Nitrous Oxide Mediated Synthesis of Monomeric Hydroxoruthenium Complexes. Reactivity of $(DMPE)_2Ru(H)(OH)$ and the Synthesis of a Silica-Bound Ruthenium Complex

Anne W. Kaplan and Robert G. Bergman*

Department of Chemistry, University of California, Berkeley, California 94720

Received April 17, 1998

Treatment of $(DMPE)_2Ru(H)_2$ with 1 equiv of N_2O affords the hydroxoruthenium complex $(DMPE)_2Ru(H)(OH)$ (**1**) in 41% yield. Further treatment with an excess of N_2O affords the dihydroxo complex $(DMPE)_2Ru(OH)_2$ (**5**) in 30% yield. Addition of phenols, thiols, and silanols to **1** yields the corresponding aryloxo-, thiolato-, and siloxoruthenium complexes **6**−**10** in 25−75% yield. The hydroxo ligand of **1** may also be exchanged with the surface silanols of silica to form the silica-bound complex $(DMPE)_2Ru(H)(OSilica)$ (**14**). Subsequent treatment of **14** with thiocresol removes the ruthenium complex as $(DMPE)_2Ru(H)(SC_6H_4Me)$ (**10**). The treatment of **1** with acetone affords the C-bound enolate complex $(DMPE)_2Ru(H)(CH_2C(O)CH_3)$ (**15**) in 34% yield. Terminal alkynes react with **1** to give the ruthenium acetylide complexes *trans*-$(DMPE)_2Ru(H)(CCPh)$ **16** (74% yield) and *trans*-$(DMPE)_2Ru(H)(CCH)$ **17** (32% yield). Reactivity may also be affected at both ends of 1,7-octadiyne to give the bimetallic complex $(DMPE)_2RuC{\equiv}C(CH_2)_4C{\equiv}CRu(DMPE)_2$ (**19**, 33% yield). The addition of Ph_3SnH, which does not contain an acidic hydrogen, to **1** affords $(DMPE)_2Ru(H)(SnPh_3)$ (**20**) in 32% yield. When **1** is treated with 1 equiv of *p*-tolualdehyde, the hydroxo oxygen is retained, the aldehydic C−H bond is broken, and the ruthenium carboxylate complex $(DMPE)_2Ru(H)(OC(O)C_6H_4CH_3)$ (**21**) is obtained in 28% yield. The structural assignment of **21** was confirmed by X-ray crystallography. Similar reactivity is observed when **1** is treated with hexafluoroacetone, in which case the C−C bond is cleaved to produce $(DMPE)_2Ru(H)(OC(O)CF_3)$ (**22**, 55% yield). Much of the observed reactivity of **1** is rationalized using the assumption that the first step involves reversible formation of a metal cation/OH^- ion pair (**23**). Attempts to trap the cation with ethylene resulted in formation of the ruthenium ethylene complex $(DMPE)_2Ru(C_2H_4)$ (**2**); there is strong evidence that **2** forms via a cationic hydridoruthenium ethylene complex. Treatment of **1** with CO forms the cationic hydrido carbonyl complex $[(DMPE)_2Ru(H)(CO)][OH]$ (**25**).

Introduction

Many catalytic processes involve intermediates that are proposed to contain late-transition-metal−heteroatom (N, O, S) bonds.[1−3] Recent work has been directed toward the synthesis of these potentially reactive species, but there remain few examples of monomeric late-metal hydroxo complexes,[3−23] species which are thought to be important in the hydration of olefins to alcohols, the hydration of nitriles to carboxamides, and the Wacker process.[3,24−27]

The preparation and characterization of the monomeric hydroxoruthenium complex $(DMPE)_2Ru(H)(OH)$ (**1**) via the oxidative addition of water to the Ru(0)

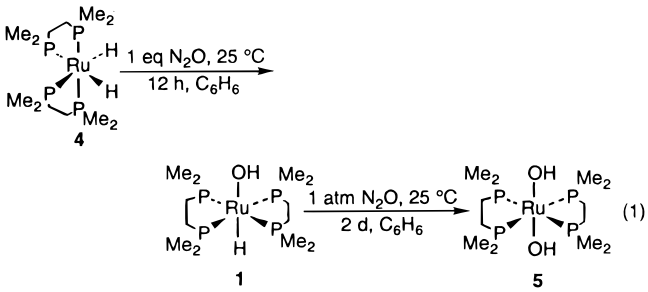
(1) Masters, C. *Homogeneous Transition-Metal Catalysis*; Chapman and Hall: New York, 1981.
(2) Chisholm, M. H. *Polyhedron* **1986**, *5*, 25.
(3) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163.
(4) Tahmassebi, S. K.; McNeil, W. S.; Mayer, J. M. *Organometallics* **1997**, *16*, 5342.
(5) Blum, O.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 229.
(6) Ros, R.; Michelin, R. A.; Bataillard, R.; Roulet, R. *J. Organomet. Chem.* **1978**, *161*, 75−90.
(7) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, 119.
(8) Bennett, M. A.; Appleton, T. *Inorg. Chem.* **1978**, *17*, 1739.
(9) Cole-Hamilton, D. J.; Young, R. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 1995.
(10) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2717.
(11) Milstein, D.; Calabrese, J. C.; Williams, I. D. *J. Am. Chem. Soc.* **1986**, *108*, 6387.
(12) Mehrotra, R. C.; Agarwal, S. K.; Singh, Y. P. *Coord. Chem. Rev.* **1985**, *68*, 101.
(13) James, B. R.; Preece, M.; Robinson, S. D. *Adv. Chem. Ser.* **1982**, *No. 196*, 145.
(14) Vaska, L.; Peone, J. *J. Chem. Soc. D* **1971**, 418.
(15) Stevens, R. C.; Bau, R.; Milstein, D.; Blum, O.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1990**, 1429.
(16) Green, L. M.; Meek, D. W. *Organometallics* **1989**, *8*, 659.
(17) Gevert, O.; Wolf, J.; Werner, H. *Organometallics* **1996**, *15*, 2806.
(18) Woerpel, K. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 7888.
(19) Edwards, A. J.; Elipe, S.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1997**, *16*, 3828.
(20) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Dalton Trans.* **1976**, 993.
(21) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941.
(22) Gemel, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1997**, *16*, 5601.
(23) Bryndza, H. E.; Fong, K. L.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444.

10.1021/om980295d CCC: $15.00 © 1998 American Chemical Society
Publication on Web 10/16/1998

complex $(DMPE)_2Ru(C_2H_4)$ (**2**) to form $[(DMPE)_2Ru(H)(OH)]_2 \cdot 2H_2O$ (**3**) and subsequent removal of the hydrogen-bound H_2O with 4 Å molecular sieves has been reported. Elevated temperatures and extended reaction times are necessary to effect this reaction.[28] More recently we have shown that **1** may be prepared under milder conditions from $(DMPE)_2Ru(H)_2$ (**4**) and N_2O.[29] This transformation represents the first example of oxygen atom transfer from N_2O into a late-transition-metal–hydrogen bond. We now report the full details of the synthesis of **1**, outline its reactivity patterns, and describe the synthesis and chemistry of a silica-bound ruthenium complex.

Results

Synthesis of Monomeric Hydroxoruthenium Complexes. Hillhouse and co-workers have found that N_2O can be used to insert oxygen atoms into nickel–carbon and the relatively oxophilic (group 4) early-metal–hydrogen bonds.[30–34] We have found that N_2O can be used to mediate oxygen atom insertion into the Ru–H bond of $(DMPE)_2Ru(H)_2$ (**4**) (eq 1). Treatment

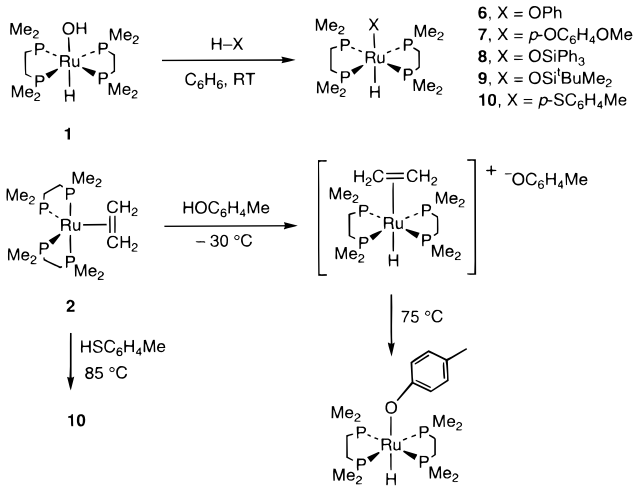


(1)

of the dihydride with 1 equiv of N_2O affords the hydroxoruthenium complex **1** in 41% yield after crystallization. Treatment of either dihydride **4** or the isolated monoinsertion product **1** with 1 atm of N_2O affords the dihydroxo complex $(DMPE)_2Ru(OH)_2$ (**5**), which can be obtained 95% pure in 30% yield (eq 1). Other oxygen atom transfer agents such as pyridine *N*-oxide, Me_3NO, and ethylene oxide do not react with **4** in benzene up to 135 °C, at which point decomposition is observed.

The hydroxo complexes **1** and **5** are sensitive to air. Both are stable to a few equivalents of water but decompose to multiple products upon dissolution in neat water. No observable decomposition is detected spectroscopically when **1** and **5** are treated with 1 equiv of oxygen in benzene, although the solutions darken from tan to light brown. Decomposition to multiple products is observed upon warming to 75 °C.

Scheme 1

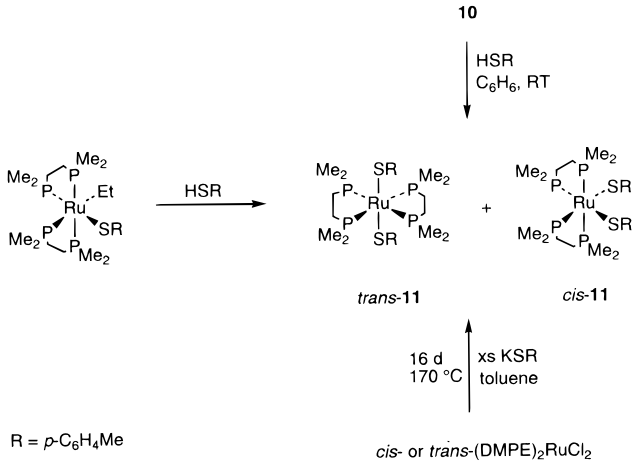


Reactivity of Monomeric Hydroxoruthenium Complexes toward Protic Reagents. We have studied the exchange chemistry of **1** and have demonstrated that a number of complexes containing ruthenium–heteroatom bonds are accessible by treatment with protic reagents at room temperature. Addition of phenols, thiols, and silanols to **1** yield the corresponding aryloxo-, thiolato-,[35] and siloxoruthenium complexes **6**–**10** in 25–75% yield (Scheme 1).[36] These reactions all occur at room temperature in benzene, and the products exhibit many diagnostic spectroscopic features. The ^1H NMR spectrum of the phenoxide **6** shows a hydride resonance at δ −23.3 ppm as a quintet (J_{HP} = 21.8 Hz). A trans geometry is indicated by $^{31}P\{^1H\}$ NMR spectroscopy, which shows a single resonance at δ 45.4 ppm for the equivalent phosphine groups. The M–H stretch is observed at 1928 cm^{-1} in the IR spectrum. Similar characteristics are observed for complexes **7**–**10**. Hydrido aryloxide and thiolate complexes are also accessible by treating $(DMPE)_2Ru(C_2H_4)$ with aryl alcohols and thiols (Scheme 1); however, elevated temperatures and longer reaction times are necessary (see Discussion).

In the reaction of **1** with thiocresol, excess thiol reacts with the hydrido thiolate product **10** to form a 3:1 mixture of cis and trans bis(thiolate) complexes with the loss of H_2 (Scheme 2). Complex **11** can also be obtained by treating $(DMPE)_2Ru(Et)(SC_6H_4Me)$ with 1 equiv of HSC_6H_4Me; the ratios of cis to trans isomers obtained is again 3:1. Pure *trans*-$(DMPE)_2Ru(SC_6H_4Me)_2$ can be crystallized selectively as red, air-stable blocky crystals by diffusion of pentane into a toluene solution of the two isomers at room temperature. Isolation of *trans*-**11** by crystallization made it possible to assign proton resonances in the ^1H NMR spectrum for both isomers. In the case of *trans*-**11**, the equivalent phosphine methyl protons appear at δ 1.35 ppm. The $^{31}P\{^1H\}$ NMR spectrum of *trans*-**11** shows a singlet for the equivalent phosphines at δ 36.4 ppm. The cis isomer of **11** shows a ^1H NMR spectrum similar to that of *trans*-**11**; ^{31}P-

(24) Jensen, C. M.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 723.
(25) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1973**, *95*, 3030.
(26) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339.
(27) Yoshida, T.; Matsuda, T.; Okano, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027.
(28) Burn, M. J.; Fickes, M. G.; Hartwig, J. F.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 5875.
(29) Kaplan, A. W.; Bergman, R. G. *Organometallics* **1997**, *16*, 1106.
(30) Koo, K.; Hillhouse, G. L.; Rheingold, A. L. *Organometallics* **1995**, *14*, 456.
(31) Matsunaga, P. T.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 2075.
(32) Matsunaga, P. T.; Mavropoulos, J. C.; Hillhouse, G. L. *Polyhedron* **1995**, *14*, 175.
(33) Vaughan, G. A.; Rupert, P. B.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1987**, *109*, 5538.
(34) Vaughan, G. A.; Sofield, C. D.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1989**, *111*, 5491.
(35) Burn, M. J.; Fickes, M. G.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1995**, *14*, 137.
(36) Yields refer to recrystallized material and do not reflect percent conversions to spectroscopically pure material, which are >90%.

Scheme 2

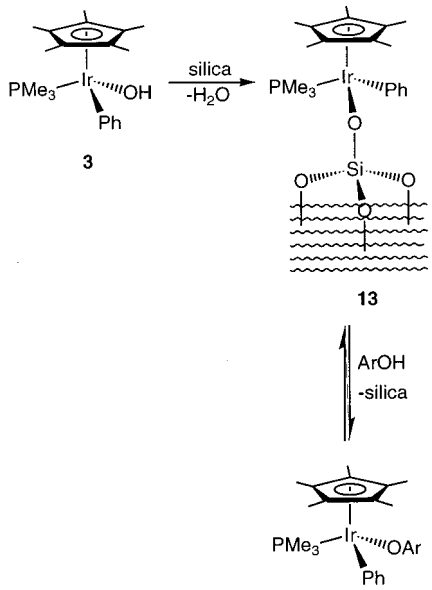


$\{^1H\}$ NMR spectroscopy is more diagnostic. Two triplets at δ 38.6 and 33.1 ppm (J_{PP} = 22.1 Hz) indicate a cis orientation of the thiocresolate ligands. In an effort to synthesize each isomer individually, *cis*- and *trans*-$(DMPE)_2RuCl_2$ were each treated with an excess of KSC_6H_4Me in toluene at 170 °C for 16 days. The rather stringent conditions required for this metathesis also effected the interconversion of cis and trans isomers, giving the same 3:1 mixture (Scheme 2).

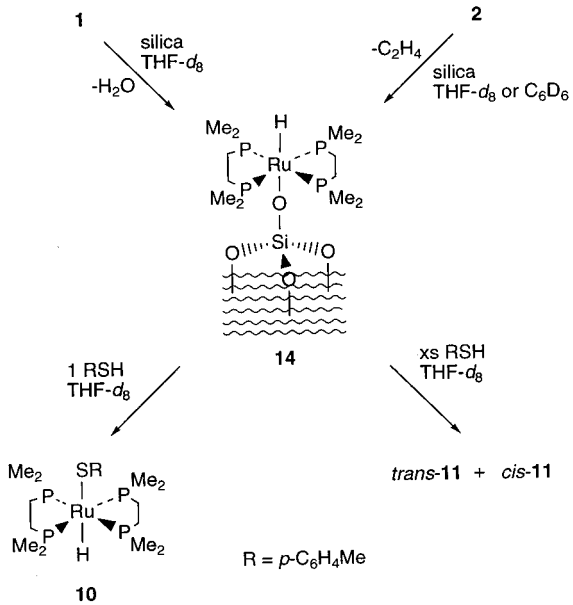
Because the reaction mixture was heterogeneous, efforts were made to increase the solubility of the potassium thiocresolate. THF was used as an alternate solvent, but no reaction occurred at 105 °C, even in the presence of 18-crown-6;[37] therefore, this route was abandoned. Lithium salts have been used to increase the solubility of the anion in heterogeneous reaction mixtures.[38] The addition of lithium cresolate, however, also had no effect on the reaction. Considering the elevated temperatures at which the bis(thiolates) are formed from the dichloride, the 3:1 *cis*-/*trans*-**11** mixture appeared to be the thermodynamic ratio. Thermolysis of purified *trans*-**11** in THF-d_8 at 135 °C for 12 days results in the same 3:1 ratio, which confirms this conclusion. A similar ratio of bis(thiolate) complexes was reported recently for the synthesis of $(DMPE)_2Ru(SPh)_2$ from $(DMPE)_2Ru(H)_2$.[39]

Silica as a Ligand. Metal oxide supported transition-metal complexes have drawn interest as hybrids of heterogeneous and homogeneous catalysts.[40−42] Meyer et al. previously reported that $Cp^*(PMe_3)(Ph)Ir(OH)$ (**12**) undergoes exchange with silica to form the supported complex $Cp^*(PMe_3)(Ph)Ir$[silica] (**13**, Scheme 3).[43]

Scheme 3



Scheme 4



More importantly, the iridium complex can be removed from silica using phenols, forming the corresponding phenoxide complexes. The reactivity of **1** toward protic reagents suggested that a similar silica-bound ruthenium complex may be accessible by treating **1** with silica.

When silica is treated with hydroxoruthenium complex **1** in THF, the new silica-bound complex **14** is formed, the silica turns tan, and the supernatant changes from tan to colorless (Scheme 4). Complex **14** is stable at room temperature. The ^{13}C CPMAS NMR spectrum of the supported complex **14** (see the Supporting Information) shows three resonances for the trans-disposed DMPE ligands at δ 31, 21, and 14 ppm. Interrupted decoupling experiments[44] were employed to identify the two upfield resonances as the CH_3 carbons. The ^{31}P CPMAS NMR displays one singlet at δ 44.0 ppm as expected, confirming the trans geometry and sup-

(37) Dall'Antonia, P.; Graziani, M.; Lenarda, M. *J. Organomet. Chem.* **1980**, *186*, 131.
(38) Ito, Y.; Nakatsuka, M.; Kise, N.; Saegusa, T. *Tetrahedron Lett.* **1980**, *21*, 2873.
(39) Field, L. D.; Hambley, T. W.; Yau, B. C. K. *Inorg. Chem.* **1994**, *33*, 2009.
(40) *Supported Metal Complexes*; Hartley, F. R., Ed.; D. Reidel: Boston, 1985.
(41) Yermakov, Y. I.; Kuznetsov, B. N.; Zakharov, V. A. *Catalysis by Supoprted Metal Complexes*; Elsevier: New York, 1981.
(42) See, for example: (a) Dufour, P.; Scott, S. L.; Santini, C. C.; Lefebvre, F.; Basset, J.-M. *Inorg. Chem.* **1994**, *33*, 2509. (b) Scott, S. L.; Dufour, P.; Santini, C. C.; Basset, J.-M. *Inorg. Chem.* **1996**, *35*, 869. (c) Scott, S. L.; Crippen, C.; Santini, C. C.; Basset, J.-M. *J. Chem. Soc., Chem. Commun.* **1995**, 1875. (d) Scott, S. L.; Basset, J.-M.; Niccolai, G. P.; Santini, C. C.; Candy, J.-P.; Lecuyer, C.; Quignard, F.; Choplin, A. *New J. Chem.* **1994**, *18*, 115.
(43) Meyer, T. Y.; Woerpel, K. A.; Novak, B. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 10290.
(44) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854.

porting the formation of one distinct silica-bound species. For comparison, CPMAS spectra were also obtained on a solid sample of **1** (see the Supporting Information). The ^{13}C CPMAS NMR spectrum of **1** contains resonances at δ 33, 24, and 14 ppm. The ^{31}P CPMAS NMR displays a singlet at δ 49 ppm. The IR spectrum of **14** shows a weak M−H stretch at 1967 cm^{-1}, which is close to that of **8** (1928 cm^{-1}), whereas the M−H stretch of **1** appears at 1836 cm^{-1}. Interestingly, it is also possible to obtain a conventional ^{31}P-{^{1}H} spectrum of **14** as a "slurry". When a 10 mm NMR tube is loaded with a suspension of **14** in THF-d_8, ^{31}P-{^{1}H} analysis in 1000 scans shows a singlet at δ 47 ppm.[45] The NMR resonances for **14** are only slightly different from those of **1**.

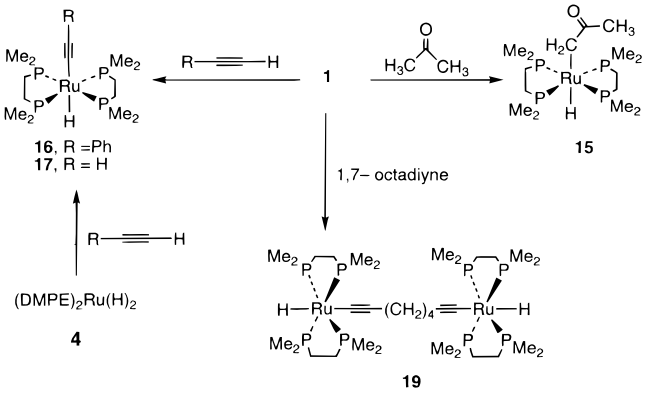
The solid-state characterization is consistent with the proposed structure of **14**. To obtain further evidence for the structure of the supported complex, the reactivity of **14** with thiocresol was exploited. The addition of exactly 1 equiv of thiocresol to **14** produces hydrido thiocresolate **10** in 95% yield (Scheme 4). Since these exchange reactions presumably involve cleavage of only the Ru−O bond, and hydroxidoruthenium complexes **1** and **10** are otherwise analogous, the structure of bound ruthenium complex **14** may be inferred. Evidence that the ruthenium complex is in fact chemisorbed by a ruthenium−oxygen bond, and not simply hydrogen-bonded to the silica surface, was obtained by monitoring the reaction of (DMPE)$_2$Ru(C$_2$H$_4$) (**2**) with silica (Scheme 4). The ruthenium−silica species formed from **2** and silica exhibits the same solid-state spectroscopic data, as well as reactivity toward thiocresol as the species generated from **1** and silica. When this reaction is followed by ^{1}H NMR in THF-d_8, 1 equiv of free ethylene is observed.

Reactions that result in attachment and removal of **1** from the silica surface appear to leave the ruthenium hydride linkage intact. When, however, an excess of thiocresol is used in removing the ruthenium complex from the surface, a mixture of bis(thiocresolates) *cis*- and *trans*-**11** is obtained, presumably by further reaction of the initially formed cresolate hydride **10** with the excess thiocresol (vide infra). Interestingly, **14** may be prepared in benzene, but **14** is unreactive toward thiocresol at room temperature in benzene, a trend also observed in the reactions of iridium−silica complex **13** with phenols. When the solvent is replaced with THF, **14** reacts with thiocresol as described above.

Treatment of 1 with Carbon Acids. Hydroxo hydride **1** is also reactive toward molecules containing acidic C−H bonds. For example, the treatment of **1** with acetone affords the C-bound enolate complex **15** in 34% yield (Scheme 5).[36] The presence of a singlet in the ^{31}P-{^{1}H} NMR spectrum at δ 43.0 ppm and two DMPE methyl peaks in the ^{1}H NMR spectrum at δ 1.38 and 1.14 ppm indicates a trans configuration. The hydride appears as a quintet at δ −16.67 ppm, and the M−H stretch in the IR is at 1928 cm^{-1}. Confirmation that the enolate is C-bound comes from the following data. DEPT experiments confirm the presence of a CH$_2$ group which appears as a quintet (J_{CP} = 4.2 Hz), indicating

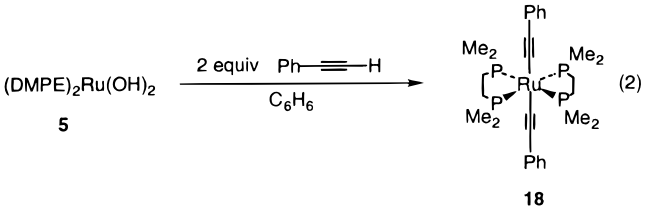
(45) A reviewer has suggested that the resonance may be due to a solution species which has leached from the silica surface. This is unlikely, since NMR analysis of the supernatant alone after taking a spectrum of the suspension contains no detectable ^{31}P resonances.

Scheme 5



coupling of the carbon to the four equivalent phosphorus atoms. In an O-bound structure, the CH$_2$ would appear as a singlet. Further, the ^{1}H NMR shift of the CH$_2$ group is at δ 1.57 ppm, which is not in the olefinic region. Finally, the presence of a carbonyl is supported by the downfield shift of δ 210.7 ppm in the ^{13}C{^{1}H} NMR spectrum and an IR stretch at 1713 cm^{-1}. It is also interesting to note that the ^{1}H chemical shift of the hydride resonance reflects the trans influence of the ligand located trans to it. For example, the chemical shift of the hydride at δ −16.67 ppm is similar to that observed for analogous bis-DMPE ruthenium alkoxides, amides, and halides (δ −18 to −25 ppm) but is substantially upfield from shifts observed when the H is trans to a hydride, stannyl, or hydrocarbyl ligand (δ −9 to −13 ppm).

Terminal alkynes react with hydroxo hydride **1** to give the ruthenium acetylide complexes **16** (74% yield) and **17** (32% yield) (Scheme 5).[36] Complex **16** has been generated independently from dihydride **4** and 1 equiv of phenylacetylene. The H and alkynyl groups in complexes **16** and **17** are also trans-disposed, as they each contain a singlet in the ^{31}P{^{1}H} NMR spectrum at δ 45.5 and 45.2 ppm, respectively. The hydrides appear as quintets at δ −11.95 and −12.37 ppm in the ^{1}H NMR spectrum. The IR spectrum of **17** exhibits a C≡C stretch at 1905 cm^{-1}. In the analogous doubly-^{13}C-labeled complex *trans*-(DMPE)$_2$Ru(H)(^{13}C^{13}CH) (**17**-$^{13}C_2$), the ^{13}C≡^{13}C stretch appeared at 1838 cm^{-1}. The monomeric nature of **17** is supported by EIMS and the presence of a terminal C−H stretch at 3269 cm^{-1}. The ^{13}C{^{1}H} NMR spectrum of **17**-$^{13}C_2$ shows the terminal acetylide carbon as a doublet at δ 91.2 ppm (J_{CC} = 110.6 Hz) and the ruthenium-bound acetylide carbon as a doublet of quintets at δ 121.8 ppm (J_{CP} = 13.7 Hz). The ^{1}H NMR spectrum of **17**-$^{13}C_2$ shows the terminal acetylide proton as a doublet at δ 2.14 ppm (J_{HC} = 35.0 Hz). Phenylacetylene also reacts with the dihydroxo complex **5** to give the bis(acetylide) complex **18**. Bis(acetylide)

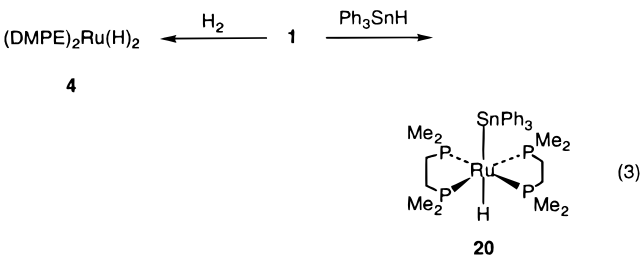


(2)

18 was recently reported by Field and co-workers to be

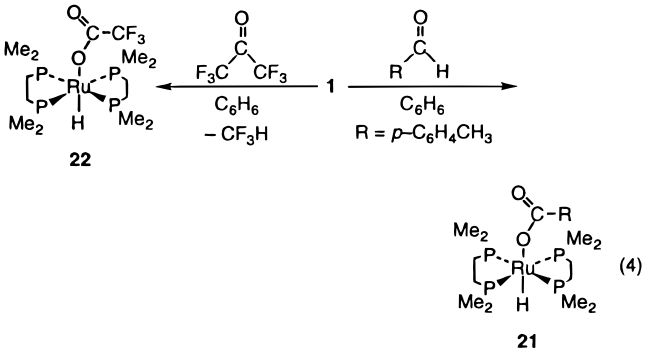
the product of addition of phenyl acetylene to **4**.[46] Interestingly, reactivity can be effected at both ends of 1,7-octadiyne to give the bimetallic complex **19** in 33% yield (Scheme 5). Complex **19** has been formulated as a dimer and not a monomer for two reasons. First, the EIMS exhibits a peak for M^+ at *m/z* 910. Second, there is no terminal C−H stretch observed in the IR spectrum. The reactivity of **1** toward internal alkynes did not result in clean products. Treatment of **1** with DMAD (dimethyl acetylenedicarboxylate) results in decomposition to multiple products. Diphenylacetylene does not react with **1**.

While the aforementioned reactions may be thought of as proceeding by protonation of the hydroxo moiety, this is not the only mode of reactivity available to the hydroxoruthenium complex **1**. The addition of Ph_3SnH, which does not contain an acidic hydrogen, to **1** affords the stannyl hydride complex **20** in 32% yield (eq 3). Both



Sn−P ($^2J_{P-Sn}$ = 174.6 Hz) and Sn−H ($^2J_{H-Sn}$ = 216.1 Hz) couplings are observed by NMR spectroscopy. Additionally, **1** reacts with dihydrogen to afford dihydride complex **4** (88% yield).

C−H and C−C Bond Activation. Treatment of (DMPE)$_2$Ru(H)(OH) with Carbonyl Compounds. An unusual reaction is observed when **1** is treated with 1 equiv of *p*-tolualdehyde (eq 4). The hydroxo oxygen



is retained, the aldehydic C−H bond is broken, and the ruthenium carboxylate complex **21** is obtained in 28% yield.[36]

Retention of the hydroxo oxygen was confirmed by ^{17}O labeling. When ^{17}O-labeled **1** is treated with *p*-tolualdehyde, the oxygen label is retained and ^{17}O NMR shifts of the product **21** appear at δ 6.7 and −10.35 ppm. It is likely that the carboxylate ligand in **21** is labile and that the oxygens scramble intramolecularly in solution to incorporate the oxygen label into both positions. The structure of **21** was confirmed by X-ray crystallography.[47] The structure was solved by direct methods and

Table 1. Crystal Data for 21

diffractometer	Enraf-Nonius CAD-4
T (°C)	−108.0
radiation	Mo Kα (λ = 0.710 73 Å)
takeoff angle	3.0°
cryst-to-detec dist	60 mm
empirical formula	$RuP_{4O2C20H40}$
fw	537.5
cryst color, habitat	orange blocks
cryst size (mm)	0.25 × 0.30 × 0.30
space group	$P2_12_12_1$ (No. 19)
unit cell dimens	a = 11.926(2) Å
	b = 12.832 (2) Å
	c = 17.159(4) Å
V, Z	2626.0(17) Å^3, 4
D_{calc}	1.36 g/cm^3
μ_{calc}	8.4 cm^{-1}
scan type	ω (0.3°/frame)
scan rate	10.0 s/frame
$2\theta_{max}$	60.0°
no. of rflns collected	4219
no. of unique rflns	4191
no. of obsd rflns, $I > 3.00\sigma(I)$	2710
no. of variables	244
R	0.039
R_w	0.040
goodness of fit	1.32
p factor	0.03
max shift/error in final cycle	<0.05
max and min peaks in final diff map	0.67/−0.20 e Å^{-3}

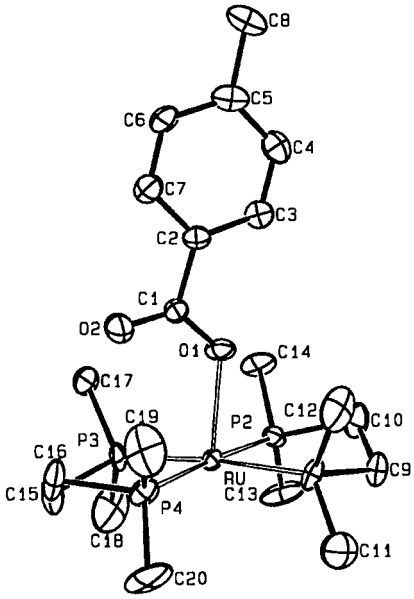


Figure 1. ORTEP diagram of (DMPE)$_2$Ru(H)(OC(O)C$_6$H$_4$-Me) (**21**).

refined using standard least-squares and Fourier techniques. Crystal and data collection parameters are shown in Table 1, and details of the structure determination are given in the Experimental section. Positional and thermal parameters are given as Supporting Information. An ORTEP diagram of **21** is shown in Figure 1. Table 2 provides intramolecular bond lengths and angles for this compound. The structure confirms the connectivity assigned to **21**. There is no apparent interaction between the carbonyl oxygen and the ruthenium center in the solid state, since the Ru···O(2) distance of 3.43 Å is 1.2 Å longer than Ru−O(1).

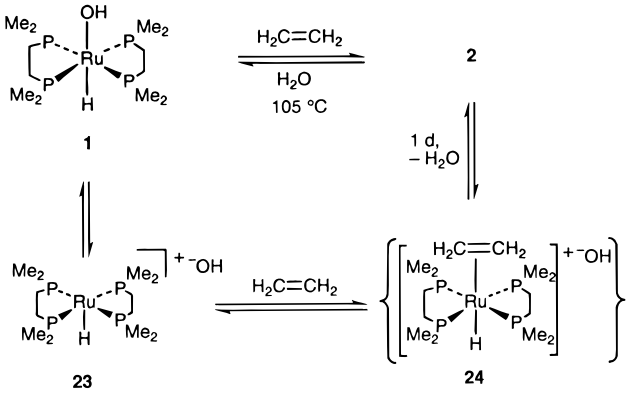
(46) Field, L. D.; George, A. V.; Hockless, D. C. R.; Purches, G. R.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1996**, 2011.

(47) Perutz and co-workers have recently solved the X-ray structure of the related complex (DMPE)$_2$Ru(H)(OCOH): Whittlesey, M. K.; Perutz, R. N.; Moore, M. H. *Organometallics* **1996**, *15*, 5166.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 21

Ru−P1	2.308(4)	Ru−O1	2.256(4)
Ru−P2	2.277(4)	O1−C1	1.256(7)
Ru−P3	2.297(3)	C1−O2	1.244(8)
Ru−P4	2.294(4)	Ru···O2	3.434(5)
P1−Ru−P2	84.19(6)	P1−Ru−O1	87.93(23)
P1−Ru−P3	174.05(15)	P2−Ru−O1	84.34(21)
P1−Ru−P4	95.44(14)	P3−Ru−O1	97.96(22)
P2−Ru−P3	95.52(13)	P4−Ru−O1	99.23(21)
P2−Ru−P4	176.40(14)	Ru−O1−C1	127.5(4)
P3−Ru−P4	84.47(5)	O2−C1−C2	117.6(6)
O1−C1−O2	125.1(5)	O1−C1−C2	116.7(5)

Scheme 6

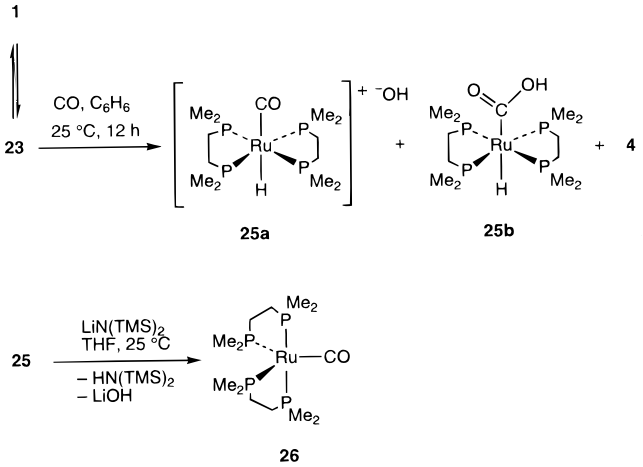


We have found that **4** and *p*-toluic acid also form complex **21** with loss of dihydrogen. When **1** is treated with hexafluoroacetone, another carboxylate complex (**22**) is formed in 55% yield (eq 4).[36] In this case, the C−C bond is broken and the release of trifluoromethane is observed by NMR spectroscopy. The $^{19}F\{^1H\}$ NMR spectrum contains a singlet at δ −74.4 ppm, consistent with the presence of a CF_3 group in the product **22**. The hydride resonates at δ − 23.40 ppm in the ^1H NMR spectrum, confirming a trans geometry and indicating that the hydride is located trans to an oxygen-based ligand. The carbonyl carbon appears as a quartet at δ 161.2 ppm, and the C−F coupling constant (J_{CF} = 32.8 Hz) is typical for two-bond coupling.

Addition of Ethylene to $(DMPE)_2Ru(H)(OH)$. Much of the observed reactivity of **1** can be rationalized using the assumption that the first step involves reversible formation of a metal cation/OH^- ion pair (**23**). Attempts to trap the cation with ethylene resulted in formation of the ruthenium ethylene complex $(DMPE)_2Ru(C_2H_4)$ (**2**) at 105 °C (Scheme 6). No reaction was observed at temperatures below 90 °C, and no intermediates were observed; however, there is strong evidence that **2** forms via the cationic hydridoruthenium ethylene complex **24**. This is provided by the reverse of the synthesis of **1** described earlier, which involves oxidative addition of water to ethylene complex **2**, the mechanism of which is described in the Discussion (vide supra).[28]

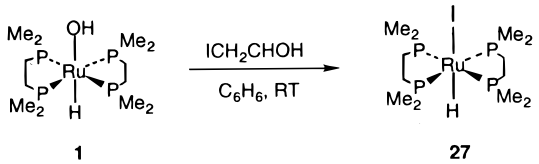
Synthesis and Reactivity of a Cationic Ruthenium Hydrido Carbonyl Complex. The proposed metal cation/OH^- ion pair **23** can indeed be trapped with CO. When a solution of **1** in C_6H_6 or THF is exposed to 1 atm of CO at room temperature, a white precipitate (**25**, 93%) is formed (Scheme 7). The product **25** is insoluble in common organic solvents, and chlorinated solvents decompose it. FAB-MS clearly shows the hydrido carbonyl cation. Negative ion FAB-MS

Scheme 7



supported the absence of a large detectable anion. Complex **25** has been characterized further by elemental analysis and IR spectroscopy. The presence of a stretch at 1950 cm^{-1} indicates the presence of a terminal CO ligand. The identification of this band was confirmed by the use of ^{13}CO. The labeled product exhibits an IR stretch at 1915 cm^{-1}, and the stretch at 1950 cm^{-1} was no longer present. Surprisingly, another stretch observed in the spectrum of the unlabeled complex **25** at 1628 cm^{-1} moved to 1604 cm^{-1} upon ^{13}CO labeling. This indicates that two CO-containing species are present in the solid state, one a terminal metal carbonyl and the other a carboxy ($RuCO_2H$) carbonyl. Further, when the supernatant from the reaction is concentrated, $(DMPE)_2Ru(H)_2$ (**4**) is isolated (7%). It is likely that the dihydride **4** results from β-hydride elimination from **25b** before it precipitates out of solution. Cation **25** may be deprotonated with $LiN(SiMe_3)_2$ in THF to form the neutral carbonyl complex $(DMPE)_2Ru(CO)$ (**26**; Scheme 7).[48] When the reaction is followed by ^1H NMR spectroscopy, the formation of 1 equiv of $HN(SiMe_3)_2$ is observed as well. The remaining insoluble white powder is presumed to be LiOH.

Halogen for Hydride Exchange at Ruthenium. Hydroxide **1** is sensitive toward ligand exchange with halogens. When **1** is dissolved in chlorinated solvents such as CCl_4, $CHCl_3$, and CH_2Cl_2, varying amounts of $(DMPE)_2Ru(H)(Cl)$, $(DMPE)_2Ru(OH)(Cl)$, and $(DMPE)_2RuCl_2$ are observed. Treatment of **1** with 2-iodoethanol in benzene yields the hydrido iodide complex **27**[49] in 57% yield (eq 5). Inequivalent DMPE Me resonances at δ

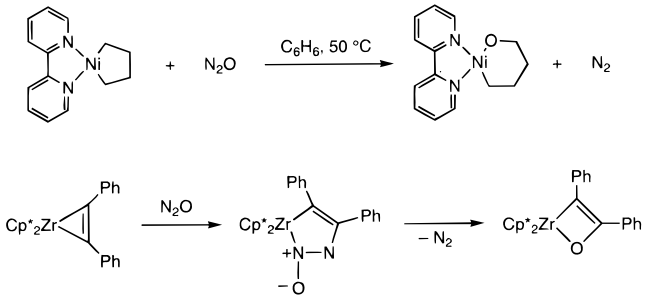


(5)

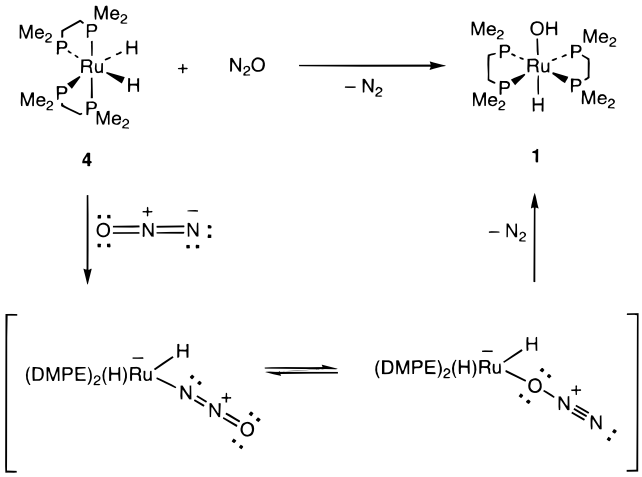
1.69 and 1.12 ppm in the ^1H NMR and a singlet at δ 38.6 ppm in the $^{31}P\{^1H\}$ NMR spectrum are consistent with its formulation as the trans isomer **27**. The

(48) Jones, W. D.; Libertini, E. *Inorg. Chem.* **1986**, *25*, 1794.
(49) This complex was originally characterized by IR and elemental analysis. We further characterized it by NMR spectroscopy. See: Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, 2605.

Scheme 8



Scheme 9



hydride resonance at δ −18.41 ppm falls into the region typically observed for hydrides located trans to halide ligands.

Discussion

Formation of Hydroxoruthenium Complexes with N_2O. As mentioned in the Results, we have found that treatment of $(DMPE)_2Ru(H)_2$ (**4**) with 1 equiv of N_2O affords the hydrido hydroxo complex **1** and that the dihydroxo complex **5** is formed upon exposure to excess N_2O (eq 1). While N_2O proves to be a convenient anhydrous reagent for inserting an O atom into a metal−hydride bond under mild conditions, not much is known about the actual mechanism of N_2O-mediated oxygen atom insertion. This is due in part to the fact that the use of N_2O to directly oxidize organic fragments on metal centers is rare. As mentioned earlier, Hillhouse and co-workers did show that N_2O can be used to insert oxygen atoms into nickel−carbon and the relatively oxophilic (group 4) early-metal−hydrogen bonds.[30−34] In the case of Ni (Scheme 8), the authors invoke coordination of N_2O to form a five-coordinate intermediate prior to N_2 loss and oxygen atom transfer.[31] They observe no intermediate in this reaction; however, an intermediate is observed in the Zr system they studied (Scheme 8). In this case, N_2O inserts into a metal−carbon bond to form a Zr−N linkage before losing N_2 to form the O-inserted product. At present, the only metal complex reported to contain N_2O as a ligand is $[Ru(NH_3)_5N_2O]^{2+}$.[50] Because of the instability of this ion, the complex could not be structurally characterized; however, theoretical studies by Hoffmann and co-workers indicate that N-linkage complexes are more stable than the analogous O-linkage complexes.[51] In our studies of the N_2O-mediated oxygen atom insertion into ruthenium hydride complexes, no intermediates are observed, yet it seems likely that N_2O coordinates initially to the ruthenium center (either via O or N with subsequent rearrangement) prior to N_2 loss with hydride migration to oxygen (Scheme 9). We cannot rule out an N_2O insertion pathway, however.

Treatment of the Hydroxoruthenium Complex 1 with Protic Reagents. The synthesis of compounds containing late-metal−heteroatom bonds has typically involved metathesis reactions of metal halide complexes with alkali-metal alkoxide, amide, thiolate, etc. reagents.[52] Alternatively, earlier work in these laboratories has shown that $(DMPE)_2Ru(C_2H_4)$ (**2**) is a useful precursor for a variety of complexes containing metal−heteroatom bonds. Complex **2** has been treated with HX (X = SAr, OAr, PPhH, NHPh) to give the corresponding $(DMPE)_2Ru(H)(X)$ complexes via a protonation mechanism (Scheme 1).[35] In contrast to the high temperatures required to form complexes containing metal−heteroatom bonds from **2**, the hydroxidoruthenium complex **1** undergoes exchange reactions with thiols, phenols, and silanols at room temperature (Scheme 1).

Similar to the exchange reactions with silanols, **1** reacts with silica to form **14**, containing a Ru−O−silica linkage. Characterization of supported metal complexes has been a challenge.[53] Physical methods such as IR and NMR spectroscopy and EXAFS have been employed[54] but have not always provided conclusive characterization. Basset and co-workers have studied the chemistry of allylrhodium complexes grafted onto silica, as well as titania and alumina.[42] A large part of these studies has focused on the reactivity of the supported complexes toward small organic compounds and identifying the organic products. By probing the reactivity of the bound complexes, they obtain circumstantial evidence for the structure of the organometallic groups on the surface. In contrast, we have developed a different method for characterizing silica-bound metal complexes.[43] For example, the ruthenium fragment of **14** may be removed from the silica surface as the thiocresolate derivative **10**, by treating **14** with *p*-thiocresol (Scheme 4). By removal of the intact metal complex, evidence is provided that significant structural changes

(50) (a) Armor, J. N.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 6874. (b) Bottomley, F.; Crawford, J. R. *J. Chem. Soc. D* **1971**, 200. (c) Bottomley, F.; Crawford, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 9092. (d) Diamantis, A. A.; Sparrow, G. J. *J. Chem. Soc. D* **1970**, 819. (e) Diamantis, A. A.; Sparrow, G. J.; Snow, M. R.; Norman, T. R. *Aust. J. Chem.* **1975**, *28*, 1231.

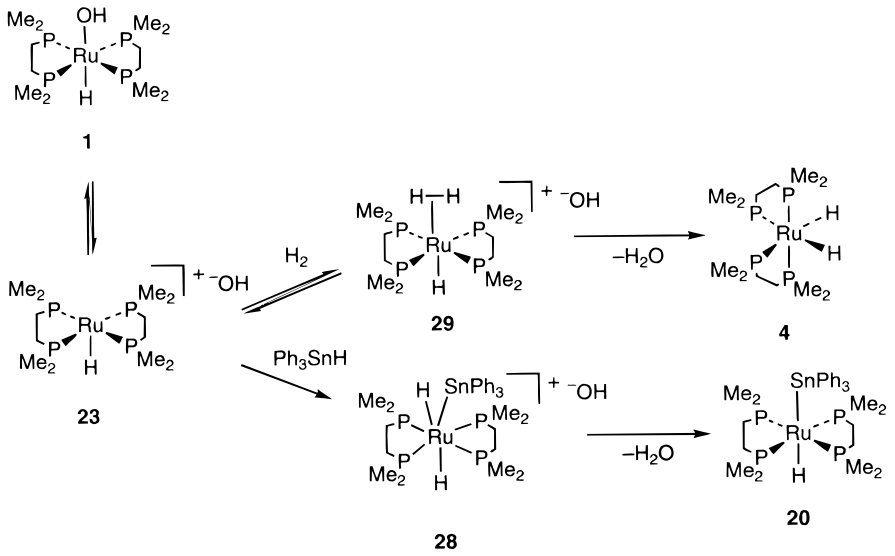
(51) Tuan, D. F.-T.; Hoffmann, R. *Inorg. Chem.* **1985**, *24*, 871.

(52) Recent examples include: (a) Newman, L. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 5314. (b) Fornies, T.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1006. (c) Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 6387. (d) Hartwig, J. F.; Anderson, R. A.; Bergman, R. G. *Organometallics* **1991**, *10*, 1875. (e) Bohle, D. S.; Jones, T. C.; Rickard, C. E. F.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1984**, 865. (f) Edwards, A. J.; Elipe, S.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1997**, *16*, 3828.

(53) Roberto, D.; Cariati, E.; Pizzotti, M.; Psaro, R. *J. Mol. Catal. A* **1996**, *111*, 97.

(54) See, for example, a discussion of a supported rhodium catalyst: (a) Schwartz, J. *Acc. Chem. Res.* **1985**, *18*, 302. (b) Foley, H. C.; DeCanio, S. J. T.; Chao, K. J.; Onuferko, J. H.; Dybowski, C.; Gates, B. C. *J. Am. Chem. Soc.* **1983**, *105*, 3074. (c) Dufour, P.; Santini, C. C.; Houtman, C.; Basset, J. M. *J. Mol. Catal.* **1991**, *66*, L23.

Scheme 10



did not occur in the bound complex while on the silica surface.

C−H Activation of Carbon Acids. We were interested in the extent to which hydroxidoruthenium complex **1** may act as a base, in particular to explore its ability to activate C−H bonds. When treated with acetone, **1** forms the C-bound enolate complex **15** (Scheme 5). Current interest in transition-metal enolate complexes comes from their possible application as synthons for carbanions, for example in the design of catalysts for the aldol reaction.[55] Enolates have been shown to bind to metal centers in an η^1-mode through the oxygen atom, or methylene group, or in an η^3-mode as an oxaallyl. Typically, late-metal enolates are C-bound, although a few examples of late-transition-metal O-bound enolates have been reported.[37,38,56] Hartwig et al. have found that the enolate ligand tends to bind through the oxygen atom rather than the methylene in the related tetrakis(trimethylphosphine)ruthenium system.[57]

Complex **1** also activates the C−H bonds of terminal alkynes. Monomeric terminal acetylide complexes **16** and **17** are formed when **1** is treated with the corresponding alkyne (Scheme 5). Similarly, when dihydroxo complex **5** is treated with 2 equiv of phenylacetylene, the bis(acetylide) complex (**18**) is obtained (eq 2). The dimeric species **19** (Scheme 5) is obtained when **1** is treated with 1,7-octadiyne. Extension of this reactivity to conjugated alkynes could be a possible approach to conjugated organometallic systems, which have attracted much recent attention.[58−65]

As noted above, much of the observed reactivity of **1** can be rationalized using the assumption that the first step involves reversible formation of a metal cation/OH^- ion pair (**23**). This is most easily applied to the reaction of **1** with weak protic acids H−X, perhaps including alkynes and acetone. In the reaction of triphenyltin hydride, we suggest that, after OH^- dissociation, the Sn−H bond oxidatively adds to the cationic ruthenium center in intermediate **23**, and then hydroxide removes a proton from the Ru in **28**[66] to arrive at the observed product **20** (Scheme 10). Similar reactivity of **1** toward H_2 would give the cationic dihydrogen hydride complex $[(DMPE)_2Ru(H_2)(H)][OH]$ (**29**), which, upon loss of water, would form the observed dihydride **4** (Scheme 10). Field and co-workers have shown that dihydrogen hydride complexes in this system are indeed stable and may be formed by protonation of **4** by simple alcohols. In fact, when **4** is dissolved in neat methanol, the corresponding dihydrogen hydride complex is formed reversibly and is able to reversibly lose hydrogen to form the five-coordinate cation $(DMPE)_2RuH^+$.[39] We believe we are observing the reverse of this reaction with H_2O.

C−H and C−C Bond Activation of Carbonyl Compounds. Initial ion pair formation can also be used to rationalize the apparent oxidations of *p*-tolualdehyde and hexafluoroacetone to the corresponding carboxylate complexes. O-Coordination of the aldehyde to the ruthenium center and subsequent hydroxide attack at the carbonyl carbon in **30** would form the metallaacetal species **31** (Scheme 11).[67] This species is likely to be unstable with respect to β-elimination, leading to the dihydride complex **4** and the carboxylic

(55) (a) Mukaiyama, T.; Banno, K.; Narasaka, K. *J. Am. Chem. Soc.* **1974**, *96*, 7503. (b) Yamamoto, Y.; Naruyama, K. *Tetrahedron Lett.* **1980**, 4607. (c) Stille, J. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 1665. (d) Evans, D. A.; McGee, L. R. *Tetrahedron Lett.* **1980**, 3975. (e) Reetz, M. T.; Vougioukas, A. E. *Tetrahedron Lett.* **1987**, *28*, 793. (f) Sato, S.; Matsuda, I.; Izumi, Y. *Tetrahedron Lett.* **1986**, 5517.

(56) Slough, G. A.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1989**, *111*, 938.

(57) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 5670.

(58) Yam, V. W.-W.; Lau, V. C.-Y.; Cheung, K.-K. *Organometallics* **1996**, *15*, 1740.

(59) Weng, W.; Bartik, T.; Brady, M.; Bartik, B.; Ramsden, J. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1995**, *117*, 11922.

(60) Narvor, N. L.; Toupet, L.; Lapinte, C. *J. Am. Chem. Soc.* **1995**, *117*, 7129.

(61) Khan, M. S.; Kakkar, A. K.; Ingham, S. L.; Raithby, P. R.; Lewis, J. *J. Organomet. Chem.* **1994**, *472*, 247.

(62) Atherton, Z.; Faulkner, C. W.; Ingham, S. L.; Kakkar, A. K.; Khan, M. S.; Lewis, J.; Long, N. J.; Raithby, P. R. *J. Organomet. Chem.* **1993**, *462*, 265.

(63) Faulkner, C. W.; Ingham, S. L.; Khan, M. S.; Lewis, J.; Long, N. J.; Raithby, P. R. *J. Organomet. Chem.* **1994**, *482*, 139.

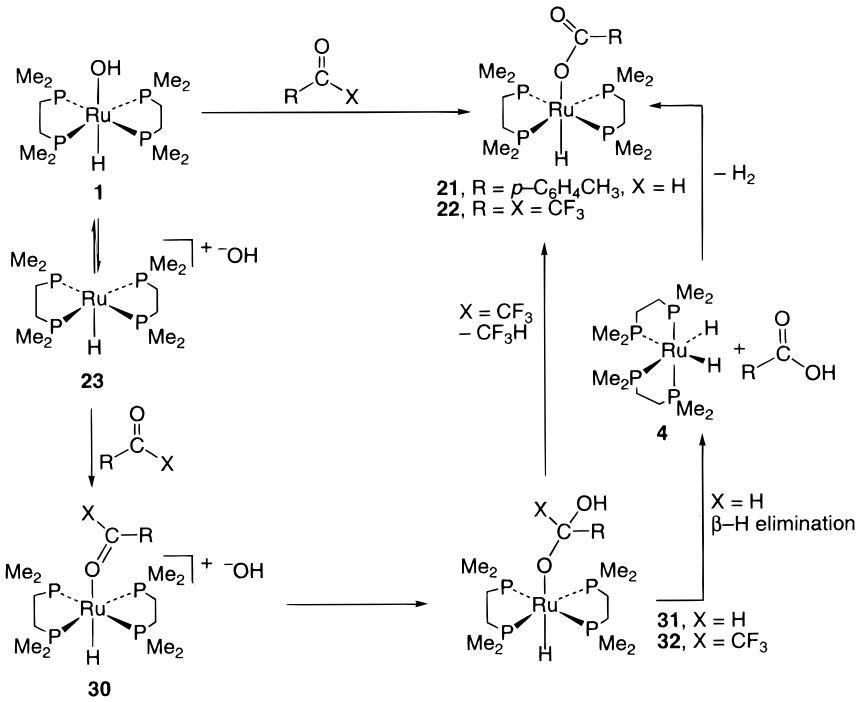
(64) Sponsler, M. B. *Organometallics* **1995**, *14*, 1920.

(65) Xia, H. P.; Jia, G. *Organometallics* **1997**, *16*, 1.

(66) It is also possible that this intermediate could involve a three-centered bond where the Sn−H bond has not been broken.

(67) An alternate mechanism in which the first step is nucleophilic attack of the ruthenium-bound hydroxo ligand on the aldehyde is also possible. This initial step would give an intermediate differing from **32** only in a proton transfer.

Scheme 11



acid, which quickly react to give **21** (vide supra).[68] Hexafluoroacetone leads to intermediate **32**, which undergoes C−C cleavage followed by proton transfer to give **22**. When the reaction of **1** with hexafluoroacetone is monitored by ^{1}H NMR, the formation of 1 equiv of CF_3H is observed.

Reversible Oxidative Addition of Water to a Ru-(0) Center. When the hydroxoruthenium complex **1** is exposed to an atmosphere of ethylene in benzene at 105 °C for 1 day, the ruthenium ethylene complex **2** is formed (Scheme 6). There is strong evidence that the reverse reaction (treatment of **2** with an excess of water at elevated temperatures to form the hydroxoruthenium complex **1**) proceeds via cationic hydridoruthenium ethylene complex **24**, which loses ethylene and forms **2** by anion addition.[69] We believe that we are observing the microscopic reverse of this process: dissociation of hydroxide, coordination of ethylene, and deprotonation of the metal center to afford the observed product **2**.

Trapping the Cationic Hydridoruthenium Complex with CO. If the hydroxo ligand is labile, it should be possible to trap the resulting $[(DMPE)_2Ru(H)]^+$ cation. When **1** is treated with CO at room temperature, the proposed cation $[(DMPE)_2Ru(H)]^+$ formed from hydroxide dissociation is indeed trapped to form the hydrido carbonyl complex **25** (Scheme 7). As described previously, attack of the dissociated $^-$OH on the coordinated carbonyl ligand and β-hydride elimination are also observed. The attack of hydroxide on the cationic metal carbonyl complex is noteworthy, as it pertains to the water gas shift (wgs) reaction. The wgs reaction is industrially important, as it is used to increase the H_2/CO ratio in synthesis gas.[70,71] Currently, this process is based upon late-metal oxide catalysts in heterogeneous high-temperature systems.[71] The studies of Yoshida and co-workers on mononuclear rhodium phosphine complexes have demonstrated the involvement of hydroxidometal complexes in the catalytic cycle.[72] Two of the key transformations associated with wgs catalysis are nucleophilic attack by $^-$OH on a cationic metal carbonyl complex and subsequent loss of CO_2 to generate a metal hydride (eq 6). The formation of **25b** and

$$\text{M–CO}^+ + {}^-\text{OH} \longrightarrow \text{M–COOH} \longrightarrow \text{M–H} + \text{CO}_2 \qquad (6)$$

dihydride **4** indicates we are observing examples of both of these steps.

Conclusions

We have found that N_2O is capable of mediating oxygen atom insertion into a late-metal−hydrogen bond to afford hydroxoruthenium complexes **1** and **5**. The hydroxo ligand is reactive; therefore, additional complexes containing ruthenium−heteroatom bonds (thiolates, siloxides, alkoxides) are accessible via exchange reactions with **1**, introducing a mild, general route into this class of molecules containing late-metal heteroatom bonds. This exchange chemistry has been extended to designing experiments employing silica as a ligand. We have successfully prepared a ruthenium-bound silica complex and have exploited the exchange reactivity of the complex to provide strong evidence for its structural identity. It has become clear that silica can be treated as a simple[3] ligand in both Ir and Ru systems and would be particularly useful if utilized in catalytic systems.

(68) When they are followed by NMR spectrometry, the reactions of both **1** with toluic acid and **4** with toluic acid occur immediately on mixing.

(69) Characterization of an analogous intermediate may be found in ref 35.

(70) Storch, H.; Golumbic, N.; Anderson, R. B. *The Fischer-Tropsch and Related Syntheses*; Wiley: New York, 1951.

(71) *Catalyst Handbook*, Springer-Verlag: West Berlin, 1970; Chapters 5 and 6.

(72) Yoshida, T.; Okano, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 3411 and references therein.

Complex **1** has been shown to activate C−H, Sn−H, and C−C bonds under mild conditions, partially due to the lability and high basicity of the hydroxo ligand. Support for reactivity of **1** involving hydroxide dissociation is found in the reactions of ethylene, H_2, and particularly CO. In the last case, the five-coordinate cation resulting from OH dissociation is trapped by the entering CO molecule.

Experimental Section

General Methods. Unless otherwise noted, all reactions and manipulations were carried out in dry glassware under a nitrogen or argon atmosphere at 20 °C in a Vacuum Atmospheres 553-2 drybox equipped with a MO-40-2 inert-gas purifier or using standard Schlenk techniques. The amount of O_2 in the drybox atmosphere was monitored with a Teledyne model #316 trace oxygen analyzer. Glass reaction vessels fitted with ground-glass joints and Kontes Teflon stopcocks are referred to as bombs. The other instrumentation and general procedures used have been described previously.[73]

NMR Spectroscopy. Solution NMR experiments were performed on a Bruker AMX spectrometer resonating at 400.13 MHz for ^{1}H, 161.98 MHz for ^{31}P, and 100.61 MHz for ^{13}C that was equipped with a QNP probe. All solid-state NMR spectra were acquired on a Chemagnetics CMX-360 NMR spectrometer, using magic angle spinning (5 kHz for carbon, 4−4.5 kHz for phosphorus) and proton decoupling. A pulse length of 5 μs and a delay of 1 s between scans were used. It was checked that this was sufficient to allow for complete relaxation of the observed nuclei by recording spectra with various delays. Carbon spectra were obtained at 90 MHz, phosphorus at 145.7 MHz, and oxygen at 48.8 MHz. Phosphorus chemical shifts are given with respect to 85% H_3PO_4 by using KH_2PO_4 as an external standard (3.88 ppm). Carbon chemical shifts are given with respect to TMS by using hexamethylbenzene as an external standard (17.3 ppm).

Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. Dimethoxybenzene and phenols were sublimed prior to use. *p*-Nitrophenol was recrystallized from C_6H_6. *p*-Tolualdehyde was distilled from $CaSO_4$. Water and *tert*-butyldimethylsilanol were degassed with three freeze−pump−thaw cycles. Liquid terminal alkynes and acetone were distilled from $MgSO_4$ and stored over 4 Å molecular sieves. Acetylene gas was purified by passage through two −78 °C traps separated by a concentrated H_2SO_4 trap. Amine oxides were purified according to the method of Soderquist and sublimed before use. Degussa 300 silica was dried in vacuo at 200 °C for 48 h. Solutions containing silica were agitated by attaching the reaction vessels to a Kugelrohr motor. *cis*-$(DMPE)_2RuCl_2$,[75] *trans*-$(DMPE)_2RuCl_2$,[75] $(DMPE)_2Ru(C_2H_4)$,[28] $(DMPE)_2Ru(Et)(SC_6H_4CH_3)$,[28] and $(DMPE)_2Ru(H)(p\text{-}SC_6H_4Me)$[28] were prepared by literature methods. An improved preparative method for $(DMPE)_2Ru(H)_2$ (**4**) has been used which involves Na reduction of $(DMPE)_2RuCl_2$ in the presence of 1 atm of H_2 and affords **4** in >95% yield.[75]

***trans*-(DMPE)$_2$Ru(OH)(H) (1).**[28] An 800-mL thick-walled glass vessel fused to a vacuum stopcock was charged with a stir bar and a colorless solution of **4** (2.30 g, 5.71 mmol) in C_6H_6 (100 mL). The bomb was degassed via three freeze−pump−thaw cycles, and N_2O (6.29 mmol) was condensed in. The solution was warmed to 25 °C and stirred for 12 h. The resulting brown solution was concentrated in vacuo to a dark brown residue and washed with pentane (4 × 5 mL) to remove any unreacted $(DMPE)_2Ru(H)_2$. The residue was dissolved in a minimal amount of toluene (10 mL) and layered with pentane (40 mL). After 1 day at 25 °C, the tan solution was decanted from a dark brown residue and the solution was cooled to −35 °C for 2 day. The tan crystals obtained were washed with pentane (3 × 1 mL) and dried in vacuo to afford 980 mg (41% yield) of **1**. ^{1}H NMR (C_6D_6): δ 1.52 (m, 4 H, CH_2), 1.37 (s, 12 H, P−CH_3), 1.34 (m, 4 H, P−CH_2), 1.26 (s, 12 H, P−CH_3), −5.40 (br, 1 H, Ru−O*H*), −20.27 (qn, J_{HP} = 20.8, 1 H, Ru−*H*). ^{31}P{^{1}H} NMR δ 46.9 (s). Lit.[28] ^{1}H NMR (C_6D_6): δ 1.51 (m, 4 H, CH_2), 1.37 (s, 12 H, P−CH_3), 1.33 (m, 4 H, P−CH_2), 1.26 (s, 12 H, P−CH_3), −5.41 (br, 1 H, Ru−O*H*), −20.27 (qn, J_{HP} = 20.8, 1 H, Ru−*H*). ^{31}P{^{1}H} NMR: δ 46.8 (s).

***trans*-(DMPE)$_2$Ru(OH)$_2$ (5) (Method A).** An 800-mL bomb was charged with a stir bar and a solution of **1** (1.28 g, 3.06 mmol) in C_6H_6 (100 mL). The bomb was degassed via three freeze−pump−thaw cycles, and N_2O (1 atm) was condensed into the bomb. The solution was warmed to 25 °C and stirred for 3 days. The resulting brown solution was concentrated in vacuo to a dark brown residue, which was dissolved in minimal toluene (10 mL) and layered with pentane (40 mL). After 1 day at 25 °C, the tan solution was decanted from a dark brown residue and the solution was cooled to −35 °C for 2 days. The tan crystals obtained were washed with pentane (3 × 1 mL) and dried in vacuo to afford 400 mg (30% yield) of **5**. ^{1}H NMR (C_6D_6): δ 1.55 (m, 8 H, P−CH_2), 1.27 (s, 24 H, P−CH_3), −7.00 (br, 2 H, O*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 44.6 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 29.2 (qn, J_{CP} = 13.1 Hz, P−*C*H$_2$), 11.3 (qn, J_{CP} = 5.9 Hz, P−*C*H$_3$). IR (Nujol): 3400−3100 (m, br), 1462 (s), 1423 (s), 1377 (m), 1292 (m), 1277 (m), 1184 (w), 1161 (w), 1082 (w), 941 (s), 912 (s), 889 (s), 835 (m), 796 (m), 733 (m), 700 (m), 642 (m), 515 (m), 503 (m), 492 (m), 484 (m), 441 (m), 424 (m), 409 (w) cm^{-1}. MS-EI: *m/z* 435 [M$^+$]. HRMS (EI): *m/z* calcd for $C_{12}H_{34}O_2P_4Ru$ 436.0553, obsd 436.0552. Repeated crystallizations afforded **4** in 95% purity; analytically pure material could not be obtained.

***trans*-(DMPE)$_2$Ru(OH)$_2$ (5) (Method B).** An 800-mL bomb was charged with a stir bar and a solution of **4** (500 mg, 1.24 mmol) in C_6H_6 (80 mL). The bomb was degassed via three freeze−pump−thaw cycles, and N_2O (1 atm) was condensed into the bomb. The solution was warmed to 25 °C and stirred for 3 days. The resulting brown solution was concentrated in vacuo to a dark brown residue which was dissolved in minimal toluene (10 mL) and layered with pentane (40 mL). After 1 day at 25 °C, the tan solution was decanted from a dark brown residue and the solution was cooled to −35 °C for 2 days. The tan crystals obtained were washed with pentane (3 × 1 mL) and dried in vacuo to afford 173 mg (32% yield) of **5**. Spectroscopic data are identical with those obtained from method A.

***trans*-(DMPE)$_2$Ru(H)(OC$_6$H$_5$) (6).** To a solution of **1** (80.2 mg, 0.191 mmol) in C_6H_6 (10 mL) was added phenol (20.9 mg, 0.222 mmol). After 1 day at 25 °C, the solution was concentrated to a beige powder and this solid was redissolved in toluene for recrystallization by slow pentane diffusion into the toluene solution of **16**. A second recrystallization afforded 23.6 mg (25% yield) of **16** as white crystals: mp 192 °C dec. ^{1}H NMR (C_6D_6): δ 7.35 (t, J_{HH} = 7.8 Hz, 2 H, *m*-OC$_6$*H*$_5$), 6.62 (t, J_{HH} = 6.8 Hz, 1 H, *p*-OC$_6$*H*$_5$), 6.43 (d, J_{HH} = 7.6 Hz, 2 H, *o*-OC$_6$*H*$_5$), 1.65 (m, 4 H, P−CH_2), 1.30 (s, 12 H, P−*C*H$_3$), 1.23 (m, 4 H, P−CH_2), 1.09 (s, 12 H, P−*C*H$_3$), −23.3 (qn, J_{HP} = 21.8 Hz, 1 H, Ru−*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 45.4 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 174.0 (*C*), 129.1 (*C*H), 120.5 (*C*H), 109.5 (*C*H), 31.3 (qn, J_{CP} = 12.3 Hz, *C*H$_2$), 22.9 (m, P*C*H$_3$), 15.5 (qn, J_{CP} = 5.4 Hz, P*C*H$_3$). IR (KBr): 3058 (w), 2958 (w), 2897 (m), 1928 (m), 1589 (m, br), 1562 (w, br), 1489 (m), 1479 (m, br), 1421 (w, br), 1290 (m, br), 1279 (m, br), 1164 (w, br), 1124 (w, br), 1101 (w, br), 1072 (w, br), 1020 (w, br), 989 (w, br), 935 (s, br), 910 (m, br), 889 (m), 841 (m), 795 (w), 760 (w), 727 (m), 698 (m), 644 (m), 523 (w), 459 (w) cm^{-1}. MS-EI: *m/z* 496 [M$^+$]. HRMS (EI): *m/z* calcd for $C_{18}H_{38}OP_4Ru$ 496.0917, obsd

(73) Meyer, K. E.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 3749.
(74) Soderquist, J. A.; Anderson, C. L. *Tetrahedron Lett.* **1986**, *27*, 3961.
(75) Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, 896.
(76) We thank Prof. L. Field for this suggestion.

496.0924. Anal. Calcd for $C_{18}H_{38}OP_4Ru$: C, 43.64; H, 7.73. Found: C, 43.99; H, 8.22.

***trans*-(DMPE)$_2$Ru(H)(OC$_6$H$_4$OMe) (7).** To a solution of **1** (92.3 mg, 0.220 mmol) in C_6H_6 (10 mL) was added *p*-methoxyphenol (28.4 mg, 0.228 mmol). After 3 days at 25 °C, C_6H_6 and H_2O were removed in vacuo to afford 111 mg of **17** (96%) as a white powder. ^{1}H NMR (C_6D_6): δ 7.00 (d, J_{HH} = 8.8 Hz, 2 H, *Ph*), 6.32 (d, J_{HH} = 8.8 Hz, 2 H, *Ph*), 3.61 (s, 3 H, O*Me*), 1.69 (m, 4 H, P−C*H*$_2$), 1.32 (s, 12 H, P−C*H*$_3$), 1.26 (m, 4 H, P−C*H*$_2$), 1.10 (s, 12 H, P−C*H*$_3$), −23.2 (qn, J_{HP} = 21.7 Hz, 1 H, Ru−*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 45.4 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 166.7 (*C*), 147.6 (*C*), 119.1 (*C*H), 115.1 (*C*H), 56.1 (O*C*H$_3$), 30.9 (qn, J_{CP} = 13.3 Hz, P−*C*H$_2$), 22.7 (m, P−*C*H$_3$), 15.1 (qn, J_{CP} = 5.3 Hz, P−*C*H$_3$). IR (KBr): 2958 (w), 2933 (w), 2922 (w), 2897 (m), 2829 (w), 2800 (w), 1930 (m), 1496 (m), 1419 (m), 1279 (m), 1228 (m), 1038 (w), 937 (s), 891 (m), 839 (m), 644 (m) cm^{-1}. Elemental analysis was not obtained due to similarity to **6**.

***trans*-(DMPE)$_2$Ru(H)(OSiPh$_3$) (8).** A solution of triphenylsilanol (62.6 mg, 0.226 mmol) in C_6H_6 (5 mL) was added to a solution of **1** (91.3 mg, 0.218 mmol) in C_6H_6 (15 mL). After 16 h, the C_6H_6 and water were removed in vacuo. Recrystallization from pentane vapor diffusion into a toluene solution of **18** gave 93.7 mg of **18** (63.4%) as a white powder: mp 144 °C dec. ^{1}H NMR (C_6D_6): δ 7.88 (m, 6 H, Ph), 7.29 (m, 6 H, Ph), 7.21(m, 3 H, Ph), 1.64 (m, 4 H, P−C*H*$_2$), 1.23 (m, 4 H, P−C*H*$_2$), 1.20 (s, 12 H, P−C*H*$_3$), 1.04 (s, 12 H, P−C*H*$_3$), −24.4 (qn, J_{HP} = 21.7 Hz, Ru−*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 43.93 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 146.5 (*C*), 136.5 (*C*H), 127.6 (*C*H), 127.1 (*C*H), 31.5 (qn, J_{CP} = 12.5 Hz, *C*H$_2$), 23.3 (qn, J_{CP} = 7.6 Hz, P*C*H$_3$), 15.9 (qn, J_{CP} = 5.0 Hz, P*C*H$_3$). ^{17}O NMR (C_6D_6): δ −93. IR (KBr): 3066 (w), 3045 (w), 2964 (w), 2923 (w), 2899 (w), 2802 (w), 1928 (w), 1656 (w, br), 1637 (w, br), 1589 (w, br), 1543 (w, br), 1524 (w, br), 1508 (w, br), 1483 (w, br), 1427 (m, br), 1294 (w), 1279 (w), 1117 (s, br), 937 (m), 912 (w), 889 (w), 839 (w), 795 (w), 739 (w), 729 (w), 706 (m), 644 (w), 515 (m), 478 (w) cm^{-1}. MS-EI: *m/z* 678 [M$^+$]. HRMS (EI): *m/z* calcd for $C_{30}H_{48}OSiP_4Ru$ 678.1468, obsd 678.1468. Elemental analysis was attempted but resulted in a low percent of carbon, likely due to the formation of silicon carbides.

***trans*-(DMPE)$_2$Ru(H)(OSiMe$_2$^{t}Bu) (9).** To a solution of **1** (45.9 mg, 0.0525 mmol) in C_6H_6 (20 mL) was added a solution of ^{t}BuMe$_2$SiOH (14.7 mg, 0.111 mmol) in C_6H_6 (2 mL). After 1 day at 25 °C, the solution was concentrated to a red-brown oil in vacuo to remove H_2O and the oil was redissolved in C_6H_6. After 2 days more, the solution was concentrated and redissolved. This solution was concentrated in vacuo, redissolved in toluene, and placed in a pentane diffusion chamber at 20 °C for 4 days to afford 21 mg (37.5%) of **9** as a white solid. ^{1}H NMR (C_6D_6): δ 1.61 (m, 4 H, P−C*H*$_2$), 1.45 (s, 12 H, P−C*H*$_3$), 1.29 (m, 4 H, P−C*H*$_2$), 1.28 (s, 9 H, Si−C(C*H*$_3$)$_3$), 1.14 (s, 12 H, P−C*H*$_3$), 0.21 (s, 6 H, Si(C*H*$_3$)$_2$), −23.6 (qn, J_{HP} = 21.6 Hz, 1 H, Ru−*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 43.6 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 31.44 (qn, J_{CP} = 13.6 Hz, P−*C*H$_2$), 28.4 (SiC(*C*H$_3$)$_3$), 23.1 (m, P−*C*H$_3$), 21.5 (Si*C*(CH$_3$)$_3$), 15.4 (qn, J_{CP} = 5.0 Hz, P−*C*H$_3$), 1.15 (Si(*C*H$_3$)$_2$). IR (KBr): 2958 (w), 2933 (w), 2922 (w), 2897 (m), 2829 (w), 2800 (w), 1930 (m), 1497 (m), 1419 (m), 1279 (m), 1228 (m), 1038 (w), 937 (s), 891 (m), 839 (m), 795 (w), 729 (m), 702 (m), 683 (w), 644 (m) cm^{-1}. Elemental analysis was not obtained due to similarity to **8**.

(DMPE)$_2$Ru(H)(*p*-SC$_6$H$_4$Me) (10).[35] To a solution of **1** (45.1 mg, 0.108 mmol) in C_6H_6 (5 mL) was added *p*-thiocresol (13.7 mg, 0.110 mmol). After 1 h at room temperature, the volatile materials were removed in vacuo. Recrystallization by pentane vapor diffusion into a concentrated toluene solution afforded 41.5 mg of **10** (73% yield). ^{1}H NMR (C_6D_6): δ 7.66 (d, J_{HH} = 7.8, 2 H, SC$_6$*H*$_4$Me), 6.89 (d, J_{HH} = 7.8, 2 H, SC$_6$*H*$_4$-Me), 2.19 (s, 3 H, C*H*$_3$), 1.66 (m, P−C*H*$_2$), 1.44 (s, P−C*H*$_3$), 1.23 (m, P−C*H*$_2$), 1.12 (s, P−C*H*$_3$), −18.1 (q, 1 H, J_{HP} = 22.0). ^{31}P{^{1}H} NMR (C_6D_6): δ 43.3 (s). Lit.[35] ^{1}H NMR (C_6D_6): δ 7.65 (d, J_{HH} = 7.9, 2 H, SC$_6$*H*$_4$Me), 6.88 (d, J_{HH} = 7.7, 2 H, SC$_6$*H*$_4$-Me), 2.19 (s, 3 H, C*H*$_3$), 1.67 (m, P−C*H*$_2$), 1.44 (s, P−C*H*$_3$), 1.23 (m, P−C*H*$_2$), 1.12 (s, P−C*H*$_3$), −18.0 (q, 1 H, J_{HP} = 22.0). ^{31}P{^{1}H} NMR (C_6D_6): δ 43.2 (s).

(DMPE)$_2$Ru(*p*-SC$_6$H$_4$Me)$_2$ (11) (Method A). To a solution of (DMPE)$_2$Ru(C$_2$H$_5$)(p-SC$_6$H$_4$CH$_3$) (32.5 mg, 0.0587 mmol) in THF (5 mL) was added *p*-thiocresol (8.0 mg, 0.0646 mmol). After 2 days at room temperature, the solution had turned from light yellow to peach. The solution was concentrated in vacuo to a bright orange powder. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the crude material showed only a 3:1 mixture of *cis*- and *trans*-**11**. Crude **11** was dissolved in toluene (1 mL) and placed in a pentane diffusion chamber at 20 °C for 1 day. The red crystals obtained were washed with pentane (3 × 0.5 mL) and dried in vacuo to afford 19.0 mg (50% yield) of *trans*-**11**.

***trans*-11:** mp 183 °C; ^{1}H NMR (THF-*d*$_8$) δ 7.44 (d, J_{HH} = 8.0, 4 H, *o*-SC$_6$*H*$_4$Me), 7.38 (d, J_{HH} = 8.0; 4 H, *m*-SC$_6$*H*$_4$Me), 2.08 (s, 6 H, SC$_6$H$_4$*Me*), 1.62 (m, P−C*H*$_2$), 1.35 (s, 24 H, P−*Me*); ^{1}H NMR (C_6D_6) δ 7.49 (d, J_{HH} = 8.0, 4 H, *o*-SC$_6$*H*$_4$Me), 6.80 (d, J_{HH} = 8.0; 4 H, *m*-SC$_6$*H*$_4$Me), 2.09 (s, 6 H, SC$_6$H$_4$*Me*), 1.36 (s, 24 H, P−*Me*); ^{31}P{^{1}H} NMR (THF-*d*$_8$) δ 36.89 (s); ^{31}P{^{1}H} NMR (C_6D_6) δ 36.37 (s); ^{13}C{^{1}H} NMR (C_6D_6) δ 147.3 (*C*), 136.9 (*C*H), 132.2 (*C*), 128.8 (*C*H), 30.1 (q, J_{CP} = 12.1, *C*H$_2$), 21.3 (C$_6$H$_4$*C*H$_3$), 15.3 (q, J_{CP} = 7.0, P*C*H$_3$); IR (KBr) 3070 (w), 3008 (w), 2964 (w), 2906 (m, br), 2863 (w), 2800 (w), 1593 (w), 1481 (m), 1421 (m, br), 1408 (m), 1379 (w), 1294 (m), 1278 (m), 1238 (w), 1211 (w), 1174 (w), 1130 (w), 1101 (w), 1076 (m), 1016 (w), 939 (s, br), 930 (s, br), 912, (m, br), 891 (m), 837 (m), 818 (m), 806 (m), 796 (m), 729 (m), 704 (m), 644 (m), 627 (w), 501 (m); MS-EI *m/z* 648 [M$^+$]. Anal. Calcd for $C_{26}H_{46}P_4S_2Ru$: C, 48.21; H, 7.16. Found: C, 48.64; H, 6.85.

***cis*-11:** ^{1}H NMR (THF-*d*$_8$) δ 7.67 (d, J_{HH} = 8.0; 4 H, *o*-SC$_6$*H*$_4$-Me), 6.68 (d, J_{HH} = 8.0; 4 H, *m*-SC$_6$*H*$_4$Me), 2.15 (s, 6 H, SC$_6$H$_4$*Me*), 1.79 (d, J_{HP} = 8.6, 6 H, P−*Me*), 1.26 (d, J_{HP} = 6.2, 6 H, P−*Me*), 1.14 (vt, J_{HP} = 2.6, 6 H, P−*Me*), 1.03 (vt, J_{HP} = 3.4, 6 H, P−*Me*); ^{1}H NMR (C_6D_6) δ 8.24 (d, J_{HH} = 8.0; 4 H, *o*-SC$_6$*H*$_4$Me), 6.96 (d, J_{HH} = 8.0; 4 H, *m*-SC$_6$*H*$_4$Me), 2.17 (s, 6 H, SC$_6$H$_4$*Me*), 1.69 (d, J_{HP} = 7.8, 6 H, P−*Me*), 1.24 (t, J_{HP} = 3.1, 6 H, P−*Me*), 0.94 (s, 6 H, P−*Me*), 0.63 (d, J_{HP} = 5.8, 6 H, P−*Me*); ^{31}P{^{1}H} NMR (THF-*d*$_8$) δ 38.6 (t, J_{PP} = 22.1), 33.1 (t, J_{PP} = 22.1); ^{31}P{^{1}H} NMR (C_6D_6) δ 37.6 (t, J_{PP} = 22.1), 33.0 (t, J_{PP} = 22.1).

(DMPE)$_2$Ru(*p*-SC$_6$H$_4$Me)$_2$ (11) (Method B). To a solution of *trans*-(DMPE)$_2$RuCl$_2$ (183 mg, 0.388 mmol) in toluene (25 mL) was added potassium *p*-thiocresolate (815 mg, 5.02 mmol, prepared from KH and *p*-thiocresol in hexanes). The mixture was heated to 170 °C for 16 days, at which point NMR analysis showed clean conversion to a 3:1 mixture of *cis*- and *trans*-(DMPE)$_2$Ru(*p*-SC$_6$H$_4$Me)$_2$ isomers. The reaction mixture was filtered through Celite, concentrated in vacuo, and recrystallized from toluene layered with pentane to afford 177 mg (70%) of *cis*- and *trans*-**11** as a mixture of yellow and red solids. Spectroscopic data are identical with those obtained from method A.

(DMPE)$_2$Ru(*p*-SC$_6$H$_4$Me)$_2$ (11) (Method C). To a solution of **1** (63.8 mg, 0.150 mmol) in benzene (10 mL) was added HSC$_6$H$_4$Me (41.0 mg, 0.330 mmol). After 1 h at room temperature, the resulting red solution was placed under vacuum to remove the volatile materials. Recrystallization from toluene/pentane vapor diffusion afforded 76.8 mg of **11** (79% yield). Spectroscopic data are identical with those obtained from method A.

Thermolysis of *trans*-(DMPE)$_2$Ru(*p*-SC$_6$H$_4$Me)$_2$. A solution of *trans*-**11** and *p*-xylene (integration standard) in C_6D_6 was degassed with three freeze−pump−thaw cycles, and then the tube was flame-sealed. The tube was placed in a 105 °C oil bath for 1 day. A mixture of 3:1 *cis*- and *trans*-**11** was observed in the ^{1}H NMR spectrum. The ratio of isomers did not change upon continued heating for 12 days at 135 °C.

Treatment of *trans*-(DMPE)$_2$Ru(OH)(H) (1) with Silica in C$_6$D$_6$ and Subsequent Reactions with *p*-Thiocresol. To

a solution of **1** (98 mg, 0.23 mmol) in THF (40 mL) was added silica (400 mg). The tan solution turned clear, and the silica turned tan. The reaction mixture was stirred for 4 h at room temperature. The product **14** was isolated via filtration, washed with THF (3 × 20 mL), and dried in vacuo. ^{13}C (CPMAS) NMR: δ 31.1, 21.1, 14.4. ^{31}P (CPMAS) NMR: δ 44.0. ^{31}P (C_6D_6) NMR: δ 47.0. IR (neat): 2970 (m), 2908 (s), 1967 (w), 1762 (w), 1545 (br, m), 1424 (m), 920 (br, w), 800 (br, w) cm^{-1}.

To a suspension of **14** in THF (50 mL) was added *p*-thiocresol (28 mg, 0.23 mmol). The solution was stirred for 30 min at room temperature, during which time the solution turned yellow. The solution was filtered and concentrated in vacuo to afford (DMPE)$_2$Ru(H)(*p*-SC$_6$H$_4$CMe) (**10**) in 95% yield. Spectroscopic data are consistent with reported values.[35] When **14** is treated with excess *p*-thiocresol under similar conditions, the bis(thiolate) complex **11** is obtained in 96% yield. Spectroscopic data are consistent with reported values.[39]

Treatment of (DMPE)$_2$Ru(C$_2$H$_4$) (2) with Silica and Subsequent Reactions with *p*-Thiocresol. To a solution of **2** (100 mg, 0.23 mmol) in THF (55 mL) was added silica (400 mg). The tan solution turned clear, and the silica turned tan. The reaction mixture was stirred for 4 h at room temperature. The product **14** was isolated via filtration, washed with THF (2 × 15 mL), and dried in vacuo. ^{13}C (CPMAS) NMR: δ 31.2, 21.8, 15.4. ^{31}P (CPMAS) NMR: δ 43.4. ^{31}P (C_6D_6) NMR: δ 47.1. IR (neat): 2975 (m), 2910 (s), 1966 (w), 1761 (w), 1540 (br, m), 1423 (m), 920 (br, w), 805 (br, w) cm^{-1}.

To a solution of **14** in THF (50 mL) was added *p*-thiocresol (28 mg, 0.23 mmol). The solution was stirred for 30 min at room temperature, during which time the solution turned yellow. The solution was filtered and concentrated in vacuo to afford (DMPE)$_2$Ru(H)(*p*-SC$_6$H$_4$CMe) (**10**) in 95% yield. Spectroscopic data were consistent with reported values.[35] When **14** is treated with excess *p*-thiocresol under similar conditions, the bis(thiolate) complex **11** is obtained, also in 95% yield. Spectroscopic data were consistent with reported values.[39]

***trans*-(DMPE)$_2$Ru(H)(CH$_2$C(O)CH$_3$) (15).** A 50-mL bomb was charged with a stir bar and a solution of **1** (103.6 mg, 0.247 mmol) in C_6H_6 (10 mL). The bomb was degassed via three freeze−pump−thaw cycles, and acetone (0.270 mmol) was condensed into the bomb. The solution was warmed to 25 °C and stirred for 2 h. The volatile materials were removed in vacuo to afford 108 mg (95% yield) of **15**. The product was washed with pentane (3 × 3 mL). Analytically pure **15** (39 mg, 34% yield) was obtained as tan crystals by two successive recrystallizations using pentane vapor diffusion into a toluene solution of **15** at 25 °C. ^{1}H NMR (C_6D_6): δ 2.13 (s, 3 H, C(O)-C*H*$_3$), 1.57 (m, 6 H, Ru−C*H*$_2$ and P−C*H*$_2$), 1.38 (s, 12 H, P−C*H*$_3$), 1.21 (m, 4 H, P−C*H*$_2$), 1.14 (s, 12 H, P−C*H*$_3$), −16.67 (qn, J_{HP} = 22.2 Hz, 1 H, Ru−*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 43.0 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 210.7 (*C*), 31.0 (qn, J_{CP} = 13.7 Hz, P−*C*H$_2$), 30.6 (CO*C*H$_3$), 25.7 (qn, J_{CP} = 7.6 Hz, P−*C*H$_3$), 18.0 (qn, J_{CP} = 4.2 Hz, Ru−*C*H$_2$), 15.2 (qn, J_{CP} = 5.0 Hz, P−*C*H$_3$). IR (KBr): 2958 (m), 2922 (m), 2897 (s), 1928 (s), 1713 (w), 1475 (m), 1444 (m), 1419 (s), 1365 (m), 1288 (w), 1279 (m), 1232 (w), 1074 (w), 991 (w), 935 (s), 889 (s), 862 (w), 840 (m), 795 (w), 727 (s), 702 (s), 683 (w), 644 (m), 459 (w) cm^{-1}. MS-EI *m/z* 459 [(M)$^+$]. Anal. Calcd for C$_{15}$H$_{38}$OP$_4$Ru: C, 39.21; H, 8.34. Found: C, 39.20; H, 8.32.

***trans*-(DMPE)$_2$Ru(H)(CCPh) (16) (Method A).** To a solution of **1** (98 mg, 0.23 mmol) in C_6H_6 (5 mL) was added dropwise a solution of phenylacetylene (26 mg, 0.26 mmol) in C_6H_6 (5 mL). The tan solution turned to peach after 0.5 h at 25 °C. Lyophilization, followed by dissolution of the remaining solid in pentane, filtration through Celite, and concentration in vacuo afforded 88 mg (74% yield) of **16** as an orange solid which was pure by NMR spectroscopy. Analytically pure yellow needles of **16** (33 mg, 28% yield) were obtained by two successive recrystallizations from pentane at −70 °C: mp 180 °C dec. ^{1}H NMR (C_6D_6): δ 7.47 (d, J_{HH} = 6.9 Hz, 2 H, *o*-C$_6$*H*$_5$), 7.18 (s, 2 H, *m*-C$_6$*H*$_5$), 6.95 (t, J_{HH} = 7.4 Hz, 1 H, *p*-C$_6$*H*$_5$), 1.50 (s, 12 H, P−C*H*$_3$), 1.51 (m, 4 H, P−C*H*$_2$), 1.29 (m, 4 H, P−C*H*$_2$), 1.24 (s, 12 H, P−C*H*$_3$), −11.95 (qn, J_{HP} = 20.0 Hz, 1 H, Ru−*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 45.5 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 133.5 (m, Ru−*C*), 132.5 (Ru−C*C*), 130.5 (*C*H), 127.9 (*C*H), 122.0 (*C*H), 109.3 (*ipso*-*C*), 31.6 (qn, J_{CP} = 14.1 Hz, P−*C*H$_2$), 23.7 (qn, J_{CP} = 7.0 Hz, P−*C*H$_3$), 17.1 (qn, J_{CP} = 7.0 Hz, P−*C*H$_3$); IR (KBr): 3064 (w), 2960 (w), 2926 (w), 2899 (m), 2058 (s), 1759 (w), 1632 (w), 1591 (m), 1479 (w), 1417 (m), 1290 (w), 1277 (w), 935 (s), 926 (s), 889 (m), 841 (w), 795 (w), 748 (m), 725 (m), 702 (m), 646 (m), 461 (w) cm^{-1}. MS-EI: *m/z* 503 [(M − 1)$^+$]. Anal. Calcd for C$_{20}$H$_{38}$P$_4$Ru: C, 47.71; H, 7.61. Found: C, 47.50; H, 7.67.

***trans*-(DMPE)$_2$Ru(H)(CCPh) (16) (Method B).** To a solution of **4** (60.0 mg, 0.149 mmol) in C_6H_6 (5 mL) was added dropwise a solution of phenylacetylene (16.7 mg, 0.164 mmol) in C_6H_6 (5 mL). The solution turned to peach after 1 h at room temperature. Lyophilization, followed by recrystallization from pentane at −50 °C, afforded 33.8 mg of **16** (45% yield). Spectroscopic data were identical with those obtained from method A.

***trans*-(DMPE)$_2$Ru(H)(CCH) (17).** A Schlenk flask equipped with a stir bar was charged with **1** (94.3 mg, 0.225 mmol) in C_6H_6 (10 mL). Acetylene gas was bubbled through the solution for 25 min at 25 °C. The volatile materials were removed in vacuo to afford 93 mg of **17** (97% yield) as a white powder. Recrystallization of **17** from pentane (0.5 mL) at − 50 °C affords 31 mg of **17** (32% yield) as microcrystalline needles. ^{1}H NMR (C_6D_6): δ 1.85 (s, 1 H, CC*H*), 1.56 (s, 12 H, P−C*H*$_3$), 1.57 (m, 4 H, P−C*H*$_2$), 1.30 (m, 4 H, P−C*H*$_2$), 1.24 (s, 12 H, P−C*H*$_3$), −12.37 (qn, J_{HP} = 21.5 Hz, 1 H, Ru−*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 45.2 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 121.8 (qn, J_{CP} = 13.7 Hz, Ru−*C*), 91.2 (Ru−C*C*), 31.8 (qn, J_{CP} = 13.8 Hz, P−*C*H$_2$), 24.0 (qn, J_{CP} = 6.9 Hz, P−*C*H$_3$), 17.1 (qn, J_{CP} = 3.9 Hz, P−*C*H$_3$). IR (KBr): 3269 (m), 2962 (w), 2922 (w), 2899 (m), 1905 (m), 1730 (w), 1421 (w), 1277 (w), 939 (s), 928 (s), 889 (w), 841 (w), 795 (w), 727 (w), 703 (w), 644 (w), 530 (w) cm^{-1}. MS-EI: *m/z* 427 [M$^+$ − 1]. HRMS (EI) *m/z* calcd for C$_{14}$H$_{34}$P$_4$Ru 428.0655, obsd 428.0657.

***trans*-(DMPE)$_2$Ru(H)(^{13}C^{13}CH) (17-^{13}*C*$_2$).** In a resealable NMR tube was added a solution of **1** (8.4 mg, 0.020 mmol) in C_6D_6 (0.5 mL). H^{13}C^{13}CH (0.022 mmol) was condensed into the solution via vacuum-transfer techniques. After 3 h at room temperature, the volatile materials were removed in vacuo to afford pure **17**-^{13}*C*$_2$ as a white solid (7.8 mg, 91%). ^{1}H NMR (C_6D_6): δ 1.85 (d, J = 35.0 Hz, 1 H, CC*H*), 1.56 (s, 12 H, P−C*H*$_3$), 1.57 (m, 4 H, P−C*H*$_2$), 1.30 (m, 4 H, P−C*H*$_2$), 1.25 (s, 12 H, P−C*H*$_3$), −12.39 (br, 1 H, Ru−*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 45.1 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 122.3 (dqn, J_{CP} = 13.7 Hz, J_{CC} = 100.0 Hz, Ru−*C*), 121.3 (d, J_{CC} = 100.0 Hz, Ru−C*C*), 31.8 (qn, J_{CP} = 13.8 Hz, P−*C*H$_2$), 24.0 (qn, J_{CP} = 6.9 Hz, P−*C*H$_3$), 17.1 (qn, J_{CP} = 3.9 Hz, P−*C*H$_3$). IR (KBr): 3253 (m), 2962 (w), 2922 (w), 2899 (m), 1838 (s), 1726 (w), 1632 (w), 1421 (w), 1294 (w), 1277 (w), 941 (s), 926 (s), 889 (m), 841 (w), 795 (w), 727 (w), 702 (w), 646 (w), 532 (w) cm^{-1}. MS-EI: *m/z* 429 [M$^+$ − 1].

***trans*-(DMPE)$_2$Ru(CCPh)$_2$ (18).**[46] To a solution of **4** (30.0 mg, 0.0744 mmol) in benzene was added HCCPh (16.7 mg, 0.164 mmol). The reaction mixture was stirred at room temperature for 10 days, and the volatile materials were removed in vacuo to afford **18** in 92% yield. ^{1}H NMR (THF-*d*$_8$): δ 2.09 (24 H, m, CH$_3$), 2.22 (8 H, br s, CH$_2$), 7.43 (10 H, m, CH). ^{31}P{^{1}H} NMR (THF-*d*$_8$): δ 40.6 (s). Lit.[46] ^{1}H{^{31}P} NMR (THF-*d*$_8$): δ 2.08 (24 H, m, CH$_3$), 2.21 (8 H, br s, CH$_2$), 7.43 (10 H, m, CH). ^{31}P{^{1}H} NMR (THF-*d*$_8$): δ 40.8 (s).

***trans*-(DMPE)$_2$(H)RuCC(CH$_2$)$_4$CCRu(H)(DMPE)$_2$ (19).** To a solution of **1** (99 mg, 0.24 mmol) in C_6H_6 (10 mL) was added 1,7-octadiyne (34.5 μL, 0.26 mmol). After 16 h, the solution was concentrated in vacuo to a white powder and

recrystallized from pentane (4 mL) at −50 °C to afford 35 mg of **19** as colorless microcrystals (33% yield). ^{1}H NMR (C_6D_6): δ 2.64 (br, 4 H, CH_2CH_2), 1.93 (m, 4 H, CH_2CH_2), 1.62 (s, 24 H, P−CH_3), 1.63 (m, 8 H, P−CH_2), 1.40 (m, 8 H, P−CH_2), 1.35 (s, 24 H, P−CH_3), −12.29 (qn, J_{HP} = 21.3 Hz, 2 H, Ru−*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 45.9 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 106.6 (qn, J_{CP} = 14.4 Hz, Ru*C*C), 104.0 (Ru*C*C), 32.5 (RuCC*C*H$_2$), 32.0 (qn, J_{CP} = 13.9 Hz, P−*C*H$_2$), 24.3 (qn, J_{CP} = 6.5 Hz, P−*C*H$_3$), 22.9 (RuCCCH$_2$*C*H$_2$), 17.5 (qn, J_{CP} = 6.3 Hz, P−*C*H$_3$). IR (KBr): 2083 (m), 1716 (m), 1419 (m), 1329 (w), 1290 (m), 1275 (m), 1072 (w), 935 (m), 925 (m), 910 (m), 887 (m), 836 (w), 700 (m), 644 (w), 622 (w), 509 (m), 498 (m), 447 (m) cm^{-1}; IR (Nujol): 2960 (w), 2920 (m), 2899 (s), 2850 (w), 2819 (w), 2079 (w), 1732 (s), 1632 (w), 1603 (w), 1421 (w), 1389 (w), 1350 (w), 1292 (w), 1277 (w), 1238 (w), 1193 (w), 1149 (w), 937 (s), 928 (s), 889 (w), 839 (w), 725 (w), 702 (w), 644 (w), 461 (w) cm^{-1}. MS-EI: *m/z* 910 [(M)$^+$]. HRMS (EI): *m/z* calcd for $C_{32}H_{74}P_8Ru_2$ 910.1779, obsd 910.1796.

***trans*-(DMPE)$_2$Ru(H)(SnPh$_3$) (20).** To a solution of **1** (77 mg, 0.18 mmol) in C_6H_6 (5 mL) was added dropwise a solution of triphenylstannane (67 mg, 0.19 mmol) in C_6H_6 (5 mL) at 25 °C. After 0.5 h, the volatile materials were removed in vacuo and recrystallization from pentane (4 mL) diffusion into a concentrated toluene solution (1 mL) afforded 43.3 mg of **20** as white needles (32% yield). ^{1}H NMR (C_6D_6): δ 7.90 (d, J_{HH} = 6.9 Hz, 2 H, *o*-C$_6H_5$), 7.23 (t, 2 H, *m*-C$_6H_5$), 7.08 (br, 1 H, *p*-C$_6H_5$), 1.78 (m, 4 H, P−CH_2), 1.24 (s, 12 H, P−CH_3), 1.35 (m, 4 H, P−CH_2), 1.06 (s, 12 H, P−CH_3), −13.14 (qn, J_{HP} = 22.5 Hz, 1 H, Ru−*H*). ^{1}H{^{31}P} NMR (C_6D_6): δ −13.14 (s, J_{HSn} = 216.1 Hz, Ru−*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 46.3 (s, J_{PSn} = 174.6 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 158.2 (*ipso-C*), 138.9 (*C*H), J_{CSn} = 33.8 Hz), 127.5 (*C*H), 125.9 (*C*H), 33.1 (qn, J_{CP} = 13.8 Hz, P−*C*H$_2$), 28.3 (qn, J_{CP} = 7.7 Hz, P−*C*H$_3$), 22.7 (qn, J_{CP} = 6.7 Hz, P−*C*H$_3$). IR (KBr): 3043 (w), 2966 (w), 2900 (m), 1869 (m), 1471 (w), 1419 (m), 1389 (w), 1296 (w), 1277 (w), 1059 (w), 935 (s), 903 (m), 889 (m), 854 (w), 839 (m), 723 (s), 702 (s), 679 (w), 652 (w), 638 (m), 465 (w), 453 (w) cm^{-1}. Anal. Calcd for $C_{30}H_{48}P_4RuSn$: C, 47.89; H, 6.43. Found: C, 47.52; H, 6.75.

Treatment of 1 with H$_2$. To a bomb containing a solution of **1** (55 mg, 0.131 mmol) in benzene (10 mL) was added H_2 (1 atm) via vacuum-transfer techniques. After 1 day, the volatile materials were removed in vacuo to afford 46.5 mg of **4** (88%). ^{1}H NMR (C_6D_6): δ 1.61 (s, 6 H, PCH_3), 1.40−1.33 (br m, 8 H, PCH_2), 1.35 (s, 6 H, PCH_3), 1.31 (d, 6 H, PCH_3), 1.22 (s, 6 H, PCH_3), 1.04 (d, 6 H, PCH_3), −9.57 (m, 2 H, Ru−*H*). ^{31}P{^{1}H} NMR (C_6D_6) δ 47.6 (vt, *J* = 21.5 Hz), 38.6 (vt, *J* = 21.5 Hz). Lit.[55] ^{1}H NMR (C_6D_6): δ 1.01 (d, 6 H, P−CH_3), 1.18 (s, 6 H, P−CH_3), 1.30 (d, 6 H, P−CH_3), 1.36 (s, 6 H, P−CH_3), 1.56 (s, 6 H, P−CH_3), 1.33−1.39 (br m, 8 H, P−CH_2), −9.60 (m, 2 H, Ru−*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 38.3 (vt, *J* = 21.5 Hz), 47.3 (vt, *J* = 21.5 Hz).

***trans*-(DMPE)$_2$Ru(H)(OC(O)*p*-C$_6$H$_4$CH$_3$) (21) (Method A).** To a solution of **1** (60 mg, 0.14 mmol) in C_6H_6 (3 mL) was added dropwise a solution of *p*-tolualdehyde (19 mg, 0.16 mmol) in C_6H_6 (3 mL) at 25 °C. After 1.5 h, the solution was concentrated in vacuo to a peach solid that was spectroscopically pure (76 mg, 99% yield). X-ray-quality crystals of **21** (22 mg, 28% yield) were obtained by two successive recrystallizations using pentane vapor diffusion into a toluene solution of **21** at 25 °C: mp 160 °C dec. ^{1}H NMR (C_6D_6): δ 8.32 (d, J_{HH} = 8.0 Hz, 2 H, C$_6H_4$), 7.10 (d, J_{HH} = 8.0 Hz, 2 H, C$_6H_4$), 2.12 (s, 3 H, C$_6$H$_4$CH_3), 1.98 (m, 4 H, P−CH_2), 1.37 (s, 12 H, P−CH_3), 1.36 (m, 4 H, P−CH_2), 1.15 (s, 12 H, P−CH_3), −22.45 (qn, J_{HP} = 21.3 Hz, 1 H, Ru−*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 46.6 (s); ^{13}C{^{1}H} NMR (C_6D_6): δ 171.1 (*C*=O), 138.6 (*C*), 137.9 (*C*), 130.5 (*C*H), 129.0 (*C*H$_3$), 128.6 (*C*H), 31.7 (qn, J_{CP} = 13.6 Hz, P−*C*H$_2$), 22.9 (qn, J_{CP} = 7.3 Hz, P−*C*H$_3$), 16.0 (qn, J_{CP} = 5.4 Hz, P−*C*H$_3$). IR (KBr): 2958 (w), 2895 (w), 1928 (w), 1591 (m), 1549 (s), 1421 (w), 1404 (m), 1387 (w), 1290 (w), 1279 (w), 937 (m), 924 (w), 889 (w), 841 (w), 795 (w), 785 (w), 762 (w), 727 (w), 702 (w), 646 (w), 418 (w) cm^{-1}. MS-EI: *m/z* 537 [(M)$^+$]. Anal. Calcd for $C_{20}H_{40}O_2P_4Ru$: C, 44.69; H, 7.50. Found: C, 45.06; H, 7.71.

***trans*-(DMPE)$_2$Ru(H)(OC(O)*p*-C$_6$H$_4$CH$_3$) (21) (Method B).** To a solution of **4** (60 mg, 0.149 mmol) in benzene (8 mL) was added *p*-toluic acid (22.3 mg, 0.164 mmol). After 2 h at room temperature, the solution was concentrated to a peach solid to afford 76.8 mg of spectroscopically pure **21** (96% yield).

***trans*-(DMPE)$_2$Ru(H)(^{17}OC(^{17}O)*p*-C$_6$H$_4$CH$_3$) (21-$^{17}O_2$)** was prepared in an fashion analogous to that for **21** from **1**-^{17}O[28] and *p*-tolualdehyde. ^{1}H NMR (C_6D_6): δ 8.31 (d, J_{HH} = 8.0 Hz, 2 H, C$_6H_4$), 7.10 (d, J_{HH} = 8.0 Hz, 2 H, C$_6H_4$), 2.12 (s, 3 H, C$_6$H$_4$CH_3), 1.99 (m, 4 H, P−CH_2), 1.37 (s, 12 H, P−CH_3), 1.35 (m, 4 H, P−CH_2), 1.15 (s, 12 H, P−CH_3), −22.42 (qn, J_{HP} = 21.3 Hz, 1 H, Ru−*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 46.6 (s). ^{17}O NMR (C_6D_6): δ 6.7 (br), −10.4 (br).

X-ray Crystallographic Study of (DMPE)$_2$Ru(H)(OC(O)C$_6$H$_4$CH$_3$) (21). Crystals of **21** suitable for X-ray diffraction were obtained by evaporation of a benzene solution of **21** over 2 weeks. A fragment of one of these orange blocky crystals having dimensions of 0.25 × 0.30 × 0.30 mm was mounted on a glass fiber using Paratone N hydrocarbon oil. All measurements were made on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation. The final cell parameters and specific collection parameters are given in Table 1. The 4219 raw intensity data were converted to structure factor amplitudes by correction for scan speed, background, and Lorentz and polarization effects. Space group $P2_12_12_1$ was confirmed by successful refinement. The enantiomorph was determined by parallel refinement of both the inverse and obverse structures. The structure with the lower residuals is the one reported. No decay or absorption correction was applied. The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included with isotropic thermal parameters but not refined. Five data with small intensity and F_o values much greater than F_c were removed from the least-squares refinement. The final residuals for **21** are given in Table 1. Selected bond lengths and angles are given in Table 2, and an ORTEP diagram is shown in Figure 1. Positional and anisotropic thermal parameters and complete tables of bond distances and angles are provided in the Supporting Information.

***trans*-(DMPE)$_2$Ru(H)(OC(O)CF$_3$) (22).** A bomb was charged with a solution of **1** (93.7 mg, 0.022 mmol) in benzene (10 mL). CF$_3$C(O)CF$_3$ (0.022 mmol) was condensed into the solution via vacuum-transfer techniques. After 1 day at room temperature, the volatile materials were removed in vacuo and the resulting off-white powder was recrystallized by layering pentane (3 mL) onto a toluene (12 mL) solution of **22**. Yellow crystals of **22** were obtained in 55% yield (60.9 mg). ^{1}H NMR (C_6D_6): δ 1.73 (m, 4 H, P−CH_2), 1.28 (s, 12 H, P−CH_3), 1.20 (m, 4 H, P−CH_2), 1.04 (s, 12 H, P−CH_3), −23.40 (qn, J_{HP} = 20.9 Hz, 1 H, Ru−*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 45.2 (s). ^{13}C{^{1}H} NMR (C_6D_6): CF$_3$ carbon not observed, δ 161.2 (q, J_{CF} = 32.8 Hz, *C*O), 30.5 (qn, J_{CP} = 13.7 Hz, P−*C*H$_2$), 21.5 (qn, J_{CP} = 7.0 Hz, P−*C*H$_3$), 14.6 (qn, J_{CP} = 5.5 Hz, P−*C*H$_3$). ^{19}F{^{1}H} NMR (C_6D_6): δ −74.4. IR (KBr): 2966 (w), 2902 (m), 1932 (w), 1693 (s), 1682 (s), 1421 (w), 1294 (w), 1279 (w), 1200 (s), 1167 (m), 1122 (m), 937 (s), 912 (w), 891 (m), 839 (m), 833 (w), 795 (w), 729 (m), 704 (m), 644 (w) cm^{-1}. MS-EI *m/z* 515 [M$^+$]. Anal. Calcd for $C_{14}H_{33}F_3O_2P_4Ru$: C, 32.63; H, 6.45. Found: C, 32.85; H, 6.14.

Treatment of 1 with Ethylene. A 100 mL bomb was charged with a solution of **1** (94.2 mg, 0.225 mmol) in benzene (20 mL). Ethylene (3 atm) was condensed in via vacuum-transfer techniques. The solution was heated to 105 °C for 24 h. The volatile materials were removed in vacuo, and the resulting white solid was extracted with pentane (4 × 20 mL). Concentration of the pentane extracts afforded 64.2 mg of

spectroscopically pure **2** (67% yield). ^{1}H NMR (C_6D_6): δ 1.49 (d, J = 4.2 Hz), 1.35 (m), 1.24 (m), 1.17 (vt, J = 42.2 Hz), 1.03 (s), 1.02 (m), 0.85 (m), 0.79 (t, J = 2.3 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 43.7 (t, J = 28.5 Hz), 37.0 (t, J = 28.5 Hz). Lit.[35] ^{1}H NMR (C_6D_6): δ 1.48 (d, J = 4.2 Hz), 1.35 (m), 1.22 (m), 1.17 (vt, J = 42.2 Hz), 1.06 (s), 1.02 (m), 0.85 (m), 0.79 (t, J = 2.3 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 43.9 (t, J = 28.6 Hz), 37.2 (t, J = 28.6 Hz).

***trans*-[(DMPE)$_2$Ru(H)(CO)][OH] (25a).** A bomb (120 mL) was charged with a solution of **1** (101 mg, 0.240 mmol) in benzene (15 mL). The solution was degassed (three freeze−pump−thaw cycles), and an atmosphere of CO was condensed in (1 atm) via vacuum-transfer techniques. A white precipitate formed within 5 min at room temperature. The solution was stirred for 1 day at room temperature, and the precipitate was isolated via filtration and washed with THF (3 × 5 mL). IR (Nujol): 3394 (br), 2669 (w), 2621 (w), 1950 (s), 1670 (m), 1628 (s), 1431 (m), 1379 (s), 1333 (m), 1296 (m), 1286 (m), 1250 (w), 1140 (w), 1084 (w), 976 (m), 949 (m), 941 (m), 903 (m), 849 (m), 837 (w), 804 (w), 741 (m), 715 (m) cm^{-1}. MS−FAB: m/z 431 [M$^+$]. Anal. Calcd for $C_{13}H_{34}O_2P_4Ru$: C, 34.90; H, 7.66. Found: C, 34.72; H, 7.18.

***trans*-[(DMPE)$_2$Ru(H)(^{13}CO)][OH] (25a-^{13}*C*)** was prepared from **1** and ^{13}CO in a fashion analogous to that used for **25a**. IR (Nujol): 3394 (br), 2669 (w), 2621 (w), 1915 (s), 1670 (m), 1604 (s), 1431 (m), 1379 (s), 1333 (m), 1296 (m), 1286 (m), 1250 (w), 1140 (w), 1084 (w), 976 (m), 949 (m), 941 (m), 903 (m), 849 (m), 837 (w), 804 (w), 741 (m), 715 (m) cm^{-1}.

***trans*-(DMPE)$_2$Ru(CO) (26).**[48] To a suspension of **25** (56 mg, 0,13 mmol) in THF (10 mL) was added LiNTMS$_2$ (30 mg, 0.18 mmol). Within 1 h at room temperature, the solution appeared to be homogeneous. Volatile materials were removed in vacuo, and the resulting white powder was extracted with benzene (3 × 5 mL). The benzene extracts were filtered and concentrated in vacuo to a white solid. ^{1}H NMR (C_6D_6): δ 1.31 (br). ^{31}P{^{1}H} NMR (C_6D_6): δ 40.4 (s). IR (KBr): 2953 (w), 2875 (w), 1954 (s), 1927 (sh), 1450 (sh), 1428 (m), 1389 (m), 1292 (m), 935 (s), 901 (m), 858 (w), 727 (m) cm^{-1}. Lit.[48] ^{1}H NMR (C_6D_6): δ 1.31 (br). IR (KBr): 2958 (w), 2905 (w), 1945 (s), 1925 (sh), 1453 (sh), 1429 (m), 1380 (m), 1300 (m), 942 (s), 910 (m), 860 (w), 724 (m) cm^{-1}.

***trans*-(DMPE)$_2$Ru(H)(I) (27) (Method A).**[49] To a solution of **1** (83.0 mg, 0.0949 mmol) in C_6H_6 (5 mL) was added ICH_2-CH_2OH (17.9 mg, 0.104 mmol) in C_6H_6 (5 mL). After 20 min at room temperature, the solution was concentrated in vacuo to a pale yellow solid. Recrystallization from pentane (80 mL) at −70 °C afforded 57.6 mg of **27** as white needles (57% yield). ^{1}H NMR (C_6D_6): δ 1.69 (s, 12 H, P−CH_3), 1.64 (m, 4 H, P−CH_2), 1.23 (m, 4 H, P−CH_2), 1.12 (s, 12 H, P−CH_3), −18.41 (qn, J_{HP} = 21.4 Hz, 1 H, Ru−*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 38.6 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 31.2 (qn, J_{CP} = 13.3 Hz, P−*C*H$_2$), 23.7 (qn, J_{CP} = 7.2 Hz, P−*C*H$_3$), 19.7 (qn, J_{CP} = 6.2 Hz, P−*C*H$_3$). IR (KBr): 2960 (w), 2922 (w), 2897 (m), 1923 (m), 1419 (m), 1290 (w), 1279 (w), 937 (s), 891 (m), 839 (w), 727 (m), 702 (m), 675 (w), 644 (w), 457 (w) cm^{-1}. MS-EI: m/z 529 [M$^+$]. Anal. Calcd for $C_{20}H_{38}P_4Ru$: C, 27.23; H, 6.28. Found: C, 27.50; H, 6.19.

Acknowledgment. We thank the National Institutes of Health (Grant No. GM-25459) and the Arthur C. Cope Fund, administered by the American Chemical Society, for generous financial support of this work. We are grateful to Dr. F. J. Hollander, director of the University of California Berkeley College of Chemistry X-ray diffraction facility (CHEXRAY), for solving the crystal structure of **21**. We also thank Prof. R. A. Andersen for suggesting the use of N_2O in the synthesis of **1** and for helpful discussions and Prof. R. N. Perutz for disclosure of results prior to publication. We thank the DuPont Co. for partial research support and access to facilities and are grateful to G. Cres Campbell and Dr. Emilio Bunel for recording the NMR spectra of **14**.

Supporting Information Available: Text and tables giving structural tables for **21** and figures giving CPMAS spectra of **1** and **14** (14 pages). See any current masthead page for ordering information and Internet access instructions.

OM980295D