P−H Bond Addition to a Dinuclear Ruthenium Imido Complex: Synthesis and Reactivity of an Amido Phosphido Complex

Shin Takemoto, Yu Kimura, Ken Kamikawa, and Hiroyuki Matsuzaka*

Department of Chemistry, Graduate School of Science, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan

Received December 18, 2007

Treatment of the imido complex [(Cp*Ru)$_2$(μ_2-NPh)(μ_2-CO)] (**3**; Cp* = η^5-C_5Me_5) with phenylphosphine resulted in the P−H bond addition across the Ru−N bonds to give the amido phosphido complex [(Cp*Ru)$_2$(μ_2-NHPh)(μ_2-PHPh)(μ_2-CO)] (**4**). Exposure of **4** to atmospheric carbon monoxide resulted in the formation of the phosphinidene complex [{Cp*Ru(CO)}$_2$(μ_2-PPh)(μ_2-CO)] (**6**) and aniline. With excess phenylphosphine, compound **4** gave the bis(phosphido) phosphine complex [Cp*Ru(CO)(μ_2-PHPh)$_2$-Ru(PH_2Ph)Cp*] (**5**). Treatment of **4** with 2-propanol led to an overall hydrogenolysis of the Ru−N bonds to give the hydrido phosphido complex [(Cp*Ru)$_2$(μ_2-H)(μ_2-PHPh)(μ_2-CO)] (**7**). Reaction of **4** with 4-*tert*-butylphenol resulted in a P−O bond formation yielding the hydrido aryloxyphosphido complex [(Cp*Ru)$_2$(μ_2-H)(μ_2-PPh(OC_6H_4-*t*-Bu-*p*)(μ_2-CO)] (**8**). Crystal structures of **4**, **5**, and **8** are reported.

Introduction

Phosphido-bridged di- and polynuclear transition metal complexes have attracted intense interest as multimetallic reagents or catalysts for organic/inganic transformations.[1–3] Preparation of these complexes via the activation of P−H bonds of primary or secondary phosphines on transition metal centers has received considerable study recently since it would provide insights into metal-catalyzed transformations of organophosphorus compounds.[4,5] In case of primary phosphine activation, the resulting PHR^- ligand still has a P−H bond, whose reactivity such as conversion into a phosphinidene ligand and addition to alkenes and alkynes has also been the subject of numerous studies.[6,7] Three major types of reaction modes have been known for transition metal-mediated phosphine P−H activation: (i) oxidative addition to low-valent metal centers,[4,8] (ii) addition across metal−metal bonds,[9] and (iii) protonolysis of metal−alkyl

* Corresponding author. E-mail:matuzaka@c.s.osakafu-u.ac.jp.

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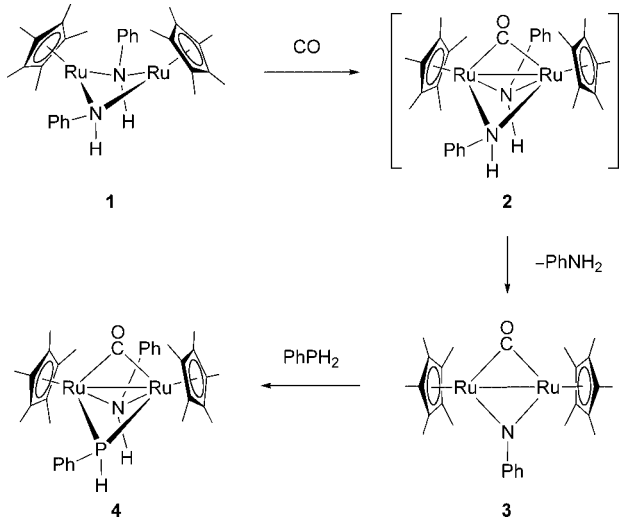
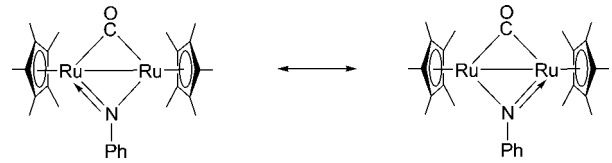
10.1021/om701260y CCC: $40.75
Publication on Web 03/18/2008

Scheme 1



and −hydride bonds.[5,10] Metal−element multiple bonds have recently been recognized as a versatile class of functional groups capable of cleaving a variety of E−H bonds (E = H, C, N, O, S, etc.).[11] However, this type of protocol has rarely been implemented for the activation of P−H bonds.[11i] Work in our laboratories has focused on the chemistry of dinuclear late transition metal complexes with heteroatom bridging ligands such as amido, imido, aryloxo, and dithiolato ligands.[12,13] Specifically, we have recently reported the formation of the diruthenium bridging imido complex [(Cp*Ru)$_2$(μ_2-NPh)(μ_2-CO)] (**3**) from the reaction of the coordinatively unsaturated amido complex [Cp*Ru(μ_2-NHPh)]$_2$ (**1**) with carbon monoxide (Scheme 1).[13] The reaction initially produces a thermally unstable yet spectroscopically identifiable μ_2-CO adduct [(Cp*Ru)$_2$(μ_2-NHPh)$_2$(μ_2-CO)] (**2**). The intermediate spontaneously eliminates 1 equiv of aniline to produce the imido complex **3**, which can be described as a hybrid of two resonance structures with a Ru−N multiple bond (Chart 1). As an extension of these studies, we sought to examine possible routes to the corresponding phosphido and phosphinidene diruthenium systems,

Chart 1



comparison of whose chemistry with that of their nitrogen analogues would be of interest. Herein we report a reaction of phenylphosphine with the imido complex **3**, which produces the amido phosphido complex [(Cp*Ru)$_2$(μ_2-NHPh)(μ_2-PHPh)(μ_2-CO)] (**4**) via P−H bond activation by the Ru−N linkage. We also describe some reactivity of **4** including conversion into a phosphinidene complex and an aryloxyphosphido complex via activation of the P−H bond of the bridging phsophido ligand.

Results and Discussion

Synthesis of Amido Phosphido Complex 4. Treatment of the imido complex **3** with 0.9 equiv of phenylphosphine in THF at −80 °C produced the amido phosphido complex **4** (Scheme 1). ^{1}H NMR analysis of the reaction mixture showed that complex **4** was formed in ∼80% yield. Use of 1 equiv of phenylphosphine resulted in significant contamination with byproducts including the bis(phosphido) phosphine complex [Cp*Ru(CO)(μ_2-PHPh)$_2$Ru(PH$_2$Ph)Cp*] (**5**; vide infra). Treatment of **3** with phenylphosphine-d_2 (PhPD$_2$, 90% *d*) in THF resulted in the formation of [(Cp*Ru)$_2$(μ_2-NDPh)(μ_2-PDPh)(μ_2-CO)] (**4**-d_2; 90% *d* for PhPD and 80% *d* for PhND), showing that almost all of the N−H and P−H hydrogen atoms in **4** result from phenylphosphine. The contamination of 10% H on the nitrogen center in **4**-d_2 in the above deuterium-labeling experiment might be due to participation of adventitious water in deuteron transfer step. Complex **4** was isolated in 33% yield as dark green crystals after recrystallization from hexanes and characterized by both spectroscopic and crystallographic techniques. The ^{1}H NMR spectrum of **4** exhibits one Cp* resonance as a doublet (δ 1.62 ppm, $^4J_{PH}$ = 1.4 Hz), indicating a symmetrical dinuclear structure with one bridging phosphido ligand. Resonances attributable to the P−H and N−H protons are observed at δ 1.74 (d, $^1J_{PH}$ = 320 Hz) and 0.82 (d, $^3J_{PH}$ = 12 Hz) ppm, respectively. In its ^{13}C{^{1}H} NMR spectrum, a resonance due to the μ_2-carbonyl carbon was observed at 256.8 ppm as a doublet ($^2J_{PC}$ = 8.6 Hz). The structure of **4** deduced by single-crystal X-ray diffraction is shown in Figure 1. Because of a site disorder between the NPh and PPh groups, the solved structure possesses a crystallographic mirror plane that contains the ruthenium atoms and the bridging CO ligand. Thus, the nitrogen and phosphorus atoms are treated as duplicate atoms in the same position with equal U_{ij} values and 50% occupancy for each. Although this prevents us from discussing bond lengths and angles around these atoms, the overall atom connectivity within the structure as well as the equatorial orientation of the two phenyl substituents have been unequivocally established. The ruthenium atoms are separated 2.6857(7) Å from each other, a distance consistent with a metal−metal bonding interaction.

We had expected that **4** might eliminate aniline to produce the phosphinidene complex [(Cp*Ru)$_2$(μ_2-CO)(μ_2-PPh)], as the bis(amido) complex **2** does to give the imido complex **3**.[13] However, compound **4** is stable in solution at room temperature and showed no sign of spontaneous aniline elimination. In the case of the bis(amido)-to-imido conversion, the electron-deficiency on the ruthenium centers caused by the loss of aniline is compensated by the formation of π-bonds between the imido

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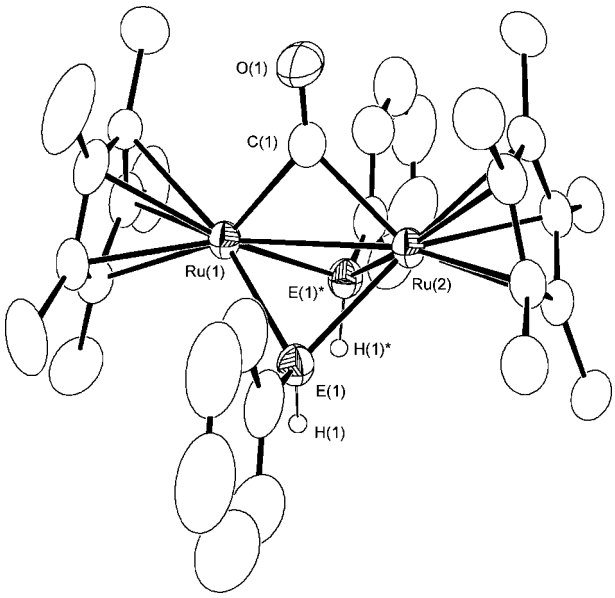
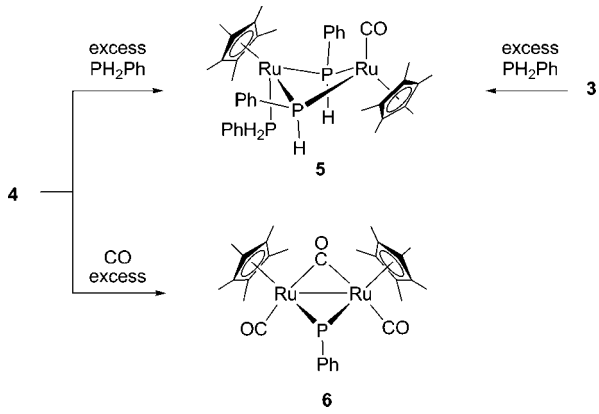


Figure 1. ORTEP drawing of **4**. Ellipsoids are drawn at the 35% probability level. All H atoms except for those on N and P atoms are omitted. The ellipsoid labeled E(1) represents P and N atoms modeled to occupy the same site with 50% occupancy. The atoms E(1) and E(1)* are symmetry related to each other.

Scheme 2



ligand and the ruthenium atoms. Furthermore, the shortening of the Ru−N bond distances strengthens the Ru−N σ-bonding interactions. Since several experimental and theoretical data suggest that a P−H bond is generally more acidic than a corresponding N−H bond,[14] the greater stability of **4** as compared to that of **2** with respect to aniline elimination could be ascribed to the decreased tendency of phosphorus 3p orbitals as compared to nitrogen 2p orbitals to participate in π-bonding,[15] though stable compounds with M−P π-bonds within a M(μ_2-PR)M framework are known.[16]

Reaction of 4 with Excess Phenylphosphine. Treatment of **4** with a 5-fold excess of phenylphosphine in THF led to the elimination of aniline and incorporation of 2 equiv of phenylphosphine to give the bis(phosphido) phosphine complex [Cp*Ru(CO)(μ_2-PHPh)$_2$Ru(PH$_2$Ph)Cp*] (**5**) (Scheme 2), which was isolated as orange crystals in 30% yield after recrystallization from toluene/acetonitrile. Complex **5** was also obtained in 84% yield by treating the imido complex **3** with excess phenylphosphine. Complex **5** was characterized by NMR spectroscopy (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}), IR spectroscopy, elemental analysis, and single-crystal X-ray diffraction. An ORTEP diagram is shown in Figure 2. The molecule exhibits a doubly bridged dinuclear structure with two bridging phosphido ligands. A phenylphosphine is bound to one ruthenium center and a terminal CO ligand coordinates to the other ruthenium site. These terminal ligands are trans to each other with respect to the four-membered Ru(1)−P(1)−Ru(2)−P(2) ring. The Ru$_2$P$_2$ ring takes an elongated butterfly shape with acute P−Ru−P angles (av. 71.5°), wide Ru−P−Ru angles (av. 105.8°), and a large Ru···Ru separation (3.73 Å). The dihedral angle between Ru(1)−P(1)−P(2) and Ru(2)−P(1)−P(2) planes is 21.6°.

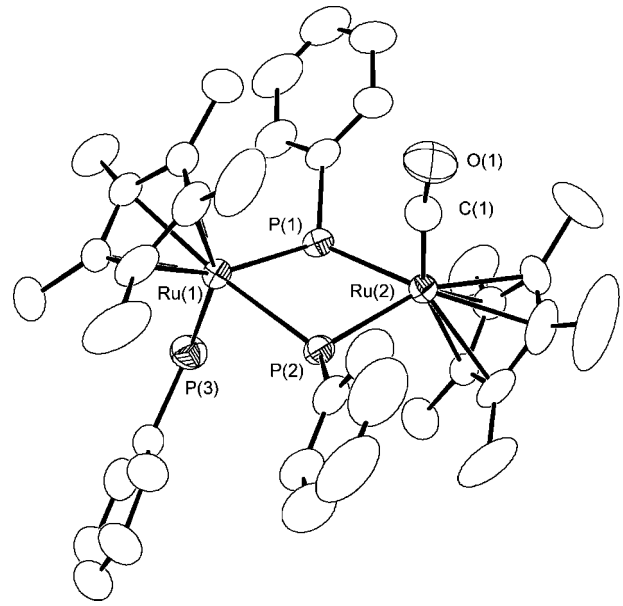


Figure 2. ORTEP drawing of **5**. Ellipsoids are drawn at the 35% probability level. All H atoms are omitted. Selected interatomic distances (Å) and bond angles (deg): Ru(1)···Ru(2) = 3.73; Ru(1)−P(1) = 2.3502(9); Ru(2)−P(1) = 2.3325(9); Ru(1)−P(2) = 2.3453(8); Ru(2)−P(2) = 2.3382(9); Ru(1)−P(3) = 2.2276(10); Ru(2)−C(1) = 1.821(3); Ru(1)−P(1)−Ru(2) = 105.77(3); Ru(1)−P(2)−Ru(2)=105.75(3);P(1)−Ru(1)−P(2)=71.25(3);P(1)−Ru(2)−P(2) = 71.69(3).

An attempted reaction of **4** with 1 equiv of phenylphosphine was conducted in THF at 50 °C to isolate a phosphine-free bis(phosphido) complex. This resulted in the formation of a 1:4:6 mixture of unreacted **4**, complex **5**, and a compound that we tentatively formulate as a bis(phosphido) complex [Cp*Ru(μ_2-CO)(μ_2-PHPh)$_2$RuCp*] on the basis of a triplet C$_5$*Me*$_5$ resonance in the ^{1}H NMR spectrum (δ 1.74, $^4J_{PH}$ = 1.6 Hz; C$_6$D$_6$), a singlet resonance in the ^{31}P{^{1}H} NMR spectrum (δ 7.38), and a triplet μ_2-*C*O resonance in the ^{13}C{^{1}H} NMR spectrum (δ 250.4, $^2J_{PC}$ = 13.7 Hz). Isolation of this material was not achieved due to its similar solubility to that of **4** and **5**. Addition of excess phenylphosphine (4 equiv) to the mixture of these compounds led to clean conversion to **5** in 46% crystallized yield based on **4**.

Reaction of 4 with Excess Carbon Monoxide: Synthesis of Phosphinidene Complex 6. Addition of carbon monoxide (1 atm) to a benzene-d_6 solution of **4** resulted in the loss of aniline (detected by ^{1}H NMR in 66% yield) and the formation of a phosphinidene complex [{Cp*Ru(CO)}$_2$(μ_2-PPh)(μ_2-CO)] (**6**, 77%; Scheme 2). From a separate experiment carried out in

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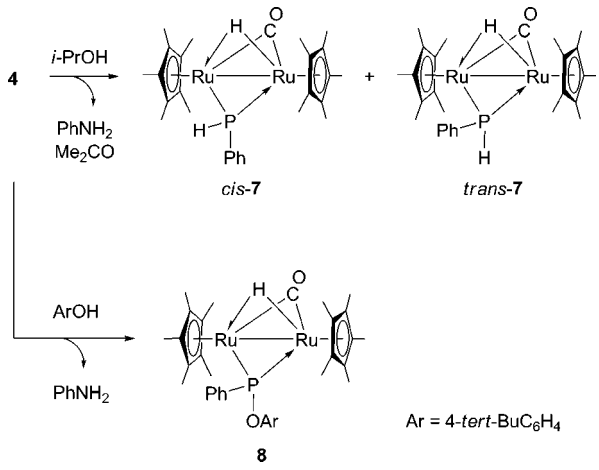
Scheme 3



THF solution, the phosphinidene **6** was isolated in 39% yield as orange crystals and characterized by NMR spectroscopy (^{1}H, ^{13}C, and ^{31}P), IR spectroscopy, and elemental analysis. The existence of the phosphinidene moiety was supported by a characteristic downfield resonance in the ^{31}P{^{1}H} NMR spectrum.[6b,10a,16] The observed ^{31}P chemical shift of δ 457.2 ppm is comparable to that observed for the isoelectronic diiron μ_2-phenylphosphinidene complex *cis*-[{CpFe(CO)}$_2$(μ_2-PPh)(μ_2-CO)] (δ 498.2 ppm), which has been shown to have a pyramidal phosphorus center by single-crystal X-ray diffraction.[6b] For comparison, μ_2-arylphosphinidene complexes with a trigonal planar phosphorus center exhibit ^{31}P resonances in a more downfield region (δ 650−690 ppm).[16] The IR spectrum of **6** shows two terminal CO bands at 1961 and 1926 cm^{-1} along with one bridging CO band at 1757 cm^{-1}. The ^{1}H NMR spectrum of **6** shows only one Cp* resonance along with signals corresponding to one phenyl group. These data are consistent with the phosphinidene-bridged cis dinuclear structure with a pyramidal phosphorus center. In the absence of single-crystal X-ray data, stereochemistry around the phosphorus atom is not obvious but a configuration such that the phenyl substituent points away from the Cp* groups is expected from steric reason.

Reaction of 4 with 2-Propanol: Synthesis of Hydrido Phosphido Complexes *cis*-7 and *trans*-7. Heating a mixture of **4** and 2-propanol (10 equiv) in C_6D_6 at 60 °C resulted in the formation of a μ-hydrido μ-phosphido complex [(Cp*Ru)$_2$(μ_2-H)(μ_2-PHPh)(μ_2-CO)] (**7**) as a 1:2 mixture of cis and trans stereoisomers (Scheme 3).[17] Herein the cis and trans denote the relative orientations of the P−H hydrogen and the hydrido ligand with respect to the Ru$_2$P ring. Aniline (56%) and acetone (69%) were detected by ^{1}H NMR analysis. Thus, the reaction is an overall transfer hydrogenolysis of the Ru−NHPh bonds with 2-propanol as a hydrogen donor. A preparative scale experiment was carried out in 2-propanol suspension. Filtration of the reaction mixture afforded **7** in 62% yield as an analytically pure red crystalline solid. The isolated solid was a 5:4 mixture of *cis*-**7** and *trans*-**7** as judged by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of **7** exhibits hydride signals of the cis and trans isomers at δ −19.58 and −20.28 ppm, respectively. The former was observed as a doublet ($^2J_{PH}$ = 50.1 Hz) whereas the latter appeared as a doublet of doublets due to coupling with both the phosphorus and the P−H hydrogen nuclei ($^2J_{PH}$ = 50.1 Hz and $^3J_{HH}$ = 8.6 Hz). The P−H resonances for the cis and trans isomers were observed at δ 5.25 ppm (d, $^1J_{PH}$ = 332.7 Hz) and δ 4.77 ppm (dd, $^1J_{PH}$ = 379.1 Hz, $^3J_{HH}$ = 8.6 Hz), respectively.

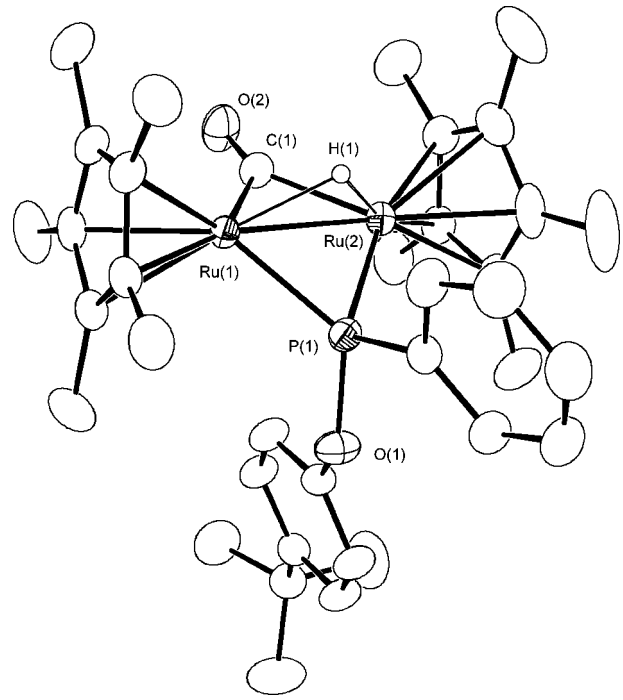


Figure 3. ORTEP drawing of **8**. Ellipsoids are drawn at the 35% probability level. All H atoms except for those on Ru atoms are omitted. Selected bond distances (Å) and angles (deg): Ru(1)−Ru(2) = 2.6124(5); Ru(1)−P(1) = 2.3502(9); Ru(2)−P(1) = 2.3325(9); Ru(1)−P(2) = 2.3453(8); Ru(2)−P(2) = 2.3382(9); Ru(1)−P(3) = 2.2276(10); Ru(2)−C(1) = 1.821(3); Ru(1)−P(1)−Ru(2) = 105.77(3); Ru(1)−P(2)−Ru(2) = 105.75(3); P(1)−Ru(1)−P(2) = 71.25(3); P(1)−Ru(2)−P(2) = 71.69(3).

Reaction of 4 with 4-*tert*-Butylphenol: Synthesis of Aryloxyphosphido Complex 8. Treatment of **4** with excess 4-*tert*-butylphenol in THF resulted in the formation of the hydrido aryloxyphosphido complex [(Cp*Ru)$_2$(μ_2-H)(μ_2-PPh-(OC$_6$H$_4$-*t*-Bu-*p*)(μ_2-CO)) (**8**; Scheme 3), which was isolated in 62% yield as dark red crystals and has been structurally characterized. The existence of a hydrido ligand in this complex was confirmed by ^{1}H NMR spectroscopy, which revealed a doublet resonance at −20.85 ppm ($^2J_{PH}$ = 51.4 Hz). The ^{31}P{^{1}H} NMR spectrum of **8** exhibited a resonance at δ 240.4 ppm, which is more downfield as compared to the ^{31}P NMR shifts of *cis*- and *trans*-**7**. An ORTEP drawing for **8** is shown in Figure 3. The hydrido ligand was located by Fourier syntheses and refined with isotropic thermal parameters. The aryloxy group exists on the phosphorus center and is trans to the hydrido ligand. The short Ru−Ru distance (2.6124(5) Å) is consistent with a Ru−Ru bond expected from the EAN rule.

When **4** was treated with excess ArOD (Ar = *p*-*tert*-butylphenyl), no deuterium was incorporated into the product **8**. Treatment of [(Cp*Ru)$_2$(μ_2-CO)(μ_2-PDPh)(NDPh)] (**4**-d_2) with ArOH also afforded **8** without incorporation of any deuterium, showing that neither the phosphido P−H nor the amido N−H in **4** is the source of the hydrido ligand in **8**. We also confirmed that deuterium is not introduced into **8** when the reaction of **4** and ArOH is carried out in THF-d_8, eliminating the possibility of the solvent acting as a source of the hydrido ligand. At present neither the origin of the hydrido nor the mechanism of the reaction is uncertain, though the overall

(17) We use the half arrow representation of the bridging hydrido complexes introduced in the following articles: (a) Baik, M.-H.; Freisner, R. A.; Parkin, G. *Polyhedron* **2004**, *23*, 2879. (b) Parkin, G. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier: Oxford, UK, 2007; Vol. 1,Chapter. 1.01.2.4.

Table 1. Crystallographic Data for 4, 5, and 8

	4	5	8
formula	$C_{33}H_{42}NOPRu_2$	$C_{39}H_{49}OP_3Ru_2$	$C_{37}H_{49}O_2PRu_2$
M	701.79	828.83	758.87
T/K	296	296	296
size (mm^3)	0.60 × 0.60 × 0.30	0.60 × 0.50 × 0.30	0.50 × 0.30 × 0.30
cryst system	orthorhombic	orthorhombic	orthorhombic
space group	*Pnnm*	$P2_12_12_1$	$P2_12_12_1$
Z	4	4	4
a (Å)	13.066(5)	9.3624(14)	10.610(3)
b (Å)	15.120(4)	19.378(4)	15.178(5)
c (Å)	16.021(5)	21.286(4)	21.350(5)
V ($Å^3$)	3164.9(18)	3861.8(13)	3438.3(16)
D_{calcd} (g/cm^3)	1.473	1.426	1.466
μ (mm^{-1})	1.030	0.934	0.955
no. of reflns collected	27298	37693	32603
no. of unique reflns	3748	8819	7839
GOF on F^2	1.032	1.039	1.036
R1 [$I > 2\sigma(I)$][a]	0.0293	0.0280	0.0253
*w*R2 (all data)[b]	0.0802	0.0725	0.0609

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum(w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

reaction is an addition of ArOH to a hypothetical phosphinidene diruthenium fragment, "$(Cp^*Ru)_2(\mu_2\text{-}CO)(\mu_2\text{-}PPh)$".

Conclusions

The imido complex $[(Cp^*Ru)_2(\mu_2\text{-}NPh)(\mu_2\text{-}CO)]$ (**3**) has been shown to cleave the P−H bond of phenylphosphine to give the amido phosphido complex $[(Cp^*Ru)_2(\mu_2\text{-}NHPh)(\mu_2\text{-}PHPh)(\mu_2\text{-}CO)]$ (**4**). This reaction represents a rare example of P−H bond activation across a metal–ligand multiple bond. Complex **4** further reacts with 2 equiv of phenylphosphine to give the bis(phosphido) phosphine complex $[Cp^*Ru(CO)(\mu_2\text{-}PHPh)_2Ru(PH_2Ph)Cp^*]$ (**5**). In contrast to the amido analogue $[(Cp^*Ru)_2(\mu_2\text{-}NHPh)_2(\mu_2\text{-}CO)]$ (**2**), the amido phosphido complex **4** is persistent toward thermal elimination of aniline. Nevertheless, interaction of **4** with carbon monoxide induces release of aniline and affords a new bridging phosphinidene complex $[\{Cp^*Ru(CO)\}_2(\mu_2\text{-}PPh)(\mu_2\text{-}CO)]$ (**6**) for which spectroscopic data and electron counting suggest pyramidal configuration at the phosphorus center. Complex **4** has also been shown to react with 2-propanol and 4-*tert*-butylphenol via elimination of aniline. In the case of 2-propanol the reaction is an overall transfer hydrogenolysis of the Ru−N bonds, yielding a hydrido phosphido complex $[(Cp^*Ru)_2(\mu_2\text{-}H)(\mu_2\text{-}PHPh)(\mu_2\text{-}CO)]$ (**7**), whereas the reaction with 4-*tert*-butylphenol results in the formation of a hydrido aryloxyphosphido complex $[(Cp^*Ru)_2(\mu_2\text{-}H)(\mu_2\text{-}PPh(OC_6H_4\text{-}t\text{-}Bu\text{-}p)(\mu_2\text{-}CO))]$ (**8**) via P−O bond formation and P−H bond cleavage.

Experimental Section

All manipulations were conducted under an atmosphere of nitrogen with standard Schlenk techniques. The imido complex **3** was prepared according to the published method.[13] Phenylphosphine was prepared by $LiAlH_4$ reduction of PCl_2Ph in diethyl ether followed by distillation under reduced pressure.[18] Other reagents were purchased from commercial vendors and used without further purification unless otherwise noted. Toluene, hexanes, THF, and diethyl ether were distilled from sodium benzophenone ketyl and degassed before use. Acetonitrile, dichloromethane, 2-propanol (Wako), and *tert*-butyl alcohol (Aldrich) were purchased as anhydrous forms and degassed before use. Deuterated solvents were obtained from Cambridge Isotope Laboratories, Inc., degassed, and stored over activated molecular sieves. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL ECP500 spectrometer at the field strength of 500.16 (^1H) and 202.48 MHz (^{31}P). $^{13}C\{^1H\}$ NMR spectra were obtained on a Varian VNMR400 spectrometer at the field strength of 100.55 MHz. Infrared spectra were obtained with a JASCO FT-IR 4100 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 Series II CHNS/O analyzer.

$[(Cp^*Ru)_2(\mu_2\text{-}NHPh)(\mu_2\text{-}PHPh)(\mu_2\text{-}CO)]$ (4). Imido complex **3** (123 mg, 0.208 mmol) was dissolved in THF (10 mL) and the solution was cooled to −80 °C. The solution was stirred and phenylphosphine (21 μL, 0.187 mmol) was added to the solution, which caused a color change of the solution from dark orange to dark green. The solution was allowed to warm slowly to room temperature and stirred overnight. The solvent was removed in vacuo and the residue was extracted with hexanes (20 mL). Concentration of the extract and cooling to −30 °C gave **4** as dark green plates. Yield 48 mg, 33%. Anal. Calcd for $C_{33}H_{42}NOPRu_2$: C, 56.48; H, 6.03; N, 2.00. Found: C, 56.14; H, 6.37; N, 2.36. ^1H NMR (C_6D_6): δ 7.30 (m, 2H, Ph), 7.15−6.95 (m, 5H, Ph), 6.79 (m, 1H, Ph), 6.67 (t, 1H, Ph), 6.20 (m, 1H, Ph), 1.74 (d, $^1J_{PH}$ = 320 Hz, PH), 1.62 (d, $^4J_{PH}$ = 1.4 Hz, 30H, Cp*), 0.82 (d, $^3J_{PH}$ = 12 Hz, NH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 256.8 (d, $^2J_{PC}$ = 8.6 Hz, μ_2-CO), 160.6 (d, J = 8.6 Hz, Ph), 140.6 (d, J = 43 Hz, Ph), 132.5 (d, J = 9.8 Hz, Ph), 132.2 (s, Ph), 129.1 (s, Ph), 127.8 (d, J = 12 Hz, Ph), 127.2 (s, Ph), 126.5 (s, Ph), 123.1 (s, Ph), 121.1 (s, Ph), 118.8 (s, Ph), 92.0 (s, C_5Me_5), 9.4 (s, C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 19.4 (s). IR (KBr): 3063 (w), 3052 (w), 2978 (m), 2953 (m), 2909 (s), 2251 (m), 1931 (m), 1761 (vs), 1591 (s), 1578 (s), 1482 (s), 1376 (s), 1240 (s), 1026 (s), 897 (m), 753 (m), 737 (m), 690 (s), 575 (s), 539 (m), 510 (s) cm^{-1}.

$[Cp^*Ru(CO)(\mu_2\text{-}PHPh)_2Ru(PH_2Ph)Cp^*]$ (5). From 3: To a solution of **3** (34 mg, 0.057 mmol) in THF (5 mL) was added phenylphosphine (32 μL, 0.285 mmol, 5.0 equiv) at −80 °C. The solution was allowed to warm slowly to room temperature and stirred overnight. The volatiles were removed in vacuo and the residue was recrystallized from toluene/acetonitrile (1 mL/7 mL) to give **5** as yellow plates. Yield 40 mg, 84%. **From 4:** To a solution of **4** (59 mg, 0.084 mmol) in THF (10 mL) was added phenylphosphine (46 μL, 0.42 mmol) at −80 °C. The solution was allowed to warm slowly to room temperature and stirred overnight. The volatiles were removed in vacuo and the residue was recrystallized from toluene/acetonitrile (2 mL/10 mL) to give **5** as yellow plates. Yield 21 mg, 30%. Anal. Calcd for $C_{39}H_{49}OP_3Ru_2$: C, 56.51; H, 5.96. Found: C, 56.30; H, 6.10. ^1H NMR (C_6D_6): δ 7.93−7.90 (m, 6H, Ph), 7.32−7.27 (m, 6H, Ph), 7.19−7.13 (m, 3H, Ph), 6.08 (dt, 2H, PH_2Ph, $^1J_{PH}$ = 320 Hz, $^3J_{PH}$ = 10 Hz), 4.25−3.12 (m, 2H,

(18) Pass, F.; Schindlbauer, H. *Monatsh. Chem.* **1959**, *90*, 148.

P*H*Ph), 1.67, 1.43 (s, 15H each, Cp*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 215.8 (t, $^2J_{PC} = 11$ Hz, CO), 137.8 (t, $J = 7$ Hz), 134.53−134.36 (m, Ph), 131.1 (dt, $J = 36$ Hz, 6 Hz, Ph), 129.7 (d, $J = 2$ Hz, Ph), 128.5 (s, Ph), 127.4 (s, Ph), 127.5 (m, Ph), 93.9, 90.3 (s, C_5Me_5), 9.98, 9.90 (s, C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 10.2 (t, $^2J_{PP} = 10$ Hz), −78.0 (d, $^2J_{PP} = 10$ Hz). IR (KBr): 3054 (w), 2965 (w), 2893 (m), 2818 (w), 2267 (s), 2217 (s), 1887 (vs), 1580 (w), 1478 (m), 1431 (m), 1375 (m), 1026 (m), 930 (m), 904 (s), 794 (s), 733 (s), 693 (s), 576 (w), 557 (w), 535 (w), 522 (m), 489 (m), 437 (m) cm^{-1}.

[{Cp*Ru(CO)}$_2$(μ_2-PPh)(μ_2-CO)] (6). A solution of **4** (59 mg, 0.084 mmol) in THF (10 mL) was stirred overnight under CO atmosphere. Removal of the solvent followed by recrystallization from toluene/acetonitrile (2 mL/5 mL) afforded **6** as red needles. Yield 22 mg, 39%. Anal. Calcd for $C_{29}H_{35}O_3PRu_2$: C, 52.40; H, 5.31. Found: C, 52.01; H, 5.64. ^1H NMR (C_6D_6): δ 8.00 (m, 2H, Ph), 7.41 (t, 2H, Ph), 7.12 (t, 1H, Ph), 1.78, (s, 30H, Cp*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 251.6 (s, μ_2-CO), 201.9 (s, CO), 158.9 (d, $^1J_{PC} = 72$ Hz, Ph), 130.7 (d, $^2J_{PC} = 12$ Hz, Ph), 127.2 (d, $^3J_{PC} = 11$ Hz, Ph), 125.6 (d, $^4J_{PC} = 12$ Hz, Ph), 100.3 (C_5Me_5), 10.4 (C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 457.2. IR (KBr): 3052 (w), 3033 (w), 2970 (w), 2902 (w), 1961 (vs), 1926 (s), 1757 (vs), 1460 (w), 1378 (m), 740 (m), 696 (m), 586 (m), 482 (m) cm^{-1}.

[(Cp*Ru)$_2$(μ_2-H)(μ_2-PHPh)(μ_2-CO)] (*cis*-7 and *trans*-7). Complex **4** (59 mg, 0.084 mmol) was suspended in 2-propanol (5 mL) and the mixture was heated in an oil bath at 60 °C with stirring for 12 h. The color of the mixture changed from dark green to dark red. The mixture was allowed to settle and cool to room temperature. Filtration and vacuum drying afforded **7** as a dark red microcrystalline solid. It was obtained as a mixture of cis and trans isomers (cis:trans = 5:4). Yield 32 mg, 63%. Anal. Calcd for $C_{27}H_{37}OPRu_2$: C, 53.10; H, 6.11. Found: C, 53.22; H, 6.24. ^1H NMR (C_6D_6) for *cis*-**7**: δ 7.64−7.07 (m, 5H, Ph), 5.25 (d, $^1J_{PH} = 332.7$ Hz, PH), 1.75 (s, 30H, Cp*), −19.58 (d, $^2J_{PH} = 50.1$ Hz, 1H, μ_2-H). $^{31}P\{^1H\}$ NMR (C_6D_6) for *cis*-**7**: δ 50.5 (s). ^1H NMR (C_6D_6) for *trans*-**7**: δ 7.64−7.07 (m, 5H, Ph), 4.77 (dd, 1H, $^1J_{PH} = 379.1$ Hz, $^3J_{HH} = 8.6$ Hz, PH), 1.79 (s, 30H, Cp*), −20.28 (dd, 1H, $^2J_{PH} = 50.1$ Hz, $^3J_{HH} = 8.6$ Hz, μ_2-H). $^{31}P\{^1H\}$ NMR (C_6D_6) for *trans*-**7**: δ 64.3 (s). IR (KBr): 3042 (w), 2975 (w), 2903 (m), 2246 (m), 2092 (w), 1906 (w), 1737 (vs), 1579 (m), 1477 (m), 1378 (m), 1029 (m), 938 (w), 803 (w), 740 (w), 693 (w), 628 (w), 586 (w), 549 (w), 525 (w), 492 (w) cm^{-1}.

[(Cp*Ru)$_2$(μ_2-H)(μ_2-PPh(OC$_6$H$_4$-*t*-Bu-*p*)(μ_2-CO)] (8). To a solution of **4** (214 mg, 0.305 mmol) in THF (15 mL) was added *p-tert*-butylphenol (458 mg, 3.05 mmol) at −80 °C. The solution was allowed to warm to room temperature and stirred for 12 h. The volatile components were removed in vacuo and the residue was extracted with toluene (10 mL). The extract was concentrated to 1 mL and layered with acetonitrile (5 mL). After solvent diffusion was complete, the dark red blocks of **8** were collected by filtration and dried in vacuo. Yield 143 mg, 62%. Anal. Calcd for $C_{37}H_{49}O_2PRu_2$: C, 58.56; H, 6.51. Found: C, 58.28; H, 6.63. ^1H NMR (C_6D_6): δ 8.05 (m, 2H, Ar), 7.42 (m, 2H, Ar), 7.22−7.08 (m, 5H, Ar), 1.67 (s, 30H, Cp*), 1.21 (s, 9H, *t*-Bu), −20.85 (d, 1H, $^2J_{PH} = 51.4$ Hz, μ_2-H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 266.4 (d, $^2J_{PC} = 9$ Hz, μ_2-CO), 154.2 (d, $J = 4$ Hz, Ar), 145.0 (s, Ar), 144.6 (d, $J = 1$ Hz, Ar), 144.4 (s, Ar), 132.2 (d, $J = 13$ Hz, Ar), 126.6 (s, Ar), 125.3 (s, Ar), 120.0 (d, $J = 8$ Hz, Ar), 93.9 (d, $J = 1$ Hz, C_5Me_5), 34.2 (s, CMe_3), 31.6 (CMe_3), 10.1 (C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 240.5 (s). IR (KBr): 2961 (m), 2904 (m), 1732 (vs), 1506 (s), 1478 (m), 1378 (m), 1221 (s), 1173 (s), 739 (m), 697 (m), 623 (m), 561 (m), 497 (m) cm^{-1}.

X-ray Crystallography. A single crystal of each sample was coated with Paratone-N hydrocarbon oil and mounted on a glass capillary. All measurements were performed on a Rigaku RAXIS Rapid diffractometer equipped with an imaging plate detector. The frame data were processed with use of the Rigaku PROCESS-AUTO program,[19] and the reflection data were corrected for absorption with an ABSCOR program.[20] The structures were solved by a direct method (SHELXS 97) and refined on F^2 by the full-matrix least-squares method by using SHELX97.[21] Anisotropic refinement was applied to all non-hydrogen atoms. Crystallographic data are summarized in Table 1. As to compound **4**, the nitrogen and phosphorus atoms (N(1) and P(1)) are site-disordered. These atoms are modeled to have the same atomic coordinates and U values with 50% occupancies. The hydrogen atom on N (and P) was located by Fourier syntheses and refined with isotropic thermal parameters. Other hydrogen atoms were placed at the calculated positions and treated as riding models. For compound **5**, all hydrogen atoms were placed at the calculated positions and treated as riding models. For compound **8**, the hydride ligand was located by Fourier syntheses and refined with isotropic thermal parameters. Other hydrogen atoms were placed at the calculated positions and treated as riding models. For all structures, the thermal ellipsoid plots were generated with the ORTEP-3 program[22] and presented at the 35% probability level.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Area (No. 18033046, "Chemistry of Coordination Space") from the Ministry of Education, Culture, Sports, Science and Technology, Japan. We are also grateful to the TOYOTA Motor Corporation for financial support.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM701260Y

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