Modulation of Reactivity and Stereochemistry of Substrate Binding by the Group X in $RuHX(CO)(P^tBu_2Me)_2$

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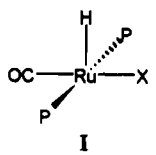
The group X has a significant influence on the reactivity of $RuHX(CO)P_2$(P = P^tBu_2Me) toward D_2, MeC_2Me, and PhC_2H. Thus, D_2 exchanges into the RuH site faster for X in the order I > Cl > F. Molecular hydrogen and $RuH(OR)(CO)P_2$ are in equilibrium with $Ru(H)_2(H_2)(CO)P_2$ and ROH (R = H or CH_2CF_3). Added Brønsted base (DBU) and H_2 will convert $RuHX(CO)P_2$ to $Ru(H)_2(H_2)(CO)P_2$ and [HDBU]X for X = I but not for X = Cl. For X = F, the conversion (with elimination of HF) does not require added base. Insertion of 2-butyne into the Ru–H bond occurs for X = I but not for X = Cl, $OSiPh_3$, OCH_2CF_3, or OPh. Phenylacetylene inserts into the Ru–H bond (*syn* stereochemistry of addition) when X = I and Cl. However, the iodide insertion product reacts further to eliminate styrene, with formation of a product where one phosphine *tert*-butyl group has oxidatively added its C–H bond to the metal. When X = OCH_2CF_3, OPh, F, or $OSiPh_3$, phenylacetylene reacts to eliminate HX and give $RuH(C_2Ph)(CO)P_2$. The CO stretching frequency of this product shows evidence of π donation from acetylide. The large downfield ^{13}C chemical shift of C_α in this compound may have the same cause. A labeling study shows that the proton eliminated in HX is that of the PhC_2H. Reaction of $RuHF(CO)P_2$ with $HSiMe_3$ yields $FSiMe_3$ and $RuH_n(SiMe_3)(CO)P_2$ (n = 1 and 3). Reaction of $RuH(C_2Ph)(CO)P_2$ with equimolar PhC_2H gives products of Ru–H addition with both regiochemistries. Reaction with excess PhC_2H gives $Ru(C_2Ph)_2(CO)P_2$, whose structure is proposed on the basis of variable-temperature ^{31}P and ^{13}C NMR studies. Reaction of these Ru–H bonds with D_2 or alkyne must occur *cis* to H (i.e., between H and X). Such attack stereochemistry is made easier when the opening of the HRuX angle is energetically facile. *Ab initio* SCF calculations show that the opening of the HRuX angle is easier for a heavier halide, which accounts for the higher reactivity observed for the iodide derivative. An internal competition experiment shows that PhC_2H reacts faster with $RuHX(CO)P_2$ when X = C_2Ph than when X = Cl. Underlying this complex reactivity is the fact that $RuHX(CO)P_2$ is a multifunctional reagent.

Introduction

We have reported spectroscopic data which indicate that the composite ($\sigma + \pi$) electron donor ability of the group X in the "π-stabilized unsaturated" compounds $RuH(X)(CO)P_2$ (P = P^tBu_2Me) (**I**) varies as follows:[1]

H < I < Br < CCPh < Cl < SPh < OPh < NHPh < OH < OCH_2CF_3 < F < $OSiPh_3$ < $OSiMe_2Ph$ < $OSiMe_3$ < OEt



I

This clearly contrasts to simple electronegativity trends. We now wish to report that the chemical reactivity of these square-pyramidal species displays a dependence on the identity of X which is sometimes subtle and at other times dramatic.

All of the chemistry reported here occurs at 25 °C, and this facility (in comparison to much of Ru(II) chemistry) highlights the ready accessibility of these $RuHX(CO)P_2$ species to ligand addition. This justifies the applicability of the phrase "operationally unsaturated" to these compounds, in spite of their Ru/X multiply-bonded ground state. It is also noteworthy that the orange to burgundy color of $RuHX(CO)P_2$ compounds in solution suggests the absence of a low-lying (spectroscopically-accessible) LUMO.

Experimental Section

General Procedures. All manipulations were carried out using standard Schlenk and glovebox techniques under prepurified argon. Bulk solvents (toluene, hexanes) were dried and deoxygenated over sodium benzophenone or potassium benzophenone and subjected to three freeze–pump–thaw cycles prior to use. Deuterated solvents were dried (C_6D_6 and C_7D_8 over sodium metal; CD_2Cl_2 over CaH_2) and vacuum-distilled prior to use. Me_3SiH was purchased from Petrarch and used as received. Phenylacetylene (98%) was purchased from Aldrich and subjected to three freeze–pump–thaw cycles prior to use. D_2 and $PhC^{13}CH$ (MSD Isotopes) and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) (98%, Aldrich) were used as received. Hydrogen gas (99.9%) was purchased from Air Products Corp. and used without further purification. ^1H (referenced to residual solvent impurity), ^2H, ^{19}F (referenced to CF_3COOH), and ^{31}P (referenced to 85% H_3PO_4) NMR spectra were collected on a Nicolet NT-360 spectrometer operating at 360, 55, 339, and 146 MHz, respectively. Low-temperature ^1H NMR spectra of $RuHX(CO)(P^tBu_2Me)_2 + H_2$ (X = Cl, I) were recorded on a Varian XL-300. ^{13}C NMR spectra were recorded on a Bruker AM-500 spectrometer operating at 125 MHz or a Nicolet NT-360 spectrometer operating at 90 MHz. Infrared spectra were recorded in C_6D_6 (NaCl cavity cell, 0.1-mm path length) on a Nicolet 510P FT-IR spectrometer to a precision of 0.3 cm^{-1}. $RuHCl(CO)(P^tBu_2Me)_2$, $RuHF(CO)(P^tBu_2Me)_2$, $RuHI(CO)(P^tBu_2Me)_2$, $RuH(OSiPh_3)(CO)(P^tBu_2Me)$, $RuH(OPh)(CO)(P^tBu_2Me)_2$, $RuH(OCH_2CF_3)(CO)(P^tBu_2Me)_2$, and $RuH(C{\equiv}CPh)(CO)(P^tBu_2Me)_2$ were prepared as described previously.[2]

Reaction of $RuHCl(CO)P^tBu_2Me)_2$ with H_2. A solution of 0.02 g (0.04 mmol) of $RuHCl(CO)(P^tBu_2Me)_2$ in 0.4 mL of C_7D_8 was placed in an NMR tube fitted with a Teflon stopcock. The solution was frozen in liquid N_2, the headspace evacuated, and 1 atm of H_2 (0.1 mmol) introduced into the tube. Upon thawing and vigorous shaking, ^1H and ^{31}P NMR spectra showed unchanged $RuHCl(CO)(P^tBu_2Me)_2$ at +25 °C. However, a signal for dissolved H_2 was not detected. At −107 °C,

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(1) Poulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190.
(2) Poulton, J. T.; Sigalas, M. P.; Folting, K.; Streib, W. E.; Eisenstein, O.; Caulton, K. G., submitted for publication.

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a new ^1H NMR signal at −9.2 ppm appeared, which was attributed to $RuH(H_2)Cl(CO)(P^tBu_2Me)_2$.

Reaction of $RuHI(CO)(P^tBu_2Me)_2$ with H_2. A solution of 0.025 g (0.04 mmol) of $RuHI(CO)(P^tBu_2Me)_2$ in 0.4 mL of C_7D_8 was placed in an NMR tube fitted with a Teflon stopcock. The solution was frozen in liquid N_2, the headspace evacuated, and 1 atm H_2 (0.1 mmol) of introduced into the tube. Upon thawing and vigorous shaking, the ^1H NMR spectrum showed a broad (100 Hz at half-height) hydride peak at −23.7 ppm. All other ^1H and ^{31}P NMR signals were unchanged. A signal for dissolved H_2 was not detected. At −105 °C, a new ^1H NMR signal at −9.7 ppm appeared which was attributed to $RuH(H_2)I(CO)(P^tBu_2Me)_2$.

Preparation of $RuDX(CO)(P^tBu_2Me)_2$ (X = Cl, I). In a typical preparation, 0.02 g of $RuHX(CO)(P^tBu_2Me)_2$ (X = Cl, I) (0.04 mmol) dissolved in 5 mL of toluene was placed in a 100-mL flask with a Teflon-coated stirbar. The solution was frozen in liquid N_2, the headspace evacuated, and 1 atm D_2 added to the headspace. After 12 h of stirring, the solvent was removed to give $RuDX(CO)(P^tBu_2Me)_2$ (X = Cl, I). Yield: 0.02 g, 100%. ^2H NMR for $RuDCl(CO)(P^tBu_2Me)_2$ (C_6H_6, 25 °C): −25.4 ppm (br, Ru–D). ^2H NMR for $RuDI(CO)(P^tBu_2Me)_2$ (C_6H_6, 25 °C): −23.6 ppm (br, Ru–D).

$Ru(H)_2(H_2)(CO)(P^tBu_2Me)_2$. A C_6D_6 solution (0.02 g) of $RuH(Cl)CO(P^tBu_2Me)_2$ (0.04 mmol) containing 0.02 g of KOH (4 mmol) was placed under 1 atm of H_2, stirred for 30 min, and then filtered. Yield: 85% by ^{31}P NMR. ^1H NMR (C_6D_6 25 °C): 1.35 (vt, 36H, P^tBu), 1.21 (vt, 6H, PMe), −6.95 ppm (br, 4H, RuH_4). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 76.3 ppm. IR: ν_{CO} = 1940 cm^{-1}. Addition of H_2O (0.04 mmol) to this sample resulted in regeneration of some $RuH(OH)(CO)(P^tBu_2Me)_2$ (by ^{31}P and ^1H NMR). Subjecting a sample of $Ru(H)_2(H_2)(CO)(P^tBu_2Me)_2$ to repeated freeze–pump–thaw cycles caused broadening and upfield movement of the $^{31}P\{^1H\}$ signal as well as broadening of all ^1H NMR signals. At −40 °C (C_7D_8), this sample displayed signals for $Ru(H)_2(H_2)(CO)(P^tBu_2Me)_2$ as well as a new ^{31}P NMR signal (71.2 ppm) and new ^1H NMR signals at 1.45 (br, PMe) and 1.09 ppm (br, P^tBu). A new hydride signal attributable to this product was not observed due to either broadness or overlap with the $Ru(H)_2(H_2)(CO)(P^tBu_2Me)_2$ hydride signal. These new signals were assigned to $RuH_2(CO)(P^tBu_2Me)_2$. Consistent with this assignment was the observation that addition of H_2 to this sample caused disappearance of the new signals and regeneration of $Ru(H)_2(H_2)(CO)(P^tBu_2Me)_2$.

Reaction of $RuH(OH)(CO)(P^tBu_2Me)_2$ with H_2. A solution of 0.02 g (0.04 mmol) of $RuH(OH)(CO)(P^tBu_2Me)_2$ in 0.4 mL of C_6D_6 was placed in an NMR tube fitted with a Teflon stopcock. The tube was frozen in liquid N_2, the head space evacuated, and 1 atm of H_2 (~0.1 mmol) admitted into the tube. Ten minutes after thawing and vigorous shaking, $^{31}P\{^1H\}$ NMR spectroscopy showed 70% conversion to $Ru(H)_2(H_2)(CO)(P^tBu_2Me)_2$ (76.3 ppm).

Comparative Rates of Exchange of D_2 with $RuHF(CO)(P^tBu_2Me)_2$, $RuHCl(CO)(P^tBu_2Me)_2$, and $RuHI(CO)(P^tBu_2Me)_2$. A 0.024-g (0.05-mmol) sample of $RuHCl(CO)(P^tBu_2Me)_2$ was dissolved in 0.4 mL of C_6D_6, and the solution was placed in an NMR tube fitted with a Teflon stopcock. The tube was attached to a calibrated gas manifold and the solution frozen in liquid nitrogen. The headspace of the tube was evacuated and 0.2 mmol of D_2 was added. Fifteen minutes after thawing and mixing, ^1H NMR spectroscopy showed 32% D incorporation (as judged by integration *vs* the phosphine methyl signal) into the metal-bound position. After 60 min, 82% D incorporation was achieved. In a procedure identical to the above, 0.2 mmol of D_2 was admitted to an NMR tube containing 0.029 g (0.05 mmol) of $RuHI(CO)(P^tBu_2Me)_2$ dissolved in 0.4 mL of C_6D_6. Fifteen minutes after thawing and mixing, ^1H NMR showed 78% D incorporation. After 60 min, >95% D incorporation was observed. In a procedure identical to the above, 0.2 mmol of D_2 was admitted to an NMR tube containing 0.023 g (0.05 mmol) of $RuHF(CO)(P^tBu_2Me)_2$ in 0.4 mL of C_6D_6. Fifteen minutes after thawing and mixing, ^1H NMR spectroscopy showed <10% D incorporation. After 60 min, 27% D incorporation was observed, and after 24 h, 72% D incorporation was observed. No evidence for elimination of HF was observed.

Reaction of $RuHF(CO)(P^tBu_2Me)_2$ with Excess H_2. A solution of 0.025 g (0.06 mmol) of $RuHF(CO)(P^tBu_2Me)_2$ in 0.4 mL of C_6D_6 was placed in a 50-mL solvent seal flask equipped with a Teflon stirbar. The flask was charged with 2 atm (~6 mmol) of H_2, and the mixture was stirred for 18 h at 25 °C, after which $^{31}P\{^1H\}$ NMR spectroscopy revealed 29% conversion to $RuH_2(H_2)(CO)(P^tBu_2Me)_2$. When this reaction was repeated in the presence of 0.1 g of CsF and in a flask treated with Surfasil silyating agent, no significant decrease in the rate of production of $RuH_2(H_2)(CO)(P^tBu_2Me)_2$ was noted.

Low-Temperature Reaction of $RuH(OCH_2CF_3)(CO)(P^tBu_2Me)_2$ with H_2. A C_7D_8 solution of 0.02 g of $RuH(OCH_2CF_3)(CO)(P^tBu_2Me)_2$ (0.04 mmol) was placed in an NMR tube fitted with a Teflon stopcock. The solution was frozen in liquid N_2, the headspace was evacuated, and 1 atm of H_2 (0.1 mmol) was added. The still-frozen solution was placed in an NMR probe precooled to −60 °C. After the solution was allowed to warm to −60 °C (10 min), the $^{31}P\{^1H\}$ NMR spectrum showed production of $Ru(H)_2(H_2)(CO)(P^tBu_2Me)_2$ (76.0 ppm, ~10%) and unreacted $RuH(OCH_2CF_3)(CO)(P^tBu_2Me)_2$ (56.3 ppm, ~90%) and no other signals (i.e., no intermediates).

$Ru[C(CH_3)CHCH_3]I(CO)(P^tBu_2Me)_2$. To a solution of 0.026 g of $RuHI(CO)(P^tBu_2Me)_2$ (0.05 mmol) in 0.04 mL of C_6D_6 was added 4.0 μL of MeC≡CMe (0.06 mmol). After 24 h, ^1H and ^{31}P NMR spectra showed complete conversion to $Ru[C(CH_3)CHCH_3]I(CO)(P^tBu_2Me)_2$. ^1H NMR (C_6D_6, 25 °C): 4.97 (q, J_{H-H} = 6 Hz, 1H, $C(CH_3)CHCH_3$), 1.91 (s, 3H, $C(CH_3)CHCH_3$), 1.68 (vt, 6H, PMe), 1.21 (vt, 18H, P^tBu), 1.19 (vt, 18H, P^tBu), 1.18 ppm (d, J = 6 Hz, 3H, $C(CH_3)CHCH_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 29.0 ppm (br). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): 205.1 (t, J_{P-C} = 18 Hz, *C*O), 152.9 (t, J_{P-C} = 9 Hz, *C*(CH_3)$CHCH_3$), 124.8 (s, $C(CH_3)CHCH_3$), 37.6 (vt, $PC(CH_3)_3$), 36.9 (vt, $PC(CH_3)_3$), 29.3 (vt, PCH_3), 29.6 (s, $PC(CH_3)_3$), 31.0 (s, $PC(CH_3)_3$), 28.1 (s, $C(CH_3)CHCH_3$), 16.6 ppm (s, $C(CH_3)CHCH_3$). IR: ν_{CO} = 1902 cm^{-1}. Repeating this reaction in the presence of 2 equiv of $(H_3C(CH_2)_5)_4NI$ resulted in no detectable decrease in rate as monitored by ^{31}P NMR spectroscopy.

$Ru(CHCHPh)F(CO)(P^tBu_2Me)_2$. To a solution of 0.02 g (0.03 mmol) of $Ru(CHCHPh)Cl(CO)(P^tBu_2Me)_2$ in 0.4 mL of C_6D_6 was added 0.04 g (2.6 mmol) of CsF. The slurry was stirred for 18 h and filtered. ^1H NMR (C_6D_6, 25 °C): 9.12 (d of d, 1H, J_{H-F} = 8 Hz, J_{H-H} = 13 Hz, C*H*=CHPh), 7.34 (d, 2H, ortho), 7.21 (t, 2H, meta), 6.95 (t, 1H, para), 6.39 (d, J_{H-H} = 13 Hz, 1H, CH=C*H*Ph), 1.21 (vt, 18H, P^tBu), 1.18 (vt, 6H, PMe), 1.14 ppm (vt, 18H, P^tBu). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 41.8 ppm (d, J_{P-F} = 22 Hz). ^{19}F NMR (C_6D_6, 25 °C): −211 ppm (d of t, J_{F-H} = 8 Hz, J_{F-P} = 22 Hz). IR: ν_{CO} = 1894 cm^{-1}.

$Ru(CHCHPh)Cl(CO)(P^tBu_2Me)_2$.[3] To a 0.5 mL C_6D_6 solution of 0.02 g of $RuHCl(CO)(P^tBu_2Me)_2$ (0.04 mmol) was added 4.5 μL of phenylacetylene (0.04 mmol). The reaction was complete with 15 min. ^1H NMR (C_6D_6, 25 °C): 8.97 (d, J_{H-H} = 13 Hz, 1H, C*H*CHPh), 7.22 (m, 2H, CHCH*Ph*), 7.17 (m, 2H, CHCH*Ph*), 6.93 (t, 1H, CHCH*Ph*), 6.21 (d, J_{H-H} = 13 Hz, 1H, CHC*H*Ph), 1.34 (vt, 6H, PMe), 1.21 (vt, 18H, P^tBu), 1.16 ppm (vt, 18H, P^tBu). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 35.4 ppm. IR: ν_{CO} = 1908 cm^{-1}.

Reaction of $RuDCl(CO)(P^tBu_2Me)_2$ and Phenylacetylene. To a 0.5 mL of a C_7H_8 solution containing 0.02 g of $RuDCl(CO)(P^tBu_2Me)_2$ (0.04 mmol) was added 4.5 μL of phenylacetylene (0.04 mmol). ^2H NMR (C_7H_8, 25 °C): 6.20 ppm (m, CHCDPh).

$Ru(CHCHPh)I(CO)(P^tBu_2Me)_2$. To a 0.5-mL C_6D_6 solution containing 0.02 g of $RuHI(CO)(P^tBu_2Me)_2$ (0.04 mmol) was added 4.5 μL of phenylacetylene (0.04 mmol). The reaction was complete in 15 min. ^1H NMR (C_6D_6, 25 °C): 8.67 (d, J_{H-H} = 13 Hz, C*H*CHPh), 7.17 (m, 2H, Ph), 7.13 (m, 2H, Ph), 6.92 (m, 1H, Ph), 5.91 (d, J_{H-H} = 13 Hz, CHC*H*Ph), 1.54 (vt, 6H, PMe), 1.24 (vt, 18H, P^tBu), 1.19 ppm (vt, 18H, P^tBu). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 31.5 ppm. IR: ν_{CO} = 1910 cm^{-1}.

$RuI(CO)(P(C(Me)_2CH_2)^tBuMe)(P^tBu_2Me)_2$. After 1 week at 25 °C, a C_6D_6 solution of $RuI(CHCHPh)(CO)(P^tBu_2Me)_2$ showed by ^1H NMR spectroscopy the presence of styrene (vinylic resonances at 5.05, 5.57, and 6.55 ppm). $^{31}P\{^1H\}$ NMR spectroscopy showed a new AB spin system: 40.8 (d, J_{P-P} = 280 Hz), 11.5 ppm (d, J_{P-P} = 280 Hz).

Reaction of $RuHF(CO)(P^tBu_2Me)_2$ with PhC_2H. A solution of 0.05 g (0.1 mmol) of $RuHF(CO)(P^tBu_2Me)_2$ in 0.5 mL of C_6D_6 was treated with 6.3 μL (0.07 mmol) of PhC_2H. After 2 h, ^1H and $^{31}P\{^1H\}$ NMR spectra showed three major products, $Ru(HCCHPh)F(CO)P_2$, $Ru(PhCCH_2)F(CO)P_2$, and $RuH(C_2Ph)(CO)P_2$ in a 6:5:2 ratio. Spectral data for $Ru(PhCCH_2)F(CO)P_2$ follow. ^1H NMR (C_6D_6, 25 °C): 8.41 (br, ortho H), 7.25 (br, meta H), 7.09 (br, para H), 5.57 (br, PhCC*H*H), 5.24 (br, PhCCH*H*), 1.35 (br, PMe), 1.25 (vt, P^tBu), 1.19 ppm (vt, P^tBu). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): −182 ppm (t, J_{F-P} = 18 Hz). IR: ν_{CO} = 1894 cm^{-1}.

(3) Assignment of the HCCHPH and the CCPh signals was made on the basis of comparison to the previously reported data for $Ru(HCCHPh)(C_2Ph)(CO)(P^iPr_3)_2$: Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295.

(4) This compound has been independently synthesized by addition of $HSiMe_3$ to $RuCO(P^tBu_2Me)_2$: Heyn, R. H.; Caulton, K. G. *J. Am. Chem. Soc.* **1993**, *115*, 3354.

RuH(CCPh)(CO)(P^tBu_2Me)$_2$. To a solution of 0.025 g of RuH($OSiPh_3$)(CO)(P^tBu_2Me)$_2$ (0.03 mmol) in 0.5 mL of C_6D_6 was added 3.4 μL of phenylacetylene. After 2 h, ^1H and $^{31}P\{^1H\}$ NMR spectra revealed 95% conversion to RuH(CCPh)(CO)(P^tBu_2Me)$_2$. ^1H NMR (C_6D_6, 25 °C): 7.60 (d, J = 7 Hz, 2H, Ph), 7.18 (t, J = 7 Hz, 2H, Ph), 7.01 (t, J = 7 Hz, 1H, Ph), 1.64 (vt, 6H, PMe), 1.21 (vt, 18H, P^tBu), 1.19 (vt, 18H, P^tBu), −27.9 ppm (t, J_{P-H} = 19 Hz, 1H, Ru–H). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 53.2 ppm. IR: ν_{CO} = 1906 cm^{-1}, ν_{CC} = 2072 cm^{-1}. Reaction of RuH(OCH_2CF_3)(CO)(P^tBu_2Me)$_2$ or RuH(OPh)(CO)(P^tBu_2Me)$_2$ with equimolar phenylacetylene also yielded RuH(CCPh)(CO)(P^tBu_2Me)$_2$.

Reaction of RuD($OSiPh_3$)(CO)(P^tBu_2Me)$_2$ with PhC≡CH. A sample of 0.03 g of RuD($OSiPh_3$)(CO)(P^tBu_2Me)$_2$ (0.04 mmol), prepared from RuDCl(CO)(P^tBu_2Me)$_2$ and $KOSiPh_3$, was treated with 4.5 μL of phenylacetylene. ^1H NMR spectroscopy showed *no* hydride signal at −27.9 ppm for the resulting hydrido acetylide, indicating complete retention of the metal-bound D label.

Ru(C_2Ph)$_2$(CO)(P^tBu_2Me)$_2$. A mixture of 0.10 g (0.2 mmol) of RuHCl(CO)(P^tBu_2Me)$_2$, 0.02 g (0.2 mmol) of LiC_2Ph, and 0.1 g (1.0 mmol) of PhC_2H was refluxed in 50 mL of hexanes for 4 h. The hot solution was filtered through Celite to remove LiCl and the solvent volume reduced to ~10 mL. After the mixture was cooled to −20 °C for 8 h, 0.068 g of burgundy-colored solid was collected by filtration and dried under vacuum. Yield: 51%. ^1H NMR (C_6D_6, 25 °C): 7.57 (d, 4H, ortho), 7.20 (t, 4H, meta), 7.03 (t, 2H, para), 1.76 (vt, 6H, PMe), 1.29 ppm (vt, 36H, P^tBu). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 47.6 ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): 206.0 (t, J_{P-C} = 13 Hz, CO), 131.1 (t, J_{P-C} = 13 Hz, *C*CPh), 130.5, 129.8, 128.5, 125.1, 123.6 (phenyl and *CC*Ph), 36.4 (vt, P*C*(CH_3)$_3$), 29.7 (s, PC(*C*H$_3$)$_3$), 7.71 ppm (vt, P*C*H$_3$). IR: ν_{CO} = 1933 cm^{-1}, ν_{CC} = 2074 cm^{-1}. Anal. Calcd for $RuOP_2C_{35}H_{52}$: C, 64.50; H, 7.98. Found: C, 64.72; H, 7.77.

Ru(CHCHPh)(C_2Ph)(CO)(P^tBu_2Me)$_2$. To a solution of 0.02 g (0.03 mmol) of Ru(CHCHPh)Cl(CO)(P^tBu_2Me)$_2$ in 0.5 mL of C_6D_6 was added 0.004 g (0.04 mmol) of LiC_2Ph. The solution was stirred for 6 h and filtered to remove LiCl. ^1H NMR (C_6D_6, 25 °C): 8.62 (d, J_{H-H} = 13 Hz, *H*CCHPh), 6.9–7.7 (m, phenyl), 6.28 (d, J_{H-H} = 13 Hz, HCC*H*Ph), 1.52 (vt, PMe), 1.21 (vt, P^tBu), 1.13 ppm (vt, P^tBu). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 40.9 ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): 205.7 (t, J_{P-C} = 10 Hz, *C*O), 153.5 (t, J_{P-C} = 10 Hz, H*C*CHPh), 133.3 (t, J_{P-C} = 2 Hz, *C*CPh),[3] 130.8, 129.0, 128.9, 125.7, 124.6, 124.3 (HC*C*HPh, *CC*Ph, and phenyl carbons), 36.5 (vt, P*C*(CH_3)$_3$), 36.2 (vt, P*C*(CH_3)$_3$), 30.1 (vt, PC(*C*H$_3$)$_3$), 29.9 (vt, PC(*C*H$_3$)$_3$), 7.43 ppm (vt, P*C*H$_3$). IR: ν_{CO} = 1910 cm^{-1}, ν_{CC} = 2074 cm^{-1}.

Ru(PhCCH$_2$)(CCPh)(CO)(P^tBu_2Me)$_2$. To a solution of 0.02 g (0.03 mmol) of Ru(C_2Ph)$_2$(CO)(P^tBu_2Me)$_2$ in 0.4 mL of C_7D_8 was added 0.03 mmol of H_2 with the aid of a calibrated gas manifold. After the tube was shaken for 5 min, ^1H and $^{31}P\{^1H\}$ NMR spectra showed formation of Ru(PhCCH$_2$)(C_2Ph)(CO)(P^tBu_2Me)$_2$ and Ru(CHCHPh)(C_2Ph)(CO)(P^tBu_2Me)$_2$ in a 5:1 ratio. Spectral data for Ru(PhCCH$_2$)(C_2-Ph)(CO)(P^tBu_2Me)$_2$ follow. ^1H NMR (C_7D_8, 25 °C): 8.05 (br, ortho H), 7.6–7.0 (meta and para H), 5.58 (br, PhCC*H*H), 5.10 (br, PhCCH*H*), 1.44 (br, PMe), 1.26 (P^tBu), 1.22 ppm (P^tBu). $^{31}P\{^1H\}$ NMR (C_7D_8, 25 °C): 38.7 ppm (br). IR: ν_{CO} = 1910 cm^{-1}, ν_{CC} = 2074 cm^{-1}. Selected low-temperature NMR data are as follows. ^1H NMR (C_7D_8, −40 °C): 8.55 (d, J_{H-H} = 7 Hz, ortho H), 7.82, (d, J_{H-H} = 7 Hz, ortho H), 6.03 and 5.46 (s, daughters of 5.58 ppm signal, PhCC*H*H), 5.26 and 5.08 ppm (s, daughters of 5.10 ppm signal, PhCCH*H*). $^{31}P\{^1H\}$ NMR (C_7D_8, −40 °C): 39.6 (br), 36.5 ppm (br); 1.35:1 integration. Addition of more H_2 to this mixture resulted in production of RuH(C_2Ph)(CO)(P^tBu_2Me)$_2$ and styrene.

Reaction of RuH(C≡CPh)(CO)(P^tBu_2Me)$_2$ with PhC≡CH. A sample of 0.03 g of RuH(C≡CPh)(CO)(P^tBu_2Me)$_2$ (0.05 mmol) was treated with 5.6 μL of PhCCH (0.05 mmol). After 5 min, ^1H and $^{31}P\{^1H\}$ NMR spectra showed two major products identified as Ru(CHCHPh)(C_2Ph)(CO)(P^tBu_2Me)$_2$ and Ru(PhCCH$_2$)(C_2Ph)(CO)(P^tBu_2Me)$_2$ in a 3:2 molar ratio.

Attempted Reaction of RuHCl(CO)(P^tBu_2Me)$_2$ with DBU under H_2. A solution of 0.02 g of RuHCl(CO)(P^tBu_2Me)$_2$ (0.04 mmol) and 12.4 μL of DBU (0.16 mmol) in 0.5 mL of C_6D_6 was placed under 1 atm of H_2. $^{31}P\{^1H\}$ NMR spectroscopy showed no conversion to Ru(H_2)$_2$(H_2)(CO)(P^tBu_2Me)$_2$ after 48 h.

Reaction of RuHI(CO)(P^tBu_2Me)$_2$ with DBU under H_2. A solution of 0.02 g of RuHI(CO)($PtBu_2Me$)$_2$ (0.04 mmol) and 12.4 μL of DBU (0.16 mmol) in 0.5 mL of C_6D_6 was placed under 1 atm of H_2 in an NMR tube fitted with a Teflon stopcock. After 16 h, a solid had formed and it was centrifuged to the top of the tube. ^1H and $^{31}P\{^1H\}$ NMR spectra showed complete consumption of RuHI(CO)(P^tBu_2Me)$_2$ and conversion to RuH_4(CO)(P^tBu_2Me)$_2$.

Reaction of RuH(CCPh)(CO)(P^tBu_2Me)$_2$ with Excess H_2. A solution of 0.02 g of RuH(CCPh)(CO)(P^tBu_2Me)$_2$ in 0.5 mL of C_6D_6 was placed in a 100-mL flask. The solution was frozen in liquid N_2, the headspace evacuated, and 1 atm of H_2 added. After 1 h of stirring, ^1H and $^{31}P\{^1H\}$ NMR spectra showed complete conversion of RuH(CCPh)(CO)(P^tBu_2-Me)$_2$ to Ru(H)$_2$(H_2)(CO)(P^tBu_2Me)$_2$. Also present, by ^1H NMR, was ethylbenzene. No styrene or phenylacetylene was detected.

Comparative Rates of Reactions of PhCCH with RuHCl(CO)(P^tBu_2-Me)$_2$ and RuH(C≡CPh)(CO)(P^tBu_2Me). An NMR tube containing the compounds RuHX(CO)(P^tBu_2Me)$_2$ where X = Cl and C_2Ph was treated with successive increments of PhC_2H. $^{31}P\{^1H\}$ NMR spectroscopy indicated that *all* RuH(C≡CPh)(CO)P_2 was selectively consumed by PhCCH before any consumption of RuHCl(CO)P_2 (to give Ru(HC=CHPh)Cl(CO)P_2).

Reaction of RuHCl(CO)(P^tBu_2Me)$_2$ with Me_3SiH. A solution of 0.02 g (0.04 mmol) of RuHCl(CO)(P^tBu_2Me)$_2$ in 0.4 mL of C_6D_6 was placed in an NMR tube fitted with a Teflon stopcock. To this solution was added 0.04 mmol of Me_3SiH using a calibrated gas manifold. Both ^1H and $^{31}P\{^1H\}$ NMR spectra showed unchanged RuHCl(CO)(P^tBu_2Me)$_2$.

Reaction of RuDCl(CO)(P^tBu_2Me)$_2$ with Me_3SiH. A solution of 0.02 g (0.04 mmol) of RuDCl(CO)(P^tBu_2Me)$_2$ in 0.4 mL of C_6D_6 was placed in an NMR tube fitted with a Teflon stopcock. To this solution was added 0.36 mmol of Me_3SiH using a calibrated gas manifold. After 10 min, ^1H NMR spectroscopy showed a hydride signal at −24.5 ppm for RuHCl(CO)(P^tBu_2Me)$_2$, whose integral intensity (*vs* the PMe signal) indicated that 73% exchange had occurred. The Si–H signal at 4.10 ppm integrated for 0.32 H *vs* the Me groups of Me_3SiH. A new singlet at −0.01 ppm was present due to Me_3SiD.

Reaction of RuHI(CO)(P^tBu_2Me)$_2$ with Me_3SiH. A solution of 0.02 g (0.03 mmol) of RuHI(CO)(P^tBu_2Me)$_2$ in 0.4 mL of C_6D_6 was placed in an NMR tube fitted with a Teflon stopcock. To this solution was added 0.03 mmol of Me_3SiH using a calibrated gas manifold. While the $^{31}P\{^1H\}$ NMR spectrum was unchanged, the ^1H NMR hydride signal had broadened (~80 Hz at half-height). Upon removal of solvent by vacuum and addition of fresh C_6D_6, the hydride signal regained its sharp triplet structure.

Reaction of RuDI(CO)(P^tBu_2Me)$_2$ with Me_3SiH. A solution of 0.02 g (0.03 mmol) of RuDI(CO)(P^tBu_2Me)$_2$ in 0.4 mL of C_6D_6 was placed in an NMR tube fitted with a Teflon stopcock. To this solution was added 0.36 mmol of Me_3SiH using a calibrated gas manifold. After 10 min, ^1H NMR spectroscopy showed a hydride signal at −23.7 ppm for RuHI(CO)(P^tBu_2Me)$_2$, whose integral intensity (*vs* the PMe signal) indicated that 100% exchange had occurred.

Reaction of RuHF(CO)(P^tBu_2Me)$_2$ with Me_3SiH. A solution of 0.02 g (0.04 mmol) of RuHF(CO)(P^tBu_2Me)$_2$ in 0.4 mL of C_6D_6 was placed in an NMR tube fitted with a Teflon stopcock. To this solution was added 0.04 mmol of Me_3SiH using a calibrated gas manifold. After 10 min, ^1H and $^{31}P\{^1H\}$ NMR spectra showed complete conversion to RuH_2(CO)(P^tBu_2Me)$_2$. ^{19}F NMR spectroscopy showed Me_3SiF (−157.8 ppm, 10-line pattern with ^{29}Si satellites, J_{H-F} = 7 Hz, J_{F-Si} = 138 Hz) as the only fluoro-containing product. Addition of more Me_3SiH to this solution resulted in production of Ru(H_2)(H)$_2$(CO)(P^tBu_2Me)$_2$, RuH($SiMe_3$)(CO)(P^tBu_2Me)$_2$, and $RuH_3(SiMe_3)$(CO)(P^tBu_2Me)$_2$. Spectral data for RuH($SiMe_3$)(CO)(P^tBu_2Me)$_2$[4] follow. ^1H NMR (C_6D_6, 25 °C): 1.29 (vt, 6H, PMe), 1.24 (vt, 18H, P^tBu), 1.10 (vt, 18H, P^tBu), 0.56 (s, 9H, SiMe), −1.08 ppm (t, J_{P-H} = 26 Hz, Ru–H). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 62.8 ppm. IR: ν_{CO} = 1908 cm^{-1}. Data for $RuH_3(SiMe_3)$(CO)(P^tBu_2Me)$_2$ are as follows. Selected ^1H NMR (C_7D_8, 25 °C): −9.26 ppm (br, Ru–H). ^1H NMR (C_7D_8, −40 °C): 1.25 (vt, 6H, PMe), 1.16 (vt, 18H, P^tBu), 1.14 (vt, 18H, P^tBu), 0.83 (s, 9H, SiMe), −9.10 (m, 2H), −9.46 ppm (m, 1H). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 63.0 ppm.

Reaction of RuH(OR)(CO)(P^tBu_2Me)$_2$ (R = CH_2CF_3 or $SiPh_3$) with Me_3SiH. In both cases, the reaction proceeded in a manner analogous to that of the reaction of RuHF(CO)(P^tBu_2Me)$_2$ with Me_3SiH. RuH_2(CO)(P^tBu_2Me)$_2$ was produced with elimination of Me_3SiOCH_2-CF_3 or $Me_3SiOSiPh_3$. The presence of $Me_3SiOCH_2CF_3$ in the RuH(OCH_2CF_3)(CO)(P^tBu_2Me)$_2$ + Me_3SiH reaction mixture was verified by ^1H NMR spectroscopy.[5]

Results

Reactivity toward Dihydrogen. Neither RuHCl(CO)P_2 nor RuHI(CO)P_2 shows major ^1H or ^{31}P NMR spectral changes

(5) For ^1H NMR data for $Me_3SiOCH_2CF_3$, see: Johnson, T. J.; Coan, P. S.; Caulton, K. G. *Inorg. Chem.*, in press.

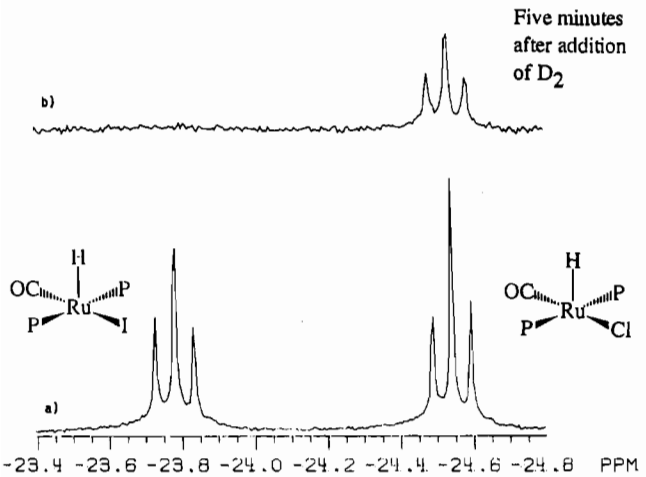


Figure 1. Hydride-region ^1H NMR spectra (C_6D_6, 25 °C): (a) equimolar $RuHCl(CO)(P^tBu_2Me)_2$ and $RuHI(CO)(P^tBu_2Me)_2$, (b) mixture in (a) 5 min after addition of substoichiometric D_2.

under 1 atm of H_2 in toluene-d_8 at +25 °C. However, a signal for dissolved H_2 is not detectable in the presence of $RuHCl(CO)P_2$ or $RuHI(CO)P_2$ (+25 to −105 °C). This observation suggests that both $RuHCl(CO)P_2$ and $RuHI(CO)P_2$ bind H_2 weakly. The spectra of both compounds at −105 °C under H_2 show new signals in the hydride region which are attributed to an H_2 adduct. The low temperature necessary for observation of an H_2 adduct again illustrates an unfavorable H_2-binding equilibrium for $RuHCl(CO)P_2$ and $RuHI(CO)P_2$. The related compound $RuHCl(CO)(P^iPr_3)_2$ shows significant binding of H_2 below 25 °C.[6]

Nevertheless, both $RuHCl(CO)P_2$ and $RuHI(CO)P_2$ readily (<1 h, 1 atm of D_2, 25 °C) incorporate deuterium into their RuH site. Proton and deuterium NMR studies indicate that neither the solvent protons nor the alkyl groups of the phosphine are deuterated within 4 h.[7] A competitive isotope-exchange experiment enables determination of the halide dependence of the rate of metal deuteration. Figure 1a shows the hydride-region ^1H NMR spectrum of a 1:1 mixture of $RuHCl(CO)P_2$ and $RuHI(CO)P_2$ (~0.05 mmol of each). The headspace of the sample tube was then filled with 1 atm of D_2 (~0.1 mmol), and the tube was briefly shaken. The spectrum in Figure 1b, collected 5 min after the addition of D_2, shows the complete exchange of the Ru–H resonance of the iodide but only incomplete (50% by integration against the PMe resonance) exchange for the chloride. The presence of chloride thus decreases the rate of exchange of Ru–H with D_2 in comparison to the case of iodide. We leave for the Discussion an explanation of this, as well as how the Ru–H can exchange with D_2 when the open coordination site in $RuHX(CO)P_2$ is *trans* to hydride (see **I**).

When X in $RuHX(CO)P_2$ is an oxygen-based ligand, molecular hydrogen shows a remarkable ability to split the Ru–X bond. When X = OH, the transformation in eq 1 was observed.

$$RuH(OH)(CO)P_2 + 2H_2 \rightleftharpoons \underset{\textbf{II}}{Ru(H_2)(H)_2(CO)P_2} + H_2O \quad (1)$$

Although this was established to be an equilibrium reaction, it can be shifted completely to product **II**[6] by addition of KOH (to a toluene solution), which absorbs the liberated water. The reaction is reversible, since addition of water to compound **II** regenerates $RuH(OH)(CO)P_2$. Compound **II** is likewise produced from $RuH(OR_f)(CO)P_2$ ($R_f = CH_2CF_3$) and hydrogen (1 atm, 25 °C, <30 min), with release of R_fOH. This reaction occurs rapidly (<5 min) even at −60 °C, and no intermediates are detected (^1H and ^{31}P NMR spectra) even at −80 °C. This reaction is also reversible. Addition of R_fOH to $RuH_4(CO)P_2$ reestablishes equilibrium concentrations of $RuH(OR_f)(CO)P_2$ and $Ru(H_2)(H)_2(CO)P_2$. In the presence of pyridine, $Ru(H_2)(H)_2(CO)P_2$ loses H_2 to form $Ru(H)_2(py)(CO)P_2$.

Scheme I

$$RuHF(CO)P_2 + H_2O \rightarrow RuH(OH)(CO)P_2 + HF$$

$$RuH(OH)(CO)P_2 + 2H_2 \rightarrow Ru(H)_2(H_2)(CO)P_2 + H_2O$$

Hydrogenolysis (1 atm of H_2) of $RuH(CCPh)(CO)P_2$ is complete within 1 h at 25 °C to give $Ru(H)_2(H_2)(CO)P_2$. The hydrocarbyl ligand is found exclusively as ethylbenzene.

Ru–Halide Hydrogenolysis. Since oxygen-based X groups in $RuHX(CO)(P^tBu_2Me)_2$ eliminate HX upon exposure to H_2, we sought to induce similar behavior when X = Cl or I by adding a Brønsted base. It was hoped that this would make HX elimination more thermodynamically favorable. When a C_6D_6 solution of $RuHCl(CO)(P^tBu_2Me)_2$ and 5 equiv of DBU (a noncoordinating base) is placed under 1 atm of H_2, $^{31}P\{^1H\}$ NMR spectroscopy shows no production of $Ru(H)_2(H_2)(CO)(P^tBu_2Me)_2$ after 48 h. However, the wholly analogous reaction with $RuHI(CO)(P^tBu_2Me)_2$, by $^{31}P\{^1H\}$ NMR (12 h), results in complete consumption of reagent with production of $Ru(H)_2(H_2)(CO)(P^tBu_2Me)_2$. A considerable amount of solid ($H\text{–}DBU^+I^-$) is also present. Because a solution of $RuHI(CO)(P^tBu_2Me)_2$ and DBU shows no spectroscopic changes in the absence of H_2, we propose that DBU deprotonates the coordinated H_2 of $RuH(H_2)I(CO)(P^tBu_2Me)_2$ to give $[Ru(H)_2I(CO)(P^tBu_2Me)_2^-][H\text{–}DBU^+]$. Loss of I^- and coordination of a second mole of H_2 lead to formation of $Ru(H)_2(H_2)(CO)(P^tBu_2Me)_2$. Observation of net dehydrohalogenation for X = I and not for X = Cl is consistent with our proposal that the equilibrium constant for eq 2

$$RuHX(CO)(P^tBu_2Me)_2 + H_2 \rightleftharpoons RuH(H_2)X(CO)(P^tBu_2Me)_2 \quad (2)$$

is larger for X = I than for X = Cl due to greater inhibition of H_2 binding by the more strongly donating Cl. It is also consistent with a higher bond dissociation energy for RuCl than for RuI.

The compound $RuHF(CO)(P^tBu_2Me)_2$ provides an opportunity to compare the reactivity of a hydrido fluoride to that of the heavier halides. The reactivity of $RuHF(CO)(P^tBu_2Me)_2$ with H_2/D_2 differs noticeably from that of the chloride and iodide compounds. The addition of 100 equiv of H_2 to $RuHF(CO)(P^tBu_2Me)_2$ results in detectable conversion (29%) to $Ru(H)_2(H_2)(CO)(P^tBu_2Me)_2$ after 18 h at 25 °C. No added base is needed to accomplish this transformation. To ensure that this reaction was not catalyzed by trace H_2O (Scheme I), the reaction was repeated in silylated glassware with CsF added as a drying agent.[8] There was no detectable rate difference, suggesting that adventitious H_2O does not play a part in the elimination of HF from $RuHF(CO)(P^tBu_2Me)_2$.

While this result indicates that HX elimination is more favorable for the fluoro compound than for the chloro and iodo compounds, no information is obtained concerning the binding of H_2 by $RuHF(CO)(P^tBu_2Me)_2$ as compared to the case of the chloro and iodo analogs. Therefore the reaction of $RuHF(CO)(P^tBu_2Me)_2$ with 4 equiv of D_2 was investigated. After 1 h at 25 °C, ^1H NMR spectroscopy indicates that 27% of the metal-bound H has been replaced by D. No formation of $Ru(H)_2(H_2)(CO)P_2$ is detected by ^1H and ^{31}P NMR spectroscopies. This observation of slower exchange with D_2 compared to the cases

(6) Gusev, D. G.; Vymenits, A. B.; Bakhmutov, V. I. *Inorg. Chem.* **1992**, *31*, 1.

(7) ^2H NMR spectroscopy indicates that ~10% deuteration of the ^{t}Bu groups of $RuHCl(CO)(P^tBu_2Me)_2$ occurs after 2 days under 1.5 atm of D_2.

(8) CsF was chosen as a drying agent because it would not effect halide metathesis and it would not act as a Brønsted base, which could effect dehydrohalogenation, as observed in the $RuHI(CO)P_2 + DBU/H_2$ reaction.

of $RuHCl(CO)P_2$ (78% exchange after 1 h) and $RuHI(CO)P_2$ (>95% exchange after 1 h) indicates that the equilibrium constant for eq 2 is smaller for X = F than for X = Cl or I. This is consistent with F being a better donor that Cl or I and thus inhibiting the binding of H_2.

In summary, the experimental evidence indicates that the identity of the halide in the reaction of $RuHX(CO)P_2$ with H_2/D_2 leads to dramatic differences in reactivity. The D_2 exchange rates indicate that the magnitude of the equilibrium constant for eq 2 as a function of halide follows the order F < Cl < I. It is the larger binding constant for X = I and hence the higher concentration of $RuH(H_2)I(CO)P_2$ present which allow observable production of $Ru(H)_2(H_2)(CO)P_2$ in the presence of DBU. For X = F, the binding constant is smaller, leading to the slower rate of exchange with D_2. However, unlike the case for X = Cl or I, there is a significant driving force for the elimination of HF, leading to the production of $Ru(H)_2(H_2)(CO)P_2$ without the need for a base such as DBU. Filled/filled M d_π–X p_π repulsions in the six-coordinate H_2 adducts may play a role in the driving force for HF elimination. It was recently demonstrated[9] that the stability of the saturated six-coordinate series $Ir(H)_2(H_2)X(P^tBu_2Me)_2$ as a function of X follows the order I > Br > Cl. This destabilizing effect results from repulsion between filled M d_π and filled X p_π orbitals, which is more pronounced for chloride, the best donor of the three halides studied. Extrapolation of these results to the $RuHX(CO)(P^tBu_2Me)_2$ system indicates that this destabilization should be greatest for X = F. Thus, the favorability of HF elimination as a means to alleviate this filled/filled repulsion is enhanced. The driving force for HF elimination may also be due in part to the stronger H–X bond formed for X = F (137 kcal/mol) compared to X = Cl (102 kcal/mol) and X = I (71 kcal/mol).[10] In the case of X = F, use of a large excess of H_2 (100 equiv) increases the amount of $RuH(H_2)F(CO)P_2$ present, thus facilitating the production of observable amounts of $Ru(H)_2(H_2)(CO)P_2$ after 18 h. The reaction of $RuHF(CO)P_2$ with 4 equiv of D_2 results in exchange of Ru–H and D. However, this amount of D_2 is insufficient to produce an observable amount of $Ru(H)_2(H_2)(CO)P_2$, even after 1 week at 25 °C.

Reactivity toward Primary Silanes. The reactivity of $RuHX(CO)(P^tBu_2Me)_2$ species with primary silanes also shows a marked dependence on the identity of X. The addition of 1 equiv of Me_3SiH to $RuHCl(CO)(P^tBu_2Me)_2$ results in no observable spectroscopic (^1H and ^{31}P NMR) changes.[11] The signals for the methyl protons (0.01 ppm, d, J_{H-H} = 4 Hz) and the Si–H proton (4.10 ppm, m, J_{H-H} = 4 Hz) are unchanged from those recorded in the absence of $RuHCl(CO)(P^tBu_2Me)_2$. However, addition of 9 equiv of Me_3SiH to $RuDCl(CO)(P^tBu_2Me)_2$ results in the growth of an Ru–H signal in the ^1H NMR spectrum. Integration indicates that 73% of the metal-bound D has been replaced by H after 10 min. Exchange between Si–H and Ru–D is also supported by a decrease in the integral intensity of the Si–H signal and the growth of a singlet at –0.01 ppm, assigned to the methyl signal of Me_3SiD. When D_2 and Me_3SiH are both added to a catalytic amount of $RuHCl(CO)(P^tBu_2Me)_2$, the reaction depicted in eq 3 occurs.[12]

$$Me_3SiH + D_2 \rightleftharpoons Me_3SiD + HD \qquad (3)$$

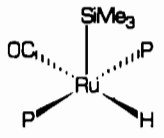
The iodo analogue, $RuHI(CO)(P^tBu_2Me)_2$, shows a broadening of the Ru–H ^1H NMR signal when exposed to 1 equiv of Me_3SiH, indicating a spectroscopically detectable shortening of the lifetime of $RuHI(CO)(P^tBu_2Me)_2$. The silane methyl and Si–H signals are unchanged and retain observable J_{H-H} and J_{Si-H}. After removal of Me_3SiH by stripping the solution to dryness and addition of fresh C_6D_6, the Ru–H signal regains its sharp triplet structure. The observation of this change for the iodo compound compared to the chloro may again be due to the poorer donor power of iodide. In accord with this conclusion are the comparative rates of exchange of $RuDX(CO)P_2$ (X = Cl, I) with Me_3SiH. Reminiscent of the comparative rates of D_2 exchange, $RuDI(CO)(P^tBu_2Me)_2$ shows a faster rate of exchange with Me_3SiH (100% exchange observed after 10 min with 9 equiv Me_3SiH) than does $RuHCl(CO)(P^tBu_2Me)_2$.

In the case of X = F or an oxygen-based ligand such as OCH_2CF_3 or $OSiPh_3$, reactivity is again dominated by cleavage of the Ru–X bond.[13] When 1 equiv of Me_3SiH is added to $RuHF(CO)(P^tBu_2Me)_2$, ^{19}F NMR spectroscopy confirms that the only F-containing product of the reaction is Me_3SiF, easily identified by the 10-line pattern (J_{H-F} = 7 Hz) at –157.8 ppm as well as the presence of ^{29}Si ($I = {}^1/_2$, 4.7% natural abundance) satellites (J_{Si-F} = 138 Hz[14]). The metal-containing product of this reaction is therefore $RuH_2(CO)(P^tBu_2Me)_2$.[15] This compound can be trapped with pyridine to form $Ru(H)_2(CO)(P^tBu_2Me)_2(py)$. If a Lewis base is not added, $RuH_2(CO)(P^tBu_2Me)_2$ decomposes to several products (as assayed by ^{31}P NMR spectroscopy) after 5 h.

If more than 1 equiv of Me_3SiH is added to the $RuH_2(CO)(P^tBu_2Me)_2$ solution, ^{31}P NMR shows a broad signal at 73.0 ppm as well as signals for two other products at 63.1 and 62.8 ppm. The broad signal at 73.0 ppm was previously observed when a solution of $RuH_2(H_2)(CO)(P^tBu_2Me)_2$ was subjected to repeated freeze–pump–thaw cycles to remove H_2. At –20 °C, this broad signal resolved into sharp signals at 76.0 and 71.2 ppm for $RuH_2(H_2)(CO)(P^tBu_2Me)_2$ and $RuH_2(CO)(P^tBu_2Me)_2$, respectively. Therefore, the observation of this signal indicates the presence of the participants in eq 4. The source of the H_2 can

$$RuH_2(CO)(P^tBu_2Me)_2 + H_2 \rightleftharpoons Ru(H)_2(H_2)(CO)(P^tBu_2Me)_2 \qquad (4)$$

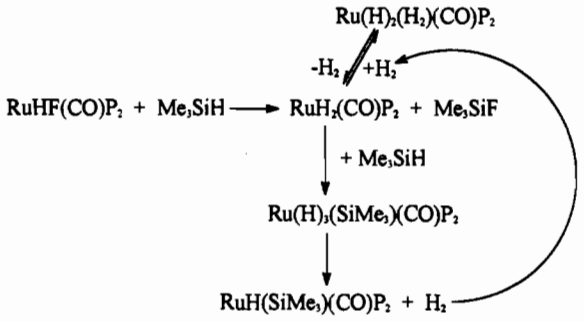
be deduced from the presence of the product signal at 62.8 ppm which has been assigned by ^1H and ^{31}P NMR spectroscopy to $RuH(SiMe_3)(CO)(P^tBu_2Me)_2$. This compound, prepared independently[4] from the reaction of the 14-electron fragment $Ru(CO)(P^tBu_2Me)_2$ with Me_3SiH, is suggested to have the structure shown in **III** on the basis of analogy to the crystallographically-characterized $RuH(SiHPh_2)(CO)(P^tBu_2Me)_2$.[16] The H_2 present is a byproduct of production of $RuH(SiMe_3)(CO)(P^tBu_2Me)_2$ from $RuH_2(CO)(P^tBu_2Me)_2$ and Me_3SiH.[17] The suspicion that an intermediate may be involved in this transformation has led to the identification of the third product ($\delta(^{31}P)$ = 63.1 ppm) as having the formula $RuH_3(SiMe_3)(CO)(P^tBu_2Me)_2$. This compound can be prepared by adding 1 equiv of H_2 to $RuH(SiMe_3)(CO)(P^tBu_2Me)_2$. The room-



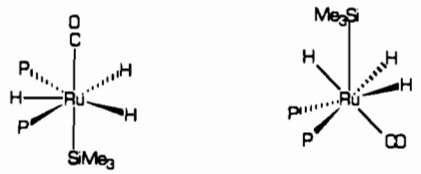
III

(9) Hauger, B. E.; Gusev, D. G.; Caulton, K. G. *J. Am. Chem. Soc.*, submitted for publication.
(10) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: London, 1984; p 949.
(11) A similar osmium compound $OsHCl(CO)(P^iPr_3)_2$ has been reported to react with Et_3SiH to form $Os(H)_2Cl(SiEt_3)(CO)(P^iPr_3)_2$: Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1991**, *10*, 462.
(12) For $HSiMe_3 + C_6D_6 \rightleftharpoons DSiMe_3 + C_6D_{6-x}H_x$ catalyzed by $OsH(SiMe_3)(PMe_3)_4$ see: Berry, D. H.; Procopio, L. J. *J. Am. Chem. Soc.* **1989**, *111*, 4099.
(13) Similar R_3Si–OR bond formation reactions were recently reported. See ref 5.
(14) For other examples of J_{Si-F} for fluorosilanes, see: Webb, G. A., Ed. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 276.
(15) The possibility that $RuH_2(CO)(P^tBu_2Me)_2$ is stabilized by solvent is currently under investigation.
(16) Heyn, R. H.; Huffman, J. C.; Caulton, K. G. *New J. Chem.*, in press.
(17) The H_2 generated prevents complete consumption of $RuH_2(CO)P_2$ by serving as a trapping agent.

Scheme II



temperature ^{1}H NMR spectrum of $RuH_3(SiMe_3)(CO)(P^tBu_2Me)_2$ exhibits a broad hydride signal at –9.25 ppm which is resolved at –20 °C into two signals at –9.10 and –9.43 ppm in a ratio of 2:1. The presence of fine structure on the signal of intensity 2 is not consistent with a dihydrogen ligand. This signal is therefore assigned to two equivalent hydrides. Structures consistent with the low-temperature NMR data are shown in **IV**.[18,19]

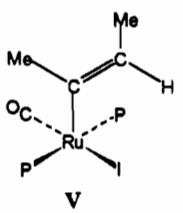


IV

The reaction of $RuHF(CO)(P^tBu_2Me)_2$ with 2 equiv of Me_3SiH is summarized in Scheme II. This reaction sequence can also be accessed by adding Me_3SiH to $Ru(H)_2(H_2)(CO)(P^tBu_2Me)_2$, which serves as a source of $RuH_2(CO)(P^tBu_2Me)_2$ as shown in eq 4.

Reactivity toward Alkynes. (1) Internal Alkyne. We first sought to explore simple binding of an unactivated alkyne to $RuHX(CO)P_2$ species. This is of special interest since the metal center is at most a two-electron electrophile (~16-valence electron count), while alkynes represent a potential four-electron donor.

One immediately encounters halide-based selectivity in that, for X = Cl or F, MeC_2Me fails to react over 1 week. Only unreacted $RuHCl(CO)P_2$ and free butyne are detected in C_6D_6. For X = I, there is a reaction to give the product **V** of *syn* (*cis*)

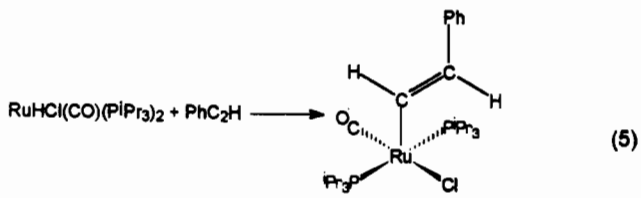


V

addition of Ru–H to the triple bond. This reaction is complete in 24 h, and no intermediate is detected (^{1}H and ^{31}P NMR), either at 25 °C or at –80 °C. The ^{1}H and ^{31}P NMR spectra of $RuHI(CO)P_2$ after 60 min under equimolar MeC_2Me at –40 °C show unreacted $RuHI(CO)P_2$, MeC_2Me, and $RuI(CMeCHMe)(CO)P_2$ (10% conversion). The ^{31}P NMR spectrum at –40 °C shows an AB spin system for the insertion product with J_{P-P} = 273 Hz. The inequivalence of the P^tBu_2Me groups is believed to be due to hindered rotation about the Ru–P axis caused by the steric demands of the MeCCHMe group. No other X groups ($OSiPh_3$, OR_f, and OPh) show reactivity with MeC_2Me under similar conditions. All of these, of course, are stronger donors than iodide.

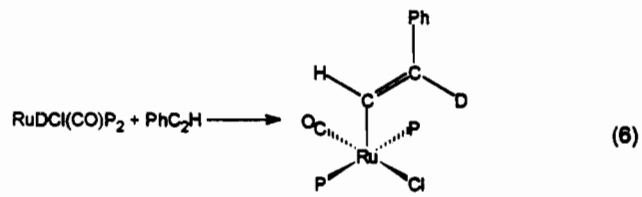
The mechanistic possibility of I^- dissociation as a preliminary step prior to alkyne coordination was considered. However, when this reaction is performed in the presence of 2 equiv of $(H_3C(CH_2)_5)_4NI$, no decrease in rate is detected, suggesting that dissociation of I^- is not involved.

(2) Terminal Alkyne. (a) Insertion. The group of Werner[20] has already demonstrated the reaction in eq 5. The crystal structure of $Os(HC{=}CHPh)Cl(CO)(P^iPr_3)_2$ shows that the final



(5)

product has the Ph and Os substituents oriented *trans* with respect to the double bond and the Ph group is located on C_β in relation to Os. This reaction could proceed by direct insertion of the alkyne into the Ru–H bond, or a vinylidene intermediate could be involved. We have addressed this question by studying the reaction of PhC_2H with the deuterated metal complex $RuDCl(CO)(P^tBu_2Me)_2$ (eq 6) to establish the fate of the two



(6)

hydrogens. With chemical shift assignments based on the literature,[21] it was possible to show that the deuterium location in the product is consistent with conventional *syn* addition of Ru—D to the C≡C bond. This rules out the alkyne migration (i.e., vinylidene) species $RuD(C{=}CHPh)Cl(CO)P_2$ as an intermediate in this mechanism.

It is interesting to note that $RuHCl(CO)_2(PMe_2Ph)_2$ also inserts into phenylacetylene.[22] However, a reaction of 5 days at 25 °C is required (compared to <1 h at 25 °C for $RuHCl(CO)(P^tBu_2Me)_2$) presumably due to the necessity of ligand dissociation from the coordinatively saturated $RuHCl(CO)_2(PMe_2Ph)_2$. The much faster reaction of $RuHCl(CO)(P^tBu_2Me)_2$ with phenylacetylene can be attributed to the unsaturation of this compound.[23]

Phenylacetylene reacts analogously (but slightly faster) with the iodo complex.[24] However, the iodide differs from the chloride

(18) (a) A question naturally arises concerning the proposed metal oxidation states for the similar compounds $Ru(H)_2(H_2)(CO)(P^tBu_2Me)_2$ and $Ru(H)_3(SiMe_3)(CO)(P^tBu_2Me)_2$. We believe that the $Ru(H)_2(CO)P_2$ fragment can oxidatively add the weaker Si–H bond (72 kcal/mol) but not the stronger H–H bond (104 kcal/mol).[18b] This conclusion is supported by the observation that $OsHCl(CO)(P^iPr_3)_2 + H_2$ forms the Os^{II}/H_2 adduct $OsH(H_2)Cl(CO)(P^iPr_3)_2$[18c] but $OsHCl(CO)(P^iPr_3)_2 + Et_3SiH$ results in oxidative addition of the Si–H bond.[11] (b) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1987; p 169. (c) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sanchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431.

(19) For other $M(H)_3(SiR_3)L_3$ (M = Fe, Ru, Os) compounds, see: (a) Knorr, M.; Gilbert, S.; Schubert, U. *J. Organomet. Chem.* **1988**, *347*, C17. (b) Haszeldine, R. N.; Malkin, L. S.; Parish, R. V. *J. Organomet. Chem.* **1979**, *182*, 323. (c) Procopio, L. J.; Berry, D. H.; *J. Am. Chem. Soc.* **1991**, *113*, 4039.

(20) Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295.

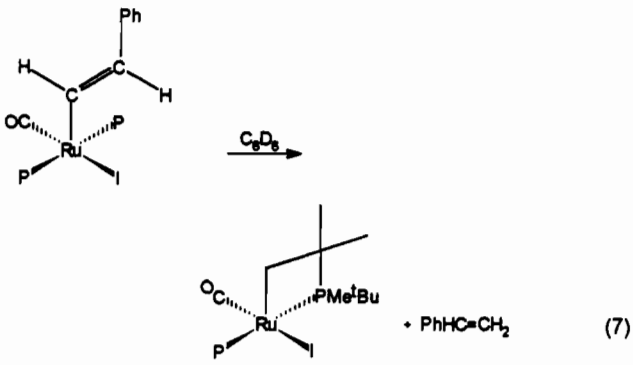
(21) Assignment of signals to the vinyl H_α and H_β positions follows that of Werner, which is, in turn, based on that for $Pt(CHCH_2)Br(PPh_3)_2$ reported by: Mann, B. E.; Shaw, B. L.; Tucker, N. I. *J. Chem. Soc. A* **1971**, 2667.

(22) Bray, J. M.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1989**, 589.

(23) $RuHCl(CO)(PPh_3)_3$ reacts with PhC_2H to give $Ru(HCCHPh)Cl(CO)(PPh_3)_2 + PPh_3$. This reaction is complete within 30 min at 25 °C, reflecting the facile loss of PPh_3 from $RuHCl(CO)(PPh_3)_3$. See: Torres, M. R.; Vegas, A.; Santos, A.; Ros, J. *J. Organomet. Chem.* **1986**, *309*, 169.

(24) Under comparable conditions, this reaction is complete for the iodide within 1 h, at which time the chloride reaction remains incomplete. There is no ^{1}H or ^{31}P NMR evidence for an adduct between $RuHI(CO)P_2$ and PhC_2H in toluene-d_8 at –80 °C.

in that the former reacts further (eq 7).[25] Over the course of 1

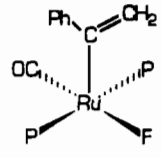


(7)

week at 25 °C in C_6D_6, ^1H NMR spectroscopy reveals the release of styrene. Both ^1H and ^2H NMR spectra show that solvent-derived deuterium is not involved (i.e., is not the source of the hydrogen which converts the coordinated vinyl group to styrene). The $^{31}P\{^1H\}$ NMR spectrum of the metal-containing product, an AB pattern with a large (280 Hz) $^2J_{P-P}$ value and one (30 ppm) upfield chemical shift, is diagnostic[26] of attack on a ligand C–H bond and production of a Ru–C bond in a four-membered ring. The ^1H NMR spectrum shows an AB pattern for the inequivalent protons of the metalated carbon. Neither Ru(HC=CHPh)Cl(CO)(P^tBu_2Me)$_2$ nor Ru(HC=CHPh)F(CO)(P^tBu_2Me)$_2$ (*vide infra*) eliminates styrene after 14 days at 25 °C.

The complete absence of the metalation reaction for RuX(CHCHPh)(CO)P_2 when X = Cl and F must be explained by the metal being less electron deficient (i.e., a higher lying LUMO) for the chloride and fluoride than for the iodide. This correlates with greater donor character for chloride and fluoride than for iodide. Steric considerations may also contribute to metalation. The larger size of iodide compared to chloride and fluoride could promote close approach of a C–H bond to Ru, thus facilitating metalation.

As observed in the case of reactivity with H_2/D_2, RuHF(CO)P_2 again displays differences in reactivity toward PhC_2H compared to the chloride and iodide compounds. The reaction of RuHF(CO)P_2 with 1 equiv of PhC_2H after 2 h results in the formation of three products as assayed by ^{31}P and ^1H NMR spectroscopies. The first of these is Ru(HC=CHPh)F(CO)P_2,[27] similar to the initial product formed in the RuHCl(CO)P_2 and RuHI(CO)P_2 reactions. This compound was synthesized independently from the reaction of Ru(HC=CHPh)Cl(CO)P_2 with CsF. On the basis of NMR and IR data, the second product from this reaction has been identified as Ru(PhC=CH$_2$)F(CO)P_2 and results from a different regiochemistry of alkyne insertion, as shown in VI.



VI

The third product is RuH(C_2Ph)(CO)P_2,[1] identified by its characteristic ^1H and $^{31}P\{^1H\}$ NMR signals. This product results from elimination of HF in a manner similar to the behavior of oxygen-based X groups (*vide infra*). An explanation for the observed HF elimination may be related to a hydrogen-bonding interaction between the electronegative F and the alkyne proton prior to insertion. Upon addition of PhC_2H to a solution of

(25) There is no metalation of the chloro vinyl complex after 1 week at 25 °C.
(26) Garrou, P. *Chem. Rev.* **1981**, *81*, 229.
(27) The observation of J_{H-H} = 13 Hz is consistent with a *trans* arrangement of the vinylic protons.

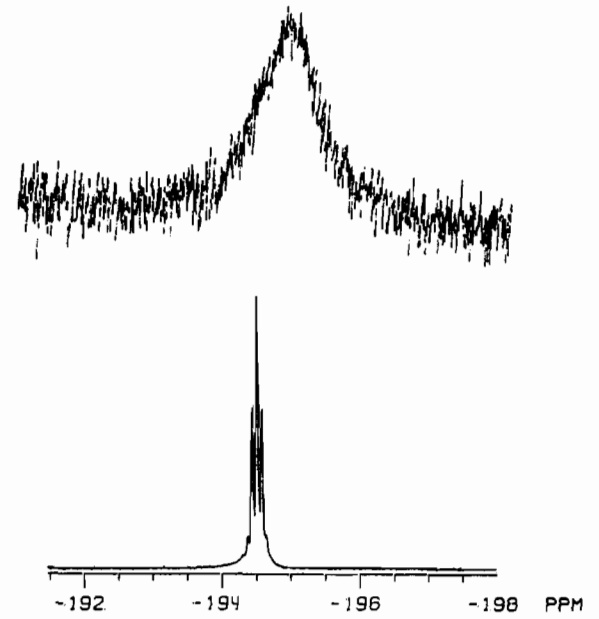
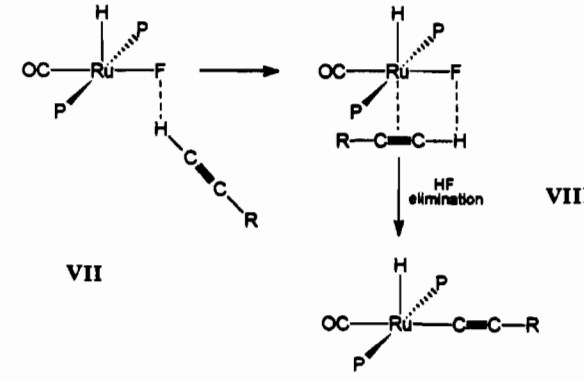


Figure 2. ^{19}F NMR spectrum (339 MHz, 25 °C, C_6D_6) of RuHF(CO)(P^tBu_2Me)$_2$ before (bottom) and after (top) addition of equimolar $^tBuC_2H$.

RuHF(CO)P_2, one immediately observes changes in the NMR signals for RuHF(CO)P_2: loss of J_{P-F} by ^{31}P NMR, loss of J_{H-F} by ^1H NMR, and a broadening of the fluoride signal by ^{19}F NMR. These changes suggested that an interaction may be present between F and the alkyne proton. However, this intermediate reacts quickly (<1 h) to give the final products, thus precluding further characterization. In an effort to learn more about this interaction, a bulkier alkyne, *tert*-butylacetylene, was used. This alkyne will not insert into the Ru–H bond of RuHX(CO)P_2 (X = I, Cl, F, OCH_2CF_3), presumably for steric reasons. However, it will interact with the fluoride of RuHF(CO)P_2. Figure 2 shows the ^{19}F NMR spectra of a sample of RuHF(CO)P_2 before and after addition of equimolar $^tBuC_2H$. In addition to this change observed by ^{19}F NMR spectroscopy, other spectroscopic changes are also observable. The ^1H NMR spectrum of the sample of equimolar RuHF(CO)P_2 and $^tBuC_2H$ shows a triplet at −24.00 ppm (J_{H-P} = 20 Hz) with no observable J_{H-F} compared to the doublet of triplets observed at −23.96 ppm (J_{H-P} = 19 Hz, J_{H-F} = 3 Hz) prior to addition of $^tBuC_2H$. The $^{31}P\{^1H\}$ NMR spectrum of this RuHF(CO)P_2/$^tBuC_2H$ solution shows a singlet at 52.3 ppm compared to the doublet observed at 52.1 ppm (J_{P-F} = 24 Hz) in the absence of $^tBuC_2H$. The solution IR spectrum of this equimolar mixture shows a new ν_{CO} at 1922 cm^{-1} compared to 1892 cm^{-1} for pure RuHF(CO)P_2. Unlike the case of the PhC_2H reaction, no elimination of HF and formation of RuH($C_2{}^t$Bu)(CO)P_2 are observed after 24 h at 25 °C. This result suggests that coordination of the alkyne to Ru is necessary for elimination of HF (VIII). All of the observed



VII VIII

spectroscopic changes are reversed upon removal of $^tBuC_2H$. These

spectroscopic changes are not consistent with coordination of the alkyne to ruthenium and are therefore attributed to an interaction between the fluoride and the alkyne H as depicted in **VII**. This interaction, which is absent for the chloro and iodo compounds, may facilitate elimination of HF.

(b) Elimination of HX (X = Alkoxide, Siloxide). As observed in the reaction toward H_2, a more Brønsted basic X group also alters the reactivity of $RuHX(CO)P_2$ toward a terminal alkyne. Oxygen-based ligands become active participants in the reaction. Phenylacetylene reacts with 2 h with $RuHX(CO)P_2$ (X = OR_f, OPh, $OSiPh_3$) to eliminate HX and form $RuH(C_2Ph)(CO)P_2$ (eq 8). This product is remarkable for being a five-coordinate

$$RuHX(CO)P_2 + PhC_2H \rightarrow RuH(C_2Ph)(CO)P_2 + HX \quad (8)$$

d^6 species devoid of ligands bearing lone pairs. However, filled acetylide π orbitals are available to provide a source of π donation to ruthenium (**IX**). Consistent with this explanation is the low

$$Ru\text{-}C{\equiv}C\text{-}Ph \leftrightarrow Ru^{-}{=}C{=}C^{+}\text{-}Ph$$

A

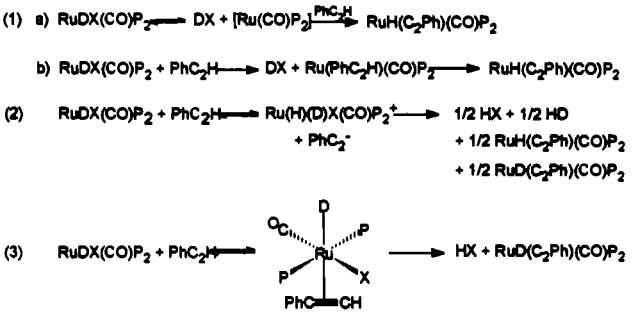
IX

CO stretching frequency for $RuH(C_2Ph)(CO)P_2$ (1906 cm^{-1}, which is comparable to that of $RuHBr(CO)P_2$).[28] The participation of the π system of the acetylide was recently proposed elsewhere.[29]

We have sought further spectroscopic evidence for such π donation by acetylide. The $^{13}C\{^1H\}$ NMR chemical shift for C_α of $RuH(C{\equiv}CPh)(CO)(P^tBu_2Me)_2$ is 140.7 ppm. This signal is significantly downfield of the 104.9 ppm C_α resonances found for the saturated complexes $Ru(C{\equiv}CPh)_2(CO)_2(PEt_3)_2$ (104.9 ppm)[30] and *cis,trans*-$RuH(C{\equiv}CPh)(CO)_2(PMe_2Ph)_2$ (111.7 ppm).[31] The downfield location of the C_α resonance for $RuH(C{\equiv}C\text{-}Ph)(CO)(P^tBu_2Me)_2$ is consistent with the presence of some allenic contribution from resonance structure **A** in **IX**. Similar effects on ^{13}C NMR chemical shifts have been observed in both organic[32] and organometallic[33] systems containing a C≡C unit capable of resonance stabilization. For comparison to a system devoid of π-acid ligands, the ^{13}C NMR chemical shift of C_α in $CpRu(PMe_3)_2(CC^tBu)$ is 91.5 ppm.[33]

We have considered the three mechanisms shown in Scheme III for eq 8. The scheme specifically deals with a deuterium-labeled metal. Mechanism 1 involves either preliminary (reaction 1a) or acetylene-induced (reaction 1b) reductive elimination of metal-bound hydride together with X. If the reagent ruthenium compound is Ru–D-labeled, both mechanisms result in complete disappearance of label from the metal complex. Mechanism 2 involves protonation of the metal by the weakly Brønsted acidic alkyne. The equivalence (either structure-based on resulting from probable fluxionality) of H and D in the cationic intermediate (as an intimate ion pair with PhC_2^-) then predicts 50% loss of label. Mechanism 3 begins with alkyne coordination. One (kinetically likely) isomer of many is shown; any one with X *cis* to alkyne will suffice. Elimination of alkyne hydrogen with the

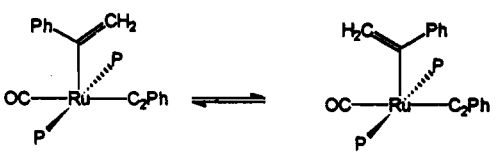
Scheme III



Brønsted basic group X (see Discussion) completes a reaction in which no label is lost.

The experimental result is that $RuD(OSiPh_3)(CO)P_2$ reacts with PhC_2H with complete retention of deuterium by the metal (both ^1H and ^2H NMR evidence). Mechanism 3 is therefore supported.

Reaction of $RuH(C_2Ph)(CO)(P^tBu_2Me)_2$ with PhC_2H. We find that $RuH(C_2Ph)(CO)P_2$ reacts with PhC_2H (1 equiv, 25 °C, <15 min, C_6D_6) to give two major products[34] (integration 100:65 by $^{13}P\{^1H\}$ NMR).[35] Each of these products has been identified in part by independent synthesis. The major product is $Ru(CH{=}CHPh)(C_2Ph)(CO)P_2$ and results from insertion of PhC_2H into the Ru—H bond of $RuH(C_2Ph)(CO)P_2$. This compound was independently synthesized by the reaction of the previously discussed $Ru(CH{=}CHPh)Cl(CO)P_2$ with LiC_2Ph. The observation of J_{H-H} = 13 Hz for the vinylic protons of $Ru(CH{=}CHPh)(C_2Ph)(CO)P_2$ confirms their *trans* stereochemistry.[36] The second product has been identified as $Ru(PhC{=}CH_2)(C_2Ph)(CO)P_2$ and results from a different regiochemistry of alkyne insertion (as shown in **VI** for X = F). This compound shows a broad $^{31}P\{^1H\}$ NMR signal at 25 °C which is resolved into two signals at –40 °C. Two broad signals for the hydrogens on C_β are observed at room temperature, each of which is resolved into two singlets (four signals in total) at –40 °C. This variable-temperature behavior is consistent with hindered rotation about the Ru—C bond due the increased steric demands of the phenyl group on C_α as shown in **X**. The compound



X

$Cp_2HMo((F_3C)C{=}CH_2)$ displays similar conformational isomerism.[37] Evidence for steric crowding was noted in $Ru(H_3CC{=}HCH_3)I(CO)P_2$, which also contains an R group on C_α. The lack of an observable J_{H-H} for the vinylic protons of Ru-

(28) We have considered that there might be significant vibrational mixing of C≡C and C≡O stretching motions, with the consequence that the lower of the two observed frequencies is "repelled" from the unmixed ν_{CO} value by the higher energy $\nu_{C\equiv C}$ motion to an uncharacteristically low value. However, the vibrational spectrum of $RuH(^{13}CCPh)(CO)P_2$ shows ν_{CO} changed by less than 2 cm^{-1} from its ^{12}C isotopomer.

(29) Hanna, J.; Geib, S. J.; Hopkins, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 9199 and references therein.

(30) Sun, Y.; Taylor, N. J.; Carty, A. J. *J. Organomet. Chem.* **1992**, *423*, C43. It has been concluded from structural data that there is not much Ru–C multiple bonding in these compounds: Sun, Y.; Taylor, N. J.; Carty, A. J. *Organometallics* **1992**, *11*, 4293.

(31) Bray, J. M.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1989**, 589.

(32) Rubin, Y.; Knobler, C. B.; Diederich, F. *J. Am. Chem. Soc.* **1990**, *112*, 1607.

(33) Lemke, F. R.; Bullock, R. M. *Organometallics* **1992**, *11*, 4261.

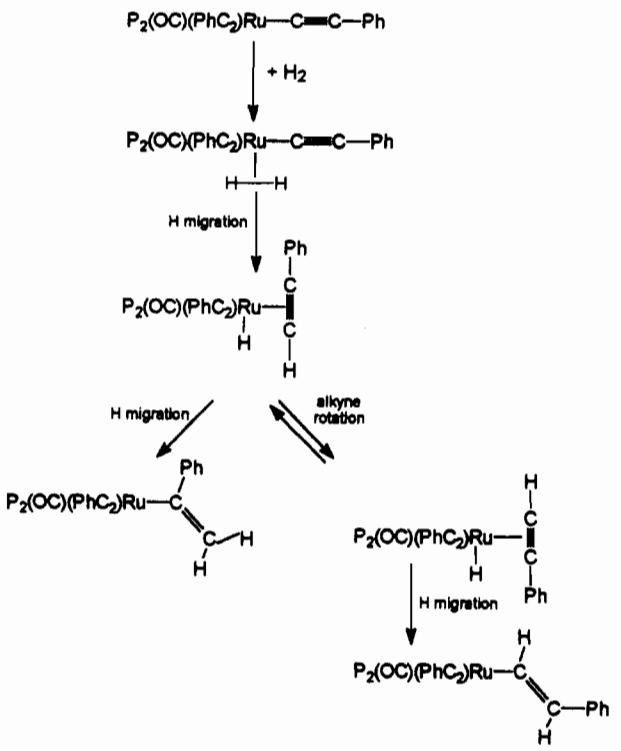
(34) In addition, the compound $Ru(C_2Ph)_2(CO)(P^tBu_2Me)_2$ has been identified as a minor product (~10%) of this reaction. This result contrasts with the observation that the reaction of $OsH(H_2)(C_2Ph)(CO)(P^iPr_3)_2$ (a source of $OsH(C_2Ph)(CO)(P^iPr_3)_2$ via H_2 loss) reacts with PhC_2H to give predominantly (87%) $Os(C_2Ph)_2(CO)(P^iPr_3)_2$: Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1993**, *12*, 663.

(35) It is interesting to note that internal competition experiments reveal that PhC_2H reacts faster with $RuH(X)(CO)P_2$ when X = C_2Ph than when X = Cl. This is consistent with higher reactivity for the compound containing the weaker π donor, acetylide.

(36) Typical values of the *trans* J_{H-H} for the –CH=CHR group are 13–20 Hz. For examples, see: (a) Reference 21. (b) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1971**, *27*, 373. (c) Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97. (d) Booth, B. L.; Hargreaves, R. G.; *J. Chem. Soc. A* **1969**, 2766. (e) Reference 20.

(37) Nakamura, A.; Otsuka, S. *J. Mol. Catal.* **1975**, 285.

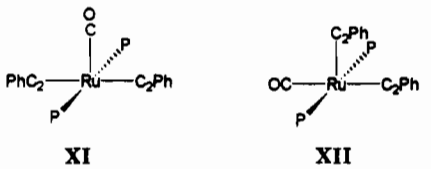
Scheme IV



$(PhC{=}CH_2)(C_2Ph)(CO)P_2$ at −40 °C is consistent with a *gem* arrangement for these two protons.[38]

It is interesting to note that the addition of H_2 to $Ru(C_2Ph)_2(CO)(P^tBu_2Me)_2$ results in the formation (5:1 mole ratio) of $Ru(PhC{=}CH_2)(C_2Ph)(CO)(P^tBu_2Me)_2$ and $Ru(HC{=}CHPh)(C_2Ph)(CO)(P^tBu_2Me)_2$. The formation of the insertion product with Ph on C_α as well as the C_β product presents an interesting mechanistic question. A mechanism consistent with the observed products is depicted in Scheme IV.

Synthesis, Spectra, and Structure of $Ru(C_2Ph)_2(CO)(P^tBu_2Me)_2$. It is possible to further elaborate the ligands in $Ru(CHCHPh)Cl(CO)P_2$. Reaction with LiC_2Ph yields $Ru(CHCHPh)(C_2Ph)(CO)P_2$, which then reacts with excess PhC_2H to eliminate styrene, with production of $Ru(C_2Ph)_2(CO)P_2$. This sequence need not be executed stepwise but can be carried out in one pot from $RuHCl(CO)P_2$, provided stoichiometric LiC_2Ph and excess PhC_2H are employed. The group of Werner has reported the synthesis of $Ru(C_2Ph)_2(CO)(P^iPr_3)_2$.[38d] However, the question of the structure of this compound was not addressed.[39] Possible geometries for $Ru(C_2Ph)_2(CO)P_2$ are **XI** and **XII**. (Both have



XI

XII

at least one C_2Ph *cis* to the empty site as required by Scheme IV.) The observation (at 25 °C) of one virtual triplet by ^1H NMR spectroscopy for the potentially diastereotopic ^{t}Bu groups of $Ru(C_2Ph)_2(CO)(P^tBu_2Me)_2$ as well as the observation of one acetylide C_α triplet (J_{P-C} = 14 Hz) by $^{13}C\{^1H\}$ NMR spectroscopy at natural abundance) are consistent with the geometry shown in **XI**. However, rapid exchange of the inequivalent C_2Ph groups in structure **XII** is equally consistent with the data. Therefore, multinuclear low-temperature NMR studies were undertaken to investigate whether $Ru(C_2Ph)_2(CO)(P^tBu_2Me)_2$ is a fluxional molecule.

When a toluene-d_8 solution of $Ru(C_2Ph)_2(CO)P_2$ is cooled to −80 °C, the $^{31}P\{^1H\}$ NMR spectrum shows two singlets at 46.0 and 45.8 ppm in a ratio of ~2:1. The absence of doublets from P–P coupling indicates that the phosphines remain equivalent within a molecule at −80 °C and thus requires assignment of the two lines to two distinct molecules. The two signals could be due to the presence of **XI** and **XII**, assuming interconversion is slow at −80 °C. Alternatively, the data are equally consistent with slow interconversion between conformers which differ in rotational conformation about the Ru–P bonds. This has been observed[1] in low-temperature $^{31}P\{^1H\}$ NMR spectra of other $RuHX(CO)(P^tBu_2Me)_2$ systems. The alkyl-region ^1H NMR spectrum at −80 °C shows two ^{t}Bu chemical shifts, consistent with the presence of two species. The aromatic region suffers from accidental degeneracy since only one well resolved set of ortho, meta, and para phenyl signals is present.

In the hope that the C_α positions would be less likely to display accidental degeneracy, a sample of $Ru(C_2Ph)_2(CO)P_2$ was prepared in one pot from $RuHCl(CO)P_2$ using 90% ^{13}C-enriched Li*CCPh and H*CCPh. The $^{31}P\{^1H\}$ NMR spectrum (25 °C, CD_2Cl_2) of this labeled compound displays a five-line pattern that results from the presence of three isotopomers: $Ru(C_2Ph)_2(CO)P_2$, $Ru(*CCPh)(C_2Ph)(CO)P_2$, and $Ru(*C_2Ph)_2(CO)P_2$. The doublet and triplet for $Ru(*CCPh)(C_2Ph)(CO)P_2$, and $Ru(*C_2Ph)_2(CO)P_2$, respectively, each display J_{P-C} = 14 Hz, which duplicates the value observed for the C_α triplet in the natural-abundance $^{13}C\{^1H\}$ NMR spectrum of unlabeled $Ru(C_2Ph)_2(CO)P_2$. The presence of the doubly labeled $Ru(*C_2Ph)_2(CO)P_2$ allows for the observation of a J_{C-C} in the event that the acetylide ligands are inequivalent (as in **XII**) at low temperature. The $^{31}P\{^1H\}$ spectrum observed at −85 °C in CD_2Cl_2 shows two distinct five-line patterns which we assign to the presence of $Ru(C_2Ph)_2(CO)P_2$, $Ru(*CCPh)(C_2Ph)(CO)P_2$, and $Ru(*CCPh)_2(CO)P_2$ isotopomers of two distinct Ru–P rotamers. The major five-line pattern displays J_{P-C} = 14 Hz while the minor pattern has J_{P-C} = 12 Hz. A phosphorus signal possessing two distinct J_{P-C} values due to a doubly labeled species with inequivalent acetylides is not observed. Thus, on the ^{31}P NMR time scale (146 MHz, −85 °C), no evidence for structure **XII** is present.

Finally, the $^{13}C\{^1H\}$NMR spectrum of the labeled sample at −85 °C in CD_2Cl_2 shows only two C_α triplets, the major at 128.9 ppm with J_{P-C} = 14 Hz and the minor at 131.1 ppm with J_{P-C} = 12 Hz. No $^{13}C-^{13}C$ coupling is observed, indicating that the acetylide ligands in each rotamer remain equivalent at −85 °C.

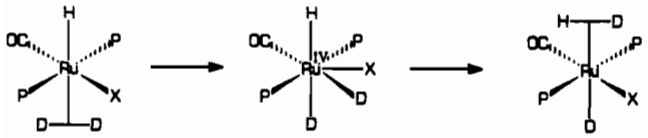
These observations indicate that the two species observed at low temperature do not result from the freezing out of a dynamic process that interconverts structures **XI** and **XII** since both low-temperature species possess equivalent acetylide ligands. In conclusion, these multinuclear variable-temperature NMR studies indicate that $Ru(C_2Ph)_2(CO)P_2$ displays equivalent acetylide ligands from +25 to −85 °C. While this is consistent with structure **XI**, structure **XII** with a low barrier to acetylide site exchange cannot be rigorously excluded.

Infrared spectroscopy shows that $Ru(C_2Ph)_2(CO)P_2$ has a comparatively high ν_{CO} value (1933 cm^{-1}) relative to all of the five-coordinate $RuYZ(CO)P_2$ compounds discussed in this work. (Only one ν_{CC} is visible.) For comparison to other acetylide-containing compounds, ν_{CO} for $RuH(C_2Ph)(CO)(P^tBu_2Me)_2$ is 1908 cm^{-1} and ν_{CO} for $Ru(HC{=}CHPh)(C_2Ph)(CO)(P^tBu_2Me)_2$ is 1910 cm^{-1}. In both of these compounds, the C_2Ph group is believed to be *trans* to CO with H or HC=CHPh at the apex of the square-based pyramid. The much higher ν_{CO} for $Ru(C_2Ph)_2(CO)(P^tBu_2Me)_2$ suggests a fundamental difference

(38) J_{H-H} values for $-CR{=}CH_2$ are typically small (1–5 Hz). For examples, see: (a) Scordia, H.; Kergoat, R.; Kubicki, M. M.; Guerchais, J. E. *J. Organomet. Chem.* **1983**, *249*, 371. (b) Amaudrutm, J.; Leblanc, J.-C.; Moise, C.; Sala-Pala, J. *J. Organomet. Chem.* **1985**, *295*, 167. (c) Reference 22. (d) Reference 20.

(39) A square-base pyramidal structure with CO at the apex and the C_2Ph groups *trans* has been proposed for a similar osmium compound, $Os(C_2Ph)_2(CO)(P^iPr_3)_2$: Werner, H.; Meyer, U.; Esteruelas, M. A.; Sola, E.; Oro, L. A. *J. Organomet. Chem.* **1989**, *366*, 187.

Scheme V

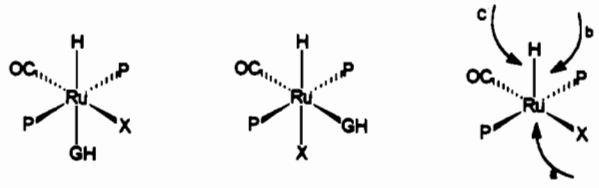


in the structure of this compound compared to the other C_2Ph-containing species described here. Structure **XI** with CO *trans* to an empty site would account nicely for the higher ν_{CO} observed for $Ru(C_2Ph)_2(CO)(P^tBu_2Me)_2$. Therefore, infrared spectroscopy supports structure **XI**.

Discussion

Degree of Substrate Binding. We reported earlier[1] that the species $RuH(OCH_2CF_3)(CO)P_2$ binds pyridine (in toluene solvent) but that this involves a modest formation constant, so that excess pyridine was required for >90% formation of adduct. Pyridine is a base with only moderate steric bulk (especially toward the flat channel created by the ^{t}Bu groups of $RuHX(CO)(P^tBu_2Me)_2$). It is therefore not surprising that there is no spectroscopic evidence, even at −80 °C, of binding of the bulkier ligands MeC_2Me and PhC_2H to this complex. Even H_2 binding is quite weak (X = F, Cl, I) at the low concentration of H_2 when it is saturated in toluene.[40] Since the compounds $RuHX(CO)P_2$ (X = F, Cl, I) exchange with D_2 within minutes at 25 °C, each must bind H_2 (or D_2) to a *kinetically-significant* extent, even if the equilibrium mole fraction of the adduct is extremely small. We conclude that the equilibrium constant for H_2 binding is smaller for the better donor fluoride complex since it is less Lewis acidic (i.e., "less unsaturated"). This will contribute to slower exchange for the fluoride. For alkynes, weak binding is a consequence of both steric and electronic (π-donor) effects, and spectroscopically undetectable species nevertheless permit rearrangement to σ-vinyl products to proceed to *completion*.

Stereochemistry of Substrate Binding. The reactivity of $RuH(X)(CO)P_2$ (X = halide) toward G–H (G = H, C_2Ph) is noteworthy in that, while addition of H_2 (or D_2) or PhC_2H to the "obvious" site (i.e., **a**, *trans* to hydride as in **XIII**) yields a



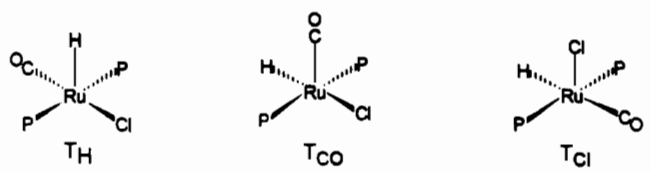
XIII **XIV**

stereochemistry which allows reactivity between G–H and the Ru–X bond, reaction between G–H and the Ru–H bond is precluded. Isomer **XIV**, where H and G–H are *cis*, is required, yet the body of evidence concerning intramolecular rearrangements of octahedral d^6 compounds indicates that a unimolecular rearrangement of **XIII** to **XIV** will be a high-energy (thus slow) process.[41] Moreover, for phosphines as bulky as P^tBu_2Me, such as intramolecular rearrangement is especially disfavored since any mechanism would aggravate repulsion with and between phosphine ligands.

We have considered a mechanism that effects H/D_2 exchange by means of a Ru^{IV} intermediate as shown in Scheme V. A similar mechanism has been proposed for the intramolecular exchange between the *trans* hydride and dihydrogen observed in $MH(H_2)(\widehat{PP})_2^+$ (M = Fe, Ru, Os; $\widehat{PP}$ = dppe, depe) by the group of Morris.[42] It is interesting to note that $[Ru(H)(H_2)(depe)_2]^+$ shows separate ^{1}H NMR (200 MHz) signals for the hydride and dihydrogen ligands from −73 to +37 °C, indicating that H/H_2 exchange is slow on the NMR time scale. The H/D_2 exchange reactions of $RuHX(CO)P_2$ (X = halide) with excess D_2 are complete within minutes at 25 °C. While the mechanism in Scheme V cannot be ruled out, we do not believe it to be operative in the $RuHX(CO)P_2$ system. For this mechanism, both steric and electronic factors suggest that the rate of H/D_2 exchange as a function of X should follow the ordering F > Cl > I, in contrast to our observations. The increased donor ability of F (which enhances the oxidizability of the metal) and its small size (which lessens steric congestion) should facilitate the formation of the seven-coordinate Ru^{IV} intermediate. In addition to these shortcomings regarding the H/D_2 exchange, Scheme V does not provide a means for obtaining the *cis* arrangement of H and alkyne necessary for insertion into the Ru–H bond.

The group of Werner has reported that $OsHCl(CO)(P^iPr_3)_2$ reacts quantitatively with 1 equiv of H_2 to give $OsH(H_2)Cl(CO)(P^iPr_3)_2$.[43] In the proposed octahedral geometry, the hydride and dihydrogen are *trans*. The ^{1}H NMR spectrum of this compound (20 °C, C_6D_6, 400 MHz) shows distinct, well-resolved signals for both the hydride and the dihydrogen ligands, indicating that H/H_2 exchange is slow on the NMR time scale. In the $RuHX(CO)P_2$ (X = halide) system, exchange of Ru–H with D_2 is a fast process which shows a noticeable dependence on X. If the mechanism for H/D_2 exchange involved oxidation of the metal to M^{IV} as the Scheme V, H/D_2 (or H/H_2) exchange should be faster for the more easily oxidized metal Os. To account for all of these observations, we therefore propose that the isomer required for G–H reactivity with the Ru–H bond (**XIV**) is not formed from **XIII** but rather by attack on $RuHX(CO)P_2$ from direction **b** (in the RuHX plane).

Energetics of Substrate Binding. We have done both *ab initio* calculations and MO analysis, with the help of extended Hückel calculations, in order to understand the influence of X on the reactivity of $RuH(X)(CO)P_2$.[44] The calculation at the *ab initio* SCF level of the potential energy surface (Figure 3) $E = f(\alpha,\beta)$, where α and β are respectively the H–Ru–X (shown for X = Cl) and H–Ru–CO angles, shows that T_H is not situated in a deep



well but in a shallow valley. This valley, which joins T_H to T_{CO} (CO *trans* to the empty site), corresponds to an opening of the Cl–Ru–H (α) angle while the H–Ru–(CO) angle (β) is maintained close to 90°. In contrast, opening the H–Ru–CO (β) angle with the Cl–Ru–H angle maintained at 90° (transformation of T_H into T_X) requires considerable energy. In general, the addition of a nucleophile between H and X (**b**) leading to an isomer where the nucleophile is trans to CO is easy compared to attack between

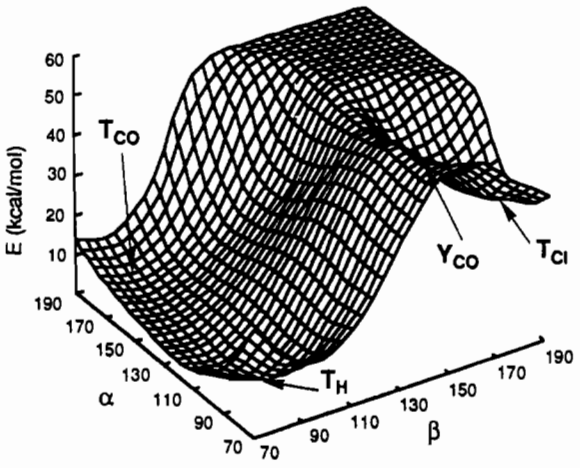
(40) We cannot therefore *prove* that an H_2 adduct mediates the exchange of RuH with D_2. Direct attack of D_2 on the hydride ligand is equally consistent with the available data but conflicts with the "central dogma" of coordination chemistry that substrate coordination mediates all reactions.

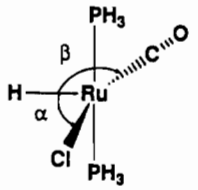
(41) For example, the intramolecular rearrangement of *fac*-$W(CO)_3(^{13}CO)$(dppm) to *mer*-$W(CO)_3(^{13}CO)$(dppm) requires 2 weeks at 25 °C to achieve equilibrium: Darensbourg, D. J.; Zalewski, D. J.; Plepys, C.; Campana, C. *Inorg. Chem.* **1987**, *26*, 3727.

(42) (a) Bautista, M. T.; Cappillani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4876. (b) Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780.

(43) Andrillo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sanchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431. No information concerning the observation of H/H_2 or H/D_2 exchange is presented.

(44) The details on the calculation procedure are given by: Poulton, J. T.; Sigalas, M. P.; Eisenstein, O.; Caulton, K. G. Submitted for publication. In this potential energy surface (PES), the two phosphines are maintained perpendicular to the RuHCl(CO) plane and only α and β are varied. Optimization of T_{Cl}, which is the only secondary minimum on this PES (19.7 kcal/mol), confirms that it is a high-energy structure.





E(kcal/mol)	
T_H	0.
T_{CO}	6.8
T_{Cl}	26.8
Y_{CO}	38.1

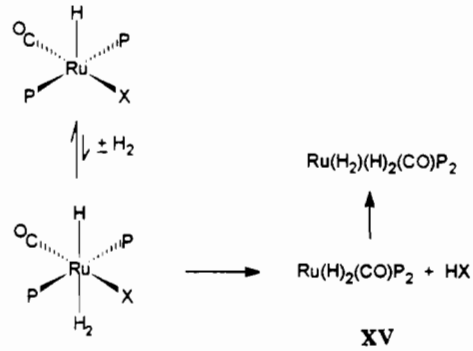
Figure 3. *Ab initio* potential energy surface for $RuHCl(CO)(PH_3)_2$ with changes in ∠H–Ru–Cl(α) and ∠H–Ru–CO(β).[44]

H and CO (**c**), to give an isomer where the nucleophile is trans to X. The calculations show that isomer T_X lies at high energy for all X groups. It is also clear that the *slope* of the valley in the direction of increasing H–Ru–X angle should be important in the determining the ratio of attack along **a** *vs* **b**. The representative structure (although not a minimum) along the more accessible valley is T_{CO}. As this structure becomes higher in energy, attack along **b** (*vs* **a**) becomes more difficult. This should diminish the amount of product in which CO is *trans* to the incoming nucleophile (i.e., in which the *hydride and X are both cis to the incoming nucleophile*). The energy difference from our *ab initio* calculations between T_H and T_{CO} is equal to 12.3 kcal/mol for X = F and 6.8 kcal/mol for X = Cl. It is thus easier to open the Cl–Ru–H angle than the F–Ru–H angle.[44] Attack along **c** remains unfavorable since T_F is considerably higher than T_{CO}.

While it has been established[45] that the ligand trans to the empty site in a square pyramid should have the strong σ-donating power, H and CO have comparable trans effects (i.e., they have equivalent capabilities to be *trans* to the empty site). As a result, the greater stability of T_H *vs* T_{CO} originates mainly from a push–pull mechanism between the π donor X and the π acceptor CO (i.e., a three-orbital, four-electron interaction).[1] In T_H, the two lone pairs of the halide are stabilized by π^*_{CO} in a push–pull mechanism while in the T_{CO} structure only one such stabilization occurs.

The monotonic behavior of electronic properties with change of halide as shown by the variation in CO stretching frequency[1] suggests that the F/Cl calculation may be extrapolated to the Cl/I case. Therefore, the difference in energy between T_{CO} and T_H should be smaller for I than for Cl. The same factors which keep this *five*-coordinate isomer relatively low in energy should act to keep *six*-coordinate isomer **XIV** close (<10 kcal/mol higher) in energy to **XIII**. Since the calculations show that T_{CO} is not an energy minimum, it will not develop an equilibrium concentration, and thus we envision H_2 approach from attack angle **b** on the ground-state structure (T_H) of $RuHX(CO)P_2$ as the mechanism of exchange. The rate of RuH/D_2 exchange will

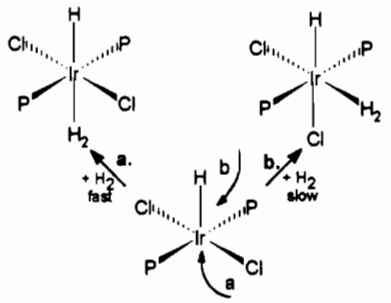
Scheme VI



XV

now depend on the energy of **XIV** relative to **XIII**, and the stronger π donor X (i.e., chloride *vs* iodide) will have the higher energy and thus the slower rate. In summary, both the D_2 binding constant and the energy to achieve the necessary intermediate **XIV** are made more unfavorable as the donor ability of X is increased (I < Br < Cl < F).

In the present case, *both* directions of approach (**a** and **b**) by H_2 have rates sufficient for a half-life of exchange of less than 5 min. This contrasts markedly to the case[46] of $IrHCl_2P_2$, where



reaction a (the "obvious" addition site) occurs in less than 5 min, while the other attack route (path **b**) requires hours (exchange of $IrHCl_2P_2$ with D_2 only *begins* to become evident after several hours at 25 °C).

The reality of two attack paths is also evident from our results of $RuHI(CO)P_2$ reacting with MeC_2Me. Here, although we see no evidence for alkyne binding *trans* to hydride (even at −80 °C), this isomer would not readily lead to Ru–H addition to the triple bond. Hence, it is again necessary to invoke addition of alkyne *cis* to hydride (path **b**). In contrast to the D_2 reaction, however, this reaction is slow (half-life of ~10 h at millimolar concentrations). This is consistent with steric hindrance as shown by the lack of alkyne binding even *trans* to hydride.

Hydrogen Transfer to X. Although rate and equilibrium constants prevent buildup of detectable concentrations of intermediates in the hydrogenolysis reactions of Ru–O bonds, some mechanistic discussion is warranted. Because the X group is already *cis* to the open coordination site (**XIII**), elimination of HX can occur after substrate attack from *either* the **a** or **b** direction. In Scheme VI, the primary product of H_2 binding[47] has diminished π donation from X to Ru and thus enhanced Brønsted basicity at X. For X = Cl or F, the thermodynamics of subsequent proton transfer to X are apparently endergonic (but are found to be improved by added base DBU, in the base-promoted heterolytic splitting of H_2 observed[48] for other late transition metals). The enhanced Brønsted acidity[49] of coordinated H_2,

(45) Rachidi, I. E.-I.; Eisenstein, O.; Jean, Y. *New J. Chem.* **1990**, *14*, 671. Riehl, J.-F.; Jean, Y.; Eisenstein, O.; Pélissier, M. *Organometallics* **1992**, *11*, 729.

(46) Gusev, D. G.; Bakhmutov, V. I.; Grushin, V. V.; Volpin, M. E. *Inorg. Chim. Acta* **1990**, *117*, 115.

(47) We propose H_2 to add but not oxidize the metal to Ru(IV) because the CO ligand diminishes the reducing power of this metal complex. This assumption is to some extent affirmed by the finding that $RuH_4(CO)P_2$ is $Ru^{II}(H_2)(H)_2(CO)P_2$.

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leads to H–F and H–O bond formation and elimination. Another factor which contributes to the occurrence of H–F and H–O elimination reactions is the increased filled/filled repulsion between M d_π and X p_π orbitals in the six-coordinate H_2 adducts which is alleviated by HX elimination.

It is important to note that species **XV**, which is a 16-electron species devoid of any stabilization of internal π donation, is not stable. It is a Lewis acid which strongly binds H_2. In contrast, when a species $RuHX(CO)P_2$ contains a π-donor ligand X, such π donation in the five-coordinate species raises the energy of its LUMO and thus inhibits binding of H_2. This is why we fail to see detectable concentrations of H_2 adducts when X = Cl or even our weakest π donor, iodide.

A labeling study has shown that it is the alkyne hydrogen which is lost to $OSiPh_3$ in eq 9. While we have detailed a

$$RuH(OSiPh_3)(CO)P_2 + PhC_2H \rightarrow RuH(C_2Ph)(CO)P_2 + HOSiPh_3 \quad (9)$$

mechanism (reaction 3 in Scheme III) in which this proton transfer is intramolecular within a six-coordinate alkyne adduct, the labeling study does not rigorously exclude proton transfer to X during a bimolecular encounter prior to Ru/C bond formation (**XVI**). The observation of interaction between the fluoride of

$P_2(OC)HRu—OSiPh_3$
$\vdots$
$H—CCPh$

XVI

$RuHF(CO)P_2$ and the H of $^tBuC_2H$ might be interpreted as favoring such a mechanism. However, no elimination of HF is observed in this reaction after 1 day at 25 °C. We therefore believe that proton transfer to X prior to Ru–C bond formation is less likely because of the modest acidity of terminal alkynes but especially because of the diminished Brønsted basicity of coordinated Ph_3SiO^- in the *five*-coordinate compound. Even the *free* siloxide is less basic than an alkyne. The act of π coordination (substrate-promoted activation) will make the alkyne more Brønsted acidic (by stabilizing the resulting anion) and will diminish siloxide → Ru π donation, thereby making that oxygen more Brønsted basic. The latter is particularly true since there is now four-electron destabilization between ruthenium and not only $OSiPh_3$ but also the four-π-electron alkyne system serving as only a two-electron donor. It is generally true that a terminal alkyne in a two-electron-donor bonding role (e.g., **XVII** of eq 10)

$$(dppe)(CO)_3W(PhC_2H) \rightarrow (dppe)(OC)_3W{=}C{=}CHPh \quad (10)$$

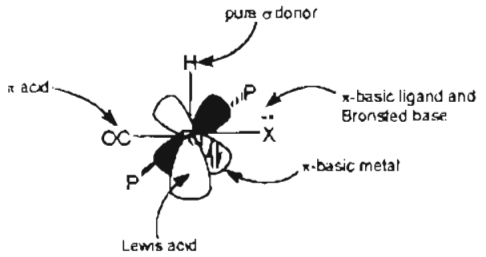
XVII

exhibits facile migration to an isomer, which relieves the four-electron destabilization.[50] The lack of a reactive coligand in **XVII** (analogous to $OSiPh_3$) leaves rearrangement to vinylidene as the only viable way to alleviate the destabilization.

Steric factors will also influence the observed elimination of HX. The preferred rotational conformation of PhCCH after binding will be influenced by the bulky nature of the X group ($OSiPh_3$, OCH_2CF_3, OPh). The most favorable orientation will be like that with the bulky Ph substituent of the alkyne oriented away from X. The H is then *syn* to X and properly positioned for HX elimination.

The idea that the filled π orbitals of an acetylide ligand can function as a donor alternative to X group lone pairs is supported by both ν_{CO} and ^{13}C NMR spectral data. The mere occurrence of eq 9 (Ru–O bond gives way to a Ru–acetylide bond) reveals the considerable thermodynamic strength of the latter bond. For an electropositive metal (Sc), where L → M π donation should be maximum, it was noted without explanation that the Sc–$C_2{}^tBu$ bond dissociation energy is unusually large.[51]

Alkynes reveal a dramatic (qualitative) difference when X is halide or siloxide. This originates in part from π donation by X preventing substrate binding in the case of 2-butyne, but it results from active bond making/breaking participation for PhC_2H when X is F or $OSiPh_3$. This arises because compound I is a multifunctional reagent (**XVIII**). The incorporation of so many



XVIII

functionalities in a monometallic compound is atypical in organometallic chemistry of noncluster compounds but provides an unusual opportunity to probe for selective organometallic reactivity.

Conclusions

Reactivity differences as dramatic as those reported here appear to be previously unrecognized, due perhaps to a lack of systematic study of the effect of variations as subtle as halide identity. This work suggests that such effects might be used profitably to modify catalytic reactivity and selectivity. The studies by Schrock[52] on the influence of the group OR_f on olefin metathesis reactivity should serve to stimulate further reliance on this approach.

Overall, the examples of proton transfer from coordinated reaction partner to ligand X in $RuHX(CO)P_2$ must be viewed as supporting evidence for the strongly polar ("ionic") character of the Ru–X bond (especially for X = OR, as supported by the calculations)[2] and thus the Brønsted basicity of the group X.

In conclusion, the reactivity of $RuHX(CO)P_2$ with G–H (G = H, SiR_3, C_2Ph) occurs exclusively at the Ru–H bond for X = Cl and I. However, for fluoride or for an oxygen-based X such as OCH_2CF_3 or $OSiPh_3$, reactivity is dominated by cleavage of the Ru–X bond. The reactivity of $RuHF(CO)P_2$ is unique. This compound displays reactivity at both the Ru–H bond and the Ru–F bond.

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