Ligand Redistribution Reactions of Five-Coordinate d^6 Species: $RuHX(CO)P_2$, IrH_2XP_2, and Cp*RuXP

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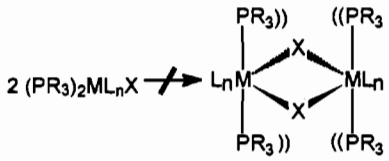
For the species $RuHXP_2(CO)$, IrH_2XP_2, and Cp*RuXP (P = bulky phosphine, X = halide or pseudohalide), both homometallic halide exchange ([M]XP + [M]YP′ ⇄ [M]YP + [M]XP′) and heterometallic halide exchange ([M]X + [M]′Y ⇄ [M]Y + [M]′X) are found to be quite rapid. In addition, hydride exchange occurs for $RuHCl(CO)P_2$ and $RuDCl(CO)P'_2$, as well as for $IrH_2Cl(P^tBu_2Ph)_2$ and $IrD_2Cl(P^tBu_2Me)_2$. Exchange is generally faster for halides than for hydrides yet is much slower for the groups phenoxide, $OSiPh_3$, and C_2Ph. These equilibria favor the better donating halide being bonded to the less electron-rich metal center. A variable-temperature ^1H NMR study of the degenerate exchange $Cp^*Ru(P^tBu_2Me)Cl + Cp^*Ru'(P^tBu_2Me)Br \rightleftarrows Cp^*Ru(P^tBu_2Me)Br + Cp^*Ru'(P^tBu_2Me)Cl$ establishes a second-order rate law with $\Delta H^‡ = 8.6 \pm 0.8$ kcal/mol and $\Delta S^‡ = -20 \pm 3$ cal/(mol K). These results clearly indicate the transient existence in solution of halide- and/or hydride-bridged dimers of monomeric metal complexes.

Introduction

We have been studying a series of unsaturated d^6 compounds which are formally unsaturated yet involve X → Ir π donation.[1] Our use of bulky ligands (phosphines and Cp*) in the species IrH_2XP_2, $RuHX(CO)P_2$, and Cp^*RuXP[2] was motivated by a desire to avoid loss of unsaturation by formation of six-coordinate dimers (eqs 1 and 2). We have therefore undertaken the present



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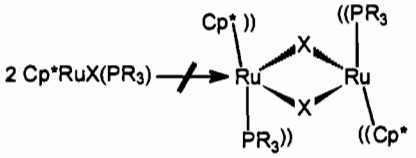

(2)

study to systematically examine the occurrence of *facile* X-ligand redistribution (eq 3) we have observed between pairs of these

$$MX + M'X' \rightleftharpoons MX' + M'X \qquad (3)$$

bulky five-coordinate molecules. We have selected for study a broad range of X groups, including not only halides but also alkoxides, hydrides (no ligand lone pair), and an acetylide (no lone pair, but π-bonding electrons). The exchange observed was surprising not only because there were two bulky ligands on each molecule but also because these did not have the planar *four*-coordinate structure which forms the basis for most previous examples of facile ligand redistribution.[3] In particular, we know of no cases of X-ligand exchange between five-coordinate species.

Experimental Section

General Procedures. All reactions were performed in inert atmosphere (either N_2 or argon). Protio solvents were dried, distilled, and stored in gastight solvent bulbs. NMR solvents were vacuum-transferred from appropriate desiccants and stored in a glovebox. $RuHCl(CO)(P^iPr_3)_2$ was synthesized according to the method of Werner,[4] and all $RuHX(CO)P_2$ and $RuDX(CO)P_2$ compounds were synthesized by metathesis of the analogous chloride.[5] IrH_2XP_2 compounds were synthesized as described elsewhere.[6,7] Cp*RuXP (X = Cl, Br, I; P = PCy_3, or P^tBu_2Me) compounds were synthesized by addition of a bulky phosphine to $[Cp^*Ru(\mu\text{-}X)]_4$.[8,9] All ligand exchange reactions were interrogated by ^1H and/or $^{31}P\{^1H\}$ NMR within 10 min of mixing. If at this time no exchange was observed, ^1H and/or ^{31}P NMR spectra were collected at 15-min intervals for the first 2 h of reaction time, after which spectra were collected at 8-h intervals. The integrations of total (i.e., both X) L_nM and of L′M were evaluated during the time evolution of the reactions to confirm material balance. Triethylamine was dried over CaH_2 and distilled under nitrogen. ^1H (360 MHz) and ^{31}P (146 MHz) NMR spectra were obtained on a Bruker 500, a Nicolet 360, or a Varian XL300 instrument.

H/D Exchanges. (a) Reaction of $RuHCl(CO)(P^tBu_2Me)_2$ and $RuDI(CO)(P^tBu_2Me)_2$. To 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 added 0.025 g (0.04 mmol) of $RuDI(CO)(P^tBu_2Me)_2$. After 10 min, ^1H NMR showed a decline in the hydride signal of $RuHCl(CO)(P^tBu_2Me)_2$ (−24.5 ppm) and the appearance of a hydride signal for $RuHI(CO)(P^tBu_2Me)_2$ at −23.7 ppm. At this time, ^1H and ^{31}P NMR showed approximately equimolar Ru/HCl, Ru/DCl, Ru/HI, and Ru/DI. The same distribution of products could be obtained from equimolar $RuDCl(CO)(P^tBu_2Me)_2$ and $RuHI(CO)(P^tBu_2Me)_2$. Repeating this reaction with 1 equiv of NEt_3 added to 0.02 g (0.04 mmol) of $RuHCl(CO)(P^tBu_2Me)_2$ in 0.2 mL of C_6D_6 and to 0.025 g (0.04 mmol) of $RuDI(CO)(P^tBu_2Me)_2$ in 0.2 mL of C_6D_6 resulted in no detectable decrease in the rate of exchange.

(b) Reaction of $RuHI(CO)(P^tBu_2Me)_2$ and $RuHCl(CO)(P^iPr_3)_2$. To a solution of 0.025 g (0.04 mmol) of $RuHI(CO)(P^tBu_2Me)_2$ in 0.5 mL of C_6D_6 was added 0.02 g (0.04 mmol) of $RuHCl(CO)(P^iPr_3)_2$. After 5 min, hydride signals for $RuHCl(CO)(P^tBu_2Me)_2$ and $RuHI(CO)(P^iPr_3)_2$ were visible.

(c) Reaction of $RuDCl(CO)(P^tBu_2Me)_2$ and $RuHCl(CO)(P^iPr_3)_2$. To a solution of 0.02 g (0.04 mmol) of $RuDCl(CO)(P^tBu_2Me)_2$ in 0.5 mL

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of C_6D_6 was added 0.02 g (0.04 mmol) of $RuHCl(CO)(P^iPr_3)_2$. Within 15 min, a hydride signal for $RuHCl(CO)(P^tBu_2Me)_2$ was visible. A steady state composition containing approximately equimolar $RuDCl(CO)(P^tBu_2Me)_2$, $RuHCl(CO)(P^tBu_2Me)_2$, $RuHCl(CO)(P^iPr_3)_2$, and $RuDCl(CO)(P^iPr_3)_2$ was achieved in 1 h. This assay was accomplished by integrating the hydride *vs* the PCH_3 protons.

(d) Reaction of $IrH_2Cl(P^tBu_2Ph)_2$ and $IrD_2Cl(P^tBu_2Me)_2$. An 8.0-mg (0.04-mmol) sample of $IrD_2Cl(P^tBu_2Me)_2$ and 7.6 mg (0.011 mmol) of $IrH_2Cl(P^tBu_2Ph)_2$ (hydride chemical shift −32.090 ppm) were weighed into an NMR tube. The solids were dissolved in C_6D_6. After 15 min, signals for $IrHDCl(P^tBu_2Ph)_2$, $IrHDCl(P^tBu_2Me)_2$, and $IrH_2Cl(P^tBu_2Me)_2$ (−32.056 ppm) were observed. Selected NMR data for $IrHDCl(P^tBu_2Me)_2$: ^1H NMR (C_6D_6, 500 MHz, 25 °C) −32.103 ppm (t, $^2J_{HP}$ = 13 Hz). Selected NMR data for $IrHDCl(P^tBu_2Ph)_2$: ^1H NMR (C_6D_6, 500 MHz, 25 °C) −32.234 ppm (t, $^2J_{HP}$ = 13 Hz).

(e) Reaction of $IrH_2I(P^tBu_2Ph)_2$ and $IrH_2Cl(P^tBu_2Me)_2$. Equimolar $IrH_2I(P^tBu_2Ph)_2$ was added to a toluene-d_8 solution of $IrH_2Cl(P^tBu_2Me)_2$. Within 30 min, the $^{31}P\{^1H\}$ NMR spectrum showed the presence of $IrH_2I(P^tBu_2Ph)_2$, $IrH_2Cl(P^tBu_2Ph)_2$, $IrH_2I(P^tBu_2Me)_2$, and $IrH_2Cl(P^tBu_2Me)_2$ in approximately equimolar ratios. No AM pattern was observed. This result was confirmed by ^1H NMR spectroscopy.

(f) Reaction of $RuH(OCH_2CF_3)(CO)(P^tBu_2Me)_2$ and $RuHCl(CO)(P^iPr_3)_2$. To a solution of 0.022 g (0.04 mmol) of $RuH(OCH_2CF_3)(CO)(P^tBu_2Me)_2$ in 0.5 mL of C_6D_6 was added 0.02 g (0.04 mmol) of $RuHCl(CO)(P^iPr_3)_2$. Exchange was observed after 10 min, at which time ^1H NMR showed $RuHCl(CO)(P^tBu_2Me)_2$ (20%), $RuH(OCH_2CF_3)(CO)(P^iPr_3)_2$ (20%), $RuH(OCH_2CF_3)(CO)(P^tBu_2Me)_2$ (30%), and $RuHCl(CO)(P^iPr_3)_2$ (30%). Selected NMR data for $RuH(OCH_2CF_3)(CO)(P^iPr_3)_2$: ^1H NMR (C_6D_6, 25 °C) −23.0 ppm (t, J_{HP} = 19 Hz).

(g) Reaction of $RuH(C_2Ph)(CO)(P^tBu_2Me)_2$ and $RuHCl(CO)(P^iPr_3)_2$. To a solution of 0.02 g (0.04 mmol) of $RuH(C_2Ph)(CO)(P^tBu_2Me)_2$ in 0.5 mL of C_6D_6 was added 0.02 g (0.04 mmol) of $RuHCl(CO)(P^iPr_3)_2$. Exchange was not observed until after 45 min, at which time ^{31}P NMR showed $RuHCl(CO)(P^tBu_2Me)_2$ (10%), $RuH(C_2Ph)(CO)(P^iPr_3)_2$ (10%), $RuH(C_2Ph)(CO)(P^iPr_3)_2$ (40%), and $RuHCl(CO)(P^iPr_3)_2$. Selected NMR data for $RuH(C_2Ph)(CO)(P^iPr_3)_2$: ^1H NMR (C_6D_6, 25 °C) −27.8 ppm (t, J_{HP} = 19 Hz); $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C) 62.6 ppm.

(h) Reaction of $RuH(OPh)(CO)(P^tBu_2Me)_2$ and $RuHCl(CO)(P^iPr_3)_2$. To a solution of 0.022 g (0.04 mmol) of $RuH(OPh)(CO)(P^tBu_2Me)_2$ in 0.5 mL of C_6D_6 was added 0.02 g (0.04 mmol) of $RuHCl(CO)(P^iPr_3)_2$. Exchange was observed after 75 min, at which time ^1H NMR showed $RuHCl(CO)(P^tBu_2Me)_2$ (10%), $RuH(OPh)(CO)(P^iPr_3)_2$ (10%), $RuH(OPh)(CO)(P^tBu_2Me)_2$ (40%), and $RuHCl(CO)(P^iPr_3)_2$ (40%). Selected NMR data for $RuH(OPh)(CO)(P^iPr_3)_2$: ^1H NMR (C_6D_6, 25 °C) −23.6 ppm (t, J_{HP} = 17 Hz).

(i) Reaction of $RuH(OSiPh_3)(CO)(P^tBu_2Me)_2$ and $RuHCl(CO)(P^iPr_3)_2$. To a solution of 0.029 g (0.04 mmol) of $RuH(OSiPh_3)(CO)(P^tBu_2Me)_2$ in 0.5 mL of C_6D_6 was added 0.02 g (0.04 mmol) of $RuHCl(CO)(P^iPr_3)_2$. Exchange was observed after 105 min, at which time ^1H NMR showed $RuHCl(CO)(P^tBu_2Me)_2$ (10%), $RuH(OSiPh_3)(CO)(P^iPr_3)_2$ (10%), $RuH(OSiPh_3)(CO)(P^tBu_2Me)_2$ (40%), and $RuHCl(CO)(P^iPr_3)_2$ (40%). Selected NMR data for $RuH(OSiPh_3)(CO)(P^iPr_3)_2$: ^1H NMR (C_6D_6, 25 °C) −23.9 ppm (t, J_{HP} = 19 Hz).

(j) Reaction of $RuHI(CO)(P^tBu_2Me)_2$ and $IrH_2Cl(P^tBu_2Ph)_2$. To a solution of 0.017 g (0.035 mmol) of $RuHCl(CO)(P^tBu_2Me)_2$ in 0.5 mL of C_6D_6 was added 0.020 g (0.026 mmol) of $IrH_2I(P^tBu_2Ph)_2$. After 10 min, an equilibrium mixture (established by later observation of unchanged ^{31}P NMR intensities) of the four species was obtained with the following ^{31}P NMR relative intensities: $RuHCl(CO)(P^tBu_2Me)_2$, 36; $RuHI(CO)(P^tBu_2Me)_2$, 1.0; $IrH_2Cl(P^tBu_2Ph)_2$, 6.0; $IrH_2I(P^tBu_2Ph)_2$, 17.8. These experiments used a pulse angle of 60°, and the T_1 value of $RuHCl(CO)(P^tBu_2Me)_2$ was measured as 7.3 s.[10] Repeating this reaction in the presence of 10 equiv of NEt_3 resulted in no noticeable decrease in rate.

(k) Reaction of $RuHI(CO)(P^tBu_2Me)_2$ and $Cp^*Ru(PCy_3)Cl$. To a solution of 0.026 g (0.04 mmol) of $RuHI(CO)(P^tBu_2Me)_2$ in 0.5 mL of C_6D_6 was added 0.019 g (0.035 mmol) of $Cp^*Ru(PCy_3)Cl$. After 10 min, $RuHCl(CO)(P^tBu_2Me)_2$, $RuHI(CO)(P^tBu_2Me)_2$, and $Cp^*Ru(PCy_3)I$ were visible by ^{31}P NMR. No $Cp^*Ru(PCy_3)Cl$ was observed.

(10) A delay of 20 s between acquisitions was used to ensure complete relaxation of the phosphorus nuclei and therefore more accurate integration. We feel that $RuHCl(CO)(P^tBu_2Me)_2$ will have approximately the same T_1 as $RuHCl(CO)(P^iPr_3)_2$.

Control Reactions. (a) Reaction of $RuHCl(CO)(P^tBu_2Me)_2$ with P^iPr_3. To a solution of 0.02 g (0.04 mmol) of $RuHCl(CO)(P^tBu_2Me)_2$ in 0.5 mL of C_6D_6 was added 0.006 g (0.04 mmol) of P^iPr_3. Phosphine exchange products $RuHCl(CO)(P^iPr_3)_2$ and $RuHCl(CO)(P^tBu_2Me)(P^iPr_3)$ were visible by ^1H and ^{31}P NMR within 30 min, with a steady state achieved after 4 h. Selected NMR data for $RuHCl(CO)(P^tBu_2Me)(P^iPr_3)$: ^1H NMR (C_6D_6, 25 °C) −24.4 ppm (d of d, J_{HP} = 17 Hz, J_{HP} = 19 Hz, Ru–H); $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C) 58.8 (d, J_{PP} = 275 Hz, P^iPr_3), 48.6 ppm (d, J_{PP} = 275 Hz, P^tBu_2Me). A similar result was obtained from the reaction of $RuHCl(CO)(P^iPr_3)_2$ and 1 equiv of P^tBu_2Me.

(b) Reaction of $RuHCl(CO)(P^tBu_2Me)_2$ and $RuHCl(CO)(P^iPr_3)_2$. To a solution of 0.02 g (0.04 mmol) of $RuHCl(CO)(P^tBu_2Me)_2$ in 0.5 mL of C_6D_6 was added 0.02 g (0.04 mmol) of $RuHCl(CO)(P^iPr_3)_2$. After 36 h at 25 °C, <10% conversion to $RuHCl(CO)(P^tBu_2Me)(P^iPr_3)$ was observed by ^1H and ^{31}P NMR.

Activation Parameters: Degenerate Exchange of $Cp^*RuCl(P^tBu_2Me)$ and $Cp^*RuBr(P^tBu_2Me)$. In the drybox, $Cp^*RuCl(P^tBu_2Me)$ (18.1 mg, 41.9 μmol) and $Cp^*RuBr(P^tBu_2Me)$ (20.3 mg, 42.6 μmol) were dissolved in 0.580 mL of toluene-d_8, the solution was added to an NMR tube, and the tube was flame-sealed under vacuum. A ^1H NMR spectrum was taken at low temperature (−59 °C) for determination of natural line widths. Then, ^1H NMR spectra were taken at several temperatures near the coalescence temperature. Temperatures were calibrated using the peak separation of ethylene glycol. The experiment was repeated using lower concentrations of reactants: $Cp^*RuCl(P^tBu_2Me)$ (6.2 mg, 14.4 μmol) and $Cp^*RuBr(P^tBu_2Me)$ (8.6 mg, 18.1 μmol) in 0.600 mL of toluene-d_8. Rate constants in these experiments varied over the range 156 s^{-1} (26 °C) to 1208 s^{-1} (72 °C). Independent fitting of the data at the different concentrations gave $\Delta H^\ddagger$ = 8.1(3) and 10.4(9) kcal/mol and $\Delta S^\ddagger$ = −21(1) and −15(3) cal deg^{-1} mol^{-1} at the lower and higher concentrations, respectively. Uncertainties given are solely those of the least-squares fitting procedure. However, there is a sizable experimental error in $\Delta S^\ddagger$, since this value suffers from uncertainty in concentration of reactants. Activation entropy values from each concentration are *inconsistent* with a dissociative mechanism.

Results

Ligand redistribution is a general class of reactions.[11] The "transmetalation" of MR with M′X is a widely used example. Examples for main group metals have been reviewed,[12] with the conclusion that reaction rates are greatly facilitated if M and M′ are Lewis acidic. Examples involving transition metals are of more recent vintage and broader scope: redistributions of halide, hydride, alkyl (e.g., from RMgX and RLi), phosphine, CO, and even Cp (C_5H_5) ligands have been reported,[3] but with widely varying rates. Several cases of these reactions are well-documented for saturated (18e) and d^8 square planar (16e) complexes, yet very few have been reported for 16e species other than d^8 square planar.

General Information. Halide exchange reactions were found to proceed quite rapidly at room temperature in nonpolar solvents and were generally complete within the time required to obtain the earliest NMR spectrum. Exchanges involving bulky pseudohalides and hydrides (deuterides) were slower and were monitored periodically by ^1H and ^{31}P NMR.[13] In the reactions discussed here, phosphine dissociation is mechanistically insignificant.[14-16] When it occurs, the rate is orders of magnitude slower than that of H or X exchange.

(11) We employ the term as a description of stoichiometry, with no implication of mechanism.
(12) Moedritzer, K. *Adv. Organomet. Chem.* **1968**, *6*, 171.
(13) For spectral data, see: Poulton, J. T.; Sigalas, M. P.; Folting, K.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 1476, as well as ref 5.
(14) Phosphine transfer would lead to AM patterns in $^{31}P\{^1H\}$ NMR spectra for $RuHX(CO)P_2$ and IrH_2XP_2 and noticeably different ^{31}P chemical shifts for Cp^*RuXP species.
(15) Transfer of *coordinated* phosphine seems implausible because μ-PR_3 intermediates will be of high energy (since none have ever been detected in ground state structures). Only PF_3 has been shown in one case to function as a μ_3 ligand. See: Balch, A. L.; Davis, B. J.; Olmstead, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 8592.
(16) While $RuHCl(CO)(P^iPr_3)_2$ and equimolar P^tBu_2Me react to give phosphine exchange products within 30 min, reaction of $RuHCl(CO)(P^iPr_3)_2$ and $RuHCl(CO)(P^tBu_2Me)_2$ results in <10% conversion to $RuHCl(CO)(P^tBu_2Me)(P^iPr_3)$ after 36 h.

Hydride Exchanges. (a) Ru(II). Reaction of equimolar $RuHCl(CO)(P^tBu_2Me)_2$ and $RuDI(CO)(P^tBu_2Me)_2$ in C_6D_6 leads to decline in the ^1H NMR signal of the hydrido chloride (−24.5 ppm) and the appearance of the hydride signal of the hydrido iodide (−23.7 ppm). A steady state is reached within 10 min at 25 °C. Equimolar $RuDCl(CO)(P^tBu_2Me)_2$ and $RuHI(CO)(P^tBu_2Me)_2$ also produce $RuHCl(CO)(P^tBu_2Me)_2$ and $RuDI(CO)(P^tBu_2Me)_2$ within 10 min at 25 °C in C_6D_6. The following equilibrium (eq 4) has therefore been reached from

$$RuHCl(CO)(P^tBu_2Me)_2 + RuDI(CO)(P^tBu_2Me)_2 \rightleftharpoons RuDCl(CO)(P^tBu_2Me)_2 + RuHI(CO)(P^tBu_2Me)_2 \quad (4)$$

both directions. Each of these experiments reaches the same ^1H NMR intensity ratios of [Ru]HCl/[Ru]DCl = 1 and [Ru]HI/[Ru]DI = 1, indicating that there is no major equilibrium deuterium isotope effect. This fact is not surprising since hydrides occupy the apical positions in the ground state structures and therefore are not subjected to significantly different *trans* influences.

The mechanism of eq 4 could involve rupture of Ru–H and Ru–D bonds or of Ru–Cl and Ru–I bonds. In order to establish whether hydride or halide exchange is occurring, we examined the reaction of $RuHI(CO)(P^tBu_2Me)_2$ with $RuHCl(CO)(P^iPr_3)_2$. After 5 min in C_6D_6, the hydride signals of $RuHCl(CO)(P^tBu_2Me)_2$ and $RuHI(CO)(P^iPr_3)_2$ are seen. Halide transfer can thus be unequivocally demonstrated as *sufficient* to accomplish eq 4. The question of H/D exchange has been further probed by observing the reaction of $RuDCl(CO)(P^tBu_2Me)_2$ and $RuHCl(CO)(P^iPr_3)_2$. This reaction does produce $RuHCl(CO)(P^tBu_2Me)_2$ (by ^1H NMR), indicating that H/D exchange does occur. However, this exchange is noticeably slower, with a steady state achieved in ~1 h as opposed to 10 min for the Cl/I exchange.

(b) Ir(III). A mixture of $Ir(H)_2Cl(P^tBu_2Ph)_2$ and $Ir(D)_2Cl(P^tBu_2Me)_2$ shows (^1H NMR) the production of $IrHDCl(P^tBu_2Ph)_2$ and $IrHDCl(P^tBu_2Me)_2$ within 15 min. These are resolvable from the reagent complexes, at 500 MHz, as a result of the deuterium isotope effect on the chemical shift.

Degenerate Exchanges. (a) Ru(II). Halide/halide ligand redistribution occurs faster than halide/pseudohalide exchange when the pseudohalide is bulky. This phenomenon is best illustrated by exchange reactions of $RuHCl(CO)(P^iPr_3)_2$ with $RuHX(CO)(P^tBu_2Me)_2$ (X = OCH_2CF_3, C_2Ph, OPh, $OSiPh_3$), all done under the same conditions with the same concentrations of reactants (eq 5). When X = OCH_2CF_3, exchange is complete

$$RuHCl(CO)(P^iPr_3)_2 + RuHX(CO)(P^tBu_2Me)_2 \overset{?}{\rightarrow} RuHX(CO)(P^iPr_3)_2 + RuHCl(CO)(P^tBu_2Me)_2 \quad (5)$$

within 10 min (40% conversion). However, for X = C_2Ph, exchange is only detectable (10% conversion) after 45 min. When X = OPh, no exchange is observed after 10 min. Only after 75 min are the products of Cl/OPh exchange detected (20% conversion). In the case of X = $OSiPh_3$, the reaction is even slower: the exchange products are first observed after 105 min (20% conversion). Only the OCH_2CF_3 exchange represents rapid achievement of equilibrium. Clearly, these results are consistent with steric bulk slowing the exchange, which is characteristic of an associative mechanism with a second-order rate law and inconsistent with an ionic mechanism (via free bulky X^-). Exchange via the naked carbanion PhC_2^- in a nonpolar solvent is likewise implausible. The slower rate for C_2Ph than for OCH_2CF_3 may reflect the lack of a lone pair, and thus less efficient bridge formation, presumably via the alkyne π-system.

(b) Ir(III). We wished to establish whether these exchanges are general for this type of complex or unique to $RuHX(CO)P_2$. We therefore decided to examine ligand exchange in another unsaturated system, with a similar molecular geometry. Reaction of approximately equimolar $IrH_2Cl(P^tBu_2Me)_2$ and $IrH_2I(P^tBu_2Ph)_2$ in toluene-d_8 yields (by $^{31}P\{^1H\}$ NMR) a mixture of ClPh, ClMe, IPh, and IMe compounds after 30 min (eq 6).

$$\begin{array}{ccc} IrH_2I(P^tBu_2Ph)_2 & + & IrH_2Cl(P^tBu_2Me)_2 \\ \text{I/Ph} & \rightleftharpoons & \text{Cl/Me} \\ IrH_2Cl(P^tBu_2Ph)_2 & + & IrH_2I(P^tBu_2Me)_2 \\ \text{Cl/Ph} & & \text{I/Me} \end{array} \quad (6)$$

Enthalpically-Driven Exchanges. On the basis of previous studies of halide (and pseudohalide) donor power ($\sigma + \pi$),[13] we felt that it would be informative to investigate exchange between different types of metal centers. One would predict that the better donor ligand would reside preferentially with the less electron-rich metal center. The established ranking of donor power is I < Cl.

Reaction of equimolar $IrH_2I(P^tBu_2Ph)_2$ and $RuHCl(CO)(P^tBu_2Me)_2$ in C_6D_6 gives, in the time required to acquire NMR data, an equilibrium mixture of these and the [Ir]Cl and [Ru]I analogs. Combination of $RuHI(CO)(P^tBu_2Me)_2$ and $IrH_2Cl(P^tBu_2Ph)_2$ (at a Ru:Ir ratio of 1:1.2) also leads to production of $RuHCl(CO)(P^tBu_2Me)_2$ and $IrH_2I(P^tBu_2Ph)_2$. This establishes that we have indeed achieved equilibrium from either side. This equilibrium (eq 7) does *not* result in a statistical distribution of

$$RuHI(CO)(P^tBu_2Me)_2 + IrH_2Cl(P^tBu_2Ph)_2 \rightleftharpoons RuHCl(CO)(P^tBu_2Me)_2 + IrH_2I(P^tBu_2Ph)_2 \quad (7)$$

the four metal halides but rather a definite preference for the product side of equilibrium 7. Integration of a $^{31}P\{^1H\}$ NMR spectrum of the above $RuHI(CO)(P^tBu_2Me)_2$ / $IrH_2Cl(P^tBu_2Ph)_2$ reaction[17] allows the determination of K_{eq} = 107 and thus ΔG° = −2.8 kcal/mol for equilibrium 7. Assuming $\Delta S \approx 0$ (since both sides of equilibrium 7 contain the same number of particles), the product side is enthalpically favored by 2.8 kcal/mol. This preference is not sterically based since the larger halide is on the complex with the larger phosphine (P^tBu_2Ph). Since we have established independently that chloride is a better donor ($\sigma + \pi$) ligand than iodide, we interpret the thermodynamic preference as placing the better donor (Cl) on the stronger electrophile; that is, $RuH(CO)P_2$ is more Lewis acidic than IrH_2P_2.

Reaction of $Cp^*Ru(PCy_3)Cl$ with a slight excess of $RuHI(CO)(P^tBu_2Me)_2$ in C_6D_6 gives, in the time required to acquire NMR data, an equilibrium mixture (eq 8) containing only $Cp^*Ru(PCy_3)I$, $RuHI(CO)(P^tBu_2Me)_2$, and $RuHCl(CO)(P^tBu_2Me)_2$. No $Cp^*Ru(PCy_3)Cl$ is observed. Clearly, this equilibrium does *not* result in a statistical distribution of the four metal halides. Rather, an enthalpic preference is observed for the production of $RuHCl(CO)(P^tBu_2Me)_2$ and $Cp^*Ru(PCy_3)I$, with $Cp^*Ru(PCy_3)Cl$ acting, effectively, as the limiting reagent. Again, we interpret the thermodynamic preference as placing the better donor (Cl) on the stronger electrophile, $RuH(CO)P_2$.

$$Cp^*Ru(PCy_3)Cl + RuHI(CO)(P^tBu_2Me)_2 \rightleftharpoons Cp^*Ru(PCy_3)I + RuHCl(CO)(P^tBu_2Me)_2 \quad (8)$$

Mechanism. (a) Acid Catalysis. We have considered the possibility (eq 9) that the exchange between $MHYL_n$ and $MHXL_m$

(17) The spectra 10 min and 1 day after mixing were identical.

could be catalyzed by trace (adventitious) HX. The oxidative

$$MHYL_n + HX \rightarrow M(H)_2XYL_n \rightarrow MHXL_n + HY$$

$$HY + M'HXL_m \rightarrow M'(H)_2XYL_m \rightarrow M'HYL_m + HX \quad (9)$$

addition steps are possible because all reagent complexes are operationally unsaturated,[1] and oxidation states Ir(V) and Ru(IV) are known in related chemistry (e.g., $Ir(H)_5P_2$ and $Cp^*RuP(H)_3$). We tested this idea by looking for a retardation of the redistribution rate between $Ir(H)_2Cl(P^tBu_2Ph)_2$ and $RuHI(CO)(P^tBu_2Me)_2$ in the presence of 10 equiv of NEt_3 per metal atom.[18] We observed that ligand redistribution was complete within the time required for recording the $^{31}P\{^1H\}$ NMR spectrum. Thus, an effort to greatly reduce the concentration of HX ($[NHEt_3]Cl$ is insoluble in benzene) causes no observed rate decrease and demonstrates that the mechanism in eq 9 is not the sole mechanism for exchange.[19]

(b) Rate Law and Activation Parameters. It was found for the degenerate exchange in eq 10 ($P = P^tBu_2Me$) that coalescence

$$Cp^*RuPCl + Cp^*(Ru')PBr \rightleftarrows Cp^*RuPBr + Cp^*(Ru')PCl \quad (10)$$

of the ^1H NMR signals of the Cp* methyl groups of the two species could be observed in toluene-d_8. This observation provides the opportunity to determine the form of the rate law and the activation parameters, ΔH^* and ΔS^*, of this exchange by measuring the line widths of the resonances (and therefore the rate of exchange) as a function of temperature. The mechanism of exchange for Cp*RuPX is likely to be the same as for $RuHX(CO)P_2$ and for IrH_2XP_2.

Spectra can be simulated for this system,[20] when one knows (1) the slow-exchange signal separation, (2) the natural line widths, (3) the integral ratio of the two lines, and (4) the rate of conversion of [M]Br to [M]Cl.[21] The first three values were measured and the fourth was varied until simulated spectra matched those measured experimentally. In this way, exchange rates were determined over a range of temperatures. Each rate was then divided by the concentration of [M]Cl, to yield rate constant k, according to eq 11.

$$1/\tau_{[M]Br} = r_{[M]Br \rightarrow [M]Cl} = k\{[M]Cl\} \quad (11)$$

Shown in Figure 1 is an Eyring plot of two data sets acquired from experiments at two different concentrations. Approximate collinearity of the two sets of points confirms the hypothesis that the exchange process is second order.[22] The large negative value of ΔS^* (-20 ± 3 cal/(mol K) for a least-squares fit to all data points in Figure 1) indicates a decrease in overall number of particles in the transition state and is consistent with exchange occurring via a dimetal species. It is also interesting that the enthalpic barrier for exchange ($\Delta H^* = 8.6 \pm 0.8$ kcal/mol) is quite high for a simple Lewis acid/base reaction. The high free energy barrier ($\Delta G^*(298\ K) = 14.6$ kcal/mol) is attributed to the steric bulk of the attendant ligands.

Discussion

Halide Exchange. Several features of a $(\mu\text{-X})(\mu\text{-Y})$ transition state for the $RuHX(CO)P_2$ exchanges are noteworthy. The first

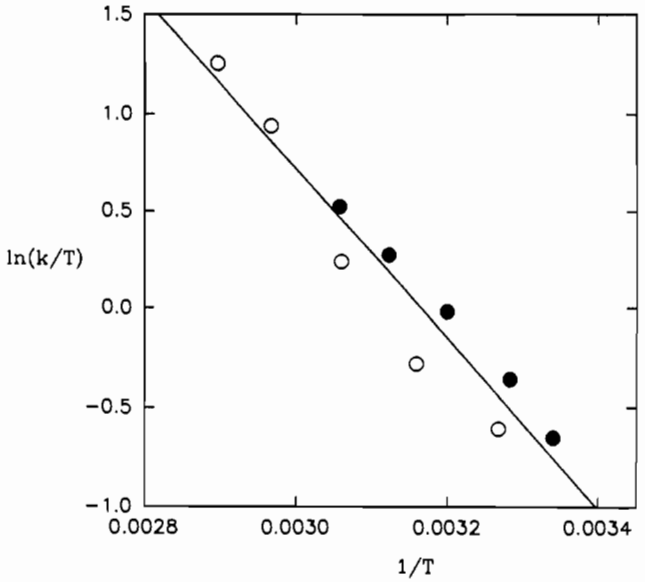
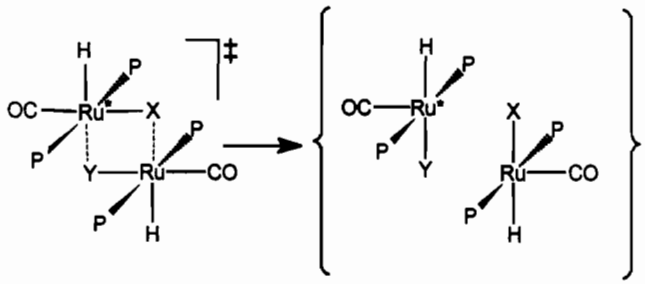


Figure 1. Eyring plot of temperature dependence of the observed rate constant for halide exchange in eq 10: open circles, 0.023 M $Cp^*Ru(P^tBu_2Me)Cl$ and 0.030 M $Cp^*Ru(P^tBu_2Me)Br$; filled circles, 0.072 M $Cp^*Ru(P^tBu_2Me)Cl$ and 0.073 M $Cp^*Ru(P^tBu_2Me)Br$.

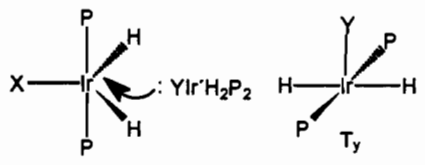
is that two problems exist in going through the "obvious" transition state, where halide bridge formation is *trans* to the hydride ligands. Sterically, this transition state (**A**) is disfavored because it involves



A

maximum contact between the phosphines.[23] The second point is that the geometry of both product molecules is "wrong" (i.e., not the ground state structure) in that the hydride is basal and the CO apical. This means that, as the fragments separate from the transition state,[24] there must be simultaneous enlargement of the Y–Ru*–CO and X–Ru–CO angles from 90°.

For the Ir/Ir exchanges, attack of a nucleophile upon $Ir(H)_2XP_2$ could, in general, occur either *cis* or *trans* to the group X. *Trans* attack (**B**) is clearly unproductive, since the nonbonded character



B

of X and Ir' necessitates a multistep reaction to complete the

(18) We first showed that this amount of NEt_3 left the ^{31}P NMR spectrum of $Ir(H)_2Cl(P^tBu_2Ph)_2$ unchanged over 1 h in benzene. The same mole ratio of NEt_3 combined with $RuHI(CO)(P^tBu_2Me)_2$ (also in benzene) results in ^1H and $^{31}P\{^1H\}$ NMR changes consistent with reversible binding of the Lewis base NEt_3 to the unsaturated Ru.

(19) This rules out *any* mechanism involving free HX, e.g., reductive elimination of HI from $Ir(H)_2I(P^tBu_2Ph)_2$.

(20) The program DNMR5 was employed.

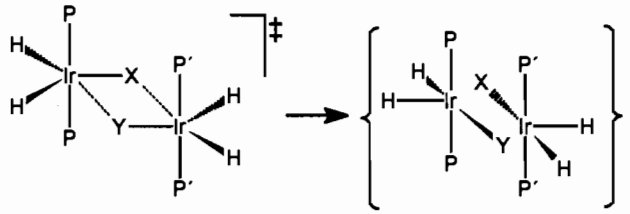
(21) The reverse rate is fixed by the populations of the two sites and the given rate of conversion of [M]Br to [M]Cl.

(22) I.e., line shapes were simulated with a second-order kinetic model. Therefore, gross deviations from collinearity would be expected if the reaction were not second order.

(23) It is worth noting that the isoelectronic species $[Rh(P^nBu_3)_2Cl_2(\mu\text{-}Cl)]_2$ avoids end-to-end P/P repulsions by placing two phosphines axial on one metal but equatorial on the other metal. See: Muir, J. A.; Muir, M. M.; Rivera, A. J. *Acta Crystallogr.* **1974**, *B30*, 2062.

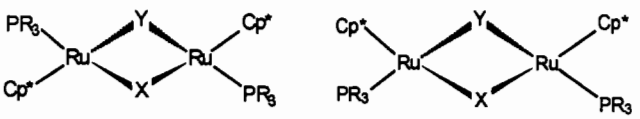
(24) The large brackets around the geminate pair following the transition state are meant to suggest the five-coordinate structure which must relax to the product ground state structure as the geminate partners diffuse apart.

halide exchange. It is also relevant that *ab initio* calculations[25] show that a mechanism which goes through a T_y intermediate (which is what will be created if Y attacks *trans* to X) is of high energy (mainly because two hydrides are mutually *trans*). *Cis* attack (**C**), which is preferred on the basis of *ab initio* calculations, effects pairwise halide exchange and leads naturally to the thermodynamically preferred product structure.



C

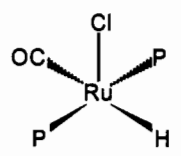
Exchange in the Cp*RuPX system could occur via a transition state (**D**) which involves either *cis* or *trans* Cp* ligands. Electronically, formation of either transition state is equally



D1 **D2**

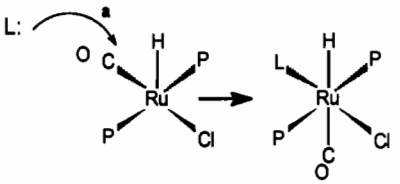
accessible, since the LUMO of $Cp^*Ru(PR_3)X$ has a node coplanar with the plane of symmetry of the molecule.[26] Bimetallic complexes, $Cp^*LRu(\mu\text{-}X)_2RuLCp^*$, resembling the required transition state for this exchange have been synthesized, with L = pyridine[27] and L = ethylene.[28] In both of these cases, the Cp* ligands occupy *trans* positions. However, a similar complex with *cis* Cp*'s is known for a chelating phosphine (bis-diphenylphosphinomethane).[29] Therefore, the exact configuration of the transition state remains uncertain.

H/D Exchange: Ru(II). While halide exchange has an obvious transition state derived from the ground state five-coordinate structure, the apical location of the hydride in $RuHX(CO)P_2$ requires some type of distortion from the ground state geometry in order to accomplish H/D exchange in a bimolecular fashion. Theoretical calculations[30] have shown that structure **E** lies 27

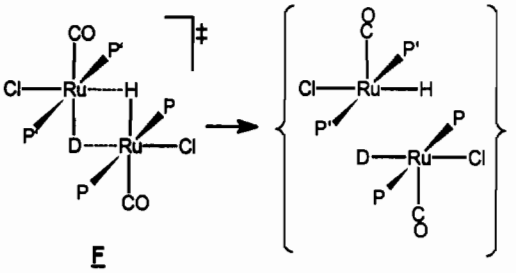


E

kcal/mol higher in energy than the ground state structure with H at the apex of the square-base pyramid. Moreover, since structure **E** is not a minimum on the potential energy surface, a detectable concentration of **E** will not exist (i.e., there is no equilibrium). However, the five-coordinate energy surface implies that attack of an incoming ligand is facile via direction **a** (in the



HRuCO plane). When L = D_2, this approach direction is responsible for exchange of metal-bound H with D_2. A similar mechanism may be operative in the present case where L would represent an Ru–D bond as shown in **F**.



F

This mechanism traverses a structure with CO at the apex of the square-based pyramid. This structure has been shown[30] to be ~7 kcal/mol higher in energy than the observed ground state geometry for $RuHCl(CO)P_2$. The involvement of this high-energy geometry, as well as the necessity for significantly more distortion from the ground state structure to the transition state (compared to that required to effect Cl/I exchange), accounts for the slower rate of H/D exchange compared to Cl/I exchange. The presence of halide lone pairs enabling more efficient bridge formation certainly also plays a part in the faster rate of halide exchange. It is also true that an $Ru_2(\mu\text{-}H)_2$ transition state will be of higher energy than an $Ru_2(\mu\text{-}Cl)_2$ case because shorter bond distances to hydride induce greater end-to-end phosphine/phosphine repulsions.

Conclusions

Exchange at saturated metal centers generally occurs relatively slowly by dissociation of one ligand, which then frees an orbital for the incoming ligand. For example, the reaction described by eq 12 requires several hours at room temperature.[31]

$$Cp^*Rh(PPh_3)(CH_3)_2 + Cp^*Rh(PPh_3)(NCMe)_2^{2+} \rightarrow 2Cp^*Rh(PPh_3)(CH_3)(NCMe)^+ \quad (12)$$

The reaction was found to be first order in $Cp^*Rh(PPh_3)(NCMe)_2^{2+}$, and exchange with free acetonitrile was found to be much faster than methyl transfer, although a complete mechanistic scheme was not presented.[32] Dissociative mechanisms have been proposed for several reactions involving d⁸ square planar complexes as well. The system described by eq 13 is strongly retarded by

$$PtMe_2(SMe_2)_2 + PtCl_2(SMe_2)_2 \rightarrow 2PtClMe(SMe_2)_2 \quad (13)$$

free SMe_2, and a mechanism proceeding via $PtMe_2(SMe_2)$ was preferred.[33] It was concluded that Lewis base ligand loss is *not mandatory* for Me/X redistribution but that such a mechanism is far faster than other mechanisms.

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An *associative* (halide-bridging) mechanism was proposed for the reaction shown in eq 14, however.[34] These $MX(CO)P_2$

$$RhCl(CO)P_2 + IrBr(CO)P_2 \rightleftharpoons RhBr(CO)P_2 + IrCl(CO)P_2 \quad (14)$$

compounds were also demonstrated to exchange CO via a bridged intermediate (or transition state) and to exchange phosphine (much more slowly) via phosphine dissociation.[35]

It now is clear for the molecules studied here that, while the only spectroscopically-detectable species are monomers, dimers *can* mediate ligand exchange reactions. Unlike the majority of previously known d^6 transition metal centers, the d^6 five-coordinate unsaturated complexes $RuHX(CO)P_2$, IrH_2XP_2, and Cp^*RuXP studied here undergo facile ligand exchanges via associative pathways. Since these compounds already contain low-lying LUMO's, no prior dissociation of ligands is necessary, and the reactions can be fast. While steric bulk frustrates dimerization, dimers are found as transition states or short-lived reaction intermediates. The role that steric factors play in these reactions was demonstrated quite clearly by examining the effect of increasing the size of the exchanging (X) ligand.

It was also shown that one can understand the favored side of an equilibrium by pairing the more electron-donating ligand with the less electron-rich metal center. This effect was most evident in the example of $Cp^*RuCl(PCy_3)$ acting as the limiting reagent in a reaction with $RuHI(CO)P_2$.

The Schlenk equilibrium (eq 15) and "transmetalation" (eq 16) are examples of ligand redistribution reactions of major

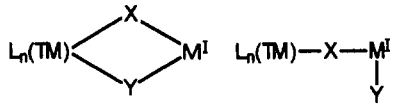
$$2RMgX \rightleftharpoons MgR_2 + MgX_2 \quad (15)$$

$$ZnRX + HgCl_2 \rightarrow ZnXCl + RHgCl \quad (16)$$

significance. Indeed, all of the reactions (eq 17 where TM = transition metal) we have used to synthesize the series of molecules

$$L_n(TM)X + M^IY \rightarrow L_n(TM)Y + M^IX \quad (17)$$

$RuHX(CO)P_2$ and Cp^*RuPX (X = halide, OR, SR, NHPh, etc.) are redistributions (which in this case go by the name "metathesis"). What remains a question for future study is whether such metathesis reactions are always faster when $L_n(TM)X$ is unsaturated (via transition state **G**) than when $L_n(TM)X$ is saturated (via transition state **H**).



G **H**

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Supplementary Material Available: A table of ^{31}P NMR chemical shifts (1 page). Ordering information is given on any current masthead page.

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