Characterization and Reactivity of an Unprecedented Unsaturated Zero-Valent Ruthenium Species: Isolable, Yet Highly Reactive

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Received March 25, 1996[⊗]

Abstract: Magnesium reduction of *cis,cis,trans*-$RuCl_2(CO)_2L_2$ (L = P^tBu_2Me) yields isolable $Ru(CO)_2L_2$, shown by solution spectroscopies and X-ray diffraction to have *trans* phosphines but *cis* carbonyls, in a nonplanar structure which resembles a trigonal bipyramid with one equatorial ligand missing. This unusual geometric structure is traced by *ab initio* (MP2) study to enhanced back-donation to CO by zero-valent Ru. This molecule reacts in time of mixing to add CO, MeNC, O_2, CS_2, C_2H_4, or PhC≡CPh. Rapid oxidative addition occurs with H_2, HCl, Cl_2, and PhC≡CH. Oxidative addition is slower with MeCl, Me_3SiH, and MeOH, which leads to more complicated reaction schemes. Reaction with PPh_2H gives not oxidative addition but addition and displacement, yielding $Ru(CO)_2(PPh_2H)_2(P^tBu_2Me)$ and equimolar free P^tBu_2Me. Magnesium reduction of *cis,cis,trans*-$RuCl_2(CO)_2L'_2$ proceeds analogously for L′ = P^iPr_3, but for L′ = PPh_3, decomposition and ligand scavenging give $Ru(CO)_2(PPh_3)_3$. Reduction of *cis,trans*-$RuCl_2(CO)(CNMe)L_2$ gives the product of oxidative addition of a ^tBu C−H bond: $RuH(CO)(CNMe)[\eta^2\text{-}P(CMe_2CH_2)^tBuMe]L$, showing the influence of electron density at unsaturated Ru(0) on its persistence.

Introduction

We report here a new aspect to the chemistry of zero-valent ruthenium; the isolation and characterization of unsaturated $Ru(CO)_2(P^tBu_2Me)_2$. This permits the determination of the unusual geometric and thus the electronic structure of this molecule. In addition, most reactions of *saturated* Ru(0) molecules with nucleophiles begin with ligand dissociation, and thus determining the details of the reactions of the unsaturated transient with the reagent partner remains difficult. In the work presented here, since we begin with this persistent unsaturated species, heretofore unobserved mechanistic detail is within reach. Since our reactions occur at and below 25 °C, we are often able to observe the primary (kinetic) products. Finally, the persistence of $Ru(CO)_2(P^tBu_2Me)_2$ lies in part in its steric bulk as well as in the resistance of the P^tBu_2Me to intramolecular C−H oxidative addition. We have tried to modulate the properties of this unusual species by altering the steric and electronic properties of the ligands. Part of this work has been reported in a preliminary communication where we comment that all other d^8 four-coordinate species of Rh^I, Ir^I, Pd^{II}, and Pt^{II} are *planar*.[1]

Experimental Section

General. All manipulations were carried out using standard Schlenk and glovebox techniques under prepurified argon. Benzene, pentane, THF, and toluene were dried over sodium benzophenone ketyl, distilled, and stored in gas tight solvent bulbs. Methanol and 2-methoxyethanol were degassed under vacuum and used without further purification. Benzene-d_6 and toluene-d_8 were dried over sodium metal and vacuum-distilled prior to use. Phosphines (P^iPr_3 and PPh_2H) and 1,2-dibromoethane were purchased from Aldrich Chemical Co. and used without purification. Diphenylacetylene, phenylacetylene, and carbon disulfide were purchased from Aldrich and used after purifying by appropriate methods (sublimation or distillation). Gaseous reagents (H_2, O_2, CO, HCl, Cl_2, C_2H_4, and MeCl) were purchased from Air Products and used as received. Trimethylsilane was purchased from Petrarch Systems and used as received. Formaldehyde (37% in water) was purchased from Baker Analyzed and used as received. Methyllithium (in diethyl ether, Aldrich) was used after its concentration was determined by appropriate titration prior to use. Methyl isocyanide was synthesized according to a published method.[2] Ruthenium trichloride hydrate was a generous loan from Johnson Matthey and used as received. $RuHCl(CO)(P^tBu_2Me)_2$,[3] *cis,cis,trans*-$RuCl_2(CO)_2(P^tBu_2Me)_2$,[4] $RuCl_2(CO)(P^tBu_2Me)_2$,[5] and *cis,cis,trans*-$RuCl_2(CO)_2(PPh_3)_2$[6] were synthesized as reported. ^1H (300 MHz) NMR spectra were recorded on a Varian XL300 spectrometer. ^{31}P NMR spectra were obtained on a Nicolet NT-360 spectrometer at 146 MHz. ^1H NMR chemical shifts are reported in ppm downfield of tetramethylsilane using residual solvent resonances as internal standards. ^{31}P NMR chemical shifts are relative to external 85% H_3PO_4. Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AR, or on a Perkin-Elmer 2400 CHN/S elemental analyzer at the Chemistry Department, Indiana University.

***cis,cis,trans*-$RuCl_2(CO)_2(P^iPr_3)_2$.** Carbon monoxide was passed through a solution of ruthenium trichloride hydrate (2.31 g, 10.0 mmol) in 2-methoxyethanol (55 mL) at 130 °C until the solution color changed to pale yellow (ca. 12 h). After a small amount of insoluble material

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[⊗] Abstract published in *Advance ACS Abstracts*, October 1, 1996.

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S0002-7863(96)00967-5 CCC: $12.00

was filtered away, $\mathrm{P^iPr_3}$ (3.50 g, 21.8 mmol) was added, and then the solution was refluxed for 10 min. The solution was concentrated to ca. 15 mL under reduced pressure and cooled to room temperature, yielding two crops of white crystals; yield 4.75 g (8.62 mmol, 86%). ^{1}H NMR ($\mathrm{C_6D_6}$, 23 °C): δ 1.26 (dvt, $J_{\mathrm{HP}} \approx J_{\mathrm{HH}} = 7.0$ Hz, 36H, $\mathrm{PCC}H_3$), 2.79 (sept of vt, $J_{\mathrm{HH}} = 7.0$ Hz, $J_{\mathrm{HP}} = 3.9$ Hz, 6H, $\mathrm{PC}H\mathrm{Me_2}$). ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$, 23 °C): δ 38.4 (s). IR: ν_{CO} ($\mathrm{C_6D_6}$) 2029 and 1960 cm^{-1}. Anal. Calcd for $\mathrm{RuC_{20}H_{42}Cl_2O_2P_2}$: C, 43.80; H, 7.72. Found: C, 44.00; H, 7.69.

$\mathbf{Ru(CO)_2(P^tBu_2Me)_2}$ (3). (a) From the Metalated Species. A Schlenk flask was charged with $\mathrm{RuHCl(CO)(P^tBu_2Me)_2}$ (303 mg, 0.62 mmol). Toluene (12 mL) was added, and the orange solution was cooled to −78 °C. MeLi (1.4 M, 0.47 mL, 0.66 mmol) was added via syringe, and the now darker orange mixture was warmed to −40 °C with stirring for 20 min. The Schlenk flask was degassed three times by freeze/pump/thaw cycles, and carbon monoxide (450 Torr in 36 mL at 290 K, 0.90 mmol) was introduced into the flask. After the solution was stirred for 30 min at −40 °C, the remaining CO was removed from the flask by pumping at low temperature (<−40 °C). The solution was warmed under argon to room temperature and then kept stirring for 4 h. During this period, the solution color changed from pale yellow to dark red. The volatiles were removed, and the red residue was extracted with pentane (5 mL × 3). The combined solution was concentrated and cooled, yielding very dark red crystals; yield 137 mg (0.29 mmol, 46%). ^{1}H NMR ($\mathrm{C_6D_6}$, 23 °C): δ 1.19 (vt, $J_{\mathrm{HP}} = 6.6$ Hz, 36H, P-^{t}Bu), 1.38 (vt, $J_{\mathrm{HP}} = 2.1$ Hz, 6H, P-Me). ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$, 23 °C): δ 65.4 (s). IR: ν_{CO} (Nujol) 1902 and 1831 cm^{-1}. Anal. Calcd for $\mathrm{RuC_{20}H_{42}O_2P_2}$: C, 50.30; H, 8.86; P, 12.97. Found: C, 50.03; H, 8.88; P, 13.18.

(b) Reduction of cis,cis,trans-$\mathbf{RuCl_2(CO)_2(P^tBu_2Me)_2}$. Magnesium turnings (52 mg, 2.12 mmol) and THF (1 mL) were placed in a Schlenk flask, and 1,2-dibromoethane (26 μL, 0.30 mmol) was added via syringe. The mixture was gently stirred until the evolution of ethylene ceased. To the flask was added a solution of *cis,cis,trans*-$\mathrm{RuCl_2(CO)_2(P^tBu_2Me)_2}$ (1.00 g, 1.82 mmol) in THF (30 mL) by means of cannula transfer. The mixture was stirred at room temperature until all the magnesium turnings were consumed (ca. 20 h). During this period, the color of the solution changed from colorless to deep red. The volatiles were removed, and the dark red residue was extracted with pentane (20 mL × 3). After the insoluble material was filtered away, the solution was concentrated and cooled, yielding two crops of dark red crystals totaling 0.70 g (1.47 mmol, 80%). All the spectroscopic data are consistent with those described above.

$\mathbf{Ru(CO)_2(P^iPr_3)_2}$. This compound was synthesized from *cis,cis,-trans*-$\mathrm{RuCl_2(CO)_2(P^iPr_3)_2}$ and stoichiometric activated magnesium turnings in THF as described above in 83% yield. ^{1}H NMR ($\mathrm{C_6D_6}$, 23 °C): δ 1.19 (dvt, $J_{\mathrm{HP}} = J_{\mathrm{HH}} = 6.8$ Hz, 36H, $\mathrm{PCC}H_3$), 2.07 (sept of vt, $J_{\mathrm{HH}} = 6.8$ Hz, $J_{\mathrm{HP}} = 3.4$ Hz, 6H, $\mathrm{PC}H\mathrm{Me}$). ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$, 23 °C): δ 71.2 (s). IR: νCO (Nujol) 1898 and 1829 cm^{-1}. Anal. Calcd for $\mathrm{RuC_{20}H_{42}O_2P_2}$: C, 50.30; H, 8.86. Found: C, 50.47; H, 8.78.

$\mathbf{Ru(CO)_3(P^tBu_2Me)_2}$ (4). A solution of $\mathrm{Ru(CO)_2(P^tBu_2Me)_2}$ (10 mg, 0.021 mmol) in $\mathrm{C_6D_6}$ (0.5 mL) was placed in an NMR tube fitted with a Teflon stopcock. The solution was frozen in liquid $\mathrm{N_2}$, the headspace was evacuated, and excess CO (1 atm) was introduced into the tube. When the solution warmed to room temperature and the tube was shaken, the solution color immediately changed from deep red to pale yellow. ^{1}H and ^{31}P{^{1}H} NMR and IR spectra showed complete conversion to $\mathrm{Ru(CO)_3(P^tBu_2Me)_2}$, which was previously reported.[7]

$\mathbf{Ru(CNMe)(CO)_2(P^tBu_2Me)_2}$ (5). A pentane (5 mL) solution of $\mathrm{Ru(CO)_2(P^tBu_2Me)_2}$ (100 mg, 0.21 mmol) was placed in a Schlenk flask fitted with a rubber septum. To this solution was added methyl isocyanide (8.7 mg, 0.21 mmol) via syringe at room temperature. Immediately, the dark red solution color changed to yellow. The solution was concentrated to ca. 2 mL and cooled to −40 °C to give bright yellow needles; yield 79 mg (0.15 mmol, 73%). ^{1}H NMR ($\mathrm{C_6D_6}$, 23 °C): δ 1.35 (vt, $J_{\mathrm{HP}} = 6.6$ Hz, 36H, P−^{t}Bu), 1.41 (vt, $J_{\mathrm{HP}} = 2.6$ Hz, 6H, P−Me), 2.53 (t, $J_{\mathrm{HP}} = 2.0$ Hz, 3H, $\mathrm{CH_3NC}$). ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$, 23 °C): δ 68.8 (s). IR: ν_{CO} ($\mathrm{C_6D_6}$) 1881 and 1829 cm^{-1}, ν_{CN} ($\mathrm{C_6D_6}$) 2078 cm^{-1}. Anal. Calcd for $\mathrm{RuC_{22}H_{45}NO_2P_2}$: C, 50.95; H, 8.75; N, 2.70. Found: C, 50.77; H, 8.54; N, 2.67.

$\mathbf{Ru(\boldsymbol{\eta}^2\text{-}O_2)(CO)_2(P^tBu_2Me)_2}$ (6). $\mathrm{Ru(CO)_2(P^tBu_2Me)_2}$ (100 mg, 0.21 mmol) was dissolved in pentane (5 mL) in a Schlenk flask, and the flask was freeze/pump/thaw degassed three times. The solution was cooled to −78 °C, and $\mathrm{O_2}$ (1 atm) was admitted to the flask at this temperature. Immediately, the deep red solution became pale orange. The remaining $\mathrm{O_2}$ gas was removed from the flask with the solvent by evacuation. The remaining pale orange solid was recrystallized from pentane to give two crops of the title compound in pure form; yield 92 mg (0.18 mmol, 86%). ^{1}H NMR (toluene-d_8, 23 °C): δ 1.15 (vt, $J_{\mathrm{HP}} = 3.2$ Hz, 6H, P−Me), 1.25 (vt, $J_{\mathrm{HP}} = 6.5$ Hz, 36H, P−^{t}Bu). ^{31}P{^{1}H} NMR (toluene-d_8, 23 °C): δ 47.7 (s). IR: ν_{CO} (pentane) 1991 and 1921 cm^{-1}. Anal. Calcd for $\mathrm{RuC_{20}H_{42}O_4P_2}$: C, 47.14; H, 8.31. Found: C, 47.00; H, 8.17.

$\mathbf{Ru(\boldsymbol{\eta}^2\text{-}CS_2)(CO)_2(P^tBu_2Me)_2}$ (7). A pentane (20 mL) solution of $\mathrm{Ru(CO)_2(P^tBu_2Me)_2}$ (200 mg, 0.42 mmol) was placed in a Schlenk flask fitted with a rubber septum and cooled to −78 °C. To this solution was added $\mathrm{CS_2}$ (27 μL, 0.45 mmol) via syringe. Immediately, a light orange precipitate formed from the dark red solution. Removing the mother liquor and washing the remaining solid with cold pentane (10 mL × 2) gave the title compound in essentially pure form; yield 212 mg (0.38 mmol, 91%). ^{1}H NMR ($\mathrm{C_6D_6}$, 23 °C) δ 1.13 (vt, $J_{\mathrm{HP}} = 6.6$ Hz, 18H, P^{t}Bu), 1.16 (vt, $J_{\mathrm{HP}} = 6.6$ Hz, 18H, P−^{t}Bu), 1.19 (vt, $J_{\mathrm{HP}} = 3.0$ Hz, 6H, P−Me). ^{31}P{^{1}H} NMR (toluene-d_8, -80 °C): δ 52.3 (s). IR: ν_{CO} ($\mathrm{C_6D_6}$) 1993 and 1933 cm^{-1}, ν_{CS} ($\mathrm{C_6D_6}$) 1125 cm^{-1}. Anal. Calcd for $\mathrm{RuC_{21}H_{42}O_2P_2S_2}$: C, 45.55; H, 7.65. Found: C, 45.76; H, 7.51.

$\mathbf{Ru(\boldsymbol{\eta}^2\text{-}C_2H_4)(CO)_2(P^tBu_2Me)_2}$ (8). A solution of $\mathrm{Ru(CO)_2(P^tBu_2Me)_2}$ (10 mg, 0.021 mmol) in toluene-d_8 (0.5 mL) was placed in an NMR tube fitted with a Teflon stopcock. The solution was frozen in liquid $\mathrm{N_2}$, the headspace was evacuated, and ethylene (1 atm, ca. 0.12 mmol) was introduced into the tube. Upon thawing and vigorous shaking, the ^{31}P{^{1}H} NMR spectrum showed reversible coordination of ethylene to the complex (see text for detail). Below −50 °C, the title compound is the only observable species by NMR. ^{1}H NMR (toluene-d_8, −50 °C): δ 0.59 (br, 6H, P−Me), 1.21 (vt, $J_{\mathrm{HP}} = 6.1$ Hz, 36H, P−^{t}Bu), 1.58 (t, $J_{\mathrm{HP}} = 5.6$ Hz, 4H, $\mathrm{C_2H_4}$). ^{31}P{^{1}H} NMR (toluene-d_8, −60 °C): δ 58.4 (s).

$\mathbf{Ru(\boldsymbol{\eta}^2\text{-}PhC{\equiv}CPh)(CO)_2(P^tBu_2Me)_2}$ (9). To a solution of $\mathrm{Ru(CO)_2(P^tBu_2Me)_2}$ (10 mg, 0.021 mmol) in toluene-d_8 (0.5 mL) was added diphenylacetylene (4.0 mg, 0.022 mmol). Immediately, the deep red solution became yellow. Although the ^{31}P{^{1}H} NMR spectrum showed complete consumption of $\mathrm{Ru(CO)_2(P^tBu_2Me)_2}$, isolation of the title compound was unsuccessful due to the equilibrium with phosphine dissociation (see text). ^{1}H NMR (toluene-d_8, −40 °C): δ 0.68 (br, 6H, P−Me), 1.12 (vt, $J_{\mathrm{HP}} = 5.8$ Hz, 36H, P−^{t}Bu), 7.04 (t, $J_{\mathrm{HH}} = 7.2$ Hz, 2H, *p*-H), 7.29 (t, $J_{\mathrm{HH}} = 7.8$ Hz, 4H, *m*-H), 7.94 (d, $J_{\mathrm{HH}} = 7.2$ Hz, 4H, *o*-H). ^{31}P{^{1}H} NMR (toluene-d_8, −40 °C): δ 60.9 (s). IR: ν_{CO} (pentane) 1960 and 1896 cm^{-1}, ν_{CC} (pentane) 1744 cm^{-1}.

$\mathbf{Ru(CO)_2(PPh_2H)_2(P^tBu_2Me)}$ (11). To a solution of $\mathrm{Ru(CO)_2(P^tBu_2Me)_2}$ (10 mg, 0.021 mmol) in $\mathrm{C_6D_6}$ (0.5 mL) was added 7.4 μL of diphenylphosphine (8.0 mg, 0.042 mmol). Immediately, the deep red solution became bright yellow. Although the ^{31}P{^{1}H} NMR spectrum showed complete conversion into $\mathrm{Ru(CO)_2(PPh_2H)_2(P^tBu_2Me)}$ and free $\mathrm{P^tBu_2Me}$, isolation of $\mathrm{Ru(CO)_2(PPh_2H)_2(P^tBu_2Me)}$ in pure form was unsuccessful due to the poor crystallinity of the compound. ^{1}H NMR ($\mathrm{C_6D_6}$, 23 °C): δ 1.23 (d, $J_{\mathrm{HP}} = 13.0$ Hz, 18H, P-^{t}Bu), 1.34 (d, $J_{\mathrm{HP}} = 5.7$ Hz, 3H, P-Me), 6.48 (dm, $J_{\mathrm{HP}} = 280$ Hz, 2H, PH), 6.93−7.03 (m, 12H, *m*- and *p*-H), 7.55 (m, 8H, *o*-H). ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$, 23 °C): δ 24.4 (d, $J_{\mathrm{PP}} = 72.3$ Hz, 2P, $\mathrm{PPh_2H}$), 66.6 (t, $J_{\mathrm{PP}} = 72.3$ Hz, 1P, $\mathrm{P^tBu_2Me}$). IR: ν_{CO} (pentane) 1858 cm^{-1}.

$\mathbf{Ru(H)_2(CO)_2(P^tBu_2Me)_2}$ (12). A solution of $\mathrm{Ru(CO)_2(P^tBu_2Me)_2}$ (100 mg, 0.21 mmol) in pentane (5 mL) was placed in a Schlenk flask and freeze/pump/thaw degassed three times. The solution was warmed to room temperature, and $\mathrm{H_2}$ (1 atm) was admitted. Immediately, the deep red solution became pale yellow. After filtration, the solution was concentrated to ca. 1 mL under reduced pressure and cooled to −78 °C under $\mathrm{H_2}$ atmosphere, yielding pale yellow crystals; yield 88 mg (0.18 mmol, 88%). ^{1}H NMR (toluene-d_8, 23 °C): δ −7.96 (t, $J_{\mathrm{HP}} = 22.7$ Hz, 2H, Ru−H), 1.22 (vt, $J_{\mathrm{HP}} = 6.7$ Hz, 36H, P−^{t}Bu), 1.36 (vt, $J_{\mathrm{HP}} = 2.2$ Hz, 6H, P−Me). ^{31}P{^{1}H} NMR (toluene-d_8, 23 °C): δ 74.0 (s). IR: ν_{CO} (Nujol) 1999 and 1966 cm^{-1}. Anal. Calcd for $\mathrm{RuC_{20}H_{44}O_2P_2}$: C, 50.09; H, 9.25. Found: C, 50.09; H, 9.45.

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(7) Heyn, R. H.; Macgregor, S. A.; Nadasdi, T. T.; Ogasawara, M.; Eisenstein, O.; Caulton, K. G. *Inorg. Chim. Acta*, in press.

***cis,trans*-$RuHCl(CO)_2(P^tBu_2Me)_2$ (13).** A solution of $Ru(CO)_2(P^tBu_2Me)_2$ (10 mg, 0.021 mmol) in C_6D_6 (0.5 mL) was placed in an NMR tube fitted with a Teflon stopcock. The solution was frozen in liquid N_2, the headspace was evacuated, and HCl (0.021 mmol) was condensed into the tube using a calibrated gas manifold. When the solution warmed to room temperature and the tube was shaken, the solution color immediately changed from deep red to colorless. ^1H and $^{31}P\{^1H\}$ NMR and IR spectra showed complete conversion to $RuHCl(CO)_2(P^tBu_2Me)_2$, which was previously reported.[3]

$RuCl_2(CO)_2(P^tBu_2Me)_2$ (14 and 15). A solution of $Ru(CO)_2(P^tBu_2Me)_2$ (10 mg, 0.021 mmol) in toluene-d_8 (0.5 mL) was placed in an NMR tube fitted with a Teflon stopcock. The solution was frozen in liquid N_2, the headspace was evacuated, and Cl_2 (0.021 mmol) was condensed into the tube using a calibrated gas manifold. When the solution warmed to room temperature and the tube was shaken, the solution color immediately changed from deep red to pale yellow. The $^{31}P\{^1H\}$ NMR spectrum showed complete conversion of $Ru(CO)_2(P^tBu_2Me)_2$ into *cis*-$RuCl_2(CO)_2(P^tBu_2Me)_2$ and *trans*-$RuCl_2(CO)_2(P^tBu_2Me)_2$ in a 2:1 molar ratio. Heating the solution at 70 °C for 2 h isomerized the *trans* isomer to the *cis* isomer completely.

$RuH(C{\equiv}CPh)(CO)_2(P^tBu_2Me)_2$ (16). A pentane (5 mL) solution of $Ru(CO)_2(P^tBu_2Me)_2$ (100 mg, 0.21 mmol) was placed in a Schlenk flask fitted with a rubber septum. To this solution was added 26 μL of phenylacetylene (24.2 mg, 0.24 mmol) was added via syringe at room temperature. Immediately, the dark red solution color changed to colorless. The solution was concentrated to ca. 2 mL and cooled to −40 °C to give colorless needles; yield 92 mg (0.16 mmol, 76%). ^1H NMR (C_6D_6, 23 °C): δ −6.63 (t, J_{HP} = 19.7 Hz, 1H, Ru−H), 1.21 (vt, J_{HP} = 6.5 Hz, 18H, P−^{t}Bu), 1.35 (vt, J_{HP} = 6.5 Hz, 18H, P−^{t}Bu), 1.63 (vt, J_{HP} = 3.0 Hz, 6H, P−Me), 6.99 (m, 1H, *p*-H), 7.15 (m, 2H, *m*-H), 7.50 (m, 2H, *o*-H). $^{31}P\{^1H\}$ NMR (C_6D_6, 23 °C): δ 60.2 (s). IR: ν_{CO} (C_6D_6) 2020 and 1958 cm^{-1}, ν_{CC} (C_6D_6) 2103 cm^{-1}, ν_{RuH} (C_6D_6) 1919 cm^{-1}. Anal. Calcd for $RuC_{28}H_{48}O_2P_2$: C, 58.01; H, 8.35. Found: C, 57.73; H, 8.34.

Reaction of $Ru(CO)_2(P^tBu_2Me)_2$ with MeCl. A solution of $Ru(CO)_2(P^tBu_2Me)_2$ (10 mg, 0.021 mmol) in C_6D_6 (0.5 mL) was placed in an NMR tube fitted with a Teflon stopcock. The solution was frozen in liquid N_2, the headspace was evacuated, and chloromethane (0.032 mmol) was condensed into the tube using a calibrated gas manifold. After the solution was maintained at 80 °C for 2 h, the $^{31}P\{^1H\}$ NMR spectrum showed complete conversion of $Ru(CO)_2(P^tBu_2Me)_2$ into $Ru(COCH_3)Cl(CO)(P^tBu_2Me)_2$,[8] $RuMeCl(CO)(P^tBu_2Me)_2$,[8] and $Ru(CO)_3(P^tBu_2Me)_2$ in a 5:1:1 molar ratio.

Reaction of $Ru(CO)_2(P^tBu_2Me)_2$ with Me_3SiH. A solution of $Ru(CO)_2(P^tBu_2Me)_2$ (10 mg, 0.021 mmol) in C_6D_6 (0.5 mL) was placed in a Teflon valve NMR tube and freeze/pump/thaw degassed. Trimethylsilane (0.21 mmol) was condensed into the tube. After 2 days at room temperature, $Ru(H)_2(CO)_2(P^tBu_2Me)_2$ was produced as the only phosphorus-containing species detected by $^{31}P\{^1H\}$ NMR. ^1H NMR revealed $Me_3Si{-}SiMe_3$ as the only silicon-containing product.

Reaction of $Ru(CO)_2(P^tBu_2Me)_2$ with CH_2O. A C_6D_6 (0.5 mL) solution of $Ru(CO)_2(P^tBu_2Me)_2$ (10 mg, 0.021 mmol) was placed in an NMR tube fitted with a rubber septum. Equimolar aqueous formaldehyde was added to this solution via syringe at room temperature. After 24 h at room temperature, the solution color changed from deep red to pale yellow. The $^{31}P\{^1H\}$ NMR spectrum showed complete conversion of $Ru(CO)_2(P^tBu_2Me)_2$ into $Ru(H)_2(CO)_2(P^tBu_2Me)_2$ and $Ru(CO)_3(P^tBu_2Me)_2$. The ratio between the two products depends on the amount of formaldehyde employed (see text for detail).

Reaction of $Ru(CO)_2(P^tBu_2Me)_2$ with MeOH. A solution of $Ru(CO)_2(P^tBu_2Me)_2$ (10 mg, 0.021 mmol) in a mixture of C_6D_6 (0.4 mL) and MeOH (0.1 mL) was placed in an NMR tube. After 3 h at room temperature, the solution color changed from deep red to pale yellow. The $^{31}P\{^1H\}$ NMR spectrum showed formation of $Ru(H)_2(CO)_2(P^tBu_2Me)_2$ (ca. 60%) and $Ru(CO)_3(P^tBu_2Me)_2$ (ca. 35%) with some other small amount of uncharacterized products (ca. 5%).

Magnesium Reduction of *cis,cis,trans*-$RuCl_2(CO)_2(PPh_3)_2$. Magnesium turnings (18 mg, 0.74 mmol) and THF (0.5 mL) were placed in a Schlenk flask, and 1,2-dibromoethane (16 μL, 0.19 mmol) was added via syringe. The mixture was gently stirred until the evolution of ethylene ceased. A suspension of *cis,cis,trans*-$RuCl_2(CO)_2(PPh_3)_2$ (0.41 g, 0.54 mmol) in THF (10 mL) was added to the flask by means of cannula transfer. The mixture was stirred at room temperature until all the magnesium turnings were consumed. During this period, the color of the solution changed from colorless to dark reddish brown. The volatiles were removed, and the dark red residue was extracted with benzene (10 mL × 3). After the insoluble material was filtered away, the solution was evaporated to dryness, leaving a brown solid. $^{31}P\{^1H\}$ NMR and IR data reveal formation of $Ru(CO)_2(PPh_3)_3$[9] as the main product (>90% purity based on $^{31}P\{^1H\}$ NMR); yield 225 mg (0.24 mmol, 44% based on Ru).

***cis,trans*-$RuCl_2(CO)(CNMe)(P^tBu_2Me)_2$.**[10] To an orange solution of $RuCl_2(CO)(P^tBu_2Me)_2$ (684 mg, 1.31 mmol) in toluene (30 mL) was added 75 μL of methyl isocyanide (57 mg, 1.38 mmol) by means of syringe at room temperature. The obtained pale yellow solution was refluxed for 5 min. After filtration, the solution was concentrated to ca. 10 mL and recrystallized from hot toluene to give two crops of colorless crystals; yield 582 mg (1.04 mmol, 79%). ^1H NMR (THF-d_8, 23 °C): δ 1.45 (vt, J_{HP} = 6.3 Hz, 36H, P−^{t}Bu), 1.69 (vt, J_{HP} = 3.3 Hz, 6H, P−Me), 3.52 (s, 3H, CH_3NC). $^{31}P\{^1H\}$ NMR (THF-d_8, 23 °C): δ 40.9 (s). IR: ν_{CO} (C_6D_6) 1956 cm^{-1}, ν_{CN} (C_6D_6) 2174 cm^{-1}. Anal. Calcd for $RuC_{21}H_{45}Cl_2NOP_2$: C, 44.92; H, 8.08; N, 2.49. Found: C, 44.79; H, 8.23; N, 2.71.

$RuH(CO)(CNMe)[\eta^2\text{-}P(CMe_2CH_2)^tBuMe](P^tBu_2Me)$ (17a and 17b). A solution of $RuHCl(CO)(P^tBu_2Me)_2$ (10 mg, 0.021 mmol) in toluene-d_8 (0.5 mL) was placed in an NMR tube. The solution was cooled to −78 °C, and MeLi (15 μL in 1.4 M ether solution, 0.021 mmol) was added into the tube by syringe. Warming to −40 °C formed a diastereomeric mixture of $RuH(CO)[\eta^2\text{-}P(CMe_2CH_2)^tBuMe](P^tBu_2Me)$ as reported.[7] When methyl isocyanide (1.15 μL, 0.021 mmol) was added into the NMR tube and the tube was shaken, the solution color changed immediately from red-orange to pale yellow. ^1H and $^{31}P\{^1H\}$ NMR spectra showed complete conversion to the title compounds as a diastereomeric mixture. **17a**: $^{31}P\{^1H\}$ NMR (toluene-d_8, −40 °C) δ 23.2 (d, J_{PP} = 240 Hz, 1P, metalated *P*), 65.1 (d, J_{PP} = 240 Hz, 1P, P^tBu_2Me); ^1H NMR (toluene-d_8, −40 °C) δ −7.29 (t, J_{PH} = 21.8 Hz, Ru-*H*). **17b:** $^{31}P\{^1H\}$ NMR (toluene-d_8, −40 °C) δ 13.9 (d, J_{PP} = 240 Hz, 1P, metalated *P*), 64.3 (d, J_{PP} = 240 Hz, 1P, P^tBu_2Me); ^1H NMR (toluene-d_8, −40 °C) δ −7.48 (t, J_{PH} = 21.7 Hz, Ru−*H*).

Magnesium Reduction of $RuCl_2(CO)(CNMe)(P^tBu_2Me)_2$. Magnesium turnings (21 mg, 0.84 mmol) and THF (0.5 mL) were placed in a Schlenk flask, and 1,2-dibromoethane (40 μL, 0.46 mmol) was added via syringe. The mixture was gently stirred until the evolution of ethylene ceased. $RuCl_2(CO)(CNMe)(P^tBu_2Me)_2$ (205 mg, 0.37 mmol) in THF (8 mL) was added to the flask by means of cannula transfer. The mixture was stirred at room temperature until all the magnesium turnings were consumed (ca. 12 h). During this period, the color of the solution changed from colorless to dark brown. The volatiles were removed, and the dark brown residue was extracted with toluene (5 mL × 3). After the insoluble material was filtered away, the solution was evaporated to dryness, leaving ca. 150 mg of red-orange-colored solid. The $^{31}P\{^1H\}$ NMR spectrum showed formation of **17a** and **17b** as main products in addition to a singlet at δ 64.1 ppm with a small amount of some uncharacterized species.

X-Ray Structure Determinations. (a) $Ru(CO)_2(P^tBu_2Me)_2$. The crystal was attached to a glass fiber using silicone grease and was transferred to the goniostat where it was cooled to −171 °C for characterization and data collection. A systematic search of selected ranges of reciprocal space yielded a set of reflections which exhibited monoclinic (2/m) diffraction symmetry. Data collection was undertaken as shown in Table 1. Plots of the four standard reflections (6,0,0; 0,−6,0; 0,0,6; 5,−3,−5) measured every 300 reflections showed no

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[9] (a) Cavit, B. E.; Grundy, K. R.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1972**, 60. (b) Gaffney, T. R.; Ibers, J. A. *Inorg. Chem.* **1982**, *21*, 2851.

[10] Although the ^1H NMR spectrum shows only one ^{t}Bu signal, we propose the conformation of CO and CNMe taking a *cis* position. Addition of MeNC to a THF solution of $RuCl_2(CO)(P^tBu_2Me)_2$ gives the yellow product whose $^{31}P\{^1H\}$ NMR chemical shift is δ 37.7. This complex (presumably *trans* isomer) isomerizes into *cis* isomer at toluene reflux temperature within 15 min. This reaction pattern is identical to that which is shown for two isomers of $RuCl_2(CO)_2(P^tBu_2Me)_2$.[4,5]

Table 1. Crystallographic Data

	$Ru(CO)_2(P^tBu_2Me)_2$	$Ru(CO)_2(O_2)(P^tBu_2Me)_2$
formula	$C_{20}H_{42}O_2P_2Ru$	$C_{20}H_{42}O_4P_2Ru$
a (Å)	11.601 (3)	16.312(1)
b (Å)	14.320(3)	14.686(1)
c (Å)	15.404(3)	20.778(2)
β (deg)	107.65(1)	106.19(1)
V (Å^3)	2438.47	4780.30
Z	4	8
fw (g/mol)	477.6	509.6
space group	$P2_1/n$	$P2_1/c$
T (°C)	−171	−172
λ (Å^a)	0.71069	0.71069
ρ_{calc} (g/cm^3)	1.301	1.416
μ (cm^{-1})	7.69	7.95
$R(F_o)^b$	0.0666	0.0608
$R_w(F_o)^c$	0.0712	0.0575

[a] Graphite monochromator. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $Rw = [\Sigma w(|F_o| - |F_c|)^2/w|F_o|^2]^{1/2}$ where $w = 1/\sigma^2(|F_o|)$.

systematic trends. Examination of the 0k0 data showed that 0k0 reflections were systematically extinct for $k = 2n + 1$. The h01 zone was problematic: reflections having $h + 1 = 2n + 1$ were, in general, weak; the average intensity for $h + 1 = 2n + 1$ was 24 vs 1731 for $h + 1 = 2n$. The maximum intensity for a reflection having $h + 1 = 2n + 1$ was 235 for 6,0,−7, and it should be noted that 156 of the 308 h01 reflections with $h + l = 2n + 1$ had intensities greater than 50.0. The original assumption was that there were no systematic extinctions in the h01 zone and the space group was assumed to be $P2_1$ (or $P2_1/m$) rather than $P2_1/n$. **$P2_1$:** The structure was solved by locating the two unique Ru atoms using MULTAN-78. The remaining non-hydrogen atoms were located in successive iterations of least-squares refinement, followed by difference Fourier calculations. The two independent molecules in the asymmetric unit were mirror images of each other. The refinement did not proceed smoothly, several thermal parameters behaved abnormally and chemically equivalent distances and angles showed significant differences between the two molecules. This is typical in cases where the space group is really centrosymmetric rather than acentric. **$P2_1/n$**: When this space group is chosen, the significant space group violations must be ignored. The structure was solved again using MULTAN-78. The identical solution could be obtained by shifting the center of symmetry between the two molecules in $P2_1$ to the origin. The structure was refined using anisotropic thermal parameters on all non-hydrogen atoms and with fixed calculated hydrogen atoms. The number of parameters refined was 227, including the scale factor and an overall isotropic extinction parameter. The final difference map contains a peak of 2.9 e/Å^3. This peak is located 2.14 Å from C(18) (65501). The next highest peak of 1.1 e/Å^3 is located 1 Å from one phosphorus. The deepest hole is −1.7 e/Å^3. The space group violations for space group $P2_1/n$ are significant. They could possibly be explained by the presence of a small fragment of different alignment; however, no abnormalities were noted during the initial search. The possibility that the crystal might have undergone a phase transition was investigated by heating the crystal from −171 to −50 °C; the space group violations remained. Another crystal from the same sample was mounted as above and transferred to the goniostat at −50 °C, a search was carried out, and the identical unit cell was obtained. Results of the structure determination are shown in Table 2 and Figure 1.

(b) $Ru(\eta^2\text{-}O_2)(CO)_2(P^tBu_2Me)_2$. A larger crystal was cleaved to obtain a suitably sized fragment, which was affixed to the end of a glass fiber using silicone grease. The mounted sample was transferred to the goniostat where it was cooled to −172 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space located a set of reflections with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/c$ (Table 1). Subsequent solution and refinement of the structure confirmed this choice. Data were collected (6° < 2θ < 45°) using a standard moving-crystal, moving-detector technique with fixed background counts at each extreme of the scan. Raw intensities were corrected for Lorentz and polarization terms and for absorption. The structure was solved by Patterson and Fourier techniques. A difference Fourier phased on the non-hydrogen atoms located many of the hydrogen atoms, and these were placed in idealized fixed positions in the subsequent least-squares refinements. Two independent molecules are present in the asymmetric unit. During the refinement, three carbon atoms (C(26), C(42), and C(51)) refused to properly converge while being refined anisotropically. Since the crystal used was cleaved from a larger mass, the behavior of these atoms may be due to a poor absorption correction. The three atoms were assigned isotropic thermal parameters for the final refinement. A careful examination was made to ensure that the cell chosen was indeed proper. The initial examination revealed several surprising facts. (1) The two molecules are not only nearly identical but related by an apparent translational vector of 0.259, 0.746, −0.253 ($^1/_4$, $^3/_4$ $-^1/_4$). (2) The midpoint of the two Ru atoms lies at 0.370, 0.127, 0.125 ($^3/_8$, $^1/_8$, $^1/_8$). (3) Examination of the intensity data reveals areas in reciprocal space with "pseudoextinctions"; for example h00 exists for only $h = 4n$. In spite of the above, there does not appear to be an error in space group assignment. This conclusion is based on the following: (a) $P2_1/c$ is difficult to missassign, (b) examination of the Ru···Ru vectors fails to show any missed symmetry, (c) two different cell reduction programs fail to find a better cell. Results are shown in Table 3 and Figure 2.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $Ru(CO)_2(P^tBu_2Me)_2$

Ru(1)−P(2)	2.3596(22)
Ru(1)−P(12)	2.3542(22)
Ru(1)−C(22)	1.886(10)
Ru(1)−C(24)	1.854(9)
O(23)−C(22)	1.153(11)
O(25)−C(24)	1.177(10)
P(2)−Ru(1)−P(12)	165.56(8)
P(2)−Ru(1)−C(22)	96.49(26)
P(2)−Ru(1)−C(24)	89.91(25)
P(12)−Ru(1)−C(24)	94.25(25)
P(12)−Ru(1)−C(22)	90.70(26)
C(22)−Ru(1)−C(24)	133.3(4)
Ru(1)−C(22)−O(23)	168.2(8)
Ru(1)−C(24)−O(25)	168.7(7)

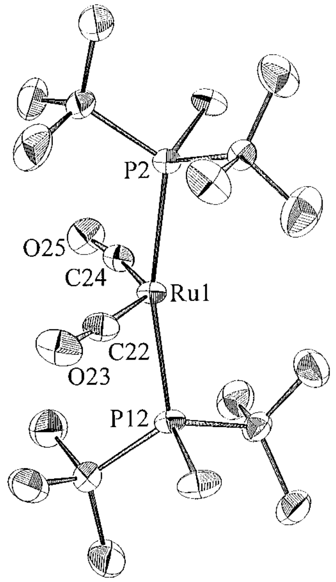

Figure 1. ORTEP view, with selected atom numbering, of $Ru(CO)_2(P^tBu_2Me)_2$.

Computational Method. Calculations were performed using the *ab initio* core-potential (ECP) method and employed the Gaussian 92 package of programs.[11] For Ru and Rh, the ECPs of Hay and Wadt,[12]

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Table 3. Selected Bond Distances (Å) and Angles (deg) for $Ru(CO)_2(O_2)(P^tBu_2Me)_2$

	molecule A	molecule B
Ru(1)−P(4)	2.435(3)	2.433(3)
Ru(1)−P(14)	2.431(3)	2.434(3)
Ru(1)−O(2)	2.042(8)	2.029(7)
Ru(1)−O(3)	2.032(8)	2.028(7)
Ru(1)−C(24)	1.891(12)	1.876(12)
Ru(1)−C(26)	1.860(12)	1.887(13)
O(2)−O(3)	1.472(10)	1.467(10)
C(51)−O(52)	1.134(13)	1.148(13)
P(4)−Ru(1)−P(14)	163.93(11)	164.38(11)
P(4)−Ru(1)−O(2)	84.22(23)	84.62(23)
P(4)−Ru(1)−O(3)	82.22(23)	82.41(23)
P(4)−Ru(1)−C(24)	97.6(3)	93.2(3)
P(4)−Ru(1)−C(26)	93.4(4)	96.6(4)
P(14)−Ru(1)−O(2)	86.27(23)	85.19(22)
P(14)−Ru(1)−O(3)	82.01(23)	82.08(23)
P(14)−Ru(1)−C(24)	97.7(3)	92.5(3)
P(14)−Ru(1)−C(26)	91.8(4)	98.0(4)
O(2)−Ru(1)−O(3)	42.3(3)	42.4(3)
O(2)−Ru(1)−C(24)	108.4(4)	160.7(4)
O(2)−Ru(1)−C(26)	162.5(4)	109.8(4)
O(3)−Ru(1)−C(24)	150.7(4)	118.3(4)
O(3)−Ru(1)−C(26)	120.2(4)	152.2(4)
C(24)−Ru(1)−C(26)	89.1(5)	89.5(5)
Ru(1)−O(2)−O(3)	68.5(4)	68.8(4)
Ru(1)−O(3)−O(2)	69.2(4)	68.8(4)
Ru(1)−C(24)−O(25)	175.9(11)	178.4(10)
Ru(1)−C(26)−O(27)	177.6(11)	176.4(10)

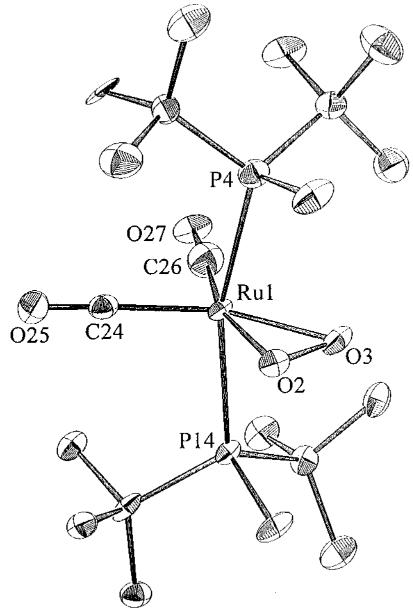
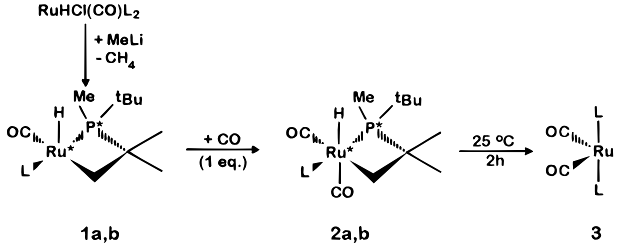


Figure 2. ORTEP view, with selected atom numbering, of "molecule A" of $Ru(O_2)(CO)_2(P^tBu_2Me)_2$.

in which the 4s and 4p subvalence shell electrons are included in the valence shell, were chosen along with a [3111/3111/311] Gaussian basis set. For P, the ECP and [31/31] basis set of Barthelat *et al.* were employed.[13] For C and O, we chose the (9s/5p) primitives of Huzinaga with the contraction scheme of Dunning and Hay.[14] H atoms were described by (4s) primitives contracted into a [1s] basis set.[15] PH_3 groups were given a fixed geometry (P−H = 1.42 Å, M−P−H = 120.0°). All geometries were fully optimized at the MP2 level under the C_{2v} symmetry constraint. For the structures that did not correspond to minima (i.e., the square-planar structure of $Ru(CO)_2(PH_3)_2$ and the bent structure of $[Rh(CO)_2(PH_3)_2]^+$), geometries were optimized with fixed angles at the metal. The geometry of $Ru(CO)_2(PH_3)_2$ was reoptimized with C_1 symmetry to confirm the geometry found in C_{2v} symmetry. No significant difference was found. Previous work on other unsaturated Ru complexes has shown that experimental geometries can be reproduced at this level of calculation without the need to incorporate polarization functions on metal-bound atoms.[7]

Scheme 1



Results

Preparation and Characterization of $Ru(CO)_2(P^tBu_2Me)_2$. Addition of methyllithium to a toluene solution of RuHCl(CO)-$(P^tBu_2Me)_2$ at −78 °C and warming the solution to −40 °C give clean conversion to a diastereomeric mixture (Scheme 1, asterisks indicate chiral centers) of **1a** and **1b** with approximately 3:1 molar ratio as reported.[7] Complexes **1a** and **1b** absorb 1 equiv of CO at −40 °C to give **2a** and **2b** with the solution color change from red-orange to pale yellow. This transformation was confirmed by NMR measurements.[16] $^{31}P\{^1H\}$ NMR of **2a** and **2b** shows the two new sets of AM patterns at −40 °C with a large $^2J_{PP}$ value (220 Hz), which shows a *trans* relationship of the two phosphine ligands. The molar ratio between the two diastereomers **2a** and **2b** is identical to that of **1a** and **1b**, suggesting that CO acts purely as a trapping reagent. In ^1H NMR, the hydride resonances of **2a** and **2b** are observed in the lower field region (δ −5.9 and −6.2, respectively) at −20 °C in toluene-d_8, compared to those of **1a** and **1b** (δ −25.0 and −26.7 at −40 °C in toluene-d_8). This observation is consistent with the coordination of the second carbonyl at the position *trans* to the hydride. The mixture **2a** and **2b** is only stable at low temperature. Remarkably ($Ru^{II} \rightarrow Ru^0$), it undergoes demetalation (i.e., C−H reductive elimination) of the metalated phosphine to form the four-coordinate complex $Ru(CO)_2(P^tBu_2Me)_2$, **3**, at room temperature in 2 h. During this period, the solution color changes from pale yellow (saturated) to very deep red (unsaturated). The thermodynamics of this reaction are quite surprising, i.e., an 18-electron, coordinatively saturated species (**2a** and **2b**) isomerizes into a 16-electron coordinatively unsaturated complex (**3**).

Complex **3** shows one $^{31}P\{^1H\}$ NMR signal at 23 °C. This signal is very sharp, and even at −90 °C does not show obvious broadening. In the ^1H NMR, one virtual triplet for ^{t}Bu protons and one virtual triplet for its P−Me hydrogens are observed. All these are consistent with the phosphine ligands being equivalent and taking transoid geometry. Therefore, from these NMR studies, there is no evidence for an agostic interaction, which would make the two phosphines in **3** inequivalent. The ^{31}P NMR chemical shift of **3** in benzene, toluene, pentane, or THF shows no obvious solvent dependency; i.e., there is no (or no strong) interaction of these solvents with the vacant site

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[15] Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

[16] **2a:** $^{31}P\{^1H\}$ NMR (toluene-d_8, −20 °C): δ 17.1 (d, J_{PP} = 220 Hz, 1P, metalated *P*), 63.4 (d, J_{PP} = 220 Hz, 1P, P^tBu_2Me); ^1H NMR (toluene-d_8, −20 °C): δ −5.9 (ddt, J_{PH} = 25.5 and 17.1 Hz, J_{HH} = 2.9 Hz, Ru-*H*). **2b:** $^{31}P\{^{1H}\}$ NMR (toluene-d_8, −20 °C): δ 11.8 (d, J_{PP} = 220 Hz, 1P, metalated *P*), 63.1 (d, J_{PP} = 220 Hz, 1P, P^tBu_2Me); ^1H NMR (toluene-d_8, −20 °C): δ -6.2 (t, J_{PH} = 21.8 Hz, Ru-*H*).

of **3**. The complex is highly soluble; it dissolves into even saturated hydrocarbons such as pentane and Nujol. The IR spectrum of **3** in Nujol gives the two CO stretching vibrations with unequal intensities at 1831 and 1902 cm^{-1}. These values are low and consistent with a low oxidation state of ruthenium. The observation of two infrared CO absorptions indicates that two carbonyl ligands are *not trans*. The intensity of the two ν(CO) bands, together with the equation $\tan^2 \theta = I_{as}/I_s$ where I is the intensity of the appropriate ν(CO) band and 2θ is the angle between the two CO vectors, gives $2\theta = 130°$. This generally supports the retention of the nonplanar solid-state structure ($\angle$C−Ru−C = 133°, see below) in solution. However, in the solid state, the Ru−C−O moieties are bent to ca. 168° in a cisoid mode, so the angle of two CO vectors in the crystals is ca. 110°, indicating some fluxionality of the molecules in solution.

The four-coordinate complex **3** also can be synthesized from *cis,cis,trans*-$RuCl_2(CO)_2(P^tBu_2Me)_2$ by reduction with stoichiometric activated magnesium in THF according to eq 1.[17] The

$$\textit{cis,cis,trans}\text{-}RuCl_2(CO)_2L_2 + Mg \rightarrow Ru(CO)_2L_2 + MgCl_2$$

$$L = P^tBu_2Me \text{ or } P^iPr_3 \qquad (1)$$

reaction proceeds almost quantitatively, and the isolated yield of **3** goes up to 80%. Triisopropylphosphine has electronic and steric properties similar to those of P^tBu_2Me. However, reaction of $RuHCl(CO)(P^iPr_3)_2$ with MeLi does not give analogous products to **1a** and **1b**, which are obtained from $RuHCl(CO)(P^tBu_2Me)_2$ and MeLi. The ^{31}P NMR spectrum of the reaction mixture of $RuHCl(CO)(P^iPr_3)_2$ and MeLi (1:1 molar ratio) shows formation of several uncharacterized species in addition to remaining $RuHCl(CO)(P^iPr_3)_2$. Therefore, the original synthetic route of $Ru(CO)_2(P^tBu_2Me)_2$, successive metalation and demetalation, is not applicable to the synthesis of a P^iPr_3 analogue. However, the reductive route to Ru(0) using magnesium yields $Ru(CO)_2(P^iPr_3)_2$ from *cis,cis,trans*-$RuCl_2(CO)_2(P^iPr_3)_2$ in 83% isolated yield. In $Ru(CO)_2(P^iPr_3)_2$, the phosphorus nuclei are equivalent, as are the ^{i}Pr groups. ^{1}H NMR shows one doublet of virtual triplets for PCH*Me*$_2$ and multiplet for PC*H*Me$_2$. All this is consistent with *trans* phosphines. Two ν_{CO} bands are seen at 1898 and 1829 cm^{-1} in the IR spectrum, and the OC−Ru−CO angle is calculated as 129° from their intensity.

Both four-coordinate complexes, $Ru(CO)_2(P^tBu_2Me)_2$ and $Ru(CO)_2(P^iPr_3)_2$, are very air-sensitive, however, they are fairly thermally stable; a benzene solution of either complex shows no decomposition at room temperature for up to 10 days. Refluxing the benzene solution of **3** causes slow decomposition (ca. 20% in 6 h) into $Ru(CO)_2(P^tBu_2Me)_3$, free phosphine, and some other uncharacterized compounds. The crystals, which are kept in the glovebox under argon at room temperature, do not show any detectable change during 8 months.[18]

The structure of $Ru(CO)_2L_2$ (Table 2) might be described as a trigonal bipyramid (Figure 1) lacking one equatorial ligand. The molecule is four-coordinate and nonplanar, but like no previously observed four-coordinate X-ray structure. The C−Ru−C angle (133.3(4)°) is larger than TBP, and the phosphines bend ($\angle$P−Ru−P = 165.56(8)°) almost negligibly toward the opposite "side" from the carbonyl ligands. There are no Ru/C or H distances short enough to be interpreted as an agostic interaction with ^{t}Bu or methyl substituents on P.

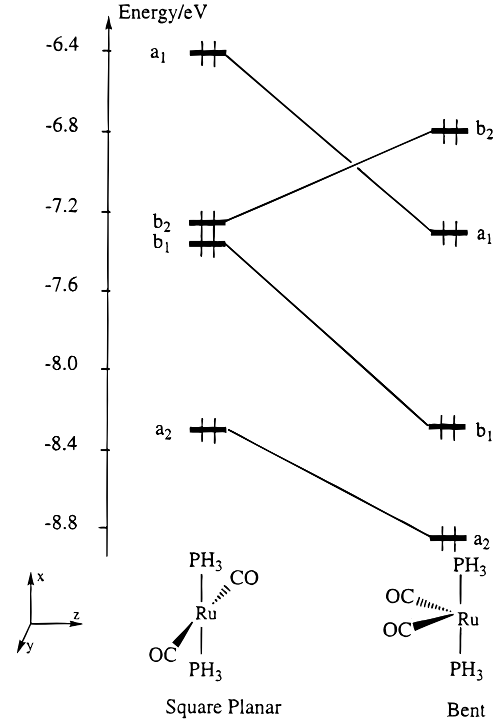
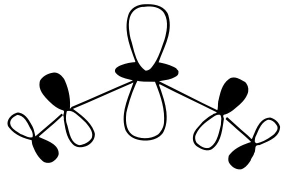


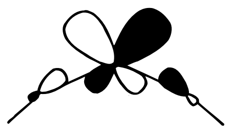
Figure 3. Walsh diagram relating the frontier orbitals of planar and bent $Ru(CO)_2(PH_3)_2$, based on *ab initio* calculations.

Electronic Origin of the Structure. Density functional studies[19] on $Ru(CO)_4$ support this as a singlet ground state with C_{2v} symmetry (i.e., nonplanar), analogous to $Ru(CO)_2L_2$. Earlier EHT studies[20] traced this nonplanar structure to a d^8 electron count, influenced by π-acceptor ligands. Our reported[1] core potential *ab initio* calculations (MP2) on $Ru(CO)_2(PH_3)_2$ reproduce well the structural features observed for $Ru(CO)_2(P^tBu_2Me)_2$, showing that the observed structure is not caused by the very bulky ligand P^tBu_2Me. In addition, the calculations at the same level showed that isoelectronic $Rh(CO)_2(PH_3)_2^+$ prefers a planar structure, in agreement with experiment.

A Walsh diagram (Figure 3) reveals the origin of the structural preferences. The antibonding a$_1$ orbital is less antibonding upon bending because of diminished overlap between the 5σ CO orbital (HOMO) and z^2 and because back-donation into π^*_{CO} becomes possible (**A**) as already suggested.[20] This increased stabilizing interaction with z^2 is one of the factors which leads to shorter calculated M−(CO) distances in the bent than in the planar structure. The b$_1$ (xz) orbital is also stabilized by back-donation which only occurs in the bent structure. The b$_2$ orbital (angles drawn to scale) is strongly destabilized in the bent structure because of increased overlap with the 5σ of CO (**B**) and diminished overlap with π^*_{CO}. However, cisoid bending of the M−C−O angle as in **B** diminishes the destabilization by minimizing the overlap between b$_2$ and the 5σ of CO. The



A



B

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[17] Sodium amalgam also can be employed as a reductant of this reaction. However, large excess of Na/Hg is required and the yield of **3** is relatively low (ca. 40%).

[18] The complexes are unreactive toward dinitrogen, so N_2 gas can be employed as an inert media instead of Ar gas.

[19] Li, O.; Schreckenbach, G.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 486.

[20] Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

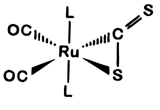
lowering of a_2 upon bending is unexpected since bending the C−Ru−C angle should diminish the overlap between a_2 and π^*_{CO}, thus raising the energy of a_2. The calculated (opposite) behavior may be due to two effects: (1) a general field effect according to which the destabilization of z^2 by the four ligands in the planar structure destabilizes all other (even the nonbonding) d orbitals; (2) the shorter M−CO distance in the bent structure compensating for the smaller overlap due to imperfect alignment of the a_2 and π^*_{CO} orbitals.

In contrast to the above, the d orbital energies of Rh(I) lie farther from the π^*_{CO}. The calculated stabilization of the a_1 and b_1 orbitals is therefore less on bending $Rh^I(CO)_2(PH_3)_2{}^+$, and the destabilization of b_2 by the now closer 5σ of CO is greater. In short, it is the greater reducing power of Ru(0) than Rh(I) which leads to different structures for $Ru(CO)_2L_2$ and (planar) $Rh(CO)_2L_2{}^+$. Thus, the presence of a π-acceptor ligand is a necessary (but not sufficient) condition for a nonplanar d^8 ML_4 complex.[21]

Reaction of 3 with Donor Ligands. Compound **3** absorbs 1 equiv of CO quickly and irreversibly to form adduct **4**. The reaction proceeds very cleanly and yields $Ru(CO)_3(P^tBu_2Me)_2$, quantitatively based on $^{31}P\{^1H\}$ NMR. All the spectroscopic data (^1H and $^{31}P\{^1H\}$ NMR and IR) are consistent with those reported previously.[7] Similarly, **3** reacts with methyl isocyanide quantitatively in the time of mixing to give $Ru(CNMe)(CO)_2(P^tBu_2Me)_2$, **5**. It is a bright yellow, crystalline solid, and ^1H and $^{31}P\{^1H\}$ NMR and IR data suggest a similar structure to **4**, i.e., two bulky phosphine ligands are taking the apical sites and the three strong π-acid ligands (two CO and a MeNC) are on the equatorial plane. Two ν_{CO} frequencies (1894 and 1844 cm^{-1}) are low enough to be consistent with Ru(0) oxidation state.

Complex **3** adds stoichiometric O_2 and CS_2 in the time of mixing at 25 °C to give $Ru(\eta^2\text{-}O_2)(CO)_2(P^tBu_2Me)_2$, **6**, and $Ru(\eta^2\text{-}CS_2)(CO)_2(P^tBu_2Me)_2$, **7**, respectively. The crystals of **6**, suitable for X-ray analysis, were obtained by recrystallization from cold pentane. Figure 2 shows the crystal structure of **6** as a distorted octahedron with $\angle O2{-}Ru1{-}O3 = 42.3(3)°$, $\angle P4{-}Ru1{-}P14 = 163.93(11)°$, and $\angle C24{-}Ru1{-}C26 = 89.1(5)°$. The O2−O3 distance (1.472(10) Å) is somewhat longer than in other crystallographically characterized η^2-O_2 ruthenium complexes, $[RuH(O_2)(dippe)_2]BPh_4$[22] (d(O−O) = 1.360(1) Å) and $[Ru(O_2)(\eta^5\text{-}C_5Me_5)(dppe)]PF_6$[23] ($d$(O−O) = 1.398(5) Å). Note that the oxidation states of the ruthenium centers in these two complexes are higher than the oxidation state in **6**, i.e., weaker back-donation to the O_2 ligands should be expected in these molecules than that in **6**. The reported O−O bond length in H_2O_2 is 1.49 Å;[24] this value is almost identical with that in **6**. Thus the dioxygen ligand in **6** is best considered as a peroxide ligand. Therefore, **6** must be formally considered as a Ru(II) complex with a strong back-donation to the coordinated O_2. In the IR spectrum, ν_{CO} are detected at relatively higher frequency (1991 and 1921 cm^{-1}, or about 90 cm^{-1} above those of **3**), also supporting a +2 oxidation state of the ruthenium center in **6**, although these frequencies are considerably below those of a typical Ru^{2+} species such as *cis,cis,trans*-$RuCl_2(CO)_2(P^tBu_2Me)_2$ (2029 and 1962 cm^{-1}). The angle of OC−Ru−CO is calculated as 102° from the intensities of the ν_{CO} bands in the IR spectrum in pentane solution. This value is somewhat larger than that of the X-ray data (89.1°). ^1H NMR spectrum of **6** shows only one virtual triplet for ^tBu groups, which is consistent with C_{2v} symmetry of the molecule as shown in Figure 2. The coordination of O_2 to **6** is irreversible; evacuation to 0.01 mmHg at 50 °C (higher temperature causes the decomposition of the complex) does not show any dissociation of the O_2 ligand.

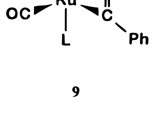
The spectroscopic features of $Ru(\eta^2\text{-}CS_2)(CO)_2(P^tBu_2Me)_2$, **7**, are consistent with structure **7**. The phosphorus nuclei are equivalent, as indicated by a singlet in the $^{31}P\{^1H\}$ NMR spectrum at −80 °C. This equivalence requires that the dangling S in structure **7** must lie in the $Ru(CO)_2$ plane. The ^tBu groups of the phosphines appear as two virtually coupled triplets in the ^1H NMR spectrum, consistent with no mirror plane of symmetry perpendicular to the $Ru(CO)_2(CS_2)$ plane. This rules out η^1-C and η^2-S,S structures for the CS_2 ligand. An η^2-CS coordination is thus the most likely.[25] A similar structure was reported for an analogous complex $Ru(\eta^2\text{-}CS_2)(CO)_2(PPh_3)_2$.[26] The IR spectrum of **7** shows a strong band at 1125 cm^{-1}, as expected for this type of compound,[27] in addition to two CO stretches with equal intensities at 1993 and 1933 cm^{-1}. Remarkably, these are as high as in the O_2 complex, **6**. Complex **7** is thermally unstable; its solution in C_6D_6 darkens from pale yellow to a blackish color in 2 h, even at room temperature. The $^{31}P\{^1H\}$ NMR spectrum reveals decomposition of **7** into free phosphine and some other uncharacterized compounds. However, the isolated complex (solid) shows no obvious decomposition during 10 days at 25 °C under Ar.



7

Under ethylene atmosphere (1 atm), **3** ligates one molecule of C_2H_4 per ruthenium reversibly to form $Ru(\eta^2\text{-}C_2H_4)(CO)_2(P^tBu_2Me)_2$, **8**. Below −60 °C, it shows a broad signal in the $^{31}P\{^1H\}$ NMR spectrum at ca. 58 ppm. Above −40 °C, coordinated ethylene dissociates and the signal of **3** emerges. The ratio of **3** and **8** is approximately 1:20 at −40 °C, 2:3 at −20 °C, and 7:1 at 0 °C. At and above 20 °C, the signals of **3** and **8** coalesce into one broad signal, indicating rapid equilibrium between the two complexes. The coordinated ethylene is observed at 1.58 ppm as a triplet at −50 °C in ^1H NMR; this indicates that, even at this temperature, there is a fast rotation of the ethylene ligand.

Reaction with diphenylacetylene is immediate, giving $Ru(\eta^2\text{-}PhC{\equiv}CPh)(CO)_2(P^tBu_2Me)_2$, **9**, which dissociates slightly (<5%) in an equilibrium process, to release free phosphine above −40 °C in toluene; the $^{31}P\{^1H\}$ NMR signal of **9** then becomes broader. At higher temperatures (>0 °C), the resonances of **9** and free phosphine coalesce into one very broad signal ($w_{1/2} \approx 400$ Hz at 23 °C), and its chemical shift at this temperature (δ 58.9) is slightly higher than that of **9** at −40 °C



9

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[21] Hoffmann, R.; Minot, C.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 2001.

[22] Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **1993**, *115*, 9794.

[23] Kirchner, K.; Mauthner, K.; Mereiter, K.; Schmid, R. *J. Chem. Soc., Chem. Commun.* **1993**, 892.

[24] Savariault, J.-M.; Lehmann, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 1298.

[25] Mealli, C.; Hoffmann, R.; Stockis, A. *Inorg. Chem.* **1984**, *23*, 56.

[26] Grundy, K. R.; Harris, R. O.; Roper, W. R. *J. Organomet. Chem.* **1975**, *90*, C34.

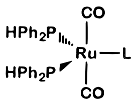
[27] Butler, I. S.; Fenster, A. E. *J. Organomet. Chem.* **1974**, *66*, 161.

(δ 60.9). Although Ru(η^2-PhC≡CPh)(CO)$_2$(P^{t}Bu$_2$Me), **10**, is not detectable by either ^{31}P{^{1}H} NMR or IR, probably due to its low concentration, we propose the equilibrium as eq 2

$$\underset{\mathbf{9}}{\mathrm{Ru}(\eta^2\text{-PhCCPh})(\mathrm{CO})_2\mathrm{L}_2} \rightleftharpoons \underset{\mathbf{10}}{\mathrm{Ru}(\eta^2\text{-PhCCPh})(\mathrm{CO})_2)\mathrm{L}} + \mathrm{L} \qquad (2)$$

between **9**, **10**, and free P^{t}Bu$_2$Me from these observations. An analogous complex, Ru(η^2-PhC≡CPh)(CO)$_2$(PEt$_3$)$_2$,[28] is isolable and does not show the phosphine dissociation shown for **9**, even at 80 °C in benzene. Since P^{t}Bu$_2$Me is more basic than PEt$_3$, the driving force of this phosphine dissociation from **9** seems to be a steric repulsion between the bulky phosphines and the coordinated PhC≡CPh. This equilibrium is further supported by the capacity of the alkyne to change from two-electron donor character in **9** to four-electron donation in **10**. Two ν_{CO} bands are detected for **9** at 1960 and 1896 cm^{-1}, which are ca. 60 cm^{-1} above those of **3** but below those of **6**, indicating weaker π-acceptor character of diphenylacetylene in **9** than of the O$_2$ ligand in **6**.

At 23 °C in C$_6$D$_6$, **3** reacts with PPh$_2$H (2 equiv) not by P−H oxidative addition, but by displacement of one of P^{t}Bu$_2$Me to give Ru(CO)$_2$(PPh$_2$H)$_2$(P^{t}Bu$_2$Me), **11**, and free phosphine. The reaction with 1 equiv of PPh$_2$H shows the same products, in addition to the remaining **3**. Steric hindrance among three phosphines in the probable intermediate, Ru(CO)$_2$(PPh$_2$H)(P^{t}Bu$_2$Me)$_2$, causes one P^{t}Bu$_2$Me to dissociate to form Ru(CO)$_2$(PPh$_2$H)(P^{t}Bu$_2$Me). This species should be more reactive than **3**, adding PPh$_2$H to give **11**. This reaction is thus controlled by steric effects. The ^{31}P{^{1}H} NMR spectrum of **11** shows an AM$_2$ pattern with the $^2J_{PP}$ coupling constant of 72.3 Hz. This value is too small for a *trans* coupling, but is also inconsistent with a coupling at a 90° P−Ru−P angle (~20 Hz expected). These observations support the structure **11**. Indeed, in the IR spectrum, one strong ν_{CO} is detected at relatively low frequency (1858 cm^{-1}). A similar complex, Ru(CO)$_2$(PPh$_3$)$_3$, with *trans* carbonyls was reported previously and showed a ν_{CO} of 1905 cm^{-1}.[9a]

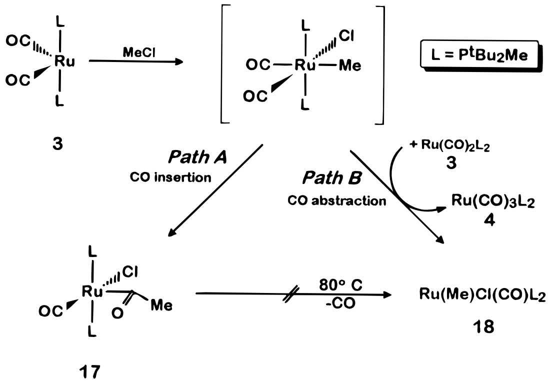


11

No reaction is found with CO$_2$ (1 atm), N$_2$ (1 atm), acetonitrile (10 equiv), or pyridine (10 equiv). There is no reason to attribute these first two negative results to steric factors. Acetonitrile can be estimated as isosteric with isocyanide, which reacts with **3** immediately; however, no reaction was observed by ^{31}P{^{1}H} NMR even at −90 °C in toluene for each case. In acetonitrile as a solvent, **3** does not show any obvious line broadening in the ^{31}P{^{1}H} NMR spectrum at room temperature. A common feature of these four reagents is weaker π-acidity than that of all the other reagents described above, which exhibit great reactivity toward **3**. It is concluded from these observations that Ru(CO)$_2$(P^{t}Bu$_2$Me)$_2$ is not a strong σ-Lewis acid (as might have been anticipated by its 16-electron count), but relies heavily on its π-basicity for ligand binding. This is consistent with the idea that the high energy of the HOMO also results in a LUMO of high energy.

Reaction of 3 with Oxidants. The reaction of **3** with H$_2$ proceeds quite rapidly with a prompt color change from deep red to pale yellow and is quantitative by ^{31}P{^{1}H} NMR. The dihydride complex **12** is isolated in pure form as pale yellow crystals in 88% yield. It shows a single high field resonance at δ −7.96 as a triplet in the ^{1}H NMR. The ^{t}Bu and the methyl groups of the phosphines show virtual triplets in their ^{1}H NMR signals. Two ν_{CO} bands are seen at 1999 and 1966 cm^{-1}, consistent with **12** as *cis,cis,trans*-RuH$_2$(CO)$_2$(P^{t}Bu$_2$Me)$_2$.

Scheme 2



Complex **3** adds 1 equiv of HCl or Cl$_2$ immediately to give *cis,trans*-RuHCl(CO)$_2$(P^{t}Bu$_2$Me)$_2$, **13**, or RuCl$_2$(CO)$_2$(P^{t}Bu$_2$Me)$_2$, respectively. All the spectroscopic data (^{1}H and ^{31}P{^{1}H} NMR and IR) agree with those reported previously.[3,4] In the ^{31}P{^{1}H} NMR spectrum, RuCl$_2$(CO)$_2$(P^{t}Bu$_2$Me)$_2$ is observed as a mixture of two isomers, **14** (*cis,trans*) and **15** (*trans,trans*). Complex **14** is the thermodynamically favorable species; complex **15** isomerizes completely into **14** in C$_6$D$_6$ at 70 °C in 2 h. Although the *cis* isomer **14** is both the kinetically and thermodynamically expected product from simple oxidative addition of Cl$_2$ to **3**, our observation of forming *some trans* isomer **15** suggests that the reaction mechanism (or at least *one* mechanism) is not concerted. However, the reaction is too fast to detect intermediates.

The reaction of **3** with equimolar phenylacetylene occurs in the time of mixing at room temperature to give the oxidative addition product, RuH(C≡CPh)(CO)$_2$(P^{t}Bu$_2$Me)$_2$, **16**. Two ^{t}Bu signals are detected in its ^{1}H NMR spectrum. This (and two ν_{CO} bands) is consistent with C_s symmetry of **16**, i.e., two bulky phosphines are *trans* and two carbonyls are *cis*. This stereochemistry is consistent with a concerted mechanism. The rearrangement of **16** to the isomeric vinylidene complex Ru(=C=CHPh)(CO)$_2$(P^{t}Bu$_2$Me)$_2$ cannot be achieved thermally, even at 110 °C after 24 h in toluene.

The reaction with MeCl is relatively slow; it is necessary to heat the reaction mixture. Complex **3** is consumed completely at 80 °C in 2 h to form three products: the main product, the acetyl complex **17**, and the two minor products, **4** and **18**. The molar ratio between the three products is approximately **17**:**4**:**18** = 5:1:1 based on the ^{31}P NMR spectrum. The mechanism of this transformation is explained in Scheme 2. The first step is an oxidative addition of MeCl to the four-coordinate complex **3** to give an unobservable intermediate, Ru(Me)Cl(CO)$_2$(P^{t}Bu$_2$Me)$_2$. This intermediate is converted into the final products in two different manners: one is an insertion of the CO ligand to the Ru−Me bond to give **17** (path A),[29] while the other is CO abstraction from the intermediate by unreacted **3** to give equimolar (as observed) **4** and **18** (path B). A similar carbonyl transfer reaction between **3** and **13** to form **4** and RuHCl(CO)(P^{t}Bu$_2$Me)$_2$ was observed independently,[8] supporting the above mentioned mechanism. The acetyl complex, **17**, does not show thermal transformation into **18** by loss of CO at 80 °C in C$_6$D$_6$.

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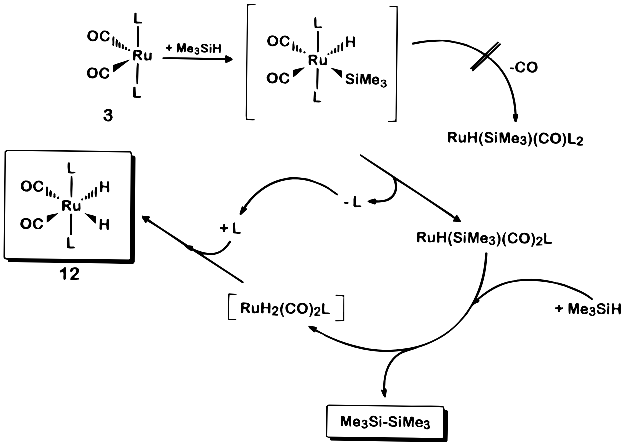
(28) Ogasawara, M.; Kawamura, K.; Ito, K.; Toyota, K.; Streib, W. E.; Komiya, S.; Caulton, K. G. Manuscript in preparation.

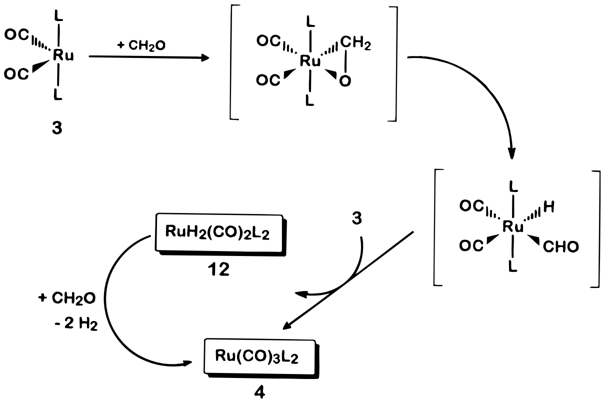
(29) A similar CO insertion was reported for an analogous complex: Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1977**, *142*, C1.

Scheme 3

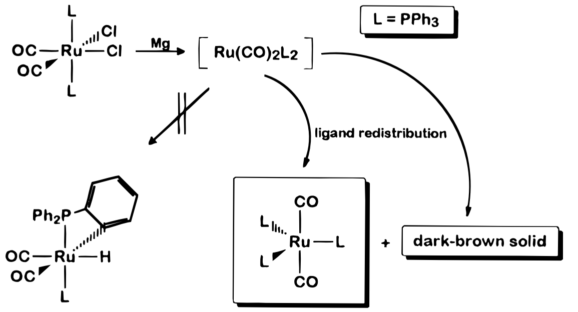


Complex **3** reacts with excess Me$_3$SiH (10 equiv) in C$_6$D$_6$ at room temperature within 2 days to give the dihydride complex **12** and Me$_3$Si−SiMe$_3$. The reaction is slow, but quite clean; at the end of the reaction, **12** is the only phosphorus-containing species detected by ^{31}P{^{1}H} NMR spectroscopy. However, during the reaction, the ^{31}P{^{1}H} NMR spectrum of the reaction mixture shows four signals: remaining **3**, **12**, free P^{t}Bu$_2$Me, and a species with a singlet at δ 43.7. Note that the final products do not contain any trace amount of free phosphine or of the 43.7 ppm species. The ^{31}P{^{1}H} NMR intensities of P^{t}Bu$_2$Me and the signal at δ 43.7 are approximately the same. From these observations, we propose the mechanism of the reaction as Scheme 3. Me$_3$SiH is added to **3** to give an undetectable intermediate, RuH(SiMe$_3$)(CO)$_2$(P^{t}Bu$_2$Me)$_2$. The three bulky ligands (two phosphines and SiMe$_3$) of this species presumably are thermodynamically unfavorable due to mutual steric repulsion. Thus, one phosphine dissociates to form equimolar free phosphine and a coordinatively unsaturated species, RuH(SiMe$_3$)(CO)$_2$(P^{t}Bu$_2$Me). We propose that this is the species at δ 43.7 in the ^{31}P{^{1}H} NMR. Indeed, the ^{1}H NMR spectrum of this mixture shows a hydride signal at δ −26.2 in addition to the hydride signal of **12**. Although the signal is observed as a broad singlet (coupling with a phosphorus is not resolved), presumably due to the low signal-to-noise ratio of the spectrum, the very high-field chemical shift of the hydride signal is consistent with the coordinative unsaturation of RuH(SiMe$_3$)(CO)$_2$(P^{t}Bu$_2$Me). Dissociation of a carbonyl from RuH(SiMe$_3$)(CO)$_2$(P^{t}Bu$_2$Me)$_2$ is ruled out by our observations; if this were the case, released CO should be trapped by remaining **3** to form **4**, which is not observed. RuH(SiMe$_3$)(CO)$_2$(P^{t}Bu$_2$Me) reacts with a second Me$_3$SiH to give Me$_3$Si−SiMe$_3$ and RuH$_2$(CO)$_2$(P^{t}Bu$_2$Me), and then the latter traps the free phosphine to give **12**.

Scheme 4



Scheme 5



Addition of 0.5 equiv of formaldehyde to the C$_6$D$_6$ solution of **3** gives a mixture of **4** and **12** in approximately 1:1 molar ratio (eq 3). However, the ratio between the two products depends on the amount of CH$_2$O employed. When CH$_2$O/**3**

$$2\mathrm{Ru(CO)_2L_2} + \mathrm{CH_2O} \rightarrow \underset{\mathbf{4}}{\mathrm{Ru(CO)_3L_2}} + \underset{\mathbf{12}}{\mathrm{Ru(H)_2(CO)_2L_2}} \quad (3)$$

(mol/mol) > 1, **4** forms as a main product in more than 90% yield with **12** as a minor product.[30] In the course of the reaction, the formation of an intermediate whose ^{31}P{^{1}H} NMR chemical shift is δ 59.3 and a small amount of free phosphine is observed. There are two candidates for the intermediate: Ru(η^2-CH$_2$O)(CO)$_2$L$_2$ and RuH(CHO)(CO)$_2$L$_2$ (see Scheme 4).[30] However, due to its low concentration and short lifetime, we could not obtain any further information about this intermediate. The detection, but ultimate disappearance, of free phosphine indicates that the final step of the reaction, H-migration from the formyl ligand, proceeds via the dissociation of the phosphine.

Complex **3** is also converted into **4** (ca. 35%), **12** (ca. 60%), and some other minor products in MeOH and C$_6$D$_6$ mixtures at room temperatures in several hours. The stoichiometry of the reaction approximates that of eq 4 and probably begins with oxidative addition of the O−H bond of methanol to **3**.[31]

$$3\mathrm{Ru(CO)_2L_2} + \mathrm{CH_3OH} \rightarrow 2\mathrm{Ru(H)_2(CO)_2L_2} + \mathrm{Ru(CO)_3L_2} \quad (4)$$

Magnesium Reduction of Other RuCl$_2$(CO)(CX)L$_2$ Complexes. The ruthenium dichloride complex, *cis,cis,trans*-RuCl$_2$(CO)$_2$(PPh$_3$)$_2$, was reduced with activated magnesium, trying to synthesize a four-coordinate complex analogous to **3** with smaller phosphines and also with a different electronic character. The reaction gives Ru(CO)$_2$(PPh$_3$)$_3$[9a] as the main ruthenium-containing product instead of the target molecule, Ru(CO)$_2$(PPh$_3$)$_2$. In addition to Ru(CO)$_2$(PPh$_3$)$_3$, an uncharacterized dark brown solid, which is insoluble in toluene, is formed. The yield of Ru(CO)$_2$(PPh$_3$)$_3$ is low (44% based on ruthenium), and it has one extra phosphine ligand in the molecule. Presumably, two Ru(CO)$_2$(PPh$_3$)$_2$ molecules are transformed into Ru(CO)$_2$(PPh$_3$)$_3$ and the dark brown solid by phosphine disproportionation. It should be noted that no *ortho*-metalated species is observed by ^{31}P NMR (see Scheme 5).

Magnesium reduction of RuCl$_2$(CO)(CNMe)(P^{t}Bu$_2$Me)$_2$ in THF gives a diastereomeric mixture of metalated species, **17a** and **17b**, as the main product in approximately 9:1 molar ratio.

In addition to **17a** and **17b**, a small singlet at δ 64.1 is observed at room temperature in the ^{31}P{^{1}H} NMR spectrum

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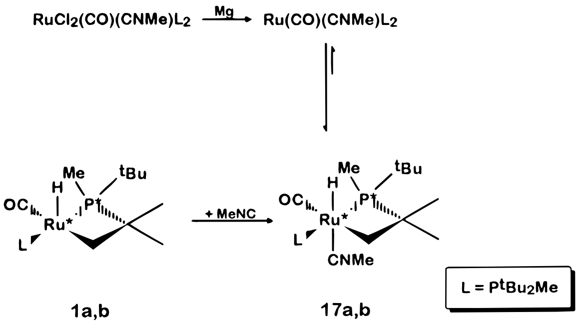
(30) The two hydrides in **12** are labile, and **12** reacts with CO to form **4** and H$_2$ gas.[7]

(31) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. E. *J. Am. Chem. Soc.* **1979**, *101*, 503.

Scheme 6



1a,b **17a,b**

of the toluene extract of the magnesium reduction products. ^{1}H and ^{31}P{^{1}H} NMR characteristics of **17a** and **17b** are identical with those prepared from **1a** and **1b** and methyl isocyanide (Scheme 6). Addition of MeNC to the cold toluene solution of **1a** and **1b** gives immediate solution color change from reddish orange to pale yellow. The molar ratio of **17a** and **17b** in this solution at −40 °C is ca. 3:1; it duplicates that of the **1a** and **1b** employed. When this solution was kept at room temperature, the solution turned light red in color and the ^{31}P{^{1}H} NMR spectrum showed an additional singlet at δ 64.1, which was also observed in the sample prepared from $RuCl_2(CO)(CNMe)(P^tBu_2Me)_2$ and Mg as described above. Note the molar ratio between **17a** and **17b** changed from 3:1 to 9:1, while the sample was kept at room temperature for 3 days. However, during this period, slow decomposition of the complexes into several uncharacterized species is also observed. The reddish colored solution, at room temperature, indicates formation of a coordinatively unsaturated species, presumably the species with the signal at δ 64.1 in the ^{31}P NMR spectrum. This change of the molar ratio of **17a** and **17b** between −40 °C and room temperature suggests an equilibrium between **17a**, **17b**, and the species whose ^{31}P NMR chemical shift is δ 64.1. Judging from our results on the $Ru(CO)_2(P^tBu_2Me)_2$ system, we propose that this species is an analogous four-coordinate complex, $Ru(CO)(CNMe)(P^tBu_2Me)_2$. Note that the ^{31}P NMR chemical shift of **3** (δ 65.4) is very close to that of $Ru(CO)(CNMe)(P^tBu_2Me)_2$ (δ 64.1). Methyl isocyanide is a weaker π-acceptor than carbonyl.[32] Substitution of one of the two carbonyls in **3** with methyl isocyanide apparently increases the electron density of the ruthenium center and thus enhances the reactivity of the complex toward oxidative addition. Consequently, $Ru(CO)(CNMe)(P^tBu_2Me)_2$ metalates one of its phosphine ligands to form **17a** and **17b**.

Discussion

Studies[33,34] of several reactions of $Ru(CO)_5$ reveal that they begin with dissociation of one CO to form transient $Ru(CO)_4$ with $\Delta H^\ddagger = 27.6$ kcal/mol (and $\Delta S^\ddagger = 15.2$ cal K^{-1} mol^{-1}). This establishes the approximate Ru−CO bond dissociation energy to form unsaturated Ru(0) unassisted by steric effects, but also permits determination that the rate of CO loss down this group is Ru > Os > Fe.[35] This helps to understand our ability to *isolate* $Ru(CO)_2L_2$. In contrast, $Ru(CO)_2(PMe_3)_2$ has been shown in matrix isolation studies to bind Ar, CH_4, and Xe.[36]

$Ru(CO)_2L_2$ has much of the reactivity which would be expected of an unsaturated molecule containing a zero-valent, 4d metal. It adds many sterically compact Lewis bases in time of mixing, and it undergoes two-electron oxidative addition with H−H, *sp*-C−H, Si−H, O−H, H−Cl, and Cl−Cl bonds. The results with Cl_2 suggest the reaction is not a concerted addition of both atoms, which should yield only the *cis* isomer of $RuCl_2(CO)_2L_2$. Alternatives include a radical reaction or the intermediate $RuCl(CO)_2L_2^+$ and Cl^-.

The first "slow" (greater than time of mixing) reaction we encounter is that with MeCl. Acetyl formation and subsequent CO dissociation of the presumed primary product, $Ru(Me)Cl(CO)_2L_2$, at a rate faster than that of the slow rate of the primary reaction permits CO to (rapidly) scavenge unreacted $Ru(CO)_2L_2$, leading to several products in a rational stoichiometry.

The reaction with $PHPh_2$, which was intended as a possible oxidative addition reaction, is instead probably a simple Lewis base addition reaction, but steric hindrance in any 1:1 adduct is so large as to cause dissociation of P^tBu_2Me, followed by binding of an additional molecule of $PHPh_2$. The reaction is thus addition and phosphine substitution: nonredox processes. Thus, the thermodynamics of this process are probably dictated by diminishing steric repulsion in the five-coordinate molecule.

The magnesium reduction method of synthesis of $Ru(CO)_2L_2$ has some generality for bulky L and is seemingly much more simple than the zinc reduction of $FeX_2(CO)_2(PEt_3)_2$,[37] which gives first the $FeX(CO)_2(PEt_3)_2$ radical, and then $FeX(CO)_2(PEt_3)_2^-$, by a sequence of apparent one-electron reductions. In contrast, Mg reduction of $MCl_2(PMe_3)_4$ (M = Ru, Os) leads to $MH(\eta^2\text{-}CH_2PMe_2)(PMe_3)_3$[38] by internal redox from the presumed intermediate $M(PMe_3)_4$. This shows the importance of the presence of two CO ligands here in maintaining a zero-valent product. Our original synthesis of $Ru(CO)_2L_2$, by formation of $RuH(CO)_2[\eta^2\text{-}P(CMe_2CH_2)^tBuMe](P^tBu_2Me)$, followed by its reductive elimination of C with H, displayed unanticipated thermodynamics. We have examined our spectra (particularly ^{31}P NMR) for evidence that either species $Ru(CO)_2L_2$ (L = P^tBu_2Me or P^iPr_3) is in detectable equilibrium with a species where a phosphine substituent has been metalated. None was found. However, the reducing power of the metal in the analogous compound where one CO has been replaced by the weaker π-acid MeNC is stronger than in the dicarbonyl complex; the zero-valent and divalent isomers are present at detectable concentrations. The results of magnesium reduction of $RuCl_2(CO)_2(PPh_3)_2$ also support the subtle electronic balance in the $Ru(CO)_2L_2$ system, which prevents the complexes from metalation to form coordinatively saturated species. The metal center in the presumed intermediate $Ru(CO)_2(PPh_3)_2$ is not strong enough as a reductant for *ortho*-metalation; thus, it transformed to the final product by an intermolecular ligand disproportionation. The electronic balance in "$Ru(CO)_2(PPh_3)_2$" is easily altered by a change of the metal or the ligand; the osmium analogue, "$Os(CO)_2(PPh_3)_2$", and "$Ru(CO)(PPh_3)_3$" show oxidative addition of aromatic C−H bonds of the ligands to form $OsH(CO)_2[PPh_2(C_6H_4)](PPh_3)$[39] and $RuH(CO)[PPh_2(C_6H_4)](PPh_3)_2$,[40] respectively.

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While, initially, our finding that $Ru(CO)_2L_2$ is not isostructural with isoelectronic $Rh(CO)_2L_2^+$ was surprising, we have been able to show that this represents a deformation to a (nonplanar) structure of lower energy as a result of the greater back-bonding ability of Ru(0) compared to that of Rh(I), in concert with the presence of two carbonyl ligands to take advantage of the metal electron density. It is ironic that the distortion away from that of $Rh(CO)_2L_2^+$ moves $Ru(CO)_2L_2$ to a structure which is very close to that of $Ru(CO)_3L_2$, with one equatorial CO removed. In this way, the $Ru(CO)_{2,3}L_2$ pair are closely analogous to the $Cr(CO)_{5,6}$ pair,[41] where removal of one CO does not result in major structural reorganization.

Conclusions

Platinum group metal complexes with d^8 16-electron count, which include $RhCl(CO)(PPh_3)_2$ and $IrCl(CO)(PPh_3)_2$ play an important role in organo-transition-metal chemistry. However, the isolable examples of such compounds of zero-valent ruthenium are very few. Our new system, $Ru(CO)_2L_2$, with its unusual geometry not found for isoelectronic $Rh(CO)_2L_2^+$, represents the first class of ruthenium complexes of this type without a π-donor ligand or an agostic interaction.

The ruthenium center in the complex is not a sufficiently strong reductant to cleave most C−H bonds. For example, intramolecular C−H oxidative addition is observed in only certain of the unsaturated, zero-valent species reported here. This feature, together with the steric protection by the bulky phosphine ligands, makes it possible to isolate $Ru(CO)_2L_2$ for L = P^iPr_3 and P^tBu_2Me.

Acknowledgment. This work was supported by the U.S. National Science Foundation and the French CNRS. M.O. held a JSPS fellowship. We thank Johnson Matthey for material support. We thank the EPSRC for a Western European NATO Research Fellowlship and the EU for a grant to S.A.M. within the Human Capital and Mobility Network No. CHRX CT 930152.

Supporting Information Available: Full crystallographic details and positional and thermal parameters for $Ru(CO)_2$-$(P^tBu_2Me)_2$ and $Ru(O_2)(CO)_2(P^tBu_2Me)_2$ (7 pages). See any current masthead page for ordering and Internet access instructions.

JA960967W

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