP_{iPr}), 3.08 (dd, J_{PP} = 12.4 Hz, J_{YP} = 69.4 Hz, PNP_{iPr}).

6b-Y. ^{1}H NMR (C_6D_6, 293 K, δ): 8.38 (t, J_{HH} = 8.8 Hz, CH of PPh_2CH, 2H), 7.89 (t, J_{HH} = 8.6 Hz, CH of PPh_2CH, 2H), 7.30 (m, CH of PPh_2CH, Ar-CH of PNP_{iPr}, CH of PhCN, 7H), 7.24 (t, J_{HH} = 7.3 Hz, CH of PPh_2CH, 1H), 7.13 (t, J_{HH} = 7.0 Hz, CH of PhCN, 1H), 7.06 − 7.01 (m, CH of PPh_2CH, Ar-CH of PNP_{iPr}, 4H), 6.94 (m, Ar-CH of PNP_{iPr}, CH of PhCN, 4H), 5.11 (s, NH), 4.88 (m, P-$CH{=}$CPhNH, 1H), 2.35 (m, CH of *i*Pr, 1H), 2.24 (s, Me of PNP_{iPr}, 3H), 2.19 (s, Me of PNP_{iPr}, 3H), 2.14 (m, CH of *i*Pr, H), 2.03 (m, CH of *i*Pr, 2H), 1.78 (s, Me of C_5Me_5, 15H), 1.48 (dd, J_{HH} = 7.3 Hz, J_{HP} = 14.7 Hz, Me of *i*Pr, 6H), 1.30 − 1.21 (m, Me of *i*Pr, 6H), 1.09 (dd, J_{HH} = 6.1, 7.3 Hz, J_{HP} = 15.3 Hz, Me of *i*Pr, 3H), 0.95 (m, Me of *i*Pr, 3H), 0.85 (dd, J_{HH} = 6.1, 7.3 Hz, J_{HP} = 15.3 Hz, Me of *i*Pr, 3H), 0.77 (dd, J_{HH} = 7.3 Hz, J_{HP} = 9.8 Hz, Me of *i*Pr, 3H), −12.53 (t, J_{HP} = 23.2 Hz, Ru-H, 1H), −13.09 (t, J_{HP} = 24.5 Hz, Ru-H, 1H). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 293 K, δ): 162.0 (d, J_{CP} = 21.1 Hz, C_{Ar}), 160.9 (d, J_{CP} = 20.1 Hz, C_{Ar}), 160.0 (P−CH=CPhNH), 145.9 (d, J_{CP} = 35.5 Hz, C_{Ar}), 143.0 (d, J_{CP} = 2.9 Hz, C_{Ar}), 140.3 (d, J_{CP} = 34.5 Hz, C_{Ar}), 136.1 (d, J_{CP} = 14.4 Hz, C_{Ar}), 132.7 (C_{Ar}), 132.3 (d, J_{CP} = 23.0 Hz, C_{Ar}), 131.9 (d, J_{CP} = 9.6 Hz, C_{Ar}), 129.4 (C_{Ar}), 128.6 (C_{Ar}), 128.3 (C_{Ar}), 128.1 (C_{Ar}), 127.7 (d, J_{CP} = 8.6 Hz, C_{Ar}), 127.3 (d, J_{CP} = 12.5 Hz, C_{Ar}), 126.7 (d, J_{CP} = 9.6 Hz, C_{Ar}), 125.7 (d, J_{CP} = 1.9 Hz, C_{Ar}), 121.9 (d, J_{CP} = 5.8 Hz, C_{Ar}), 121.2 (d, J_{CP} = 17.3 Hz, C_{Ar}), 120.3 (d, J_{CP} = 5.8 Hz, C_{Ar}), 118.6 (d, J_{CP} = 18.2 Hz, C_{Ar}), 87.5 (C_{Ar} of C_5Me_5), 80.2 (d, J_{CP} = 28.8 Hz, P-CH═CPhNH), 25.6 (*i*Pr), 24.5 (*i*Pr), 21.3 (d, J_{CP} = 6.7 Hz, *i*Pr), 20.8 (d, J_{CP} = 8.6 Hz, *i*Pr), 20.7 (Me of PNP_{iPr}), 19.8 (d, J_{CP} = 7.7 Hz, *i*Pr), 19.7 (d, J_{CP} = 8.6 Hz, *i*Pr), 19.5 (*i*Pr), 19.4 (d, J_{CP} = 7.7 Hz, *i*Pr), 18.9 (*i*Pr), 18.4 (d, J_{CP} = 11.5 Hz, *i*Pr), 17.3 (*i*Pr), 11.9 (Me of C_5Me_5). ^{31}P NMR (C_6D_6, 293 K, δ): 65.11 (s, PPh_2CH_2), 3.12 (dd, J_{PP} = 9.9 Hz, J_{YP} = 64.4 Hz, PNP_{iPr}), 2.53 (dd, J_{PP} = 9.9 Hz, J_{YP} = 74.3 Hz, PNP_{iPr}). Anal. Calcd for $C_{56}H_{74}N_2P_3RuY$: C, 63.57; H, 7.05; N, 2.65. Found: C, 63.92; H, 7.26; N, 2.33.

[(PNP_{iPr})Y(μ-H)$_2$(μ-$CH_3NCPhCH_2PPh_2$-κP:κN)Ru(C_5Me_5)] (7b-Y). An NMR tube fitted with a J. Young valve was charged with **2b-Y** (75 mg, 0.079 mmol), *N*-benzylidenemethylamine (9.4 mg, 0.079 mmol), and C_6D_6 (0.6 mL). Formation of **7b-Y** was observed by ^{1}H and ^{31}P NMR upon instant mixing of the reaction solution at 20 °C. The solvent was then removed under reduced pressure. The residue that was obtained was recrystallized in hexanes (1 mL) at −30 °C overnight. The yellow solid that separated from the mother liquid was isolated, washed with cold hexanes (2 × 0.5 mL), and dried in vacuo to give a yellow powder. Yield: 60 mg, 71%. Yellow plates of **7b-Y** were obtained as a diethyl ether solvate for an X-ray diffraction study by slow diffusion of diethyl ether into a saturated solution of **7b-Y** in tetrahydrofuran at −30 °C under a nitrogen atmosphere. ^{1}H NMR (C_6D_6, 293 K, δ): 8.14 (t, J_{HH} = 7.3 Hz, CH of PPh_2CH_2, 2H), 7.55 (t, J_{HH} = 7.3 Hz, CH of PPh_2CH_2, 2H), 7.36 (t, J_{HH} = 7.3 Hz, CH of PPh_2CH_2, 2H), 7.30 (d, J_{HH} = 6.1 Hz, CH of PPh_2CH_2, 1H), 7.24 (m, CH of PPh_2CH_2, Ar-CH of PhCHNMe, 2H), 7.18 (m, Ar-CH of PhCHNMe, Ar-CH of PNP_{iPr}, 2H), 7.12−7.08 (m, CH of PPh_2CH_2, Ar-CH of PhCHNMe, Ar-CH of PNP_{iPr}, 4H), 7.04 (d, J_{HH} = 6.1 Hz, Ar-CH of PNP_{iPr}, 1H), 6.99 (m, Ar-CH of PNP_{iPr}, 1H), 6.96 (m, Ar-CH of PNP_{iPr}, 2H), 6.86 (d, J_{HH} = 4.9 Hz, Ar-CH of PhCHNMe, 1H), 6.81 (d, J_{HH} = 8.6 Hz, Ar-CH of PhCHNMe, 1H), 3.72 (m, P−CH_2, 2H), 3.22 (m, PhC*H*NMe, 1H), 2.33 (m, CH of *i*Pr, 2H), 2.22 (s, Me of PNP_{iPr}, 3H), 2.17 (m, CH of *i*Pr, 1H), 2.07 (s, Me of PNP_{iPr}, 3H), 2.05 (s, PhCHN*Me*, 1H), 1.82 (m, CH of *i*Pr, 1H), 1.66 (s, Me of C_5Me_5, 15H), 1.64 (m, Me of *i*Pr, 3H), 1.55 (m, Me of *i*Pr, 6H), 1.47 (dd, J_{HH} = 7.3 Hz, J_{HP} = 14.7 Hz, Me of *i*Pr, 3H), 1.12 (dd, J_{HH} = 7.3 Hz, J_{HP} = 14.7 Hz, Me of *i*Pr, 3H), 1.04 (dd, J_{HH} = 8.6 Hz, J_{HP} = 15.9 Hz, Me of *i*Pr, 6H), 0.90 (m, Me of *i*Pr, 3H), −13.13 (t, J_{HP} = 24.5 Hz, Ru-H, 1H), −13.30 (t, J_{HP} = 28.1 Hz, Ru-H, 1H). $^{13}C\{^{1}H\}$

NMR (C_6D_6, 293 K, δ): 162.8 (d, J_{CP} = 21.2 Hz, C_{Ar}), 162.6 (d, J_{CP} = 17.3 Hz, C_{Ar}), 148.7 (m, C_{Ar}), 146.6 (m, C_{Ar}), 137.2 (d, J_{CP} = 15.4 Hz, C_{Ar}), 136.9 (m, C_{Ar}), 133.4 (C_{Ar}), 132.8 (C_{Ar}), 132.3 (C_{Ar}), 131.5 (m, C_{Ar}), 131.3 (d, J_{CP} = 9.6 Hz, C_{Ar}), 129.2 (C_{Ar}), 128.4 (C_{Ar}), 128.0 (C_{Ar}), 127.5 (d, J_{CP} = 7.7 Hz, C_{Ar}), 127.4 (C_{Ar}), 127.2 (d, J_{CP} = 9.6 Hz, C_{Ar}), 127.1 (C_{Ar}), 126.1 (C_{Ar}), 125.7 (C_{Ar}), 124.3 (C_{Ar}), 121.4 (m, C_{Ar}), 121.1 (d, J_{CP} = 5.8 Hz, C_{Ar}) 118.8 (d, J_{CP} = 15.4 Hz, C_{Ar}), 116.9 (d, J_{CP} = 15.4 Hz, C_{Ar}), 87.9 (C_{Ar} of C_5Me_5), 67.1 (PhCHNMe), 56.1 (d, J_{CP} = 19.3 Hz, P-CH_2), 36.5 (PhCHN*Me*), 25.1 (*i*Pr), 24.2 (*i*Pr), 21.6 (d, J_{CP} = 9.6 Hz, *i*Pr), 20.9 (d, J_{CP} = 13.5 Hz, *i*Pr), 20.8 (Me of PNP_{iPr}), 20.7 (Me of PNP_{iPr}), 20.5 (d, J_{CP} = 9.5 Hz, *i*Pr), 20.0 (d, J_{CP} = 11.6 Hz, *i*Pr), 19.6 (d, J_{CP} = 11.6 Hz, *i*Pr), 19.2 (d, J_{CP} = 13.5 Hz, *i*Pr), 19.1 (d, J_{CP} = 9.6 Hz, *i*Pr), 16.7 (d, J_{CP} = 3.9 Hz, *i*Pr), 16.3 (, J_{CP} = 5.8 Hz, *i*Pr), 12.1 (Me of C_5Me_5). ^{31}P NMR (C_6D_6, 293 K, δ): 55.16 (s, PPh_2CH_2), 6.54 (dd, J_{PP} = 19.8, 22.3 Hz, J_{YP} = 68.1 Hz, PNP_{iPr}), 4.81 (dd, J_{PP} = 19.8, 22.3 Hz, J_{YP} = 68.1 Hz, PNP_{iPr}). Anal. Calcd for $C_{57}H_{78}N_2P_3RuY \cdot 0.5\ C_6H_{14}$: C, 64.50; H, 7.67; N, 2.51. Found: C, 64.51; H, 7.59; N, 2.25.

[(PNP_{iPr})Y(μ-H)$_2$(μ-*t*BuNCCH$_2$PPh$_2$-κ*P*:η^2-*NC*)Ru(C_5Me_5)] (8b-Y). An NMR tube fitted with a J. Young valve was charged with **2b-Y** (80 mg, 0.084 mmol), *tert*-butyl isocyanide (7 mg, 0.084 mmol), and C_6D_6 (0.6 mL). Formation of **8b-Y** was observed by ^{1}H and ^{31}P NMR upon instant mixing of the reaction solution at 20 °C. The solvent was then removed under reduced pressure. The residue that was obtained was recrystallized in hexanes (1 mL) at −30 °C overnight. The yellow solid that separated from the mother liquid was isolated, washed with cold hexanes (2 × 0.5 mL), and dried in vacuo to give a yellow powder. Yield: 56 mg, 64%. Suitable crystals for an X-ray diffraction study were obtained by cooling a saturated solution of **8b-Y** in hexanes at −30 °C under a nitrogen atmosphere. ^{1}H NMR (C_6D_6, 293 K, δ): 8.09 (t, J_{HH} = 7.3 Hz, CH of PPh_2CH_2, 2H), 7.96 (t, J_{HH} = 8.6 Hz, CH of PPh_2CH_2, 2H), 7.59 (m, CH of PPh_2CH_2, 1H), 7.26 (m, CH of PPh_2CH_2, Ar-CH of PNP_{iPr}, 4H), 7.10 (m, CH of PPh_2CH_2, Ar-CH of PNP_{iPr}, 5H), 6.92 (m, Ar-CH of PNP_{iPr}, 2H), 4.88 (m, P-CH_2, 2H), 2.31 (s, Me of PNP_{iPr}, 3H), 2.19 (s, Me of PNP_{iPr}, 3H), 2.17 (m, CH of *i*Pr, 1H), 2.07 (m, CH of *i*Pr, H), 1.98 (m, CH of *i*Pr, 1H), 1.92 (m, CH of *i*Pr, 1H), 1.68 (dd, J_{HH} = 7.3 Hz, J_{HP} = 15.9 Hz, Me of *i*Pr, 3H), 1.59 (s, Me of C_5Me_5, 15H), 1.46 (dd, J_{HH} = 7.3 Hz, J_{HP} = 17.1 Hz, Me of *i*Pr, 3H), 1.25 (dd, J_{HH} = 6.1 Hz, J_{HP} = 10.7 Hz, Me of *i*Pr, 3H), 1.14 (dd, J_{HH} = 6.1 Hz, J_{HP} = 14.7 Hz, Me of *i*Pr, 3H), 1.09 (m, Me of *i*Pr, 3H), 1.06 (s, Me of *t*Bu, 9H), 0.93 (dd, J_{HH} = 7.3 Hz, J_{HP} = 13.5 Hz, Me of *i*Pr, 3H), 0.89 (m, Me of *i*Pr, 3H), 0.81 (dd, J_{HH} = 7.3 Hz, J_{HP} = 15.3 Hz, Me of *i*Pr, 3H), −13.65 (t, J_{HP} = 25.7 Hz, Ru-H, 1H), −14.21 (t, J_{HP} = 19.6 Hz, Ru-H, 1H). ^{13}C{^{1}H} NMR (C_6D_6, 293 K, δ): 271.8 (d, J_{YC} = 40.5 Hz, Y-η^2-CN*t*Bu), 164.7 (d, J_{CP} = 15.3 Hz, C_{Ar}), 158.9 (d, J_{CP} = 20.1 Hz, C_{Ar}), 150.1 (d, J_{CP} = 12.5 Hz, C_{Ar}), 145.0 (d, J_{CP} = 24.0 Hz, C_{Ar}), 141.4 (d, J_{CP} = 25.9 Hz, C_{Ar}), 136.8 (d, J_{CP} = 12.5 Hz, C_{Ar}), 133.2 (d, J_{CP} = 10.5 Hz, C_{Ar}), 133.0 (C_{Ar}), 132.8 (d, J_{CP} = 9.6 Hz, C_{Ar}), 132.7 (C_{Ar}), 132.5 (d, J_{CP} = 9.6 Hz, C_{Ar}), 129.0 (C_{Ar}), 128.7 (d, J_{CP} = 9.6 Hz, C_{Ar}), 128.4 (C_{Ar}), 127.6 (C_{Ar}), 127.5 (d, J_{CP} = 4.8 Hz, C_{Ar}), 127.2 (C_{Ar}), 127.0 (d, J_{CP} = 8.6 Hz, C_{Ar}), 126.3 (d, J_{CP} = 4.8 Hz, C_{Ar}), 123.2 (d, J_{CP} = 2.9 Hz, C_{Ar}), 119.6 (C_{Ar}), 119.4 (C_{Ar}), 115.9 (d, J_{CP} = 6.7 Hz, C_{Ar}), 86.8 (C_{Ar} of C_5Me_5), 55.7 (CMe_3), 57.3 (d, J_{CP} = 35.5 Hz, P−CH_2), 31.0 (C*Me*$_3$), 25.4 (*i*Pr), 25.0 (*i*Pr), 23.3 (d, J_{CP} = 8.6 Hz, *i*Pr), 21.2 (d, J_{CP} = 10.5 Hz, *i*Pr), 20.9 (Me of PNP_{iPr}), 20.8 (Me of PNP_{iPr}), 20.6 (d, J_{CP} = 7.7 Hz, *i*Pr), 20.5 (d, J_{CP} = 10.5 Hz, *i*Pr), 19.9 (d, J_{CP} = 7.7 Hz, *i*Pr), 19.8 (d, J_{CP} = 11.5 Hz, *i*Pr), 19.2 (d, J_{CP} = 9.6 Hz, *i*Pr), 18.8 (d, J_{CP} = 10.5 Hz, *i*Pr), 18.3 (*i*Pr), 17.3 (m. *i*Pr), 12.4 (*i*Pr), 11.8 (Me of C_5Me_5). ^{31}P NMR (C_6D_6, 293 K, δ): 68.00 (t, J_{PP} = 17.3 Hz, PPh_2CH_2), 9.04 (dd, J_{PP} = 9.9, 12.4 Hz, J_{YP} = 68.1 Hz, PNP_{iPr}), 4.64 (dd, J_{PP} = 9.9, 12.4 Hz, J_{YP} = 65.6 Hz, PNP_{iPr}). IR (Nujol, cm^{-1}): 1974 (w, Ru-H stretch), 1541, (m, N═C stretch). Anal. Calcd for $C_{54}H_{78}N_2P_3RuY$: C, 62.48; H, 7.57; N, 2.70. Found: C, 62.18; H, 7.57; N, 2.31.

[(PNP_{iPr})Y(μ-H)$_2$(μ-Rh(C_5Me_5)(CO)COCH$_2$PPh$_2$κ*P*:κ*O*)Ru(C_5Me_5)] (9b-Y). An NMR tube fitted with a J. Young valve was charged with **2b-Y** (84 mg, 0.088 mmol), Rh(C_5Me_5)(CO)$_2$ (26 mg, 0.088 mmol), and C_6D_6 (0.8 mL). The reaction mixture was mixed thoroughly at 20 °C. ^{1}H and ^{31}P NMR spectra of the reaction mixture showed full conversion to **9b-Y** in 1 h. The solvent was then removed under reduced pressure. The residue that was obtained was recrystallized in hexanes (1 mL) at −30 °C overnight. The orange-red solid that separated from the mother liquid was isolated, washed with cold hexanes (2 × 0.5 mL), and dried in vacuo to afford the title complex. Yield: 70 mg, 64%. Orange-red blocks of **9b-Y** were obtained for an X-ray diffraction study by cooling a saturated solution of **9b-Y** in hexanes at −30 °C under a nitrogen atmosphere. ^{1}H NMR (C_6D_6, 293 K, δ): 8.12 (t, J_{HH} = 7.3 Hz, CH of PPh_2CH_2, 2H), 7.65 (t, J_{HH} = 7.3 Hz, CH of PPh_2CH_2, 2H), 7.49 (m, CH of PPh_2CH_2, 1H), 7.35 (t, J_{HH} = 6.1 Hz, CH of PPh_2CH_2, Ar-CH of PNP_{iPr}, 2H), 7.24 (t, J_{HH} = 7.3 Hz, CH of PPh_2CH_2, 1H), 7.17 (m, CH of PPh_2CH_2, Ar-CH of PNP_{iPr}, 2H), 7.08 (m, CH of PPh_2CH_2, Ar-CH of PNP_{iPr}, 2H), 7.01 (m, Ar-CH of PNP_{iPr}, 1H), 6.90 (m, Ar-CH of PNP_{iPr}, 1H), 6.87 (m, CH of PPh_2CH_2, Ar-CH of PNP_{iPr}, 2H), 5.00 (m, P-CH_2, 1H), 3.99 (t, J_{HP} = 12.2 Hz, P-CH_2, 1H), 2.26 (s, Me of PNP_{iPr}, 3H), 2.13 (s, Me of PNP_{iPr}, 3H), 2.06 (m, CH of *i*Pr, 3H), 2.00 (s, Me of (C_5Me_5)Rh, 15H), 1.85 (m, CH of *i*Pr, 1H), 1.53 (s, Me of (C_5Me_5)Ru, 15H), 1.49 (m, Me of *i*Pr, 3H), 1.39 (dd, J_{HH} = 6.1, 7.3 Hz, J_{HP} = 15.3 Hz, Me of *i*Pr, 3H), 1.25 (m, Me of *i*Pr, 3H), 1.19−1.13 (m, Me of *i*Pr, 6H), 1.06 (dd, J_{HH} = 6.1, 7.3 Hz, J_{HP} = 15.3 Hz, Me of *i*Pr, 3H), 0.95 (dd, J_{HH} = 7.3 Hz, J_{HP} = 15.9 Hz, Me of *i*Pr, 3H), 0.83 (dd, J_{HH} = 6.3, 7.3 Hz, J_{HP} = 11.6 Hz, Me of *i*Pr, 3H), −13.28 (t, J_{HP} = 26.9 Hz, Ru-H, 1H), −13.52 (t, J_{HP} = 26.9 Hz, Ru-H, 1H). ^{13}C{^{1}H} NMR (C_6D_6, 293 K, δ): 280.1 (d, J_{RhC} = 56.9 Hz, Y-OC=Rh), 199.8 (d, J_{RhC} = 104.6 Hz, Rh−CO), 162.7 (d, J_{CP} = 20.0 Hz, C_{Ar}), 155.8 (d, J_{CP} = 18.5 Hz, C_{Ar}), 144.6 (d, J_{CP} = 30.8 Hz, C_{Ar}), 135.5 (m, C_{Ar}), 133.3 (m, C_{Ar}), 133.0 (C_{Ar}), 132.2 (d, J_{CP} = 9.2 Hz, C_{Ar}), 130.8 (C_{Ar}), 128.8 (C_{Ar}), 128.3 (C_{Ar}), 128.0 (d, J_{CP} = 11.6 Hz, C_{Ar}), 127.6 (d, J_{CP} = 7.7 Hz, C_{Ar}), 127.4 (C_{Ar}), 127.2 (d, J_{CP} = 9.2 Hz, C_{Ar}), 126.8 (m, C_{Ar}), 124.6 (C_{Ar}), 119.5 (d, J_{CP} = 15.4 Hz, C_{Ar}), 117.8 (d, J_{CP} = 20.0 Hz, C_{Ar}) 115.5 (d, J_{CP} = 7.7 Hz, C_{Ar}), 98.5 (C_{Ar} of (C_5Me_5)Rh), 88.5 (C_{Ar} of (C_5Me_5)Ru), 76.3 (m, P−CH_2), 25.5 (d, J_{CP} = 6.2 Hz, *i*Pr), 24.9 (*i*Pr), 23.3 (d, J_{CP} = 10.8 Hz, *i*Pr), 21.1 (*i*Pr), 20.8 (Me of PNP_{iPr}), 20.6 (d, J_{CP} = 7.7 Hz, *i*Pr), 20.3 (d, J_{CP} = 6.2 Hz, *i*Pr), 20.1 (d, J_{CP} = 7.7 Hz, *i*Pr), 19.6 (m, *i*Pr), 19.5 (*i*Pr), 19.3 (*i*Pr), 19.1 (d, J_{CP} = 10.8 Hz, *i*Pr), 18.1 (*i*Pr), 11.7 (Me of (C_5Me_5)Ru), 11.2 (Me of (C_5Me_5)Rh). ^{31}P NMR (C_6D_6, 293 K, δ): 58.59 (s, PPh_2CH_2), 11.58 (d, J_{YP} = 81.7 Hz, PNP_{iPr}), 1.85 (dd, J_{PP} = 12.4 Hz, J_{YP} = 71.8 Hz, PNP_{iPr}). IR (Nujol, cm^{-1}): 2024 (w, Ru−H stretch), 1961 (w, Ru−H stretch), 1918 (s, Rh−C═O stretch), 1304 (m, Y−O═C stretch), 1280 (m, Y−O═C stretch). Anal. Calcd for $C_{61}H_{84}NO_2P_3RhRuY \cdot C_6H_{14}$: C, 60.26; H, 7.40; N, 1.05. Found: C, 59.95; H, 7.11; N, 1.27.

[(PNP_{iPr})Y(μ-H)$_2$(μ-Co(C_5Me_5)(CO)COCH$_2$PPh$_2$κ*P*:κ*O*)Ru(C_5Me_5)] (10b-Y). The title complex was synthesized in a manner similar to that for complex **9b-Y**, starting with **2b-Y** (70 mg, 0.073 mmol), Co(C_5Me_5)(CO)$_2$ (18.3 mg, 0.073 mmol), and C_6D_6 (0.8 mL). Yield: 65 mg, 74%. Orange-red blocks of **10b-Y** were obtained for an X-ray diffraction study by slow diffusion of diethyl ether into a saturated solution of **10b-Y** in tetrahydrofuran at −30 °C under a nitrogen atmosphere. ^{1}H NMR (C_6D_6, 293 K, δ): 8.33 (t, J_{HH} = 8.6 Hz, CH of PPh_2CH_2, 2H), 7.49 (m, CH of PPh_2CH_2, 3H), 7.42 (t, J_{HH} = 7.3 Hz, CH of PPh_2CH_2, 2H), 7.29 (t, J_{HH} = 7.3 Hz, CH of PPh_2CH_2, 1H), 7.10 (m, CH of PPh_2CH_2, Ar-CH of PNP_{iPr}, 4H), 6.97 (t, J_{HH} = 7.3 Hz, Ar-CH of PNP_{iPr}, 1H), 6.89 (m, CH of PPh_2CH_2, Ar-CH of PNP_{iPr}, 3H), 5.34 (t, J_{HP} = 12.2 Hz, P-CH_2, 1H), 3.67 (dd, J_{HH} = 8.6 Hz, J_{HP} = 12.8 Hz, P-CH_2, 1H), 2.29 (s, Me of PNP_{iPr}, 3H), 2.16 (s, Me of PNP_{iPr}, 3H), 2.12 (m, CH of *i*Pr, 1H), 1.98 (m, CH of *i*Pr, 1H), 1.85 (m, CH of *i*Pr, 2H), 1.79 (s, Me of (C_5Me_5)Co, 15H), 1.55 (dd, J_{HH} = 7.3 Hz, J_{HP} = 15.9 Hz, Me of *i*Pr, 3H), 1.50 (m, Me of *i*Pr, 3H), 1.47 (s, Me of (C_5Me_5)Ru, 15H), 1.38 (dd, J_{HH} = 7.3 Hz, J_{HP} = 15.9 Hz, Me of *i*Pr, 3H), 1.17 (dd, J_{HH} = 7.3 Hz, J_{HP} = 13.5 Hz, Me of *i*Pr, 3H), 1.14 (m, Me of *i*Pr, 3H), 1.07 (dd, J_{HH} = 7.3 Hz, J_{HP} = 14.7 Hz, Me of *i*Pr, 3H), 1.00 (dd, J_{HH} = 7.3 Hz, J_{HP} = 15.9 Hz, Me of *i*Pr, 3H), 0.84 (dd, J_{HH} = 7.3, 8.6 Hz, J_{HP} = 11.6 Hz, Me of *i*Pr, 3H), −13.37 (t, J_{HP} = 26.9 Hz, Ru-H, 1H), −13.46 (t, J_{HP} = 26.9 Hz, Ru-H, 1H). ^{13}C{^{1}H} NMR (C_6D_6, 293 K, δ): 284.8 (Y-OC═Co), 213.5 (Co−CO), 162.8 (d, J_{CP} = 20.0 Hz, C_{Ar}), 156.6 (d, J_{CP} = 20.0 Hz, C_{Ar}), 145.4 (d, J_{CP} = 30.8 Hz, C_{Ar}), 137.1 (d, J_{CP} = 13.8 Hz, C_{Ar}), 133.3 (d, J_{CP} = 23.1 Hz, C_{Ar}), 132.9 (d, J_{CP} = 18.5 Hz, C_{Ar}), 131.2 (d, J_{CP} = 9.2 Hz, C_{Ar}), 130.6 (C_{Ar}), 129.1 (C_{Ar}), 128.3 (C_{Ar}), 127.6 (d, J_{CP} = 7.7 Hz, C_{Ar}), 127.5 (C_{Ar}), 127.0 (d, J_{CP} = 9.2 Hz, C_{Ar}), 126.4 (d, J_{CP} = 4.6 Hz, C_{Ar}), 124.8 (d, J_{CP} = 3.1 Hz, C_{Ar}), 118.6 (d, J_{CP} = 15.4 Hz, C_{Ar}), 117.8 (d, J_{CP} = 20.0 Hz, C_{Ar}) 116.2 (d, J_{CP} = 7.7 Hz, C_{Ar}), 93.5 (C_{Ar} of (C_5Me_5)Co), 88.2 (C_{Ar} of (C_5Me_5)Ru), 79.4 (d, J_{CP} = 16.9 Hz, P−CH_2), 25.8 (d, J_{CP} = 6.2 Hz, *i*Pr), 24.8 (*i*Pr), 23.2 (*i*Pr), 21.1 (*i*Pr), 21.0 (d, J_{CP} = 10.8 Hz, *i*Pr), 20.6 (Me of PNP_{iPr}), 20.5 (d, J_{CP} = 7.7 Hz, *i*Pr), 20.1 (d, J_{CP} = 7.7 Hz, *i*Pr), 19.9 (d, J_{CP} = 9.2 Hz, *i*Pr), 19.5 (d, J_{CP} = 7.7 Hz, *i*Pr), 19.3 (*i*Pr), 19.2 (d, J_{CP} = 4.6 Hz, *i*Pr), 19.1 (*i*Pr), 17.7 (*i*Pr), 17.6 (*i*Pr), 11.5 (Me of (C_5Me_5)Ru), 10.8 (Me of (C_5Me_5)Co). ^{31}P NMR (C_6D_6, 293 K, δ): 57.61 (s, PPh_2CH_2), 9.35 (dd, J_{PP} = 12.4 Hz, J_{YP} = 76.8 Hz, PNP_{iPr}), 1.32 (dd, J_{PP} = 12.4 Hz, J_{YP} = 66.9 Hz, PNP_{iPr}). IR (Nujol, cm^{-1}): 2006 (w, Ru−H stretch), 1946 (w, Ru−H stretch), 1905 (s, Co−C═O stretch), 1278 (m, Y−O═C stretch). Anal. Calcd for $C_{61}H_{84}NO_2P_3CoRuY{\cdot}0.5C_6H_{14}$: C, 61.58; H, 7.35; N, 1.12. Found: C, 61.79; H, 7.38; N, 1.36.

Computational Details. All density functional theory (DFT) calculations were performed using the Gaussian 09 package[36] with the B3PW91[37] functional. The heavy atoms, phosphorus (P), yttrium (Y), and ruthenium (Ru), were treated by the Stuttgart/Dresden effective core potential (ECP) and an associated basis set.[38] These include the 10 innermost core electrons of P and 28 innermost core electrons of Y and Ru. The 5 valence electrons of P, 11 valence electrons of Y, and 16 valence electrons of Ru were treated with an optimized basis set. One d polarization function with an exponent of 0.387 was augmented for P.[39] All other atoms (C, H, O, N) were treated with the 6-31G* basis set.[40] All geometric optimizations were conducted in the gas phase. Each optimized structure was analyzed by harmonic vibrational frequencies obtained at the same level and characterized as a minimum (Nimag = 0) or as a transition state (Nimag = 1). NBO analysis[41] was performed with 6-31G** for C, H, O, and N atoms and the same basis sets for P, Y, and Ru. Reported free energies and enthalpies were obtained at 1 atm and 298 K using unscaled vibrational frequencies. In order to obtain more reliable relative energies for organometallic complexes reported in this paper, single-point calculations using the M06[17] functional were taken into account by the same level of structure optimization.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, tables, figures, and CIF files giving X-ray structural data for the crystal structures determined in this paper, experimental procedures for the synthesis of **1-Ho**, **1-Dy**, **2-Ho**, and **2-Dy**, and Cartesian coordinates and energies for all of the computed structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Mrs. Akiko Karube for conducting elemental analyses. This work was supported by Grant-in-aid for Scientific Research (S) (No. 21225004) from the JSPS. W.W.N.O. is grateful to the JSPS for a short-term postdoctoral fellowship.

■ REFERENCES

(1) For examples of homomultinuclear rare-earth polyhydrides, see: (a) Ephritikhine, M. *Chem. Rev.* **1997**, *97*, 2193−2242. (b) Hou, Z. M.; Nishiura, M.; Shima, T. *Eur. J. Inorg. Chem.* **2007**, 2535−2545. (c) Konkol, M.; Okuda, J. *Coord. Chem. Rev.* **2008**, *252*, 1577−1591. For examples of homomultinuclear late transition-metal polyhydrides, see: (d) Suzuki, H. *Eur. J. Inorg. Chem.* **2002**, 1009−1023.

(2) For examples of heteromultimetallic polyhydrides containing bis(cyclopentadienyl) rare-earth units, see: (a) Evans, W. J.; Meadows, J. H.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4454−4460. (b) Alvarez, D.; Caulton, K. G.; Evans, W. J.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 5674−5676. (c) Alvarez, D.; Caulton, K. G.; Evans, W. J.; Ziller, J. W. *Inorg. Chem.* **1992**, *31*, 5500−5508. (d) Radu, N. S.; Gantzel, P. K.; Tilley, T. D. *Chem. Commun.* **1994**, 1175−1176. (e) Butovskii, M. V.; Tok, O. L.; Wagner, F. R.; Kempe, R. *Angew. Chem., Int. Ed.* **2008**, *47*, 6469−6472. (f) Sobaczynski, A. P.; Bauer, T.; Kempe, R. *Organometallics* **2013**, *32*, 1363−1369.

(3) For examples of heteromultimetallic polyhydrides containing mono(cyclopentadienyl) rare-earth units, see: (a) Shima, T.; Hou, Z. M. *Chem. Lett.* **2008**, *37*, 298−299. (b) Shima, T.; Hou, Z. M. *Organometallics* **2009**, *28*, 2244−2252. (c) Takenaka, Y.; Hou, Z. M. *Organometallics* **2009**, *28*, 5196−5203. (d) Shima, T.; Luo, Y.; Stewart, T.; Bau, R.; McIntyre, G. J.; Mason, S. A.; Hou, Z. M. *Nat. Chem.* **2011**, *3*, 814−820. (e) Shima, T.; Hou, Z. M. *Chem. Eur. J.* **2013**, *19*, 3458−3466.

(4) For examples of heteromultimetallic polyhydrides containing noncyclopentadienyl rare-earth units, see: (a) Green, M. L. H.; Hughes, A. K.; Michaelidou, D. M.; Mountford, P. *Chem. Commun.* **1993**, 591−593. (b) Bauer, T.; Wagner, F. R.; Kempe, R. *Chem. Eur. J.* **2013**, *19*, 8732−8735.

(5) (a) Li, X. F.; Nishiura, M.; Mori, K.; Mashiko, T.; Hou, Z. M. *Chem. Commun.* **2007**, 4137−4139. (b) Li, X. F.; Nishiura, M.; Hu, L. H.; Mori, K.; Hou, Z. M. *J. Am. Chem. Soc.* **2009**, *131*, 13870−13882. (c) Nishiura, M.; Hou, Z. M. *Bull. Chem. Soc. Jpn.* **2010**, *83*, 595−608. (d) Nishiura, M.; Hou, Z. M. *Nature Chem.* **2010**, *2*, 257−268. (e) Pan, L.; Zhang, K. Y.; Nishiura, M.; Hou, Z. M. *Angew. Chem., Int. Ed.* **2011**, *50*, 12012−12015.

(6) (a) Cui, D. M.; Tardif, O.; Hou, Z. M. *J. Am. Chem. Soc.* **2004**, *126*, 1312−1313. (b) Tardif, O.; Hashizume, D.; Hou, Z. M. *J. Am. Chem. Soc.* **2004**, *126*, 8080−8081. (c) Shima, T.; Hou, Z. *J. Am. Chem. Soc.* **2006**, *128*, 8124−8125. (d) Nishiura, M.; Baldamus, J.; Shima, T.; Mori, K.; Hou, Z. *Chem. Eur. J.* **2011**, *17*, 5033−5044. (e) Shima, T.; Nishiura, M.; Hou, Z. M. *Organometallics* **2011**, *30*, 2513−2524.

(7) (a) Zhang, L. X.; Suzuki, T.; Luo, Y.; Nishiura, M.; Hou, Z. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 1909−1913. (b) Cheng, J. H.; Shima, T.; Hou, Z. M. *Angew. Chem., Int. Ed.* **2011**, *50*, 1857−1860.

(8) (a) Zhang, L. X.; Nishiura, M.; Yuki, M.; Luo, Y.; Hou, Z. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 2642−2645. (b) Cheng, J. H.; Hou, Z. M. *Chem. Commun.* **2012**, *48*, 814−816. (c) Cheng, J. H.; Wang, H. Y.; Nishiura, M.; Hou, Z. M. *Chem. Sci.* **2012**, *3*, 2230−2233.

(9) Suzuki, H.; Lee, D. H.; Oshima, N.; Morooka, Y. *Organometallics* **1987**, *6*, 1569−1575.

(10) (a) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 218−220. (b) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121−127. (c) Campion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 2049−2056. (d) Miller, R. L.; Toreki, R.; Lapointe, R. E.; Wolczanski, P. T.; Vanduyne, G. D.; Roe, D. C. *J. Am. Chem. Soc.* **1993**, *115*, 5570−5588.

(11) (a) Gambarotta, S.; Floriani, C.; Chiesivilla, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690−1691. (b) Beringhelli, T.; Dalfonso, G.; Ciani, G.; Molinari, H. *Organometallics* **1987**, *6*, 194−196.

(12) Casey, C. P.; Palermo, R. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 549−550.

(13) Longato, B.; Norton, J. R.; Huffman, J. C.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 209−210.

(14) (a) Hanna, T. A.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 11363−11364. (b) Gade, L. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2659−2678.

(15) Duchateau, R.; Tuinstra, T.; Brussee, E. A. C.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. *Organometallics* **1997**, *16*, 3511−3522.

(16) Small amounts of byproducts were observed by both ^{1}H and ^{31}P NMR spectroscopy when the reaction mixture (in toluene-d_8) was cooled to −40 °C. These were not identified or isolated, however.

(17) The M06 functional is known to give better predictions of energies for organometallic compounds. See: (a) Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101-1−194101-18. (b) Zhao, Y.;

Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215−241. (c) Kulkarni, A. D.; Truhlar, D. G. *J. Chem. Theory Comput.* **2011**, *7*, 2325−2332.

(18) (a) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 5393−5396. (b) Fagan, P. J.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6959−6962. (c) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440−4451.

(19) Espinosagarcia, J.; Corchado, J. C. *J. Phys. Chem.* **1995**, *99*, 8613−8616.

(20) (a) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443−450. (b) Den Haan, K. H.; Luinstra, G. A.; Meetsma, A.; Teuben, J. H. *Organometallics* **1987**, *6*, 1509−1515. (c) Duchateau, R.; Brussee, E. A. C.; Meetsma, A.; Teuben, J. H. *Organometallics* **1997**, *16*, 5506−5516. (d) Yi, W.; Zhang, J.; Chen, Z.; Zhou, X. *Organometallics* **2012**, *31*, 7213−7221.

(21) Evans, W. J.; Forrestal, K. J.; Ziller, J. W. *J. Am. Chem. Soc.* **1998**, *120*, 9273−9282.

(22) Lee, H.; Bridgewater, B. M.; Parkin, G. *Dalton Trans.* **2000**, 4490−4493.

(23) Small quantities of unidentified products were observed as well, but these were not isolated.

(24) (a) Reger, D. L.; Tarquini, M. E.; Lebioda, L. *Organometallics* **1983**, *2*, 1763−1769. (b) Berg, F. J.; Petersen, J. L. *Organometallics* **1993**, *12*, 3890−3895. (c) Lu, E.; Chen, Y.; Leng, X. *Organometallics* **2011**, *30*, 5433−5441.

(25) Stclair, M. A.; Santarsiero, B. D.; Bercaw, J. E. *Organometallics* **1989**, *8*, 17−22.

(26) Takenaka, Y.; Shima, T.; Baldamus, J.; Hou, Z. M. *Angew. Chem., Int. Ed.* **2009**, *48*, 7888−7891.

(27) For Zr/Rh alkoxy-Fischer carbene complexes, see: (a) Erker, G.; Lecht, R.; Tsay, Y. H.; Kruger, C. *Chem. Ber.* **1987**, *120*, 1763−1765. (b) Erker, G.; Mena, M.; Hoffmann, U.; Menjon, B.; Petersen, J. L. *Organometallics* **1991**, *10*, 291−298. For Zr/Co alkoxy-Fischer carbene complexes, see: (c) Erker, G.; Lecht, R.; Kruger, C.; Tsay, Y. H.; Bonnemann, H. *J. Organomet. Chem.* **1987**, *326*, C75−C78. (d) Erker, G.; Lecht, R.; Petersen, J. L.; Bonnemann, H. *Organometallics* **1987**, *6*, 1962−1967.

(28) (a) Evans, W. J.; Fujimoto, C. H.; Johnston, M. A.; Ziller, J. W. *Organometallics* **2002**, *21*, 1825−1831. (b) Emslie, D. J. H.; Piers, W. E.; Parvez, M.; McDonald, R. *Organometallics* **2002**, *21*, 4226−4240.

(29) Cirjak, L. M.; Ginsburg, R. E.; Dahl, L. F. *Inorg. Chem.* **1982**, *21*, 940−957.

(30) *APEX2 v2013.2-0*; Bruker AXS Inc., Madison, WI, 2007.

(31) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *A64*, 112−122.

(32) Palatinus, L.; Chapuis, G. *J. Appl. Crystallogr.* **2007**, 786−790.

(33) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.

(34) Sluis, P. v. d.; Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *A46*, 194−201.

(35) Spek, A. L. *Acta Crystallogr. Sect. D* **2009**, *D65*, 148−155.

(36) Frisch, M. J., et al. *Gaussian 09, Revision A.1*; Gaussian Inc., Wallingford, CT, 2009.

(37) (a) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (c) Perdew, J. P.; Burke, K.; Wang, Y. *Phys. Rev. B* **1996**, *54*, 16533−16539.

(38) (a) Dolg, M.; Stoll, H.; Savin, A.; Preuss, H. *Theor. Chim. Acta* **1989**, *75*, 173−194. (b) Andrae, D.; Haussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123−141. (c) Bergner, A.; Dolg, M.; Kuchle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431−1441. (d) Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1993**, *85*, 441−450.

(39) Hollwarth, A.; Bohme, M.; Dapprich, S.; Ehlers, A. W.; Gobbi, A.; Jonas, V.; Kohler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 237−240.

(40) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265−3269.

(41) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926.