Inorg. Chem. **1996,** *35,* 7035−7040 **7035**

Reactivity of $RuCl_2(CO)(P^tBu_2Me)_2$ toward H_2 and Brønsted Acids: Aggregation Triggered by Protonation and Phosphine Loss

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Received May 21, 1996[⊗]

Reaction of H_2 with $RuCl_2(CO)L_2$ ($L = P^tBu_2Me$) in benzene forms $RuHCl(CO)L_2$ and HCl. The latter reacts with $RuCl_2(CO)L_2$ to give $[LH][Ru_2Cl_5(CO)_2L_2]$ and [LH]Cl. The $Ru_2Cl_5(CO)_2L_2^-$ ion is detected (NMR) as several isomers, and is shown by X-ray diffraction to have a face-shared bioctahedral structure: $LCl(OC)Ru(\mu\text{-}Cl)_3Ru(CO)ClL^-$. The loss of phosphine from Ru(II) is triggered by electrophilic attack, but *not* directly on P or on the Ru−P bond. It is shown (low-temperature NMR studies) that HCl reacts with $RuHCl(CO)L_2$ to give initially $RuCl_2(H_2)(CO)L_2$, in which H_2 is *trans* to Cl. From this study, and also direct observation of the reaction of HCl with $RuCl_2(CO)L_2$ to produce $Ru_2Cl_5(CO)_2L_2^-$, the Brønsted basicity of chloride in $RuCl_2(CO)L_2$ is established. This accounts for its reaction with PhC_2H and NEt_3 to give $Ru(C_2Ph)Cl(CO)L_2$. Crystallographic data (−173 °C) for $[P^tBu_2MeH][Ru_2Cl_5(CO)_2(P^tBu_2Me)_2]$: $a = 16.418(2)$Å, $b = 12.578(2)$Å, $c = 20.044(3)$Å, $\beta = 103.38(1)^\circ$ with $Z = 4$ in space group $P2_1/a$.

Introduction

Transition metal complexes containing one or more hydride ligands are normally synthesized[1] by halide replacement (eq 1)

$$EH_4^- + MCl \rightarrow MH + ... \qquad (1)$$

with EH_4^- (E = B, Al) reagents (and subsequent transformation of the $M(EH_4)$ primary product with ROH) or by oxidative addition of H_2 to a low-valent metal (eq 2). Only poorly

$$M^0 + H_2 \rightarrow M(H)_2 \qquad (2)$$

understood are the reactions of later transition elements with metal halides where H_2 formally disproportionates into H^+ and H^- (eq 3). Such heterolytic splitting of H_2 is usually "pro-

$$MCl + H_2 \rightarrow MH + HCl \qquad (3)$$

moted" by a Brønsted base (e.g., NEt_3), which functions to absorb HCl. The detailed mechanism of this heterolysis of H_2 is not understood,[2] and is the subject of this report.

Divalent ruthenium compounds are normally six-coordinate, with an 18-valence-electron count. With sufficiently bulky phosphines, five-coordinate 16-electron complexes become isolable: $RuCl_2(PPh_3)_3$,[3] $RuHCl(PPh_3)_3$,[4] and $RuCl_2(CO)(PCy_3)_2$.[5] These are all square-pyramidal with the anionic and two *trans* phosphine ligands in the basal positions. We have pursued the idea that there can be destabilizing interactions between halide ligand lone pairs and the filled d_π orbitals of an 18-electron metal center. Thus, coordination of a sixth ligand (especially if it is *not* a π-acid ligand) to any of these 16-electron complexes will leave chloride particularly Brønsted basic. Even the above *five*-coordinate molecules will have Brønsted basic chloride, since there are more chloride lone pairs than can be donated to the one empty metal orbital. We have tested some of these ideas by reacting $RuCl_2(CO)(P^tBu_2Me)_2$ with anhydrous HCl and even with H_2, and report here the outcome of this study.

Experimental Section

All manipulations were performed under inert atmosphere or *in vacuo* using standard Schlenk and glovebox techniques. Solvents were distilled from drying agents and stored in bulbs with Teflon valves. Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer. NMR spectra were recorded on either a Nicolet 360 MHz or a Varian XL 300 MHz instrument with chemical shifts in ppm referenced to residual solvent peaks (^1H) or external H_3PO_4 (^{31}P). Elemental analysis was performed by Desert Analytics, Tucson, AZ, or in this department on a Perkin-Elmer 2400 CHNS analyzer.

$RuHCl(CO)(P^tBu_2Me)_2$. The following is an improved procedure compared to the one reported,[6] based on using NEt_3 to scavenge evolved HCl. To a mixture of $RuCl_3{\cdot}3H_2O$ (4.0 g; 15 mmol), triethylamine (3.4 g; 33 mmol), and 2-methoxyethanol (80 mL) was added via cannula P^tBu_2Me (7.6 g; 47.4 mmol) in methoxyethanol (20 mL). The resulting solution was heated to 130 °C for 12 h. Volatiles were evaporated, and the residue was extracted with benzene (4 × 50 mL). The benzene solution was evaporated *in vacuo* to give a crude product. Recrystallization from methoxyethanol gave orange-yellow crystals, which were filtered off and washed with cold (−20 °C) methanol. Yield: 6.6 g (89%). The purity of the products was checked by ^1H and ^{31}P NMR.

$RuCl_2(CO)(P^tBu_2Me)_2$. A solution of $RuHCl(CO)(P^tBu_2Me)_2$ (2.0 g; 4 mmol) in $CHCl_3$ (20 mL) was refluxed for 4.5 h. The color of the solution changed from orange to dark brown. After the solution was cooled to room temperature, $CHCl_3$ was removed *in vacuo*. The residue was extracted four times with pentane. The combined pentane extracts were evaporated, yielding a brown solid which was recrystallized from toluene (−40 °C) to obtain 1.25 g (58%) of dark brown crystals. $^{31}P\{^1H\}$ NMR (C_6D_6): 39.0 ppm. ^1H NMR (C_6D_6): 1.44 (vt, $N = 6.6$ Hz, 6 H, PCH_3), 1.30 (vt, $N = 12.9$ Hz, 36 H, P^tBu) ppm. IR (C_6D_6): $\nu(CO) = 1937$ cm^{-1}. Anal. Calc (found) for $C_{19}H_{42}Cl_2OP_2Ru$: C, 43.84 (43.81); H, 8.14 (8.24). MS (EI): *m/z* 520 (M), with isotopic peaks consistent with the computer-simulated result for the formula

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[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1996.

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S0020-1669(96)00583-6 CCC: $12.00

$C_{19}H_{42}Cl_2OP_2Ru$. $RuCl_2(CO)L_2$ has two rotamers at temperature < −30 °C; the ^{31}P chemical shifts are 38.5 and 37.8 ppm with a ratio of 1:0.7 at −70 °C.

***trans,trans,trans*-$RuCl_2(CO)_2(P^tBu_2Me)_2$ and *cis,cis,trans*-$RuCl_2(CO)_2(P^tBu_2Me)_2$.** In an NMR tube with a Teflon stopcock, 10 mg of $RuCl_2(CO)(P^tBu_2Me)_2$ was dissolved in toluene-d_8. After three freeze−pump−thaw cycles, 1 atm of CO was introduced, and the brown solution changed to light yellow within the time of mixing. $^{31}P\{^1H\}$ NMR: 42.05 ppm (*trans* isomer). ^1H NMR: 1.47 (vt, $N = 5.7$ Hz, 6 H, PCH_3), 1.35 (vt, $N = 12.3$ Hz, 36 H, $PCCH_3$) ppm. IR: $\nu(CO) = 1981$ cm^{-1}. The solution was then kept at 80 °C in an oil bath for 2 h, during which the solution became colorless. $^{31}P\{^1H\}$ NMR: 44.8 ppm (*cis, trans* isomer). ^1H NMR: 1.65 (vt, $N = 8.1$ Hz, 6 H, PCH_3), 1.29 (vt, $N = 12$ Hz, 36 H, $PCCH_3$) ppm. IR: $\nu(CO) = 2029, 1964$ cm^{-1}.

$[HP^tBu_2Me][Ru_2Cl_5(CO)_2(P^tBu_2Me)_2]$. A Schlenk flask was charged with $RuCl_2(CO)(P^tBu_2Me)_2$ (50 mg; 0.096 mmol) and toluene (5 mL). After three freeze−pump−thaw cycles, 0.096 mmol of HCl gas was condensed (−196 °C) into the flask via a gas manifold. The solution was warmed to room temperature, and some white precipitate formed. The solution was filtered, and the solid was washed with toluene. The combined toluene solution was evaporated to dryness, and the residue was recrystallized from CH_2Cl_2 and ether to give red crystals. Anal. Calc (found) for $C_{29}H_{63}Cl_5O_2P_3Ru_2$: C, 38.02 (37.78); H, 6.93 (7.01). $^{31}P\{^1H\}$ NMR (C_6D_6): 64.3, 62.5, 28.7 ppm. ^1H NMR (C_6D_6), ppm: for the cation 0.94 (d, $J_{HP} = 15.3$ Hz, $PCCH_3$), 1.54 (d, $J_{HP} = 9.3$ Hz, PCH_3); for the major anion isomer 1.43 (d, $J_{HP} = 12.9$ Hz, $PCCH_3$), 1.45 (d, $J_{HP} = 12.9$ Hz, $PCCH_3$), 1.48 (d, $J_{HP} = 6.6$ Hz, PCH_3); for the minor anion isomer 1.37 (d, $J_{HP} = 12.9$ Hz, $PCCH_3$), 1.51 (d, $J_{HP} = 12.2$ Hz, $PCCH_3$), 1.61 (d, $J_{HP} = 5.4$ Hz, PCH_3). IR (C_6D_6): $\nu(CO) = 1948, 1957$ (sh) (weak) cm^{-1}.

Search for Intermediates by Low-Temperature Reactions. Typical method: An NMR tube was charged with $RuHCl(CO)(P^tBu_2Me)_2$ (10 mg; 0.020 mmol) and toluene-d_8 (0.5 mL). It was degassed by three freeze−pump−thaw cycles. One equivalent of HCl gas was introduced at −196 °C, and the tube was flame-sealed. The sealed tube was kept in a dry ice−acetone bath with most of the tube immersed in the bath. After the tube was shaken several times to allow mixing of the gas and liquid, it was transferred to a precooled NMR probe.

Certain low-temperature experiments seeking to detect an adduct between H_2 and $RuCl_2(CO)L_2$ gave artifactual results due to formation of an adduct with H_2O impurity. This adduct, at −27 ppm in its ^{31}P NMR, showed a temperature-dependent ^1H NMR signal in the range 3.14−3.42 ppm for the water protons. In contrast, dry sources of H_2 gave *no* change in the ^{31}P NMR spectrum in the temperature range −50 to −120 °C (in Freons).

Reaction of $RuCl_2(CO)(P^tBu_2Me)_2$ with 0.5 equiv of HCl. To a benzene solution of 10 mg of $RuCl_2(CO)(P^tBu_2Me)_2$ was added 0.01 mmol of HCl gas. The color changed from brown to orange. $^{31}P\{^1H\}$ NMR: 64.3, 62.6 ($[Ru_2Cl_5(CO)_2(P^tBu_2Me)_2]^-$) 22.0 ppm (coalesced peak of $[HP^tBu_2Me]^+$ and P^tBu_2Me).

Reaction of $RuCl_2(CO)(P^tBu_2Me)_2$ with H_2 in the Presence of NEt_3. Into a degassed benzene solution of 10 mg of $RuCl_2(CO)(P^tBu_2Me)_2$ and 3 μL of NEt_3 was introduced 1 atm of H_2. After mixing, a white precipitate formed. $^{31}P\{^1H\}$ NMR showed $RuHCl(CO)(P^tBu_2Me)_2$ as the only phosphine-containing product (50.1 ppm); this was further confirmed by ^1H NMR.

X-ray Structure Determination of $[HP^tBu_2Me][Ru_2Cl_5(CO)_2(P^tBu_2Me)_2]$. A suitable single crystal (plate) was selected from the bulk sample using inert-atmosphere handling techniques (nitrogen-filled glovebag).[7] The crystal was attached to a glass fiber using silicone grease and then transferred to a goniostat where it was cooled to −173 °C for characterization and data collection. A systematic search of selected regions of reciprocal space yielded a set of reflections which exhibited $2/m$ diffraction symmetry. The systematic extinctions of $h0l$ for $h = 2n + 1$ and of $0k0$ for $k = 2n + 1$ uniquely identified the space group as $P2_1/a$ (No. 14). This choice was confirmed by the subsequent solution and refinement of the structure. Data collection ($6 < 2\theta < 45°$) was undertaken as detailed in Table 1; an absorption correction was applied (range 0.71−0.91). The structure was solved by locating the Ru atoms in the best E map from MULTAN-78. The remaining non-hydrogen atoms were located in successive iterations of least-squares refinement followed by difference Fourier calculations. Following initial refinement, many of the hydrogen atoms were evident, at least one on each methyl group. Hydrogen atoms were then introduced in fixed idealized positions and assigned a thermal parameter of 1.0 plus the isotropic equivalent of the parent atom. During the refinement, abnormally short C−O distances were noticed in the two carbonyl groups (C(7)−O(8) and C(20)−O(21)), as well as elongated thermal ellipsoids on the carbon atoms in these groups. A disorder between CO and Cl was suspected and resolved. At the predominantly CO site, the disorder is 85% CO and 15% Cl for Cl(42) and Cl(43). A similar disorder would then be expected at the terminal Cl sites (Cl(6) and Cl(19)); however, it was not possible to observe the 15% C and O positions in a difference map computed after the occupancy of the Cl atoms had been refined to approximately 85%. The final cycles of full-matrix least-squares refinement were then completed using anisotropic thermal parameters on non-hydrogen atoms, except for C(7), O(8), C(20), O(21), Cl(42), and Cl(43), which were refined with isotropic thermal parameters. Hydrogen atoms were fixed, and the final $R(F)$ was 0.058 for the full unique data. The final difference map was essentially featureless, the largest peak was 1.33 e/Å^3 in the vicinity of Ru(1), and the deepest hole was −1.35 e/Å^3. The results of the structure determination are shown in Table 2 and Figure 1.

Table 1. Crystallographic Data for $[P^tBu_2MeH][Ru_2Cl_5(CO)_2(P^tBu_2Me)_2]$

formula $C_{29}H_{63}Cl_5O_2P_3Ru_2$	space group: $P2_1/a$
fw = 916.14	$T = -173$ °C
$a = 16.418(2)$ Å	$\lambda = 0.710\ 69$ Å^a
$b = 12.578(2)$ Å	$\rho_{calc} = 1.511$ g cm^{-3}
$c = 20.044(3)$ Å	$\mu = 12.1$ cm^{-1}
$\beta = 103.38(1)°$	$R(F_o)^b = 0.0583$
$V = 4026.69$ Å^3	$R_w(F_o)^c = 0.0601$
$Z = 4$	

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

Table 2. Selected Distances (Å) and Angles (deg) for $[P^tBu_2MeH][Ru_2Cl_5(CO)_2(P^tBu_2Me)_2]$

	Distances		
Ru(1)−Ru(2)	3.2988(10)	Ru(2)−Cl(5)	2.4890(22)
Ru(1)−Cl(3)	2.4264(22)	Ru(2)−Cl(19)	2.3952(27)
Ru(1)−Cl(4)	2.5144(25)	Ru(2)−P(22)	2.3453(23)
Ru(1)−Cl(5)	2.4857(21)	Ru(2)−C(20)	1.828(11)
Ru(1)−Cl(6)	2.359(3)	O(8)−C(7)	1.088(14)
Ru(1)−P(9)	2.3389(25)	O(21)−C(20)	1.142(14)
Ru(1)−C(7)	1.858(12)	P(32)−Cl(19)	3.857(3)
Ru(2)−Cl(3)	2.4205(22)	P(32)−Cl(4)	4.176(3)
Ru(2)−Cl(4)	2.4996(23)		
	Angles		
Cl(3)−Ru(1)−Cl(4)	80.33(8)	Cl(3)−Ru(2)−P(22)	97.06(8)
Cl(3)−Ru(1)−Cl(5)	81.26(7)	Cl(3)−Ru(2)−C(20)	98.8(3)
Cl(3)−Ru(1)−Cl(6)	167.40(10)	Cl(4)−Ru(2)−Cl(5)	79.18(8)
Cl(3)−Ru(1)−P(9)	99.10(8)	Cl(4)−Ru(2)−Cl(19)	90.13(8)
Cl(3)−Ru(1)−C(7)	97.5(4)	Cl(4)−Ru(2)−P(22)	177.25(8)
Cl(4)−Ru(1)−Cl(5)	78.96(8)	Cl(4)−Ru(2)−C(20)	92.1(4)
Cl(4)−Ru(1)−Cl(6)	87.81(11)	Cl(5)−Ru(2)−Cl(19)	91.18(9)
Cl(4)−Ru(1)−P(9)	178.27(8)	Cl(5)−Ru(2)−P(22)	102.19(8)
Cl(4)−Ru(1)−C(7)	91.4(4)	Cl(5)−Ru(2)−C(20)	171.1(4)
Cl(5)−Ru(1)−Cl(6)	92.37(9)	Cl(19)−Ru(2)−P(22)	92.23(8)
Cl(5)−Ru(1)−P(9)	102.59(8)	Cl(19)−Ru(2)−C(20)	87.4(3)
Cl(5)−Ru(1)−C(7)	170.3(4)	P(22)−Ru(2)−C(20)	86.6(4)
Cl(6)−Ru(1)−P(9)	92.87(10)	Ru(1)−Cl(3)−Ru(2)	85.78(7)
Cl(6)−Ru(1)−C(7)	86.9(4)	Ru(1)−Cl(4)−Ru(2)	82.28(7)
P(9)−Ru(1)−C(7)	87.1(4)	Ru(1)−Cl(5)−Ru(2)	83.07(6)
Cl(3)−Ru(2)−Cl(4)	80.75(8)	Ru(1)−C(7)−O(8)	177.4(11)
Cl(3)−Ru(2)−Cl(5)	81.31(7)	Ru(2)−C(20)−O(21)	175.2(10)
Cl(3)−Ru(2)−Cl(19)	169.10(9)		

Reaction of $RuCl_2(CO)(P^tBu_2Me)_2$ with PhCCH. To a benzene solution of 10 mg (0.02 mmol) of $RuCl_2(CO)(P^tBu_2Me)_2$ was added 3 μL (0.02 mmol) of PhCCH. After 5 min at room temperature, $^{31}P\{^1H\}$

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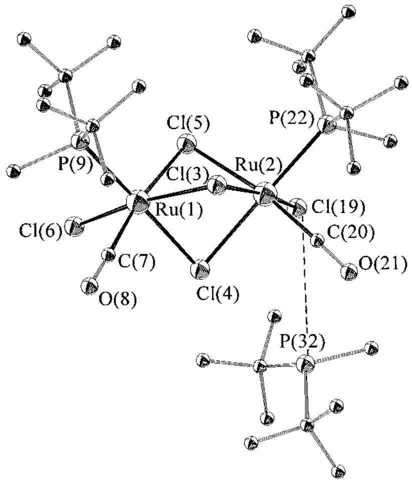


Figure 1. ORTEP drawing of the non-hydrogen atoms of $(HP^tBu_2Me)Ru_2Cl_5(CO)_2(P^tBu_2Me)_2$, showing selected atom labeling. Hydrogen bonding from the (undetected) hydrogen on P(32) of the phosphonium cation is shown as a dashed line to Cl(19).

NMR revealed $[HP^tBu_2Me][Ru_2Cl_5(CO)_2(P^tBu_2Me)_2]$ (64.3, 62.6, 28.7 ppm), $RuCl(C_2Ph)(CO)(P^tBu_2Me)_2$ (41.1 ppm), $Ru(C_2Ph)_2(CO)(P^tBu_2Me)_2$ (47.0 ppm), and P^tBu_2Me (11.8 ppm).

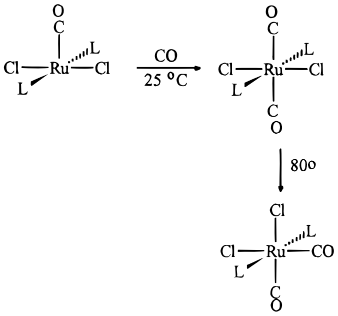
$RuCl(C_2Ph)(CO)(P^tBu_2Me)_2$. PhCCH (30 mg; 0.30 mmol) in toluene (2 mL) was added via a cannula to a 10 mL toluene solution of $RuCl_2(CO)(P^tBu_2Me)_2$ (150 mg; 0.30 mmol) and NEt_3 (90 mg; 0.90 mmol) at −40 °C. The mixture was stirred for 24 h at room temperature, during which a white solid formed. The brown mixture was filtered through a Celite pad. The filtrate was evaporated to dryness, and the residue was extracted with pentane. The pentane solution was concentrated to 3 mL. After 1 day at −40 °C, dark brown crystals precipitated and were filtered off, washed with a small amount of pentane, and dried *in vacuo*. Yield: 125 mg (74%). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 41.0 ppm. ^1H NMR (C_6D_6, room temperature): 1.34 (two overlapping vt, $J = 13.8$ Hz, 36 H, $PCCH_3$), 1.55 (vt, $J = 6.6$ Hz, 6 H, PCH_3), 7.00 (m, 1 H C_6H_5-*p*-H), 7.17 (m, 2 H, C_6H_5 *m*-H), 7.50 (dd, 2 H, C_6H_5-*o*-H) ppm. IR (C_6D_6): 2095 (ν(C≡C)), 1937 (ν(C≡O) cm^{-1}. Anal. Calc (found) for $C_{27}H_{47}ClOP_2Ru$: C, 55.32 (55.37); H, 8.08 (7.95).

***trans,trans*- and *cis,trans*-$RuCl(C_2Ph)(CO)_2(P^tBu_2Me)_2$.** Into a toluene solution of 10 mg of $RuCl(C_2Ph)(CO)(P^tBu_2Me)_2$ was introduced 1 atm of CO at −78 °C. After mixing, the solution color changed from brown to pale orange. $^{31}P\{^1H\}$ NMR at −80 °C showed one peak at 47.0 ppm assigned to *trans,trans*-$RuCl(C_2Ph)(CO)_2(P^tBu_2Me)_2$, which, at room temperature, was completely isomerized to the *cis,-trans* isomer. $^{31}P\{^1H\}$ NMR: 48.0 ppm. ^1H NMR: 1.34 and 1.33 (vt, $J = 13$ Hz, $PCCH_3$), 1.78 (vt, $J = 6.6$ Hz, PCH_3), 7.00 (tt, $J = 7$ Hz, 2 Hz, 1 H, C_6H_5 *p*-H), 7.16 (dd, $J = 8$ Hz, 7 Hz, 2 H, C_6H_5), 7.58 (dd, $J = 8$ Hz, 2 Hz, 2 H, C_6H_5) ppm. IR (C_6D_6): 2027 and 1960 cm^{-1} with equal intensities.

Results

The synthesis of $RuCl_2(CO)L_2$ ($L = P^tBu_2Me$) is conveniently accomplished by refluxing $RuHCl(CO)L_2$ in chloroform for 4 h. A number of other reagents were tried, without success. These include CH_3COCl, $PhCH_2Cl$, *N*-chlorosuccinimide, and CCl_4. This reaction is also quite specific, since it fails to convert either $RuHCl(CO)(P^iPr_3)_2$ or $OsHCl(CO)(P^tBu_2Me)_2$ to the corresponding dichloride.

The structure of $RuCl_2CO(PCy_3)_2$ shows it to be square-pyramidal with CO apical.[8] The ν(CO) value (1937 cm^{-1}) for $RuCl_2(CO)L_2$ is distinctly higher than that for $RuHCl(CO)L_2$ (where CO is *trans* to Cl); this frequency indicates CO in a site *trans* to *no* ligand. We also offer a reactivity result which is in accord with the correctness of the structure for $RuCl_2(CO)L_2$: it reacts (rapidly) with CO to give the *all-trans* isomer (only one ν(CO)). Since this has fewer push/pull interactions from Cl lone pairs to π^*(CO), this isomer is expected to be less stable than the *cis*-dicarbonyl. Indeed, the kinetic isomer is observed to isomerize *completely* to the *cis*-dicarbonyl in toluene solution.



In agreement with the expectation that back bonding will be greater in the *cis*-dicarbonyl, its asymmetric ν(CO) value is 17 cm^{-1} lower than that of the *trans*-dicarbonyl. Both the *cis* and the *trans* isomers show only a single $^{31}P\{^1H\}$ NMR chemical shift and a single ^{t}Bu proton virtual triplet.

Hydrogenolysis of $RuCl_2(CO)L_2$. Reaction of $RuCl_2(CO)L_2$ ($L = P^tBu_2Me$) with 1 atm of H_2 in toluene at 25 °C gives, with the time of our first NMR observation (20 min), complete consumption of the dichloride complex with production of some $RuHCl(CO)L_2$. Also evident by $^{31}P\{^1H\}$ NMR spectroscopy are a group of signals due to isomers of $Ru_2Cl_5(CO)_2L_2^-$ (see below) and the resonance due to protonated phosphine, $HP^tBu_2Me^+$. The reactions forming these two products are those in eqs 4 and 5, which show that the relative amounts of $RuHCl(CO)L_2$ and $Ru_2Cl_5(CO)_2L_2^-$ will be influenced by stirring rate, by the rates of the reactions in eqs 4 and 5, and by the concentrations of dissolved H_2 and HCl.

$$RuCl_2(CO)L_2 + H_2 \rightarrow RuHCl(CO)L_2 + HCl \qquad (4)$$

$$2RuCl_2(CO)L_2 + HCl \rightarrow [LH][Ru_2Cl_5(CO)_2L_2] + L \qquad (5a)$$

$$L + HCl \rightleftharpoons [LH]Cl \qquad (5b)$$

$[LH][Ru_2Cl_5(CO)_2L_2]$. This compound crystallizes well in any of the reactions described in this report where it is formed in toluene. It can be conveniently recrystallized from CH_2Cl_2/Et_2O. The $^{31}P\{^1H\}$ NMR of recrystallized material shows (25 °C) two resonances of unequal intensity at 64.2 ppm (intensity 37) and 62.3 ppm (intensity 30) and a third, due to LH^+, at 29.2 ppm (intensity 33). The intensity ratio of cation to the sum of the 60−70 ppm resonances is ~1:2, consistent with a formula $[LH][Ru_2Cl_5(CO)_2L_2]$. The ^1H NMR spectrum of this product in C_6D_6 shows ^{t}Bu and Me doublets for $HP^tBu_2Me^+$ and four ^{t}Bu *doublets* for phosphines attached to Ru. There are also two PMe doublets. If it is formed according to eq 5a (which has been independently verified), consumption of $RuCl_2(CO)L_2$ is complete at an HCl:Ru ratio of 0.5 (see eq 5a and also see below). The resulting product has a ν(CO) stretching pattern in its infrared spectrum (in C_6D_6) composed of one strong band (1948 cm^{-1}) with a weak shoulder at ~1957 cm^{-1}. All of these spectra suggest two isomeric forms for $Ru_2Cl_5(CO)_2L_2^-$.

The formula of one crystal from solid samples which reproducibly give a three-line $^{31}P\{^1H\}$ NMR spectrum was established by single-crystal X-ray diffraction to be $[LH][Ru_2Cl_5(CO)_2L_2]$, as shown in Figure 1. It is a face-shared bioctahedron with three bridging halides, which is a common way for Ru(II)

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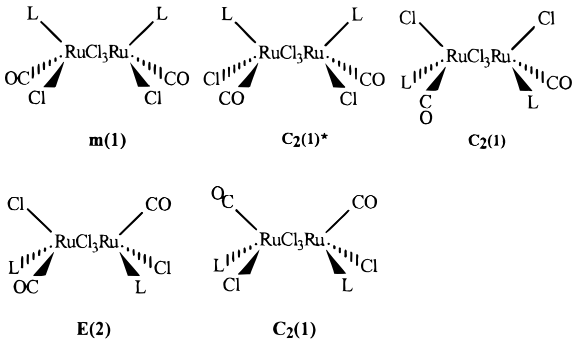
(8) Moers, F. G.; Beurskens, P. T.; Noordijk, J. H. *Cryst. Struct. Commun.* **1982**, *11*, 1655.

Chart 1

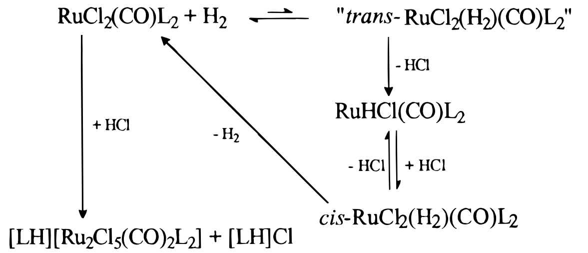


to achieve coordination number 6 when ligands are in short supply (i.e., HCl has consumed phosphine ligands under our reaction conditions). There are five possible isomers, based on the configuration of the two Ru(CO)LCl units. They are shown in Chart 1, together with their symmetry, followed by the expected number of ^{31}P NMR chemical shifts. The crystal selected for the X-ray study contains primarily the mirror-symmetric structure in Chart 1. There is however an 85:15 disorder of CO and Cl in the crystal selected. The disorder is consistent with a 70:15:15 occupation by isomer *m* and the two enantiomers of the isomer marked with an asterisk in Chart 1. The overall structure of the major (and also the minor) anion has phosphine ligands eclipsed at opposite ends, although it is clear that there are no significant repulsions between the eclipsed bulky phosphines. It is of course significant that Ru(II) molecules with *two* bulky P^{t}Bu$_2$Me ligands are always five-coordinate monomers (i.e., halide bridging is absent), yet here, with only one P^{t}Bu$_2$Me ligand per Ru, a face-shared bioctahedron is adopted. Ru−Cl bond lengths are longer to μ-Cl (average 2.473(3) Å) than to terminal Cl (average 2.377(4) Å), and Ru−(μ-Cl) distances lengthen systematically according to the ligand in the *trans* site according to Cl < CO < P^{t}Bu$_2$Me. The Ru−CO distances are short (average 1.843(15) Å), and Ru−C−O angles are essentially linear (angles exceed 175.2°). Angles at μ-Cl range from 82.3(7) to 85.8(7)°, and (μ-Cl)−Ru−(μ-Cl) angles are much less than 90° (79.0(1)−81.3(1)°). This furnishes more room for the bulky phosphines, but angles involving terminal ligands are all less than 92.9°. An analogous anion, $Ru_2(\mu\text{-}Cl)_3Cl_2(CO)_2(PPh_3)_2^-$, was isolated following protonation (CH_2ClCO_2H) of $RuHCl(CO)(PPh_3)_3$.[9] The face-shared octahedron is of extremely common occurrence for Ru(II).[10]

The phosphonium proton appears to be involved in a hydrogen bond to chloride in the solid state. The P−H vector points in the direction of terminal Cl(19), and bridging chloride Cl(4), with the P(32)/Cl(19) contact the shorter at 3.86 Å. This is only 0.25 Å longer (after correction for P *vs* N single-bond radii) than found for strong N−H···Cl hydrogen bonds.[11] Such hydrogen bonding helps to explain the benzene solubility of this salt.

Search for Reaction Intermediates. Although reaction of $RuCl_2(CO)L_2$ with H_2 at room temperature is complete within 20 min, attempts to detect its H_2 adduct were unsuccessful even at −120 °C because of a low equilibrium constant. Nevertheless, T_1 of H_2 in the presence of $RuCl_2(CO)L_2$ is 110 ms at −60 °C, much shorter than that of free dissolved H_2, and indicating weak interaction of H_2 with $RuCl_2(CO)L_2$. The reaction of H_2 and $RuCl_2(CO)L_2$ occurs at temperatures >−40 °C to form L, $[HL][Ru_2Cl_5(CO)_2L_2]$, and $RuHCl(CO)L_2$. The proposed reaction mechanism is depicted in Scheme 1 (the compound in quotation marks is unobserved). H_2 binds to $RuCl_2(CO)L_2$ to form an unobservable *trans*-$RuCl_2(H_2)(CO)L_2$ transient, which generates $RuHCl(CO)L_2$ by dissociation of HCl. The Brønsted acidity of coordinated H_2 is well established.[12] The generated HCl reacts with $RuCl_2(CO)L_2$ to form $[HL][Ru_2Cl_5(CO)_2L_2]$ and L. This could be confirmed in two ways. First, reaction of $RuCl_2(CO)L_2$ with H_2 in the presence of the HCl scavenger NEt_3 (which does not bind detectably to $RuCl_2(CO)L_2$) at room temperature in benzene gives 100% yield (^{31}P{^{1}H} and ^{1}H NMR) of $RuHCl(CO)L_2$ and $[HNEt_3]Cl$. In addition, reaction of HCl with $RuCl_2(CO)L_2$ at a 1:2 mole ratio at room temperature in benzene gives a 100% yield (^{31}P{^{1}H} NMR) of $[HL][Ru_2Cl_5(CO)_2L_2]$ and equimolar L.

Scheme 1



Characterization and Decomposition Pathways of *cis*-$RuCl_2(H_2)(CO)L_2$. We sought to evaluate whether the Ru_2 anion was formed only from HCl attack on $RuCl_2(CO)L_2$ or also from HCl reacting with the primary product $RuHCl(CO)L_2$. Our early attempts to synthesize $RuCl_2(CO)L_2$ according to eq 6 at 25 °C were completely unsuccessful (the ^{31}P{^{1}H} NMR spectrum of the product solution contained numerous resonances, indicative of an unselective reaction). This suggested that simple chloride-for-hydride replacement was not viable. Our results also showed that 2.5 equiv of HCl had to be used to completely consume the hydride. When slightly less than 1 equiv of HCl gas is combined with $RuHCl(CO)L_2$ in toluene at −70 °C (Figure 2), ^{31}P{^{1}H} NMR revealed a broad peak at 54 ppm for one rotamer of $RuHCl(CO)L_2$ (A),[13] a major peak at 48.4 ppm (B) (*cis*-$RuCl_2(H_2)(CO)L_2$), and a trace amount of $RuCl_2(CO)L_2$ (C). The assignment of the 48.4 ppm peak is further supported by the ^{1}H NMR data obtained under the same conditions: a broad peak at −9 ppm, which has $T_{1\min} = 6.9$ ms at −70 °C, for η^2-H_2. The calculated r_{H-H} distance is 0.891 Å for slow-spinning H_2 (J_{HD} for $Ru(\eta^2\text{-}HD)Cl_2(CO)L_2$ is measured as 28 Hz). In addition, two virtual triplets for diastereotopic ^{t}Bu groups on the phosphine ligands confirm a *cis* geometry. When the sample was warmed to −50 °C, the major signal sharpened while the $RuHCl(CO)L_2$ peak broadened. Trace amounts of $RuCl_2(CO)L_2$ (C) and free H_2 (in the ^{1}H NMR) were also observed. A dramatic change occurred at −40 °C. The intensity of the $RuCl_2(CO)L_2$ peak (38 ppm) increased signifi-

$$RuHCl(CO)L_2 + HCl \overset{?}{\rightarrow} RuCl_2(CO)L_2 + H_2 \qquad (6)$$

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(9) Sanchez-Delgado, R. A.; Thewalt, U.; Valencia, N.; Andriollo, A.; Márquez-Silva, R. *Inorg. Chem.* **1986**, *25*, 1097.

(10) Ohta, T.; Tonomura, Y.; Nozaki, K.; Takaya, H.; Mashima, K. *Organometallics* **1996**, *15*, 1521. Joshi, A. M.; Thorburn, I. S.; Rettig, S. J.; James, B. R. *Inorg. Chim. Acta* **1992**, *198−200*, 283. Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*; Elsevier: Amsterdam, 1984; p 497.

(11) Halepoto, D. M.; Larkworthy, L. F.; Povey, D. C.; Smith, G. W.; Ramdas, V. *Polyhedron* **1995**, *14*, 1453.

(12) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155.

(13) Notheis, J. U.; Heyn, R. H.; Caulton, K. G. *Inorg. Chim. Acta* **1995**, *229*, 187. $RuHCl(CO)L_2$ exhibits three rotamers at −70 °C. Major isomer (>90%) is at 54 ppm (singlet) (^{31}P{^{1}H} NMR). Two minor isomers are at 42 and 40 ppm.

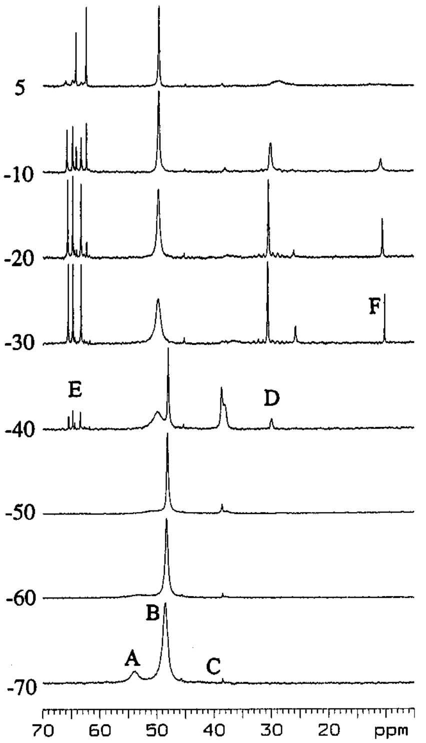
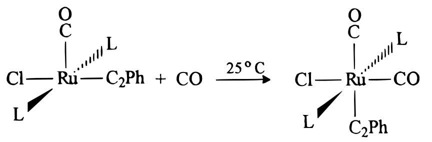


Figure 2. Variable-temperature $^{31}P\{^1H\}$ NMR spectra for the reaction of $RuHCl(CO)L_2$ with less than equimolar HCl. Reactants were combined below −70 °C, and the progress of the reaction was monitored as the temperature (shown at left) was raised.

cantly along with the $RuHCl(CO)L_2$ peak. Several peaks in the region 63−65 ppm (E) are attributed to many possible isomers of $Ru_2Cl_5(CO)_2L_2^-$. The counterion HL^+ appears at 30 ppm (D). On ^1H NMR integration, the ratio of free H_2, the proton of $RuHCl(CO)L_2$, and bound H_2 on $Ru(H_2)Cl_2(CO)L_2$ is 1:1.2:1. At −30 °C, $Ru(H_2)Cl_2(CO)L_2$ and $RuCl_2(CO)L_2$ were transformed to $[Ru_2Cl_5(CO)_2Cl_2]^-$, $RuHCl(CO)L_2$, HL^+, and L (10 ppm) (F). Detection of free L at this temperature indicates that it is dissociated from ruthenium spontaneously and is not induced by direct protonation of phosphorus itself. The conclusion is that eq 5a may be initiated by protonation of Cl on Ru. Consumption of $RuCl_2(CO)L_2$ can be caused either by reaction with H_2 in the solution or by HCl dissociated from *cis*-$RuCl_2(H_2)(CO)L_2$; both routes produce $RuHCl(CO)L_2$. The ^1H NMR intensity of the free H_2 signal decreases, indicating reaction of H_2 with $RuCl_2(CO)L_2$. However, no evidence can be obtained to rule out the dissociation of HCl from *cis*-$RuCl_2(H_2)(CO)L_2$. Above −30 °C, rearrangements of the isomers of $Ru_2Cl_5(CO)_2L_2^-$ and coalescence of HL^+ and L are the only changes (Scheme 1). The $RuHCl(CO)L_2$ which remains is due to the substoichiometric amount of HCl used. It is clear that the failure to synthesize $RuCl_2(CO)L_2$ by this reaction is due to the competing dissociation of H_2 and HCl, which reacts immediately with $RuCl_2(CO)L_2$ to form $Ru_2Cl_5(CO)_2L_2^-$.

Reaction of PhC_2H as a Brønsted Acid toward $RuCl_2(CO)L_2$. Additional evidence for the Brønsted basicity of the chloride ligands in $RuCl_2(CO)L_2$ comes from its reaction with a terminal alkyne. In the presence of NEt_3 as a proton acceptor, PhC_2H reacts cleanly with $RuCl_2(CO)L_2$ to give $RuCl(C_2Ph)(CO)L_2$ and $[HNEt_3]Cl$ as the only products. In the absence of NEt_3, the liberated HCl reacts with $RuCl_2(CO)L_2$ to give some $Ru_2Cl_5(CO)_2L_2^-$. This is an effective synthetic route to this halo/acetylide compound not only because it does not require an electropositive metal acetylide reagent but also because the reaction of LiC_2Ph with $RuCl_2(CO)L_2$ (1:1 mole ratio) gives mainly $Ru(C_2Ph)_2(CO)L_2$ and a small amount of $Ru(C_2Ph)Cl(CO)L_2$, together with unreacted $RuCl_2(CO)L_2$. Apparently, LiC_2Ph reacts more rapidly with (the more electrophilic) $RuCl(C_2Ph)(CO)L_2$ than with $RuCl_2(CO)L_2$.

The product $RuCl(C_2Ph)(CO)L_2$ shows two ^1H NMR virtual triplets for the (diastereotopic) ^{t}Bu groups, a virtual triplet for the PMe groups, and a ν(CO) value essentially identical to that of $RuCl_2(CO)L_2$. This strongly suggests that CO occupies the apical site that it does in $RuCl_2(CO)L_2$, since CO in a basal site has a lower ν(CO) value due to more efficient (*trans*) back-donation. At 25 °C, $Ru(C_2Ph)Cl(CO)(P^tBu_2Me)_2$ absorbs 1 equiv of CO (eq 7) to give $Ru(C_2Ph)Cl(CO)_2(P^tBu_2Me)_2$, which



(7)

shows two ν(CO) bands (2027, 1960 cm^{-1}; intensities 1:1). This indicates that the *cis* isomer is formed. However, on repetition of this reaction at −80 °C in toluene, a kinetic product is observed ($^{31}P\{^1H\}$ NMR signal at 47 ppm). This isomerizes within 20 min at 25 °C to the *cis* isomer. We assign the kinetic product to be the isomer with the two CO ligands mutually *trans*, which is clearly the product of approach of dissolved CO to the open site of this square-pyramidal monocarbonyl.

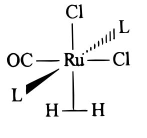
Base-induced elimination of HCl has been employed[14] to form Pt/C bonds in the polymerization of (HC≡C−aryl)PtCl. Brønsted basic halide on late transition metals may thus be of rather general occurrence.

Other Reactions. In the course of our attempts at halide metathesis of $RuCl_2(CO)L_2$ with NaI, LiBr, and CsF in acetone, we have observed the production of free P^tBu_2Me and several $^{31}P\{^1H\}$ NMR singlets between 60 and 70 ppm. These we propose to be a species analogous to that arising from HCl: $M^I[Ru_2(halide)_5(CO)_2L_2]$.

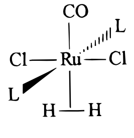
We consider that these results, taken together, show that $RuCl_2(CO)L_2$, when it adds a sixth ligand, shows a tendency to lose one of its bulky phosphine ligands, with subsequent halide-bridged aggregation of the resulting unsaturated $RuCl_2(CO)(Nu)L$ (Nu = H_2, Cl^-, ClH, F^-, or I^-). This aggregation becomes possible (while it was not for $RuCl_2(CO)L_2$) because of the diminished steric encumbrance of the metal after loss of phosphine. This is shown in Scheme 2.

Conclusions

While we have established that the thermodynamic isomer *cis*-$RuCl_2(H_2)(CO)L_2$ (**A**) is a dihydrogen complex, its *trans* isomer (**B**) is not observable in NMR. This is consistent with



A



B

the *trans* effect of CO in **B** preventing a close approach of H_2 to Ru and therefore minimal back-donation to σ^*(H−H). The formation constant for **B** is thus very low. In contrast, H_2 in isomer **A** is *trans* to a weaker σ ligand Cl, and thus H_2 can approach closer to Ru, where dπ to σ^*(H−H) overlap is more

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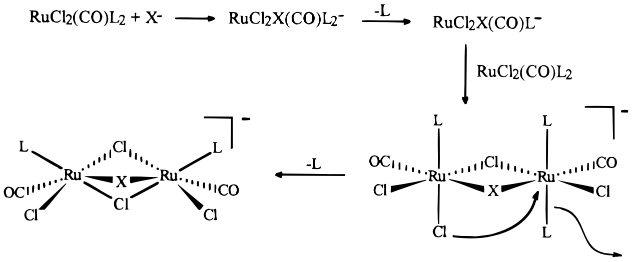
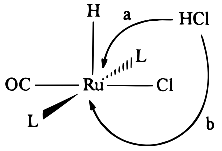
(14) James, S. L.; Verspui, G.; Spek, A. L.; van Koten, G. *Chem. Commun.* **1996**, 1309.

Scheme 2



efficient. Back-donation is even more effective in **A** because the filled−filled repulsion of Cl *trans* to H_2 raises the energy of the filled dπ orbital toward that of σ^*(H−H). Consistent with these observations, the *cis* isomer $OsCl_2(H_2)CO(P^iPr_3)_2$ (the *trans* isomer is unknown) binds H_2 so well that it is not removed under vacuum,[15] either in toluene solution or as a solid.

The results reported here show the dramatic influence of synthetic approach (HCl and $RuHCl(CO)L_2$ *vs* H_2 and $RuCl_2(CO)L_2$) on the isomeric products obtained. Our study also reveals that, in spite of the square-pyramidal geometry of $RuCl_2(CO)L_2$ with CO *trans* to a vacant site, the activation energy for H_2 addition is high enough that no *cis* $RuCl_2(H_2)(CO)L_2$ (**A**) can be formed by mixing H_2 and $RuCl_2(CO)L_2$ at low temperature. In contrast, HCl reacts with $RuHCl(CO)L_2$ to produce a product (**A**) which appears as if it has added within the H−Ru−Cl angle to produce coordinated H_2 and mutually *cis* chlorides (**C**, path **a**). This could be a concerted reaction, initiated by hydrogen bonding of HCl to coordinated hydride (or chloride), but it may also proceed via a nonconcerted path, involving $Ru(H_2)Cl(CO)L_2^+$ and free chloride, or by an intermediate with HCl added *trans* to the hydride (**C**, path **b**).



C

Finally, we cannot be certain whether the HCl reaction with $RuCl_2(CO)L_2$ begins with protonation of coordinated Cl (*cf.* H^+ + $Os(H)_2Cl_2L_2$[16]), protonation of the metal (*cf.* protonation of $W(CO)_3(PCy_3)_2$),[17] or coordination of the molecular *Cl*H to Ru (compare η^1-*Cl*H bound to Pt(II)[18]).

The reactivity of $RuXCl(CO)L_2$ with H_2 is very different for X = H (only weak adduct formation, to give an η^2-H_2 complex) and for X = Cl (hydrogenolysis of an Ru−Cl bond, with liberation of HCl). The latter case is an unusual example of simple (i.e., two-component) heterolytic splitting of H_2,[2] without the necessity of added base. However, it is clear from the work reported here that the liberation of HCl can be dangerous (here, it reacts with $RuCl_2(CO)L_2$ to give a diruthenium species). The distinct reactivity of these two $RuXCl(CO)L_2$ species may originate in part because of their different structures (H and CO apical, respectively), but the occurrence of proton transfer by coordinated H_2 to Cl suggests that the enhanced Brønsted basicity of chloride when X = Cl is a significant contributor to the observed reactivity. $RuCl_2(CO)L_2$ also shows unusual reactivity with PhC_2H: the alkyne acts like a Brønsted acid toward the chloride. $RuHCl(CO)L_2$, in contrast, adds the Ru−H bond across the alkyne triple bond.[19]

It was recently reported[20] that a solution containing a *di*chlororuthenium species ($RuH_nCl_2(P^iPr_3)_2$?) reacts with CO to give the *mono*chloro species $RuHCl(CO)_2(P^iPr_3)_2$. We suggest that this reaction involves loss of HCl (compare eq 4 here) and is thus closely related to the behavior of $RuH_2Cl_2(CO)L_2$ we report here. Moreover, the original report[6] isolated an otherwise unidentified product of reaction of HCl with $RuHCl(CO)[P^tBu_2Me]_2$; this product is that shown in Figure 1.

Acknowledgment. This work was supported by funds from the National Science Foundation and by material from Johnson Matthey/Aesar. We thank Dr. D. G. Gusev for crucial contributions to our understanding of these results.

Supporting Information Available: Tables of full crystallographic details, fractional coordinates, and anisotropic thermal parameters (3 pages). Ordering information is given on any current masthead page.

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