bands ($\epsilon > 10\,000$ M^{-1} cm^{-1}) seen in certain sulfur-containing Mo(IV,V) systems, which have been interpreted to indicate electron delocalization over the binuclear unit, are absent. However, some recent examples of oxo-bridged vanadium(IV)–vanadium(V) systems, in which delocalization has been demonstrated by EPR, show relatively weak visible absorptions.[18]

Substitution of bridging oxides by sulfide in the EDTA complexes results in broadening of these transitions and their displacement toward longer wavelengths (Figure 3) although the similar intensities of the absorption bands of the μ-oxo- and μ-sulfido-bridged complexes suggest that the same transitions are involved. However, all the complexes studied have similar stabilities with respect to reoxidation and are highly reactive toward oxygen. The decomposition mechanism of the mixed-valence complex is unclear. The reduction of a liganded carboxylate group might occur in any of the systems studied. However, the relative insensitivity of the absorption spectrum of the $Mo^{V}_2O_4^{2+}$ unit to its ligands prevented the confirmation of this possibility. The reducing strength of Mo(IV) in these mixed-valence systems undoubtedly results from the tendency to re-form the strong covalent bonding between Mo(V) atoms[16] in the $Mo_2O_4^{2+}$ or $Mo_2O_2S_2^{2+}$ moieties. The presence of bridging sulfides in the EDTA system does not appear to result in significant stabilization of the Mo(IV)–Mo(V) state.

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Nitrosyl Complexes of Rhenium. 2.[1] Neutral and Cationic Monohydride Complexes of Rhenium(I) Resulting from the Reaction of $ReH_2(NO)(PPh_3)_3$ with Perchloric Acid

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The rhenium dihydride complex $ReH_2(NO)(PPh_3)_3$ reacts with $HClO_4$ in the presence of CO with the cleavage of only one hydride ligand. Careful control of the degree of acidity and the solvent system leads to isolation of compounds such as $ReH(OR)(CO)(NO)(PPh_3)_2$ (R = Me, Et) and $[ReH(CO)(NO)(PPh_3)_3]ClO_4$. The alkoxide complexes are protonated by $HClO_4$ at the alkoxide oxygen to yield alcohol complexes $ReH(ROH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$, in which the perchlorate counterion is hydrogen bound to the coordinated alcohol. Heating $ReH(MeOH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$ in methanol results in the formal 1,2-elimination of dihydrogen with concomitant formation of $Re(OMe)(OClO_3)(CO)(NO)(PPh_3)_2$. A similar elimination reaction occurs when the alcohol complexes are reacted with halide ions to give $ReX(OR)(CO)(NO)(PPh_3)_2$ (X = Cl, Br, I). Reacting the alcohol complexes with base or $NaBH_4$, however, regenerates $ReH(OR)(CO)(NO)(PPh_3)_2$. The perchlorate complex, $Re(OMe)(OClO_3)(CO)(NO)(PPh_3)_2$, while reacting with halide ions merely with displacement of the perchlorate group, reacts with $NaBH_4$ to give $ReH_2(CO)(NO)(PPh_3)_2$ via a putative borohydride complex. The chloro–alkoxy complexes $ReCl(OR)(CO)(NO)(PPh_3)_2$ also react with $HClO_4$ to give alcohol complexes, which are considerably more labile than their hydride analogues. All structural assignments have been made on the basis of elemental analysis, infrared spectroscopy, ^1H NMR spectroscopy, and, where appropriate, deuteration studies.

Introduction

In a recent publication,[1] we described the reaction of $ReH_2(NO)(PPh_3)_3$ with HBF_4 in the presence of carbon monoxide to yield $[ReF(CO)(NO)(PPh_3)_3]BF_4$. The isoelectronic complex $OsH_2(CO)(PPh_3)_3$ behaves quite differently, affording $[OsH(CO)_2(PPh_3)_3]BF_4$ under the same conditions.[2] In the same publication we also described $ReH_2(NO)(PPh_3)_3$ as reacting with $HClO_4$ and CO with apparent decomposition. We have had cause to reinvestigate this system and have found that provided the conditions are carefully controlled, a wealth of chemistry can be obtained. In particular, we have found that in the absence of a source of good coordinating anions, cleavage of only one hydride ligand occurs, leading to a series of monohydride–nitrosyl complexes of rhenium(I). In this paper we describe a number of these complexes including $ReH(MeOH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$, which, on heating, undergoes an unusual elimination of dihydrogen.

Experimental Section

Caution! These compounds should be treated with the extreme caution normally afforded organometallic perchlorate salts, which are potentially explosive.[3] In particular, complexes **4**, **5**, **14**, and **15** described below have decomposed violently and without warning. To minimize the hazard we recommend the following precautions be taken when handling these complexes: (i) keep reaction scales to <0.5 g, (ii) avoid the use of metal spatulas since the decomposition appears to be catalyzed by finally divided metal particles, and (iii) use complexes when prepared and refrain from storing them in a sealed container.

Except where otherwise stated, all reactions were performed under an atmosphere of prepurified nitrogen (O_2 < 3 ppm). All solvents were appropriately dried, distilled, and stored over Linde type 4A molecular sieves prior to use. Infrared spectra were recorded on a Perkin-Elmer 283B spectrophotometer and calibrated against polystyrene. ^1H NMR spectra were recorded either on a Varian Associates CFT 20 spectrometer or the Nicolet 360-MHz instrument of the Atlantic Regional Magnetic Resonance Centre as CD_2Cl_2 solutions with either the $CHDCl_2$ triplet at 5.32 ppm or Me_4Si used as internal reference. ^{31}P NMR spectra were obtained on the Varian Associates XL100 spectrometer of the Atlantic Regional Laboratory of the NRC, whose services are gratefully acknowledged. Melting points were recorded on a Fisher-Johns apparatus and are uncorrected. Conductivity measurements were performed by using a conductivity bridge of local manufacture with ca. 10^{-3} M solutions in dichloromethane or nitromethane. The cell constant was determined by using a 0.0100 M aqueous KCl solution. Elemental analyses were performed by the Canadian Microanalytical Service Ltd.

Reaction of $ReH_2(NO)(PPh_3)_3$ with $HClO_4$ and CO. Synthesis of $ReH(OCH_3)(CO)(NO)(PPh_3)_2$ (1). $ReH_2(NO)(PPh_3)_3$[1] (1.00 g, 1.00 mmol) was suspended in dichloromethane–methanol (40 mL, 1:1 v/v) and the suspension degassed by rapidly bubbling carbon monoxide through for 20 min. Upon the addition of perchloric acid (0.20 mL, 70% w/v) immediate dissolution of the solid was observed with effervescence. Once dissolution was complete, 0.5 M sodium methoxide solution was added dropwise until the bright yellow solution became just slightly basic (Fisher Alkacid test paper). The passage of carbon monoxide was continued for a further 5 min after which the dichloromethane was removed slowly under reduced pressure. Pale yellow crystals were deposited from a small volume of solution and were generally sufficiently pure for further

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[1] Part 1: Cameron, T. S.; Grundy, K. R.; Robertson, K. N. *Inorg. Chem.* **1982**, *21*, 4149.

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use. When necessary, recrystallization was from dichloromethane–methanol. Yields were generally in the range of 0.62–0.75 g (75–90%); mp 149–154 °C. Anal. Calcd for $C_{38}H_{34}NP_2O_3Re$: C, 56.99; H, 4.28; N, 1.75. Found: C, 56.71; H, 4.50; N, 1.80. Λ_M (Ω^{-1} cm^2 mol^{-1}): 0.33 (CH_2Cl_2).

$ReD(OCH_3)(CO)(NO)(PPh_3)_2$ (1a). This complex was prepared as above on a 0.2 g scale by using $ReD_2(NO)(PPh_3)_3$, dichloromethane–methanol-d_1 as solvent and 30% $DClO_4$ in D_2O. Neutralization was achieved by adding sodium methoxide in methanol. The $ReD_2(NO)(PPh_3)_3$ (ν(NO) = 1650 vs cm^{-1}; ν(ReD) = 1410 m, 1270 m cm^{-1}) was prepared from $ReCl_2(OC_2H_5)(NO)(PPh_3)_2$ and $NaBD_4$ in ethanol-d_1. Recrystallization of $ReD_2(NO)(PPh_3)_3$ resulted in extensive loss of the deuterium label as a result of what appears to be rapid scrambling between the hydride and phenyl ortho protons of the phosphine ligands. Hence, the procedure of **1a** was modified slightly by adding the crude $ReD_2(NO)(PPh_3)_3$ to the CO-saturated solution along with the acid.

$ReH(OC_2H_5)(CO)(NO)(PPh_3)_2$ (2). This complex was prepared in a manner analogous to that described for **1** above by using ethanol and sodium ethoxide solution instead of methanol and sodium methoxide solution. Yields of the yellow crystals were generally in the range 0.52–0.62 g (65–75%); mp 141–143 °C dec. Anal. Calcd for $C_{39}H_{36}NP_2O_3Re$: C, 57.48; H, 4.45; N, 1.72. Found: C, 57.42; H, 4.33; N, 1.75. Λ_M (Ω^{-1} cm^2 mol^{-1}): 0.35 (CH_2Cl_2).

Synthesis of $[ReH(CO)(NO)(PPh_3)_3]ClO_4$ (3). $ReH_2(NO)(PPh_3)_3$ (0.50 g, 0.50 mmol) was suspended in dichloromethane–ethanol (40 mL, 1:1 v/v), and carbon monoxide was passed through the suspension for 15 min. Perchloric acid (0.10 mL, 70% w/v) was added to the suspension, resulting in effervescence and dissolution of the remaining solid. After carbon monoxide was passed for a further 15 min, 0.5 M sodium ethoxide solution was added dropwise to the resulting golden-yellow solution until testing with Universal Indicator paper showed it to be only slightly acidic. The solution was kept purged with carbon monoxide for a further 15 min, after which time the solvent was reduced to ca. 10 mL under reduced pressure. The resultant solution was allowed to remain sealed and undisturbed for 24–48 h, during which time large yellow crystals were deposited. The crystals were removed by filtration and recrystallized from dichloromethane–ethanol containing 1 drop of perchloric acid (ca. 0.25 g, 50%); mp 167–168 °C. Anal. Calcd for $C_{55}H_{46}NP_3ClO_6Re$: C, 58.38; H, 4.10; N, 1.24; P, 8.21. Found: C, 58.50; H, 4.23; N, 1.27; P, 9.78. Λ_M (Ω^{-1} cm^2 mol^{-1}): 15.4 (CH_2Cl_2), 76.5 (CH_3NO_2).

Reaction of $ReH(OCH_3)(CO)(NO)(PPh_3)_2$ with $HClO_4$. Synthesis of $ReH(CH_3OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$ (4). To $ReH(OCH_3)(CO)(NO)(PPh_3)_2$ (0.25 g, 0.31 mmol) suspended in 2 mL of dichloromethane was added perchloric acid (0.05 mL, 70% w/v). No reaction was visible until the addition of 5 mL of diethyl ether, which resulted in the immediate dissolution of the solid. The further addition of 50 mL of diethyl ether followed by several minutes of stirring saw the precipitation of the product as pale yellow crystals, which were collected by filtration and used immediately without further purification. Samples for analysis were recrystallized from dichloromethane–diethyl ether at −18 °C (0.27 g, 100%); mp 148–152 °C dec. Anal. Calcd for $C_{38}H_{35}NP_2ClO_7Re$: C, 50.64; H, 3.91; N, 1.55. Found: C, 50.28; H, 3.85; N, 1.57. Λ_M (Ω^{-1} cm^2 mol^{-1}): 1.9 (CH_2Cl_2), 83.5 (CH_3NO_2).

$ReH(C_2H_5OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$ (5). This complex was prepared in a manner analogous to that described above, with $ReH(OC_2H_5)(CO)(NO)(PPh_3)_2$ used as starting material. A greater volume of ether was sometimes required for precipitation of the product (0.27 g, 100%); mp 117–121 °C dec. Anal. Calcd for $C_{39}H_{37}NP_2ClO_7Re$: C, 51.18; H, 4.07; N, 1.53. Found: C, 51.76; H, 4.51; N, 1.47. Λ_M (Ω^{-1} cm^2 mol^{-1}): 2.9 (CH_2Cl_2), 82.0 (CH_3NO_2).

Elimination of H_2 from $ReH(CH_3OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$. Synthesis of $Re(OCH_3)(OClO_3)(CO)(NO)(PPh_3)_2{\cdot}H_2O$ (6). Freshly prepared $ReH(CH_3OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$ (0.25 g, 0.28 mmol) was dissolved in 20 mL of methanol, and the pale yellow solution was heated very slowly to reflux. After 15 min under reflux the color had darkened perceptibly to yellow-orange. Removal of the solvent under reduced pressure precipitated the product as an orange solid from a small volume of solution. Recrystallization was from dichloromethane–methanol in the presence of 1 drop of 70% perchloric acid (0.16–0.22 g, 63–88%); mp 147–149 °C. Anal. Calcd for $C_{38}H_{35}NP_2ClO_8Re$: C, 49.75; H, 3.85; N, 1.53. Found: C, 49.90; H, 3.98; N, 1.52. Λ_M (Ω^{-1} cm^2 mol^{-1}): 4.6 (CH_2Cl_2), 83.8 (CH_3NO_2).

Reaction of $ReH(CH_3OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$ with Nucleophiles. A. $NaBH_4$. To $ReH(CH_3OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$ (0.20 g, 0.22 mmol) suspended in 5 mL of methanol was added solid $NaBH_4$ (0.05 g, 1.3 mmol) in several small portions. Immediate effervescence was observed along with a lightening in color of the suspension. After the mixture was stirred for a further 30 min, the pale yellow solid was removed by filtration and recrystallized from dichloromethane–methanol. Comparison with an authentic sample established the product as $ReH(OCH_3)(CO)(NO)(PPh_3)_2$ (0.18 g, 97%).

B. $NaOCH_3$. To $ReH(CH_3OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$ (0.15 g, 0.17 mmol) dissolved in 25 mL of methanol was added 0.5 M sodium methoxide solution dropwise until the solution was just basic. Shortly after addition of the base, a pale yellow solid identified as $ReH(OCH_3)(CO)(NO)(PPh_3)_2$ precipitated (0.14 g, 100%).

C. LiCl. Synthesis of $ReCl(OCH_3)(CO)(NO)(PPh_3)_2{\cdot}(CH_2Cl_2)_{0.5}$ (7). Freshly prepared $ReH(CH_3OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$ (0.22 g, 0.24 mmol) and LiCl (0.013 g, 0.29 mmol) were dissolved in 60 mL of a dichloromethane–methanol mixture (1:1 v/v) and left to stir. After ca. 30 min. the pale yellow product began to separate slowly from solution. After a further 30 min, the dichloromethane was removed by evaporation under reduced pressure and the product separated and recrystallized from dichloromethane–methanol (0.17 g, 82%); mp 211–213 °C. Anal. Calcd for $C_{38}H_{33}NO_3ClP_2Re{\cdot}(CH_2Cl_2)_{0.5}$: C, 52.68; H, 3.90; N, 1.60; Cl, 8.08. Found: C, 52.43; H, 3.73; N, 1.60; Cl, 7.81. Evidence for the CH_2Cl_2 of solvation occurred in the ^1H NMR ($CDCl_3$) at δ 5.32 (s, 1 H). Λ_M (Ω^{-1} cm^2 mol^{-1}): 0.28 (CH_2Cl_2).

Prepared in similar fashion were **$ReBr(OCH_3)(CO)(NO)(PPh_3)_2{\cdot}(CH_2Cl_2)_{0.5}$ (8)** (72%, mp 216–218 °C) and **$ReI(OCH_3)(CO)(NO)(PPh_3)_2$ (9)** (77%, mp 202–203 °C).

Reaction of $ReH(C_2H_5OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$ with Nucleophiles. In a fashion entirely analogous to $ReH(CH_3OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$, $ReH(C_2H_5OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$ reacted with $NaBH_4$ and $NaOC_2H_5$ solution to regenerate $ReH(OC_2H_5)(CO)(NO)(PPh_3)_2$, which was characterized by comparison with a genuine sample. Reacting $ReH(C_2H_5OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$ with the appropriate lithium halides in a manner analogous to that described above except for the use of ethanol instead of methanol yielded, for LiCl, **$ReCl(OC_2H_5)(CO)(NO)(PPh_3)_2{\cdot}(CH_2Cl_2)_{0.5}$ (10)**: 85%, mp 209–211 °C. Anal. Calcd for $C_{39}H_{35}NClO_3P_2Re{\cdot}(CH_2Cl_2)_{0.5}$: C, 53.20; H, 4.07; N, 1.57; Cl, 7.95. Found: C, 53.50; H, 3.86; N, 1.63; Cl, 7.19. Λ_M (Ω^{-1} cm^2 mol^{-1}): 0.25 (CH_2Cl_2). When LiBr and LiI were used, **$ReBr(OC_2H_5)(CO)(NO)(PPh_3)_2$ (11)** (76%, mp 164–168 °C) and **$ReI(OC_2H_5)(CO)(NO)(PPh_3)_2$ (12)** (78%, mp 194–197 °C) were obtained, respectively.

Reaction of $Re(OCH_3)(OClO_3)(CO)(NO)(PPh_3)_2$ with Nucleophiles. A. $NaBH_4$. Synthesis of $ReH_2(CO)(NO)(PPh_3)_2{\cdot}(CH_2Cl_2)_{0.25}$ (13). To a stirred suspension of $Re(OCH_3)(OClO_3)(CO)(NO)(PPh_3)_2$ (0.20 g, 0.22 mmol) in 15 mL of methanol was added sodium borohydride (0.05 g, 1.3 mmol) in several small portions. Rapid effervescence ensued with each addition, and the suspension lightened to a pale gold. After the mixture was stirred for 30 min, the product was removed and recrystallized from dichloromethane–ethanol to give yellow crystals of the product as a quarter dichloromethane solvate (0.14 g, 80%); mp 167–170 °C. Anal. Calcd for $C_{37}H_{32}NO_2P_2Re{\cdot}(CH_2Cl_2)_{0.25}$: C, 56.49; H, 4.14; N, 1.77; Cl, 2.24. Found: C, 56.49; H, 4.16; N, 1.82; Cl, 2.28.

B. LiCl. Synthesis of $ReCl(OCH_3)(CO)(NO)(PPh_3)_2$ (7). $Re(OCH_3)(OClO_3)(CO)(NO)(PPh_3)_2$ (0.25 g, 0.27 mmol) was dissolved in 40 mL of 1:1 v/v dichloromethane–methanol and the solution heated to reflux. Within 5 min of the addition of LiCl (0.014 g, 0.33 mmol) to the boiling solution, a mass of pale yellow product precipitated. The dichloromethane was removed under reduced pressure and the yellow crystalline product removed by filtration. Characterization was by comparison to an authentic sample (0.22 g, 95%). Prepared in similar fashion were $ReBr(OCH_3)(CO)(NO)(PPh_3)_2$ (96%) and $ReI(OCH_3)(CO)(NO)(PPh_3)_2$ (92%).

If preferred, this reaction can be performed on $Re(OCH_3)(OClO_3)(CO)(NO)(PPh_3)_2$ prepared in situ by heating a solution of $ReH(CH_3OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$ freshly prepared according to earlier directions.

Reaction of $ReCl(OCH_3)(CO)(NO)(PPh_3)_2$ with $HClO_4$. Synthesis of $ReCl(CH_3OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$ (14). $ReCl(OCH_3)(CO)(NO)(PPh_3)_2$ (0.25 g, 0.30 mmol) and perchloric acid (70%, 0.05 mL) were suspended in 2 mL of dichloromethane with no apparent reaction. When 5 mL of diethyl ether was added to the stirred suspension, all the solid immediately dissolved followed by rapid precipitation of the product. A further 20–30 mL of diethyl ether was added to complete the precipitation. The bright yellow product was collected by filtration and always used immediately without further purification (0.27 g, 100%); mp 171–173 °C. Because of the risk of explosion, an elemental analysis was not obtained. Λ_M (Ω^{-1} cm^2 mol^{-1}): 0.80 (CH_2Cl_2), 93.6 (CH_3NO_2).

$ReCl(C_2H_5OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$ (16) was prepared in identical fashion from $ReCl(OC_2H_5)(CO)(NO)(PPh_3)_2$ (98%); mp 172–175 °C. Λ_M (Ω^{-1} cm^2 mol^{-1}): 1.05 (CH_2Cl_2), 83.5 (CH_3NO_2).

Results and Discussion

As described previously,[1] $ReH_2(NO)(PPh_3)_3$ reacts with excess HBF_4 in the presence of carbon monoxide to yield yellow solutions from which $[ReF(CO)(NO)(PPh_3)_3]BF_4$ can be isolated. Our

Table I. Infrared Data[a]

no.	compd	ν(CO)[b]	ν(NO)[b]	ν(ReH)[c]	others
1	$ReH(OCH_3)(CO)(NO)(PPh_3)_2$	2006	1671	1871	ν(CH), 2776 mw; ν(C–O), 1080 m; δ(ReH), 773 w
1a	$ReD(OCH_3)(CO)(NO)(PPh_3)_2$	2000	1670	1343	ν(CH), 2775 mw; δ(Re–D), 560 w
2	$ReH(OC_2H_5)(CO)(NO)(PPh_3)_2$	2004	1669	1868	ν(C–O), 1060 m; $\delta(OCH_2)$, 902 w; δ(ReH), 772 w
3	$[ReH(CO)(NO)(PPh_3)_3]ClO_4$	2022	1728	1908	δ(ReH), 768 w; $\nu(ClO_4)$, 1092 vs
4	$ReH(CH_3OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$	2045	1738	1902	ν(CH), 2815, 2825 mw; ν(C–O),[d] 1095 m; $\nu(OClO_3)$, 1132 sh, 1120 s, 1027 m, 920 m; δ(ReH), 771 w; $\nu(O{-}H{-}OClO_3)$, 3140 w br
5	$ReH(C_2H_5OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$	2052	1720	1900	ν(C–O),[d] 1074 sh; $\delta(OCH_2)$ obscured; $\nu(OClO_3)$, 1126 s, 1033 m, 928 m
6	$Re(OCH_3)(OClO_3)(CO)(NO)(PPh_3)_2$	1995	1709		ν(CH), 2818 m; ν(C–O), 1081 s; $\nu(OClO_3)$, 1129 s, 1117 sh, 1045 m, 931 m
7	$ReCl(OCH_3)(CO)(NO)(PPh_3)_2$	1988	1703		ν(CH), 2787 m; ν(C–O), 1076 s
8	$ReBr(OCH_3)(CO)(NO)(PPh_3)_2$	1987	1709		ν(CH), 2786 m; ν(C–O), 1074 s
9	$ReI(OCH_3)(CO)(NO)(PPh_3)_2$	1989	1703		ν(CH), 2796 m; ν(C–O), 1066 s
10	$ReCl(OC_2H_5)(CO)(NO)(PPh_3)_2$	1982	1705		ν(C–O), 1064; $\delta(OCH_2)$, 904
11	$ReBr(OC_2H_5)(CO)(NO)(PPh_3)_2$	1981	1700		ν(C–O), 1061; $\delta(OCH_2)$, 902
12	$ReI(OC_2H_5)(CO)(NO)(PPh_3)_2$	1987	1703		ν(C–O), 1058; $\delta(OCH_2)$, 900
13	$ReH_2(CO)(NO)(PPh_3)_2$	1977	1669	1866, 1818	δ(ReH), 778 w
14	$ReCl(CH_3OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$	2027	1758		ν(CH), 2815 mw; ν(C–O),[d] 1094 m; $\nu(OClO_3)$, 1135 s, 1026 m, 918 m
15	$ReCl(C_2H_5OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$	2028	1756		$\delta(OCH_2)$, 922 m sh; $\nu(OClO_3)$, 1144 sh, 1128 s, 1029, 918 m

[a] Nujol mulls, values in cm^{-1}. [b] All absorptions very strong. [c] Absorptions all medium to weak. [d] Assignment tentative only because of the intensity and broadness of neighboring absorptions.

Table II. ^1H NMR Data

		δ ^1H[a] (J)		
no.	compd	ReH	OR	others
1	$ReH(OCH_3)(CO)(NO)(PPh_3)_2$	3.82 t ($^2J_{HP}$ = 22.9)	2.61 s	Ph, 7.46 m
2	$ReH(OC_2H_5)(CO)(NO)(PPh_3)_2$	3.83 t ($^2J_{HP}$ = 23.1)	0.070 t, 2.72 q ($^3J_{HH}$ = 6.8)	Ph, 7.43 m
3	$[ReH(CO)(NO)(PPh_3)_3]ClO_4$[b]	1.11 dt ($^2J_{HP_{1,2}}$ = 32.3, $^2J_{HP_3}$ = 18.6)		Ph, 7.29 m
4	$ReH(CH_3OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$	4.72 t ($^2J_{HP}$ = 21.9)	1.94 d ($^3J_{HH}$ = 3.7)	OH, 6.12 q; Ph, 7.55 m
5	$ReH(C_2H_5OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$	4.63 td ($^2J_{HP}$ = 21.4, $^3J_{HReOH}$ = 0.8)	0.075 t, 2.27 dq ($^3J_{HH}$ = 7.0, $^3J_{HCOH}$ = 4.1)	OH, 5.65 td; Ph, 7.48 m
6	$Re(OCH_3)(OClO_3)(CO)(NO)(PPh_3)_2{\cdot}H_2O$		3.35 s	H_2O, 2.52 br s; Ph, 7.53 m
7	$ReCl(OCH_3)(CO)(NO)(PPh_3)_2$		3.13 s	Ph, 7.44 m
8	$ReBr(OCH_3)(CO)(NO)(PPh_3)_2$		3.21 s	Ph, 7.48 m
9	$ReI(OCH_3)(CO)(NO)(PPh_3)_2$		3.12 s	Ph, 7.45 m
10	$ReCl(OC_2H_5)(CO)(NO)(PPh_3)_2$		0.59 t, 3.27 q ($^3J_{HH}$ = 6.8)	Ph, 7.49 m
11	$ReBr(OC_2H_5)(CO)(NO)(PPh_3)_2$		0.56 t, 3.18 q ($^3J_{HH}$ = 6.8)	Ph, 7.44 m
12	$ReI(OC_2H_5)(CO)(NO)(PPh_3)_2$		0.58 t, 3.14 q ($^3J_{HH}$ = 6.8)	Ph, 7.43 m
13	$ReH_2(CO)(NO)(PPh_3)_2$	0.085 dt, −3.09 dt ($^2J_{H_1P}$ = 26.8, $^2J_{H_2P}$ = 26.1, $^2J_{H_1H_2}$ = 5.7)		Ph, 7.43 m
14	$ReCl(CH_3OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$		3.36 s	Ph, 7.52 m
15	$ReCl(C_2H_2OH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$		1.17 t, 3.62 q ($^3J_{HH}$ = 7.0)	Ph, 7.51 m

[a] Coupling constants in hertz. All signals give satisfactory integrals. [b] ^{31}P NMR: δ 11.81 (d), 7.27 (t, $^2J_{PP}$ = 20.7 Hz).

early attempts to perform a similar reaction using $HClO_4$ in place of HBF_4 led to the same initial yellow solutions, but when it was attempted to isolate the product of this reaction, gradual decomposition ensued, ending in intractable, black mixtures. We have found, however, that taking steps to remove the excess $HClO_4$ from such reaction mixtures enables stable products to be isolated. Thus, when excess perchloric acid is added to a suspension of $ReH_2(NO)(PPh_3)_3$ in CO saturated dichloromethane–methanol, the solid goes into solution with gas evolution. Rendering the solution slightly basic with sodium methoxide solution followed by evaporation of the solvent under reduced pressure results in isolation of a compound shown to be $ReH(OCH_3)(CO)(NO)(PPh_3)_2$ (**1**) by elemental analysis and IR and ^1H NMR spectroscopy. In the solid state, **1** exhibits infrared maxima at 2006 vs (ν(CO)), 1671 vs (ν(NO)) and 1871 w cm^{-1} (ν(ReH)). In addition, bands attributable to the methoxide ligand occur at 2776 mw and 1080 m cm^{-1}, of which that at 2776 cm^{-1} is diagnostic.[1] More complete infrared data for **1** and the other complexes isolated in this study can be found in Table I. The ^1H NMR spectrum confirmed the presence of the hydride ligand in **1** as well as establishing the trans disposition of the phosphine ligands. Thus the hydride signal appeared as a 1:2:1 triplet at δ 3.82 with $^2J_{HP}$ = 22.9 Hz. The unusually low-field position for the hydride resonance is close to that observed for $ReHF(CO)(NO)(PPh_3)_2$[1], and now such low values would appear to be typical for $ReHX(CO)(NO)(PPh_3)_2$ species (Table II). Until this work, the lowest values for a rhenium hydride resonance observed were −0.9 and −2.1 ppm for $ReH_2(NO)(PPh_3)_3$,[4] with more typical values being largely in the range of −4 to −8 ppm, regardless of the formal oxidation state of the metal.[5-10] It is not possible to pinpoint any particular feature(s) of these complexes responsible for these low hydride chemical shift values, especially since the closest analogues

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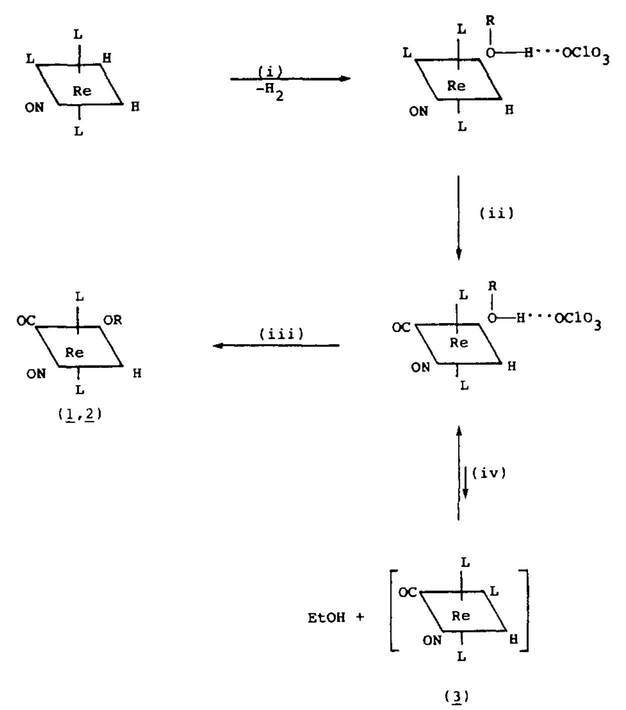
Scheme I[a]



[a] L = PPh_3. Key: (i) $HClO_4$ in ROH; (ii) CO, $-PPh_3$; (iii) base in ROH; (iv) R = Et, $+PPh_3$.

available, such as $(\pi\text{-}C_5H_5)Re(CO)(NO)H$,[8] $ReH(CO)_2(PPh_3)_3$,[7] and $ReH(CO)_3(PPh_3)_2$[7] have values more in the normal range. The preparation of $ReD(OCH_3)(CO)(NO)(PPh_3)_2$ from $ReD_2(NO)(PPh_3)_3$ and $DClO_4$ not only confirmed the assignment of the hydride signal in the ^1H NMR spectrum but also established the existence of a Fermi resonance interaction between ν(CO) and ν(ReH) (Table I), thereby establishing that these ligands are trans to one another as depicted in the schemes. A trans disposition of the hard OMe ligand and NO is as one would expect,[1] and in the absence of evidence to the contrary, all the structures depicted in the schemes have been assigned such that, where possible, the hardest anionic ligand is trans to nitric oxide.

If the experimental procedure for the isolation of **1** is modified slightly by only partially neutralizing the excess perchloric acid, a mixture of products is obtained, including some that appear to have coordinated perchlorate groups (vide infra). If the solvent is changed to dichloromethane–ethanol, however, the chemistry is somewhat different. If the procedure for the preparation of **1** is followed with ethanol and sodium ethoxide used instead of methanol and sodium methoxide, $ReH(OC_2H_5)(CO)(NO)(PPh_3)_2$ (**2**), analogous to **1**, is obtained. If, however, the reaction mixture is left slightly acidic, large crystals of $[ReH(CO)(NO)(PPh_3)_3]ClO_4$ (**3**) can be isolated over a longer period of time. The cation in **3** possesses a meridional arrangement of phosphines as indicated by ^1H and $^{31}P\{^1H\}$ NMR spectra. In the ^1H NMR spectrum, the signal due to the hydride appears as an overlapping doublet of triplets, centered at 1.11 ppm, with $^2J_{HP_{1,2}} = 32.3$ Hz and $^2J_{HP_3} = 18.6$ Hz. As required, the $^{31}P\{^1H\}$ NMR spectrum consists of a doublet (P1 and P2) at 11.81 ppm and triplet (P3) at 7.27 ppm with $^2J_{PP} = 20.7$ Hz. Because of the rather lengthy isolation procedure involved, we have not been able to isolate $[ReD(CO)(NO)(PPh_3)_3]ClO_4$ in order to determine whether the hydride is trans to the carbonyl or nitrosyl group. We have, however, assigned a trans hydride–carbonyl arrangement in the schemes by analogy with **1**.

By assuming a close correspondence between the $ReH_2(NO)(PPh_3)_3/HClO_4$ system and the $MH_2(CO)(PPh_3)_3/HBF_4$ (M = Ru, Os) systems,[2,11] a plausible scheme can be devised for the synthesis of **1**–**3** (Scheme I).

Steps 1 and 2 of the scheme have precedent in the formation of $[MH(H_2O)(CO)(PPh_3)_3]BF_4$ (M = Ru, Os)[2] and $[RuH(H_2O)(CO)_2(PPh_3)_2]BF_4$,[11] with the latter compound having been characterized by X-ray crystallography. Infrared spectra of the aquo cations above demonstrated a lowering of the symmetry of the BF_4^- ions to at least C_{3v} via a splitting of the triply degenerate bands at 1100 and 525 cm^{-1}. Rather than resulting from direct coordination of the fluoroborate anion as originally thought, the splitting was shown by X-ray analysis of $[RuH(H_2O)(CO)_2(PPh_3)_2]BF_4{\cdot}C_2H_5OH$ to result from the participation of the anion in a hydrogen-bonding network involving the coordinated water molecule and the molecule of solvation. In some cases (vide infra), we have demonstrated a similar situation for the perchlorate complexes depicted in the schemes and have attempted to illustrate this by showing the perchlorate groups hydrogen bound to the coordinated alcohol. We have had some success in isolating the two perchlorate intermediates depicted in Scheme I. Thus, reacting $ReH_2(NO)(PPh_3)_3$ with perchloric acid in the absence of CO yields a highly unstable material, which we believe to be $ReH(MeOH{\cdot}OClO_3)(NO)(PPh_3)_3$. Further work on this complex is in progress and will be reported in due course. The carbonyl containing perchlorate complex is best obtained by reversing step (iii). Thus, the addition of $HClO_4$ to a suspension of **1** in dichloromethane followed by the addition of diethyl ether yields $ReH(MeOH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$ (**4**) in almost quantitative yields. A similar procedure employing the ethoxide complex **2** gives $ReH(EtOH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$ (**5**). Complexes **4** and **5** have been completely characterized by elemental analyses and the usual spectroscopic techniques. The reader is asked to note the warning at the beginning of the Experimental Section concerning the potentially explosive nature of these complexes. In the infrared spectrum of **4**, both ν(CO) and ν(NO) increase by ca. 40 and 70 cm^{-1}, respectively, indicative of the cationic nature of the complex. Other infrared absorptions due to ν(ReH) and the coordinated methanol ligand are also observed. In particular, a weak, broad absorption at 3140 cm^{-1} is observed, which we have assigned to $\nu(O\text{–}H\text{–}OClO_3)$. When **4** is prepared from **1** in $CH_3OD/DClO_4$ mixtures, this band shifts to 2322 cm^{-1}, confirming the assignment. Attempts to prepare $ReD(MeOH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$ from **1a** resulted in isolation of **4** only, indicating exchange between the metal hydride and the hydroxyl proton of the ligated alcohol takes place, although ^1H NMR evidence suggests that this process is slow on the NMR time scale. The infrared spectrum in the 1100-cm^{-1} region demonstrates quite clearly that the perchlorate counteranion is involved in hydrogen bonding. Three principal absorptions due to $\nu(OClO_3)$ can be identified at 1620 s, 1027 s, and 920 m cm^{-1}, giving splittings that are closely comparable to those observed for the BF_4^- ion in $[RuH(OH_2)(CO)_2(PPh_3)_2]BF_4$. A very similar infrared spectrum is seen for **5**. In the ^1H NMR spectra of **4** and **5** the coordinated alcohol molecules can be identified readily and from the couplings observed it can be seen that OH and ROH exchanges are both slow on the NMR time scale. Thus **4** displays a quartet at 6.12 ppm and a doublet at 1.94 ppm due to OH and CH_3O protons of the ligated methanol, respectively, with $^3J_{HH} = 3.7$ Hz. The hydride signal occurs once again to low field at 4.72 ppm, $^2J_{HP} = 21.9$ Hz. The ^1H NMR spectrum of freshly prepared **5** exhibits signals due to both free and coordinated ethanol, indicating slow exchange between free and bound alcohol molecules. As for **4**, a separate signal is observed for the hydroxyl proton (5.65 ppm, dt) coupled to the methylene protons at 2.27 ppm (dq, $^3J_{HH} = 4.1$ Hz) and also to the hydride at 4.63 ppm (dt, $^3J_{HReOH} = 0.8$ Hz). Adding D_2O to such solutions results in loss of the signal at 5.65 ppm and the collapse of the methylene and hydride peaks to a quartet and triplet, respectively. It should be mentioned at this point that we believe that **4** and **5**, like their ruthenium analogue, are alcohol-solvated when first isolated but that the solvent molecules appear to be removed upon vacuum drying.

The key to the synthesis of $[ReH(CO)(NO)(PPh_3)_3]ClO_4$ (**3**) from **5** but not **4** lies, we believe, in the considerably greater solubility of the ethanol complex **5** by comparison to the solubility of its methanol analogue. It seems reasonable to assume that there

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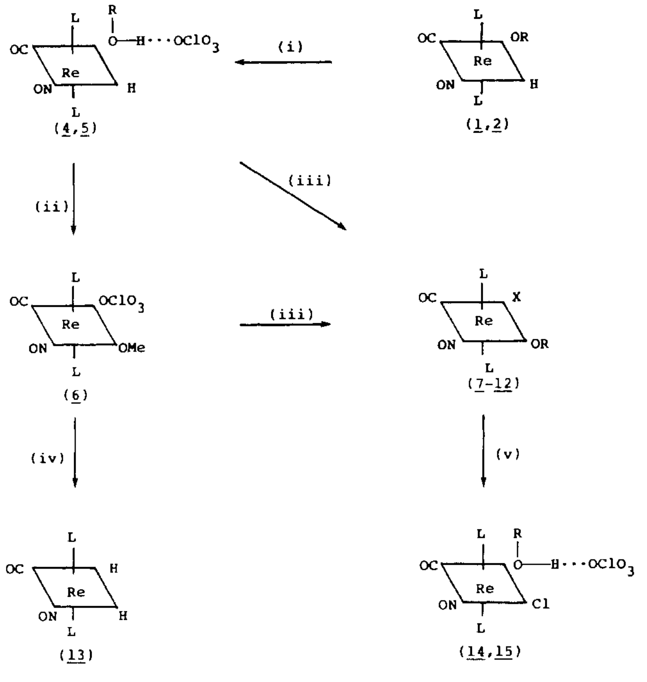
Scheme II[a]



[a] L = PPh$_3$. Key: (i) HClO$_4$ in ROH; (ii) R = Me, heating in MeOH; (iii) LiX in ROH; (iv) NaBH$_4$ in MeOH; (v) X = Cl, HClO$_4$ in ROH.

is a slowly established equilibrium between either **4** or **5** and **3** under the conditions employed. The greater solubility of **5** allows this equilibrium to be milked for the less soluble product **3**, under conditions that would result in the fairly rapid crystallization of **4**.

Both alcohol complexes **4** and **5** proved to be useful synthons in their own right (Scheme II). As anticipated, reacting **4** and **5** with base in alcohol regenerated **1** and **2**, respectively. The slow exchange rate of coordinated alcohol in **4** was confirmed by reacting **4** with sodium ethoxide, in ethanol, which resulted in the isolation of pure **1** only. The alkoxide complexes **1** and **2** were also the only products formed from either **4** or **5** and NaBH$_4$ in alcohol suspension. Heating a pale yellow methanol solution of **4** under reflux results in a deepening of the color to orange. Removal of most of the solvent under reduced pressure precipitated an orange product, identified as Re(OCH$_3$)(OClO$_3$)(CO)(NO)(PPh$_3$)$_2$·ROH (**6**). In the material deposited directly from solution, we are unsure of the nature of the solvate molecule, but presume it to be methanol in view of the method of preparation. Both the elemental analysis and ^{1}H NMR spectra of **6** were, however, obtained by using a sample that had been recrystallized in the presence of aqueous perchloric acid before being vacuum-dried, and both techniques imply the presence of a water solvate molecule. In particular, the ^{1}H NMR spectrum of **6** displays a sharp singlet at 3.35 ppm attributable to the methoxide group and a broad singlet at 2.52 ppm attributable to water. As required, the 2.52 ppm peak vanishes on the addition of D$_2$O whereas the peak at 3.35 remains unaltered. At first, the chemical shift value of the methoxide group caused us some concern as it more or less coincides with the value for free methanol, but we have isolated other methoxide complexes with comparably low shifts in both this and related studies. The reason behind these low values is presumably the same as that responsible for the low hydride chemical shifts discussed earlier. We have not ascertained whether the water of solvation is originally present in **6** or whether water is adsorbed subsequent to the vacuum drying, as seen with Pt$_2$Cl$_2$(μ-CN-*p*-tol)(μ-dppm)$_2$ for example.[12] A more contentious issue is that of whether or not the perchlorate group in **6** is directly coordinated to the metal. On the basis of the ν(CO) and ν(NO) values of 1995 and 1709 cm^{-1}, respectively, we believe that the perchlorate group is functioning as a ligand in this instance. In ReH(MeOH·OClO$_3$)(CO)(NO)(PPh$_3$)$_2$ (**4**), the complex is essentially ionic as evidenced by the high ν(CO) and ν(NO) values of 2045 and 1738 cm^{-1}. The decreases of 50 and 29 cm^{-1} respectively in these frequencies in going from **4** to **6** are approximately as one would expect in going from a cationic to a neutral complex. Unfortunately, attempts to confirm this hypothesis through conductivity measurements were inconclusive since, in dichloromethane at least, both **4** and **6** behaved essentially as nonelectrolytes. We have, however, observed other hydrogen-bound ionic complexes functioning as nonelectrolytes in this solvent.[12] In nitromethane, both **4** and **6** behaved as 1:1 electrolytes, conceivably as a result of replacement of the perchlorate ligand in **6** by solvent. The possibility, however, of **6** existing as a hydrogen-bound solvated aquo cation cannot be ruled out.

We originally anticipated that both **4** and **6** would be useful precursors to a wide variety of complexes of the types ReHX(CO)(NO)(PPh$_3$)$_2$, [ReH(CO)L(NO)(PPh$_3$)$_2$]ClO$_4$, ReX(OMe)(CO)(NO)(PPh$_3$)$_2$, and [Re(OMe)(CO)L(NO)(PPh$_3$)$_2$]ClO$_4$ via reaction with appropriate ligands X$^-$ and L. Such proved not necessarily to be the case. Thus, both **4** and **6** react with neutral ligands to give unusual products, whose synthesis and properties will be reported in due course. With anions, both **4** and **6** yield the same products, ReX(OMe)(CO)(NO)(PPh$_3$)$_2$, of which only those with X = halide (**7–9**) are reported herein, although corresponding pseudohalide complexes have been synthesized. Of interest here is the fact that the elimination of dihydrogen from **4** occurs at a faster rate than substitution of the methanol ligand, even at room temperature. Although we have never been able to isolate the ethoxy analogue of **6**, it does appear to be formed in solution at least, since reacting **5** with halide ions also produced ReX(OEt)(CO)(NO)(PPh$_3$)$_2$ (**10–12**). All the complexes **7–12** are typical examples of their class and exhibit the appropriate infrared and NMR characteristics (Tables I and II).

In view of the straightforward reactions exhibited by **6** with anionic nucleophiles such as halides, the results obtained from reacting this complex with NaBH$_4$ came as a complete surprise. In methanol suspension, **6** reacts rapidly with NaBH$_4$ with vigorous gas evolution. The resultant yellow solid proved to be the dihydride ReH$_2$(CO)(NO)(PPh$_3$)$_2$ (**13**) rather than the expected **1**. Under similar conditions, NaBH$_4$ has no effect on **1**, implying that ReH(OCH$_3$)(CO)(NO)(PPh$_3$)$_2$ is not an intermediate in the formation of **13**. We feel that the most likely explanation for this difference in reactivity between **4** and **6** results from the formation of a borohydride complex in the case of **6**, arising from displacement of the perchlorate ligand followed by MeOH elimination. The initial interaction of NaBH$_4$ with **4** on the other hand, is simply a deprotonation, resulting in more or less inert **1**. The ^{1}H NMR spectrum of **13** confirms the structure depicted in Scheme II and identifies a 0.25 mol of dichloromethane, also detected analytically. The hydride NMR signal for **13** occurs as the expected double triplet of doublets: $^2J_{\mathrm{H_1P}}$ = 26.8 Hz, $^2J_{\mathrm{H_2P}}$ = 26.1 Hz, $^2J_{\mathrm{H_1H_2}}$ = 5.7 Hz, at −3.09 and 0.09 ppm.

In view of the unusual nature of the methanol complex **4** and the novel dihydrogen elimination reaction that yields **6**, we were curious to see what effect the substitution of chloride for the hydride ligand would have on this chemistry. Accordingly, the alkoxide complexes **7** and **10** were reacted with aqueous perchloric acid in dichloromethane–diethyl ether to yield the alcohol complexes ReCl(ROH·OClO$_3$)(CO)(NO)(PPh$_3$)$_2$ (**14**, R = Me; **15**, R = Et). These two complexes were the least stable of all the complexes described herein with respect to spontaneous and explosive decomposition, so that elemental analyses were not obtained. Infrared spectra of **14** and **15** are closely comparable with those of their hydride analogues **4** and **5**. In particular, relatively high values of ν(CO) and ν(NO) are observed along with bands attributable to the alcohol ligands, and as expected, the perchlorate absorptions indicate a symmetry less than T_d. The formation and isolation of **14** and **15** are particularly rapid, and so we feel confident in their solid-state formulation. As expected by com-

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[12] Grundy, K. R.; Robertson, K. N. *Organometallics* **1983**, *2*, 1736.

parison with **4** and **5**, both **14** and **15** reacted either with base or $NaBH_4$ to regenerate the alkoxide complexes **7** and **10**, respectively. Quite unlike their hydride analogues, however, **14** and **15** can undergo rapid isomerization. Thus the solution infrared spectrum of **14** shows ν(CO) and ν(NO) at 2009 and 1776 cm^{-1}, respectively, and isolating a solid from these solutions results in a mixture containing **14** and a (dominant) new complex with ν(CO) and ν(NO) at 2007 and 1782 cm^{-1}, which also appears to possess an associated perchlorate group. The ^1H NMR spectrum of **14** is also quite unlike that of **4** in that a signal attributable to the OH--O proton is not observed. Instead, only an OCH_3 singlet is observed at 3.36 ppm, exactly coincident with the singlet arising it free methanol is added to the solution. Extracting the NMR solution with D_2O results in the complete disappearance of the signal at 3.36 ppm, implying that it is indeed due to free methanol. Exactly the same behavior was exhibited by solutions made essentially from the isomer of **14**. Although we cannot be sure of the nature of the isomers of **14** and **15**, one possibility admitted by the above evidence consists of a relatively rapid loss of alcohol (possibly reversible) from the initially formed complexes in favor of a coordinated perchlorate complex solvated with the appropriate alcohol.

$$ReCl(ROH\cdot OClO_3)(CO)(NO)(PPh_3)_2 \rightleftharpoons ReCl(OClO_3)(CO)(NO)(PPh_3)_2\cdot ROH$$

This particular behavior is not seen in **4** presumably because the hydride ligand renders the metal more class "b" in character, thereby favoring the alcohol complex over the isomer with the presumably harder perchlorate ligand.[13] If this argument has some validity it can probably also be used to explain why compound **6**, derived from **4** via dihydrogen elimination, appears to exist as a genuine perchlorate complex rather than as an alcohol cation with a hydrogen-bound perchlorate group. Despite the uncertainty in the solution structures of **14** and **15**, it seems from our preliminary observations that both can be used to generate further examples of the series $ReXY(CO)(NO)(PPh_3)_2$ via reaction in dichloromethane with crown ether solubilized salts, MY.[14]

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Registry No. **1**, 98481-35-7; **2**, 98481-36-8; **3**, 98481-38-0; **4**, 98481-40-4; **5**, 98481-42-6; **6**, 98481-43-7; **7**, 98481-44-8; **8**, 98481-45-9; **9**, 98481-46-0; **10**, 98481-47-1; **11**, 98481-48-2; **12**, 98481-49-3; **13**, 98481-50-6; **14**, 98481-52-8; **15**, 98481-54-0; $ReH_2(NO)(PPh_3)_3$, 58694-74-9; D_2, 7782-39-0.

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ed Energetica dei Composti di Coordinazione del CNR, Firenze 50132, Italy

Ruthenium(II)-6-Mercaptopurine Complex Synthesis and Solution Properties. Molecular and Crystal Structure of Bis(6-mercaptopurine)bis(triphenylphosphine)ruthenium(II) Chloride

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The preparations of the complexes $[Ru^{II}(6\text{-}MP)_2(P(C_6H_5)_3)_2]Cl_2\cdot 2C_2H_5OH\cdot 2H_2O$ (**1**) (6-MP = 6-mercaptopurine), $[Ru^{II}(6\text{-}MP\text{-}9\text{-}Me)_2(P(C_6H_5)_3)_2]Cl_2\cdot 1.5H_2O$ (**2**) (6-MP-9-Me = 6-mercapto-9-methylpurine), $[Ru^{II}(6\text{-}MP)(6\text{-}MP\text{-}H)(P(C_6H_5)_3)_2]Cl$ (**3**) (6-MP-H = N(9)-deprotonated 6-mercaptopurine), and $[Ru^{II}(6\text{-}MP\text{-}1\text{-}Me\text{-}9\text{-}Me)_2(P(C_6H_5)_3)_2]Cl_2\cdot H_2O$ (**4**) (6-MP-1-Me-9-Me = 1,9-dimethyl-6-mercaptopurine), together with the molecular and crystal structure of **1**, are reported. Complexes **1** and **2** were prepared from ethanol solution under nitrogen by treating $[Ru^{II}Cl_2(P(C_6H_5)_3)_3]$ with the stoichiometric amount of the mercapto ligand. Compound **1** crystallizes in the monoclinic system, space group $P2_1/a$ with $a = 29.504$ (4) Å, $b = 16.848$ (3) Å, $c = 10.542$ (2) Å, $\beta = 97.78$ (3)°, $V = 5192$ Å^3 (at 22 °C), $Z = 4$, $D_{calcd} = 1.45$ g cm^{-3}, and μ(Mo Kα) = 5.47 cm^{-1}. Intensities for 2991 reflections were collected by using the θ–2θ scan technique employing graphite-monochromatized Mo Kα radiation. The structure was solved by the Patterson method. Full-matrix least-squares refinement has led to final R and R_w values of 0.056 and 0.054, respectively. The structure contains $[Ru^{II}(6\text{-}MP)_2(P(C_6H_5)_3)_2]^{2+}$ cations, chloride anions, and free water and ethanol molecules. The coordination sphere about the ruthenium(II) center is approximately octahedral. The two 6-MP molecules act as bidentate ligands via the S(6) and N(7) atoms and are protonated at N(1) and N(9). The two sulfur atoms are in trans positions. The Ru–S distances are 2.417 (4) and 2.447 (4) Å, respectively, and the Ru–N bond lengths average 2.156 (14) Å. The double-bond character of the C–S group is not significantly altered by coordination, and the purine system is essentially planar. The "bite" distance S--N(7) (average value 3.10 Å in the complex) is significantly shorter than in the free ligand (3.352 Å). Strong intermolecular and intramolecular stacking interactions occur between purine systems and between purine and phenyl rings. Water, ethanol molecules, chloride ions, and H–N(1) and H–N(9) are involved in a network of hydrogen bonds. The title complex in $Me_2SO\text{-}d_6$ was studied by ^1H and ^{31}P NMR spectroscopy. The H(2) and H(8) signals of **1** and **3** were assigned by selective deuteration. The ^1H NMR spectrum was monitored as a function of added base and/or added CH_3I. On addition of base to solutions of **1**, the H(8) signal was most affected, consistent with H–N(9) deprotonation. A complex series of reactions occurs on addition of CH_3I under strongly basic conditions, and **2** was not identified as one of the products. However, when mild basic conditions were used, a simpler process was observed on addition of CH_3I. When a slight excess of CH_3I was added to a mixture containing **1** and $NaHCO_3$, the methylation occurred at N(1) and N(9) and complex **4** was isolated in 50% yield. We speculate that the N(1) proton becomes sufficiently acidic on N(9)-alkylation for additional alkylation to proceed at N(1).

Introduction

The direct alkylation of 6-oxopurine leads to a mixture of products.[1] Acyclovir, an important drug that is an antiviral compound useful in the treatment of herpes, is a 9-alkylated 6-oxopurine.[1] We previously exploited the concept that a metal complex could act both as a protecting group and as an activator of purine alkylation by stabilizing the deprotonated form of the purine.[2] However, because of the essential impossibility of a 6-oxo

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