Inorg. Chem. **1982**, *21*, 4149–4155 **4149**

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Nitrosyl Complexes of Rhenium. Synthesis of Some Fluoro Complexes of Rhenium(I), Including the Novel Cationic Complex Fluorocarbonylnitrosyltris(triphenylphosphine)rhenium(I) Tetrafluoroborate

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Received August 3, 1981

The complex previously reported as $ReCl_2(NO)(PPh_3)_2$ has been reformulated as a methoxide complex, $ReCl_2(OCH_3)(NO)(PPh_3)_2$. $ReCl_2(OCH_3)(NO)(PPh_3)_2$ reacts with $NaBH_4$ and PPh_3 in ethanol to give much improved yields of $ReH_2(NO)(PPh_3)_3$. $ReH_2(NO)(PPh_3)_3$ reacts with HCl in ethanol suspension to form air-sensitive $ReCl_2(NO)(PPh_3)_3$, which in turn reacts with CO or CNR (R = *p*-tolyl) to give $ReCl_2(CO)(NO)(PPh_3)_2$ and $ReCl_2(CNR)_2(NO)(PPh_3)$, respectively. $ReH_2(NO)(PPh_3)_3$ reacts with HBF_4 (or HPF_6) in the presence of CO to give the novel fluoro cation $[ReF(CO)(NO)(PPh_3)_3]^+$, which reacts with certain coordinating anions to give neutral $ReXF(CO)(NO)(PPh_3)_2$ (X = H, OCH_3, F). $ReHF(CO)(NO)(PPh_3)_2$ is unusual in that its stereochemistry can be determined absolutely by a combination of IR and ^1H NMR spectroscopy. The structure has been determined of fluorocarbonylnitrosyltris(triphenylphosphine)rhenium(I) perchlorate, prepared from $[ReF(CO)(NO)(PPh_3)_3]BF_4$ and $NaClO_4$ in ethanol. Solvated crystals of $[ReF(CO)(NO)(PPh_3)_3]ClO_4$ from dichloromethane–cyclohexane are monoclinic, with $a = 14.981$ (2) Å, $b = 25.560$ (3) Å, $c = 15.133$ (4) Å, $\beta = 104.84°$, space group $P2_1/n$, and $Z = 4$. Data were collected by four-circle diffractometry with 2092 reflections with $I > \sigma(I)$ being observed. Refinement was by large-block least squares to $R = 0.057$. The unit cell contains molecules of crystallization disordered about a center of symmetry. There appears to be a random mixture of cyclohexane and dichloromethane, and atomic locations have not been assigned to the solvent atoms. The structure of the cation is that of a distorted octahedron with a meridional array of phosphine ligands and the fluoride ligand (r(ReF) = 1.973 (13) Å) trans to the linear nitrosyl group.

Introduction

The chemistry of d^6 and d^8 complexes of osmium containing the Os–CO moiety is diverse and extensively developed. By comparison, however, the chemistry of rhenium complexes containing the isoelectronic [Re–NO] fragment is extremely limited. Most d^6 rhenium nitrosyl complexes take the general form $ReX_2(NO)L_3$ (X = H, Cl, Br, I and L_3 = a combination of CO, PR_3, RCN, etc.),[1-3] which can also be thought of as including the more unusual complexes such as $Re_2X_3(CO)_5(NO)$ (X = Cl, OEt),[4] $[ReX_2(CO)_2(NO)]_2$ (X = Cl, Br, I),[4,5] $[ReI_3(CO)_2(NO)]^-$,[4] and $[(\eta^5\text{-}C_5H_5)Re(CO)_2(NO)]^+$[6] and its derivatives. Five-coordinate complexes of the type $[ReX(CO)(NO)(PPh_3)_2]^+$ (X = Cl, Br) have been reported as resulting from the oxidative addition of the appropriate halogen with $Re(CO)_2(NO)(PPh_3)_2$.[7] Only a few d^8 rhenium nitrosyls are known, these being $Re(CO)_2(NO)(PPh_3)_2$[7] and $ReX(NO)_2(PPh_3)_2$ (X = H, Cl, Br, I).[7-9]

It seems obvious that the relative paucity of d^6 and d^8 rhenium nitrosyl complexes results from a synthetic limitation rather than one of inherent instability. The synthesis of such compounds through the use of nitrosonium derivatives is restricted by the limited number of suitable d^6 and d^8 precursors available, and reductive nitrosylation of rhenium(IV) and higher oxidation state rhenium seems to stop principally at d^5, $[ReNO]^{3+}$-containing complexes.[10]

In view of these difficulties, this work was initiated in an attempt to expand upon the known chemistry of low-valent rhenium nitrosyl complexes through elaboration of the chemistry of existing nitrosyl complexes. For various practical reasons, the complexes chosen to initiate the project were $ReH_2(NO)(PPh_3)_3$[2] and the anomalous $ReCl_2(NO)(PPh_3)_2$.[1] This paper describes the reformulation of $ReCl_2(NO)(PPh_3)_2$ as an alkoxide complex, $ReCl_2(OCH_3)(NO)(PPh_3)_2$, and some further chemistry of $ReH_2(NO)(PPh_3)_3$. Included is the reaction of $ReH_2(NO)(PPh_3)_3$ with HBF_4 to give a series of novel fluoro complexes, all derived from the cation $[ReF(CO)(NO)(PPh_3)_3]^+$.

Experimental Section

Except where otherwise stated, all reactions were performed under an atmosphere of prepurified nitrogen (O_2 <3 ppm). Solvents were purified by passage through a column of activated alumina followed by storage over molecular sieves. IR spectra were recorded on a Perkin-Elmer 180 spectrophotometer. Values of ν(CO), ν(NO), and ν(CN) quoted are for CH_2Cl_2 solutions; others are for Nujol or Fluorolube mulls. ^1H NMR spectra were recorded on a Varian Associates CFT20 spectrometer in $CDCl_3$ with Me_4Si as an internal reference. Melting points were recorded on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by the Guelph Chemical Laboratory, Ltd. In the absence of a quantitative analysis, all fluoro compounds were subjected to a standard qualitative test for fluorine[11] with positive results. Benzoylhydrazine was prepared from the condensation of equimolar amounts of anhydrous hydrazine and ethyl benzoate and purified by recrystallization from absolute ethanol. $ReOCl_3(PPh_3)_2$ was prepared from Re sponge with use of previously published methods.[12]

$Re(\eta^2\text{-}N_2COPh\text{-}N',O)Cl_2(PPh_3)_2$. This preparation is a modification of a previously reported procedure.[13]

To $ReOCl_3(PPh_3)_2$ (4.00 g, 4.80 mmol), triphenylphosphine (4.0 g, 15.3 mmol), and benzoylhydrazine (4.0 g, 29.4 mmol) were added 1.0 M ethanolic hydrochloric acid (30 mL, 30 mmol HCl), ethanol (50 mL), and dichloromethane (100 mL). The resultant yellow-green suspension was heated under reflux for 20 min longer than the time

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necessary for the consumption of all the starting material. The dichloromethane was removed by evaporation under reduced pressure, and the emerald green crystals were removed by filtration (4.22 g, 96%).

ReCl$_2$(OCH$_3$)(NO)(PPh$_3$)$_2$ (1a). Nitric oxide (purified by passage through a trap at −78 °C followed by a second filled with KOH pellets) was passed into a suspension of Re(η^2-N$_2$COPh-N',O)Cl$_2$(PPh$_3$)$_2$ (3.40 g, 3.72 mmol) in benzene–methanol (150 mL, 1:1 v/v). When the reaction was complete (~90 min), the vessel was flushed with nitrogen and the benzene removed by evaporation under reduced pressure. The red-brown precipitate was removed by filtration, washed with ethanol followed by hexane, and dried under vacuum (3.13 g, 86%). This material was used without further purification; mp 182–184 °C. Anal. Calcd for $C_{37}H_{33}NCl_2O_2P_2Re$: C, 52.73; H, 3.92; N, 1.66; Cl, 8.48; O, 3.80. Found: C, 53.12; H, 4.00; N, 1.67; Cl, 8.78; O, 4.35.

ReCl$_2$(OC$_2$H$_5$)(NO)(PPh$_3$)$_2$ (1b). This complex was prepared in a manner analogous to that described above with ethanol in place of methanol. On completion of the reaction a deep red-brown solution resulted rather than a suspension. Removal of the benzene under reduced pressure yielded lustrous dark brown plates (yield ca. 75%), mp 173–175 °C. Anal. Calcd for $C_{38}H_{35}NCl_2O_2P_2Re$: C, 53.27; H, 4.12; N, 1.63; Cl, 8.28; O, 3.74. Found: C, 53.06; H, 4.29; N, 1.56; Cl, 8.71; O, 5.24.

ReH$_2$(NO)(PPh$_3$)$_3$. This preparation is a modification of a previously reported procedure.[2]

ReCl$_2$(OCH$_3$)(NO)(PPh$_3$)$_2$ (3.00 g, 3.56 mmol), triphenylphosphine (3.00 g, 11.5 mmol), and sodium borohydride (0.75 g, 19.2 mmol) were heated together under reflux in ethanol (150 mL) for 45 min. The yellow, crude ReH$_2$(NO)(PPh$_3$)$_3$ was removed by filtration and washed with ethanol and hexane. The solid was dissolved in a minimum of dichloromethane and filtered through Celite to remove sodium chloride. An equal volume of ethanol was added, and when crystallization commenced, the dichloromethane was removed under reduced pressure to give bright yellow crystals of the product (3.26 g, 91%).

Reaction of ReH$_2$(NO)(PPh$_3$)$_3$ with Acids. A. HCl. Synthesis of ReCl$_2$(NO)(PPh$_3$)$_3$ (2). ReH$_2$(NO)(PPh$_3$)$_3$ (1.00 g, 1.00 mmol), concentrated hydrochloric acid (0.5 mL), and triphenylphosphine (0.10 g, 0.38 mmol) were heated together under reflux in ethanol (15 mL) for 15 min. The bright yellow product was removed by filtration and washed with ethanol and hexane (1.02 g, 95%); mp 152 °C. Anal. Calcd for $C_{54}H_{45}NCl_2OP_3Re$: C, 60.38; H, 4.23; N, 1.30; Cl, 6.60. Found: C, 60.34; H, 4.23; N, 1.27; Cl, 6.68.

B. HBF$_4$. Synthesis of [ReF(CO)(NO)(PPh$_3$)$_3$]BF$_4$ (3). (i) ReH$_2$(NO)(PPh$_3$)$_3$ (2.00 g, 2.00 mmol) was suspended in dichloromethane–ethanol (40 mL, 1:1 v/v) and carbon monoxide passed through the solution for 30 min. Upon the addition to this suspension of 48% tetrafluoroboric acid (1.25 g, 6.82 mmol) immediate effervescence was observed as the solid went into solution. The passage of carbon monoxide was continued for a further 30 min, after which the dichloromethane was removed under reduced pressure. Pale yellow crystals were deposited from a small volume of solution and were generally used without further purification. When necessary, recrystallization was from dichloromethane–cyclohexane–ethanol (trace) to give well-formed yellow needles of the product.

(ii) ReH$_2$(NO)(PPh$_3$)$_3$ (2.00 g, 2.00 mmol) in dichloromethane–ethanol (40 mL, 1:1 v/v) was treated with 48% tetrafluoroboric acid (1.25 g, 6.82 mmol) and subjected to carbon monoxide pressure (40 psi) for 20 min. Workup was as in (i).

Yields for both procedures were generally in the range of 1.3–1.8 g or 60–80%; mp 132–137 °C. Anal. Calcd for $C_{55}H_{45}NP_3BF_5O_2Re$: C, 58.10; H, 3.99; N, 1.23; P, 8.17. Found: C, 57.93; H, 4.15; N, 1.11; P, 8.68. ^{1}H NMR: δ(Ph) 7.27 m.

[ReF(CO)(NO)(PPh$_3$)$_3$]ClO$_4$. [ReF(CO)(NO)(PPh$_3$)$_3$]BF$_4$ (0.50 g, 0.44 mmol) was dissolved in a minimum of dichloromethane, and sodium perchlorate (0.50 g, 4.1 mmol) in ethanol was added. On removal of the dichloromethane under reduced pressure, yellow crystals of the product were deposited (0.50 g, 98%). Recrystallization was from dichloromethane–cyclohexane–ethanol (trace); mp 117–122 °C. Anal. Calcd for $C_{55}H_{45}NP_3ClFO_6Re$: C, 57.49; H, 3.95; N, 1.22; P, 8.09. Found: C, 56.94; H, 4.30; N, 1.23; P, 7.85.

Reaction of ReCl$_2$(NO)(PPh$_3$)$_3$ with Carbon Monoxide. Synthesis of ReCl$_2$(CO)(NO)(PPh$_3$)$_2$ (4). Carbon monoxide was bubbled into dichloromethane (20 mL) for 10 min, after which time ReCl$_2$(NO)(PPh$_3$)$_3$ (0.25 g, 0.23 mmol) was added. The carbon monoxide was continued for a further 15 min followed by the addition of ethanol (25 mL). Evaporation under reduced pressure yielded a pale yellow solid. The product was recrystallized from dichloromethane–ethanol to give lustrous pale yellow plates of ReCl$_2$(CO)(NO)(PPh$_3$)$_2$ (0.19 g, 97%), mp 252–256 °C. Anal. Calcd for $C_{37}H_{30}NCl_2O_2P_2Re$: C, 52.92; H, 3.60; N, 1.67. Found: C, 52.00; H, 3.77; N, 1.69.

Reaction of ReCl$_2$(NO)(PPh$_3$)$_3$ with *p*-Tolyl Isocyanide. Synthesis of ReCl$_2$(CNC$_7$H$_7$)$_2$(NO)(PPh$_3$) (5). ReCl$_2$(NO)(PPh$_3$)$_3$ (0.30 g, 0.28 mmol) was added to a solution of *p*-tolyl isocyanide (0.070 g, 0.60 mmol) in benzene (25 mL) and the mixture heated under reflux for 10 min. Ethanol (30 mL) was added to the cooled solution, and evaporation under reduced pressure resulted in the formation of bright yellow crystals. Recrystallization was from dichloromethane–ethanol (0.20 g, 91%); mp 253–256 °C. Anal. Calcd for $C_{34}H_{29}N_3Cl_2OPRe$: C, 52.11; H, 3.73; N, 5.36. Found: C, 51.79; H, 3.87; N, 5.13. ^{1}H NMR: δ(CH$_3$) 2.38 s, 6 H; δ(Ph) 7.34 m, 15 H.

Reaction of [ReF(CO)(NO)(PPh$_3$)$_3$]BF$_4$ with Nucleophiles. A. NaBH$_4$. Synthesis of ReHF(CO)(NO)(PPh$_3$)$_2$ (6). To [ReF(CO)(NO)(PPh$_3$)$_3$]BF$_4$ (0.30 g, 0.26 mmol) suspended in ethanol (3 mL) was added dropwise a solution of sodium borohydride (0.15 g, 3.9 mmol) in ethanol. As soon as the effervescence accompanying the addition ceased, the addition was stopped and the yellow-orange product removed by filtration. Recrystallization was from dichloromethane–ethanol to give orange crystals (0.18 g, 86%), mp 189–192 °C. Anal. Calcd for $C_{37}H_{31}NP_2FO_2Re$: C, 56.34; H, 3.96; N, 1.77; P, 7.85. Found: C, 56.61; H, 4.18; N, 1.73; P, 8.54. ^{1}H NMR: δ(ReH) 4.73 dt, $^2J_{HP}$ = 22.6 Hz, $^2J_{HF}$ = 5.7 Hz, 1 H; δ(Ph) 7.44 m, 30 H.

A procedure analogous to that above except with NaBD$_4$ and C$_2$H$_5$OD as solvent yielded ReDF(CO)(NO)(PPh$_3$)$_2$ as orange crystals. ^{1}H NMR: only a multiplet at δ 7.42 (Ph) was observed.

B. NaOCH$_3$. Synthesis of ReF(OCH$_3$)(CO)(NO)(PPh$_3$)$_2$ (7). To a suspension of [ReF(CO)(NO)(PPh$_3$)$_3$]BF$_4$ (0.35 g, 0.31 mmol) in methanol (5 mL) was added sodium methoxide in methanol (0.7 mL, 1.0 M). After 15 min of stirring, the orange product was removed by filtration and recrystallized from dichloromethane–methanol to give lustrous orange crystals (0.21 g, 83%), mp 163–173 °C. Anal. Calcd for $C_{38}H_{33}NFO_3P_2Re$: C, 55.74; H, 4.06; N, 1.71. Found: C, 54.80; H, 4.25; N, 1.69. ^{1}H NMR: δ(OCH$_3$) 3.39 s, 3 H; δ(Ph) 7.44 m, 30 H.

C. KF. Synthesis of ReF$_2$(CO)(NO)(PPh$_3$)$_2$ (8). [ReF(CO)(NO)(PPh$_3$)$_3$]BF$_4$ (0.30 g, 0.26 mmol) was dissolved in dichloromethane (15 mL), and to this was added a solution of potassium fluoride (0.031 g, 0.52 mmol) in ethanol. The solution was heated under reflux for 40 min and the dichloromethane removed under reduced pressure. Recrystallization of the crude material from dichloromethane–ethanol gave bright yellow crystals (0.13 g, 60%), mp 228–229 °C. Anal. Calcd for $C_{37}H_{30}NF_2O_2P_2Re$: C, 55.01; H, 3.87; N, 1.73; F, 4.71. Found: C, 54.99; H, 3.84; N, 1.68; F, 4.40.

Results and Discussion

In 1976, Giusto et al. reported the preparation of ReH$_2$(NO)(PPh$_3$)$_3$ from the reaction of either [Re(NO)X$_5$]$^{2-}$ salts or ReX$_3$(NO)(PPh$_3$)$_2$ derivatives with sodium borohydride and triphenylphosphine in ethanol suspension.[2] However, because of the starting materials chosen, overall yields were poor, generally less than 40% even under the most favorable of circumstances. Since it was our wish to exploit the chemistry of ReH$_2$(NO)(PPh$_3$)$_3$, we sought a route to this complex that would result in higher overall yields from the most convenient starting material, ReOCl$_3$(PPh$_3$)$_2$.[12] It seemed that the unusual complex ReCl$_2$(NO)(PPh$_3$)$_2$ reported in 1974 by Adams et al.[1] offered the best chance of achieving this goal. This compound is best prepared in the original fashion by passing nitric oxide into a benzene–methanol suspension of the benzoylazo complex ReCl$_2$(N$_2$COPh-N',O)(PPh$_3$)$_2$.[13] However, work with this material and our attempts to improve upon the reported synthesis have led us to reformulate it as a methoxide complex of rhenium(II), viz., ReCl$_2$(OCH$_3$)(NO)(PPh$_3$)$_2$.

Evidence for this reformulation is based largely upon the infrared spectra of both the methoxide complex and that of its ethoxide analogue prepared from benzene–ethanol mixtures. Unfortunately, ^{1}H NMR spectra cannot be obtained because of the complexes' paramagnetism, and elemental analysis is insufficiently sensitive to distinguish between the various

Table I. Infrared Data[a]

no.	compd	ν(NO)[b]	ν(CO)[b]	ν(ReCl)[c]	others
1a	$ReCl_2(OCH_3)(NO)(PPh_3)_2$[d]	1727		304, 276	ν(CH) 2927 w, 2902 w, 2871 w, 2801 m; ν(CO) 1042 s
1b	$ReCl_2(OC_2H_5)(NO)(PPh_3)_2$	1728		305, 284	ν(CH) 2969 w, 2928 w, 2865 w, 2840 w; ν(CO) 1046 s; $\delta(OCH_2)$ 902 m
2	$ReCl_2(NO)(PPh_3)_3$	1693, 1658		304, 276	
3	$[ReF(CO)(NO)(PPh_3)_3]BF_4$	1742	2039		ν(BF) 1050 vs
4	$ReCl_2(CO)(NO)(PPh_3)_2$[d]	1738	2007	310, 284	
5	$ReCl_2(CNR)_2(NO)(PPh_3)$	1726		303, 279	ν(CN) 2178 s, 2128 vs (CH_2Cl_2)
6	$ReHF(CO)(NO)(PPh_3)_2$	1662	1969		ν(ReH) 1835 m (CH_2Cl_2), 1854 m, 1809 s (Nujol); δ(ReH) 790 m
6a	$ReDF(CO)(NO)(PPh_3)_2$	1675	1970		ν(ReD) 1284 m; δ(ReD) 655 m
7	$ReF(OCH_3)(CO)(NO)(PPh_3)_2$	1694	1976		ν(CH) 2905 w, 2807 w, 2791 w; ν(CO) 1053 m
8	$ReF_2(CO)(NO)(PPh_3)_2$	1711	1985		
9	$ReOCl_2(OCH_3)(PPh_3)_2$				ν(CH) 2940 w, 2911 w, 2812 m; ν(CO) 1094 m
10	$ReOCl_2(OC_2H_5)(PPh_3)_2$				ν(CH) 2981 w, 2969 w, 2961 w, 2931 w, 2865 w; ν(CO) 1067 s; $\delta(OCH_2)$ 910 vs[e]

[a] Values in cm^{-1}, obtained as Nujol or Fluorolube mulls unless noted otherwise. [b] All absorptions very strong; CH_2Cl_2 solution. [c] All absorptions strong. [d] Literature values[1] are given for the following compounds. $ReCl_2(NO)(PPh_3)_2$: ν(NO) 1725 ($CHCl_3$), 1710, 1725 (Nujol); ν(ReCl) 297 s, 283 s. $ReCl_2(NO)(CO)(PPh_3)_2$: ν(NO) 1720 ($CHCl_3$), 1720, 1725 (Nujol); ν(ReCl), 311 s, 286 s. No other bands were reported. [e] Reference 12.

formulations. Although oxygen analyses support the alkoxide formulation for these complexes, oxygen analyses on compounds such as these are probably insufficiently reliable to provide anything more than corroborative evidence for the reformulation proposed. In addition to maxima due to triphenylphosphine, $ReCl_2(OCH_3)(NO)(PPh_3)_2$ (**1a**) exhibits absorptions characteristic of nitric oxide, methoxide, and *cis*-dichloride ligands (Table I). The values of ν(NO) and ν(ReCl) compare favorably with those reported for $ReCl_2(NO)(PPh_3)_2$. Furthermore, the frequencies attributed to the methoxide ligand agree well with those observed for the same ligand in $ReOCl_2(OCH_3)(PPh_3)_2$ (**9**).[12] For $ReCl_2(OC_2H_5)(NO)(PPh_3)_2$ (**1b**), however, differing values of ν(NO), ν(ReCl), ν(CO) and ν(CH) are observed. In addition, an extra band at 902 cm^{-1} attributable to $\delta(OCH_2)$ can be identified. As observed for **1a**, the ν(CH), ν(CO) and $\delta(OCH_2)$ values observed in **1b** agree well with similar absorptions seen in $ReOCl_2(OC_2H_5)(PPh_3)_2$ (**10**).[12] It is interesting to note that examination of an albeit limited variety of methoxide complexes such as $ReF(OCH_3)(CO)(NO)(PPh_3)_2$ (**7**) (vide infra), $[Os(OCH_3)(CO)(CNR)_2(PPh_3)_2]^+$[14] (R = *p*-tolyl), $[Os(OCH_3)(NO)_2(PPh_3)_2]^+$,[15] and $[Rh_2(\mu\text{-}OCH_3)(CO)_2(\mu\text{-dppm})_2]^+$[16] tends to indicate that a weak- to medium-intensity band at ca. 2800 cm^{-1} can be considered diagnostic of the presence of the methoxide ligand. The lowest frequency aliphatic CH stretching mode in ethoxide complexes generally appears at somewhat higher values of ca. 2850 cm^{-1}.

Reformulation of $ReCl_2(NO)(PPh_3)_2$ as $ReCl_2(OCH_3)(NO)(PPh_3)_2$ also enables the observed paramagnetic moment of 1.7 μ_B to be rationalized. The original authors recognized the problems posed by this value. Their arguments encompassed formulation of the complex as one of either rhenium(I) (with a linear nitrosyl) or rhenium(III) (with a bent nitrosyl). As they pointed out, the value of ν(NO) in **1a** is such that the metal–nitrosyl linkage is likely to be linear, giving a complex of rhenium(I), and five-coordinate complexes of rhenium(I) would be expected to be diamagnetic. Furthermore, it has been noted that genuine five-coordinate complexes of rhenium(III) are also likely to be diamagnetic,[17] as exemplified by $ReCl_3[o\text{-}(Me_2As)_2C_6H_4]$[18] and $ReCl_3(Ph_3PO)_2$.[12] Consequently, Adams et al. were unable to assign a structure to **1a**, on the basis of the available data.

On the other hand, formulation of **1a** as a pseudooctahedral compound of rhenium(II) (i.e., linear nitrosyl) poses no problems, since a paramagnetic moment approaching the spin-only value of 1.73 μ_B is to be expected for a low-spin d^5 complex (even one of low symmetry) exhibiting extensive spin–orbit coupling and significant electron delocalization,[19] as can be anticipated for $ReCl_2(OCH_3)(NO)(PPh_3)_2$. It should be noted that this reformulation seriously affects some of the arguments concerning charge distributions in rhenium nitrosyl complexes made by Chatt et al. in a subsequent publication.[20]

At this juncture, it should be pointed out that formulation of **1a** as a methoxide complex does present certain problems in the interpretation of the chemistry reported for this complex. Adams et al. describe a number of reactions of **1a** with neutral ligands (L) as giving six-coordinate, diamagnetic complexes of rhenium(I), $ReCl_2(NO)L(PPh_3)_2$. Although we have not reinvestigated this work, we have no doubts that these adducts are formulated correctly and are not methoxide complexes. Almost without exception, the formation of these adducts required very long reaction times and/or high temperatures and proceeded in poor to modest yields (33–75%). These conditions are most uncharacteristic for the addition of a ligand to an unsaturated complex, for it is well-known that coordinately unsaturated complexes are generally very labile. An interesting comparison is afforded by the synthesis of $ReCl_2(CO)(NO)(PPh_3)_2$ from **1a** and $ReCl_2(NO)(PPh_3)_3$ (**2**). Reacting **1a** with CO for 7 h produced $ReCl_2(CO)(NO)(PPh_3)_2$ in 55% yield.[1] By comparison, coordinately saturated **2** reacts with CO within minutes, giving the same product in 97% yield (vide infra). These results are inconsistent with **1a** being unsaturated $ReCl_2(NO)(PPh_3)_2$. Therefore, we feel that in the reactions leading to $ReCl_2(NO)L(PPh_3)_2$ from **1a**, reduction and/or disproportionation are implicated. In this regard it is interesting to note that the most rapid adduct formation occurred for L = methylhydrazine.

It is apparent that the only unequivocal method of establishing the exact nature of **1a** is by X-ray diffraction techniques. We have tried at great length to obtain single crystals of either **1a** or **1b** suitable for crystallography, but without success. Adams et al. apparently experienced the same dif-

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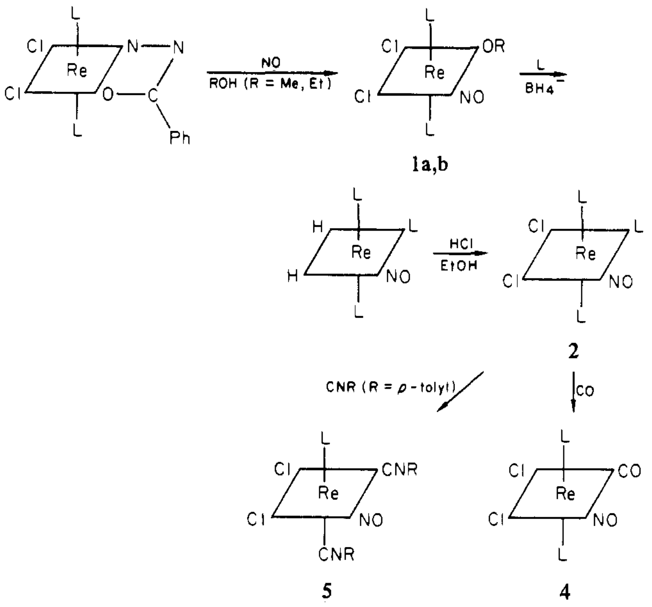
Scheme I. Synthesis and Reactions of $ReCl_2(NO)(PPh_3)_3$ ($L = PPh_3$)



ficulties since the results of their X-ray structural analysis reported to have been in progress have yet to appear.

Despite its unusual nature, $ReCl_2(OCH_3)(NO)(PPh_3)_2$ proved an ideal precursor to $ReH_2(NO)(PPh_3)_3$. In a procedure similar to that described by Giusto et al., $ReCl_2(OCH_3)(NO)(PPh_3)_2$ reacts with sodium borohydride and triphenylphosphine in ethanol suspension to give excellent yields of $ReH_2(NO)(PPh_3)_3$. In view of the report[2] that $ReH_2(NO)(PPh_3)_3$ eliminates dihydrogen at room temperature in the presence of carbon monoxide to form $Re(CO)_2(NO)(PPh_3)_2$, it was expected that similar elimination reactions could yield a variety of d^8 rhenium nitrosyl complexes. Unfortunately, in our hands, all attempts to induce elimination of dihydrogen using carbon monoxide, *p*-tolyl isocyanide, and $Ph_2PC_2H_4PPh_2$ and other phosphines met with failure, even when quite forcing conditions were employed. The same authors also reported the reaction of $ReH_2(NO)(PPh_3)_3$ with hydrogen chloride in benzene under an inert atmosphere as giving a very unstable product, tentatively formulated as "$ReCl_2(NO)(PPh_3)_2$". A reinvestigation of this reaction verified the air sensitivity of the product, but to date this material has defied analysis. However, when $ReH_2(NO)(PPh_3)_3$ is heated in ethanol suspension with hydrochloric acid, bright yellow, analytically pure $ReCl_2(NO)(PPh_3)_3$ (**2**) is obtained. This material is extremely oxygen sensitive in solution and cannot be successfully recrystallized, which presumably accounts for the difficulties encountered in all the attempts to characterize it. Stable analogues of $ReCl_2(NO)(PPh_3)_3$ have been synthesized previously with use of various alkylphenylphosphines. The X-ray crystal structure of $ReCl_2(NO)(PMePh_2)_3$ has been reported,[21] and the complex has been shown to possess a meridional array of phosphine ligands, cis chlorides, and a linear nitrosyl group. In view of the similarities in infrared spectra between $ReCl_2(NO)(PMePh_2)_3$ (ν(NO) 1690, 1670; ν(ReCl) 290, 265) and $ReCl_2(NO)(PPh_3)_3$ (see Table I) it seems logical to assume a similar structure for the latter. It seems highly likely, also, that the solution instability of $ReCl_2(NO)(PPh_3)_3$ results from a tendency to dissociate, brought about by the greater steric demands of the triphenylphosphine ligand. Lability of the phosphine ligands has been established at least qualitatively through the reaction of $ReCl_2(NO)(PPh_3)_3$ with carbon monoxide and *p*-tolyl isocyanide.

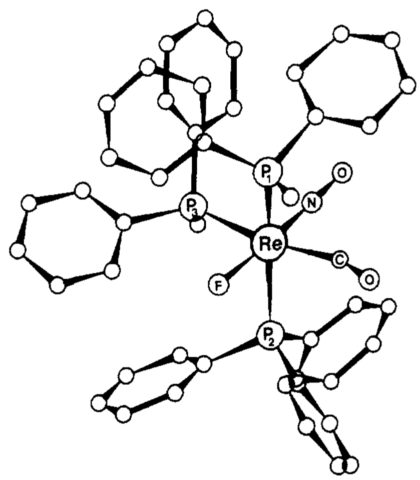


Figure 1. Structure of the cation $[ReF(CO)(NO)(PPh_3)_3]^+$. Two phenyl groups have been omitted for clarity. Relevant bond distances (Å) are given by the following: Re–F, 1.97 (1); Re–N, 1.76 (2); Re–C, 1.92 (3); Re–P (av), 2.53 (2); C–O, 1.16 (4), N–O, 1.20 (3). Relevant bond angles (deg) are given by the following: Re–N–O, 176 (2); Re–C–O, 169 (2); P_1–Re–P_2, 162 (1); P_1–Re–P_3, 95 (1); P_2–Re–P_3, 96.8 (3). The *R* factor was 0.057.

Under mild conditions, $ReCl_2(NO)(PPh_3)_3$ reacts with carbon monoxide and *p*-tolyl isocyanide (CNR) to give $ReCl_2(CO)(NO)(PPh_3)_2$ (**4**) and $ReCl_2(CNR)_2(NO)(PPh_3)$ (**5**), respectively. In both complexes the cis arrangement of chloro ligands is maintained, and a cis geometry of the isocyanide groups in **5** is also observed. With the available data, it is not possible to define the exact stereochemistry of these complexes. However, for $ReCl_2(CO)(NO)(PPh_3)_2$ it seems reasonable to assume trans triphenylphosphine groups and, with the assumption that no gross stereochemical changes have occurred, a trans arrangement of triphenylphosphine and *p*-tolyl isocyanide groups in $ReCl_2(CNR)_2(NO)(PPh_3)$. The chemistry of $ReH_2(NO)(PPh_3)_3$ and the assigned stereochemistries of the products are depicted in Scheme I.

Certain dihydrides of osmium(II) undergo cleavage reactions with noncoordinating acids to yield various hydrido cations of significant synthetic utility.[22] It was anticipated that $ReH_2(NO)(PPh_3)_3$ would behave similarly but, unfortunately, this was not the case. However, this investigation did provide some very interesting chemistry. $ReH_2(NO)(PPh_3)_3$ reacts with perchloric acid in the presence of carbon monoxide with apparent decomposition. Using tetrafluoroboric or hexafluorophosphoric acid under the same conditions, however, yields the novel fluoro cation $[ReF(CO)(NO)(PPh_3)_3]^+$ (**3**) as either the BF_4^- or PF_6^- salt. The perchlorate salt, which is quite stable, can be made via metathetical exchange of the tetrafluoroborate salt with sodium perchlorate. Cationic $[ReF(CO)(NO)(PPh_3)_3]^+$ has been characterized by elemental analysis of the BF_4^- and ClO_4^- salts, ^1H NMR study (no evidence for a metal hydride resonance up to ca. δ −25), and an X-ray structural analysis of the ClO_4^- salt.

The results of the diffraction study at the current state of refinement ($R = 0.059$) are depicted in Figure 1. Two phenyl groups have been omitted for clarity. The geometry of the cation is that of a distorted octahedron with a meridional array of phosphine ligands. Most of the intramolecular distances are unremarkable with the Re–F distance of 1.97 Å comparing well to other Re–F(terminal) distances such as 2.020 Å in $(NH_4)ReO_{1.5}F_3$[23] and 1.86 Å in $ReOF_4$.[24] The crystal chosen

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Table II. Atomic Parameters $\times 10^4$ ($\times 10^5$ for Re) for $[ReF(CO)(NO)(PPh_3)_3]ClO_4 \cdot xC_6H_{12} \cdot yCH_2Cl_2$

	x/*a*	*y*/*b*	*z*/*c*
Re	1196 (7)	33464 (4)	1386 (7)
P(1)	9648 (17)	3890 (11)	1360 (18)
P(2)	11063 (7)	2920 (5)	−785 (7)
P(3)	9247 (4)	2525 (3)	411 (5)
C(1)	8517 (66)	4245 (41)	1012 (68)
C(2)	8317 (66)	4395 (41)	100 (67)
C(3)	7352 (71)	4672 (45)	−176 (71)
C(4)	6884 (89)	4758 (52)	483 (92)
C(5)	7218 (89)	4631 (57)	1408 (91)
C(6)	8163 (74)	4347 (47)	1672 (76)
C(7)	10559 (62)	4387 (41)	1728 (63)
C(8)	10241 (69)	4876 (39)	1966 (70)
C(9)	10963 (83)	5270 (53)	2313 (84)
C(10)	11800 (82)	5191 (48)	2405 (82)
C(11)	12098 (79)	4700 (55)	2225 (81)
C(12)	11555 (72)	4286 (45)	1866 (72)
C(13)	9698 (59)	3535 (36)	2384 (59)
C(14)	8880 (64)	3278 (46)	2517 (65)
C(15)	8987 (86)	2990 (52)	3326 (88)
C(16)	9803 (89)	2879 (52)	3989 (89)
C(17)	10396 (88)	3206 (52)	3886 (92)
C(18)	10537 (76)	3466 (51)	3047 (79)
C(19)	11432 (26)	2235 (16)	−549 (27)
C(20)	11641 (30)	2090 (19)	356 (32)
C(21)	11983 (35)	1573 (24)	604 (36)
C(22)	12043 (38)	1244 (24)	−97 (42)
C(23)	11866 (41)	1365 (26)	−1007 (44)
C(24)	11532 (35)	1902 (22)	−1277 (36)
C(25)	12174 (23)	3247 (14)	−674 (24)
C(26)	12626 (26)	3472 (18)	121 (27)
C(27)	13501 (32)	3721 (20)	198 (33)
C(28)	13901 (36)	3708 (23)	−501 (38)
C(29)	13487 (43)	3426 (31)	−1304 (43)
C(30)	12568 (37)	3195 (21)	−1400 (37)
C(31)	10422 (25)	2982 (16)	−1994 (26)
C(32)	10541 (34)	3469 (24)	−2411 (34)
C(33)	9921 (31)	3533 (18)	−3331 (32)
C(34)	9363 (33)	3145 (20)	−3741 (34)
C(35)	9285 (33)	2696 (21)	−3354 (35)
C(36)	9829 (38)	2566 (24)	−2373 (39)
C(37)	9781 (17)	2067 (11)	1315 (18)
C(38)	10460 (17)	2260 (11)	2077 (17)
C(39)	10852 (20)	1893 (13)	2801 (20)
C(40)	10580 (24)	1377 (15)	2707 (24)
C(41)	9887 (22)	1195 (13)	1975 (23)
C(42)	9509 (19)	1551 (12)	1282 (19)
C(43)	8088 (18)	2672 (11)	592 (19)
C(44)	7633 (16)	3120 (10)	194 (17)
C(45)	6776 (18)	3244 (11)	334 (18)
C(46)	6359 (21)	2909 (13)	837 (22)
C(47)	6815 (20)	2442 (12)	1218 (20)
C(48)	7684 (19)	2324 (12)	1090 (19)
C(49)	8948 (16)	2110 (10)	−606 (16)
C(50)	9473 (15)	1693 (13)	−720 (16)
C(51)	9225 (21)	1382 (13)	−1492 (21)
C(52)	8437 (22)	1526 (13)	−2225 (22)
C(53)	7908 (20)	1944 (13)	−2094 (20)
C(54)	8130 (18)	2269 (11)	−1305 (19)
C(60)	10694 (18)	3983 (12)	−114 (19)
O(60)	10921 (13)	4373 (9)	−382 (14)
N(70)	9193 (14)	3456 (9)	−825 (14)
O(70)	8595 (12)	3525 (7)	−1513 (12)
F(80)	11162 (9)	3186 (5)	1198 (9)
Cl	−35 (6)	−230 (4)	2935 (6)
O(1)	−120 (20)	123 (14)	3625 (21)
O(2)	804 (29)	−170 (15)	2741 (29)
O(3)	−788 (20)	−201 (11)	2152 (21)
O(4)	−213 (28)	−721 (18)	3221 (28)

Table IV. Isotropic Temperature Factors

atom	*U*, Å^2	atom	*U*, Å^2	atom	*U*, Å^2
C(1)	799 (282)	C(23)	1069 (191)	C(44)	473 (68)
C(2)	577 (280)	C(24)	817 (157)	C(45)	610 (82)
C(3)	627 (300)	C(25)	394 (102)	C(46)	734 (93)
C(4)	1374 (400)	C(26)	540 (116)	C(47)	705 (85)
C(5)	1234 (398)	C(27)	690 (141)	C(48)	619 (80)
C(6)	822 (326)	C(28)	869 (164)	C(49)	467 (68)
C(7)	197 (261)	C(29)	1207 (200)	C(50)	518 (63)
C(8)	574 (309)	C(30)	892 (174)	C(51)	691 (89)
C(9)	767 (364)	C(31)	428 (106)	C(52)	814 (100)
C(10)	630 (374)	C(32)	818 (158)	C(53)	663 (85)
C(11)	753 (347)	C(33)	738 (136)	C(54)	576 (77)
C(12)	525 (306)	C(34)	537 (143)	C(60)	470 (75)
C(13)	532 (257)	C(35)	743 (147)	O(60)	720 (60)
C(14)	503 (288)	C(36)	1011 (174)	N(70)	316 (60)
C(15)	765 (387)	C(37)	555 (75)	O(70)	581 (50)
C(16)	1096 (383)	C(38)	461 (70)	F(80)	269 (38)
C(17)	1006 (418)	C(39)	649 (86)	Cl	936 (27)
C(18)	894 (350)	C(40)	823 (107)	O(1)	1625 (111)
C(19)	453 (106)	C(41)	786 (97)	O(2)	1769 (164)
C(20)	642 (132)	C(42)	717 (86)	O(3)	1427 (102)
C(21)	866 (163)	C(43)	551 (77)	O(4)	2039 (153)
C(22)	965 (174)				

seems to have occluded to least two different solvent molecules (presumably dichloromethane and cyclohexane), which are disordered around a center of symmetry. It was felt that further attempts at refinement would not significantly alter the more important structural features of the cation (except perhaps for the carbonyl group), and therefore atomic locations were not assigned to the solvent atoms. Atomic parameters for the other atoms are found in Table II.

Despite the disorder problems, however, the analysis does establish the gross structural and stereochemical details of the cation, with the thermal parameters supporting a trans arrangement of fluoride and nitrosyl ligands. Chatt and Heaton[25] have commented upon the stability of platinum metal hydroxide complexes when π-acid ligands of high trans influence are also present, especially in the position trans to the hydroxide. It would appear that ligands of great π acidity render the trans site (and indeed the metal as a whole) more class a in character, thereby strengthening the M–OH bond. Given that NO^+ is one of the strongest π-acid ligands available, it is not surprising to find a relatively wide range of stable metal hydroxide complexes containing nitric oxide also: e.g., *trans*-$[Ir(OH)(NO)(PPh_3)_2]^+$,[26] $Ru(OH)(CO)(NO)(PPh_3)_2$,[27] $Ru(O_2)(OH)(NO)(PPh_3)_2$,[28] and $[M(OH)(NO)_2(PPh_3)_2]^+$[15] (M = Ru, Os; OH trans to linear NO). It seems obvious that such arguments and observations should be valid for fluoro complexes as well.

The third phosphine ligand in $[ReF(CO)(NO)(PPh_3)_3]^+$ is labile, enabling neutral species of the type $ReFX(CO)(NO)(PPh_3)_2$ (**6**–**8**; X = H, OCH_3, and F, respectively) to be synthesized by reaction with the appropriate anion. Introducing a second halide by this means also results in substitution of the fluoride, yielding $ReX_2(CO)(NO)(PPh_3)_2$, X = Cl, Br. It is worth noting that $ReF_2(CO)(NO)(PPh_3)_2$ is the only product isolable from the reaction of $[ReF(CO)(NO)(PPh_3)_3]BF_4$ with carbon monoxide at elevated temperature and pressure, illustrating the comparative ease with which the BF_4^- ion can break down, as well as the affinity of rhenium(I) for fluoride ligands. $ReF(OCH_3)(CO)(NO)(PPh_3)_2$ exhibits IR maxima already discussed as being typical of the methoxide ligand, and the ^1H NMR spectrum exhibits a singlet at δ 3.39 (3 H) assigned to the methoxide group, in addition to the phenyl proton multiplet at δ 7.44. The spectroscopic properties of $ReHF(CO)(NO)(PPh_3)_2$ deserve special mention and are discussed separately below.

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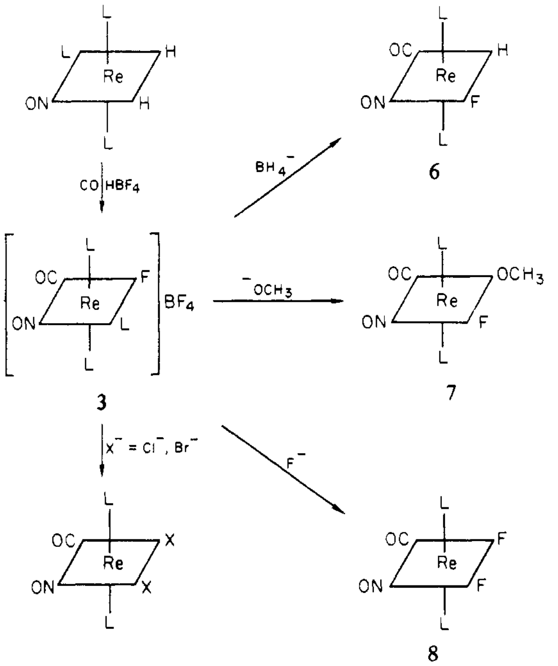
Table V. Anisotropic Temperature Factors[a]

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Re	2690 (51)	4294 (59)	3345 (57)	113 (91)	353 (36)	13 (87)
P(1)	471 (146)	422 (183)	483 (163)	−51 (138)	48 (128)	67 (138)
P(2)	376 (61)	529 (86)	396 (68)	−11 (59)	66 (55)	39 (56)
P(3)	334 (38)	491 (54)	432 (45)	13 (37)	69 (35)	−72 (35)

[a] The temperature factor T is equal to $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$.

Scheme II. Synthesis and Reactions of $[ReF(CO)(NO)(PPh_3)_3]^+$ (L = PPh_3)



Low-oxidation-state fluoro complexes of the type described in the previous paragraph are relatively rare. Various neutral and cationic fluoro complexes of Pt(II) and Pd(II) have been reported,[29] as have the complexes $MF(CO)(PPh_3)_2$ (M = Rh, Ir).[30,31] Oxidative additions to $IrF(CO)(PPh_3)_2$ resulted in the formation of $IrF(O_2)(CO)(PPh_3)_2$ and $IrFI_2(CO)(PPh_3)_2$.[32] Even fewer mixed hydride–fluoride complexes are known. To our knowledge, only $IrHFCl(CO)(PPh_3)_2$[33] and $OsHF(CO)(PPh_3)_3$[14] have been synthesized. In most of the above complexes the fluoride is quite labile so that the ready formation and stability of the fluoride complexes reported herein must be considered a rather unique facet of the low-valent chemistry of rhenium.

$ReHF(CO)(NO)(PPh_3)_2$ is unusual in that its stereochemistry can be established through a combination of IR and ^1H NMR spectroscopy. Crystalline samples of $ReHF(CO)(NO)(PPh_3)_2$ exhibit IR maxima at 1961 vs (ν(CO)), 1854 m, 1809 s (ν(ReH)), 1664 vs (ν(NO)), and 790 w cm^{-1} (δ(ReH)). In dichloromethane solution the two maxima attributed to ν(ReH) appear as a broad, single peak at 1835 cm^{-1}. The assignment of the 1854- and 1809-cm^{-1} bands to ν(ReH) was confirmed by deuteration, which also established the presence of a Fermi resonance interaction between ν(ReH) and ν(NO), thereby indicating a trans arrangement for these ligands. $ReDF(CO)(NO)(PPh_3)_2$ (**6a**) exhibits IR maxima at 1962 vs (ν(CO)), 1680 vs (ν(NO)), 1284 w (ν(ReD)), and 655 w cm^{-1} (δ(ReD)). Only one ν(ReD) band was observed since the expected higher frequency component was obscured by a ligand absorption at ca. 1320 cm^{-1}. The presence of the Fermi resonance interaction is indicated by the shift to higher frequency of ν(NO), the anomalous ν(ReH)/ν(ReD) value of 1.409 (for the lower frequency component), and the dramatic decrease in the intensity of the ν(ReH) band on deuteration. An "unperturbed" value for ν(ReH)/ν(ReD) of 1.396 can be calculated (by assuming an interaction energy between the two vibrational states, $\Delta\nu$(NO) = 16 cm^{-1}) which is in the range normally observed in the absence of any interaction.[34]

The ^1H NMR spectrum of $ReHF(CO)(NO)(PPh_3)_2$ is characterized by a multiplet at δ 7.42 (30 H, phenyl protons) and a multiplet at δ 4.73 (1 H) assigned to the hydride proton. This is a remarkably low value for a hydride resonance, especially since such resonances for hydrido–phosphine complexes generally occur to much higher field (δ −10 and above). The multiplet itself consists of a doublet of triplets, typical of an AM_2X spin system, establishing the presence of trans triphenylphosphine ligands. The value of $^2J_{HP}$ = 22.6 Hz is quite typical of those observed for other hydrido–phosphine complexes of rhenium.[2,35] ^1H NMR data are not available for either $OsHF(CO)(PPh_3)_3$ or $IrHFCl(CO)(PPh_3)_2$, and it would thus appear that the value of $^2J_{HF}$ = 5.7 Hz represents the first such value for cis ^1H–^{19}F coupling recorded.

Considering both sets of results together defines the stereochemistry of $ReHF(CO)(NO)(PPh_3)_2$ as that shown in Scheme II. Also shown are the other products derived from $[ReF(CO)(NO)(PPh_3)_3]^+$ and their probable stereochemistries. It is interesting to note that in the formation of $ReHF(CO)(NO)(PPh_3)_2$ the fluoride ligand goes from being trans to nitric oxide to being trans to carbon monoxide. It is likely that this change is kinetic in origin, arising from an associative mechanism in which the borohydride anion attacks at the least hindered site in the cation, i.e., between the fluoro and carbonyl ligands. This in turn suggests that the thermodynamically stable isomer may in fact differ from that found by having fluorine trans to nitric oxide. All attempts to isomerize $ReHF(CO)(NO)(PPh_3)_2$ by heating in solution, however, resulted in extensive decomposition and the isolation of a mixture of at least three materials, including the starting material and $ReF_2(CO)(NO)(PPh_3)_2$. No unambiguous evidence suggesting the presence of other isomers of $ReHF(CO)(NO)(PPh_3)_2$ was obtained. The chemistry of $[ReF(CO)(NO)(PPh_3)_3]^+$ and $ReHF(CO)(NO)(PPh_3)_2$ is being further investigated and will be reported in subsequent publications.

Acknowledgment. The authors acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada. We also thank Mr. E. Woods and Ms. P. Meindl for technical assistance.

Registry No. **1a**, 83095-49-2; **1b**, 83095-50-5; **2**, 83095-51-6; **3**, 83095-53-8; **4**, 53495-46-8; **5**, 83114-89-0; **6**, 83095-54-9; **7**, 83114-90-3; **8**, 83095-55-0; **9**, 83114-91-4; **10**, 17442-19-2; Re(η^2-N_2COPh-N',O)$Cl_2(PPh_3)_2$, 83149-20-6; $ReOCl_3(PPh_3)_2$, 17442-18-1;

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Inorg. Chem. **1982**, *21*, 4155–4160

$ReH_2(NO)(PPh_3)_3$, 58694-74-9; $[ReF(CO)(NO)(PPh_3)_3]ClO_4$, 83095-56-1; $[ReF(CO)(NO)(PPh_3)_3]ClO_4 \cdot xC_6H_{12} \cdot yCH_2Cl_2$, 83095-57-2; $ReCl_2(NO)(PPh_3)_2$, 53435-83-9; benzoylhydrazine, 613-94-5; deuterium, 7782-39-0.

Supplementary Material Available: Listings of interatomic bonds and interbond angles (Table III), selected torsional angles (Table VI), and observed and calculated structure factors (Table VII) (20 pages). Ordering information is given on any current masthead page.

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Structure and Synthesis of Isomers of Novel Binuclear Cobalt(III)–Phenyl Phosphate Complexes

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Received December 22, 1981

The reaction between *cis*-$[Co(en)_2Cl_2]ClO_4$ and silver phenyl phosphate in anhydrous dimethyl sulfoxide yielded the dimeric cation $\{[Co(en)_2(\mu\text{-}O_3POC_6H_5)]_2\}^{2+}$ as the major product. An X-ray structure determination of the meso diastereomer as the triflate salt monohydrate showed that it consisted of two bis(ethylenediamine)cobalt(III) moieties bridged by two phosphate ester groups; the two cobalt atoms and two bridging ligands define an eight-membered ring. Crystals were of space group $P2_1/c$ with $a = 9.454$ (5) Å, $b = 28.683$ (14) Å, $c = 7.487$ (4) Å, $\beta = 97.21$ (8)°, and $Z = 4$, R being 0.060 for 1675 reflections with $I > 2.5\sigma(I)$. The racemic diastereomer has been resolved, and the corresponding rotatory dispersion and circular dichroism spectra are discussed.

Introduction

Polynuclear metal complexes play a significant role in enhancing the rate of hydrolysis of biologically important phosphate compounds.[2-4] For example, the rate of hydrolysis of ATP is accelerated 60-fold in the presence of Cu(II) and this has been attributed to the formation of dimeric $[((ATP)CuOH)_2]^{6-}$.[2] Furthermore, the hydrolysis of pyrophosphate to orthophosphate is increased by 10^5 times at pH 7 in the presence of $[Co(1,3\text{-diaminopropane})_2(OH)(OH_2)]^{2+}$.[4] ^{31}P NMR studies indicate that the catalytically active species is a polynuclear complex containing one pyrophosphate moiety coordinated to three Co(III) centers.

As part of a continuing study into the promotion of phosphate ester hydrolysis by metal ions we now report the synthesis and characterization of a new type of Co(III) dimer containing two bridging phosphate ester moieties.[5]

Experimental Section

Reagents and Instrumentation. Analytical grade reagents were used throughout except where otherwise specified. Dimethyl sulfoxide (Mallinckrodt, AR) was dried over 4A molecular sieves. Laboratory reagent grade sulfolane (tetramethylenesulfone) was predried by passage through a column of 4A molecular sieves and then distilled from calcium hydride before use. Nitronium tetrafluoroborate (NO_2BF_4) was obtained from Pfaltz and Bauer.

^1H NMR spectra were recorded with a JEOL JNM-MH-100 (Minimar) spectrometer. Chemical shifts are quoted as downfield relative to NaTPS [sodium 3-(trimethylsilyl)propanesulfonate] in D_2O solution. For the ^{31}P NMR studies, JEOL JNM-FX-100 (^{31}P probe) or JEOL JNM-FX-90 (multiprobe) spectrometers operating at 40.32 and 36.20 MHz, respectively, with internal D_2O lock were used. All spectra were proton decoupled. ^{31}P chemical shifts are reported relative to external 85% H_3PO_4 with increasing values toward low field. $^{13}C\{^1H\}$ NMR spectra were recorded at 15.04 MHz with a JEOL FX-60Q spectrometer with chemical shift values quoted relative to 1,4-dioxane (internal reference). An autobalancing resistance bridge (Genrad 1657 RLC Digibridge) was used in conjunction with a Phillips PW 9512/00 dipping electrode for all conductance measurements. A Knauer Dampforuck-Osmometer was used for the determination of molecular weights in aqueous solution. The machine was calibrated with sodium chloride solutions (at 37 °C).

Rotatory dispersion (RD) spectra were obtained with 1-dm cells in a Perkin-Elmer P22 spectropolarimeter. Molecular rotations [M] are recorded in units of deg M^{-1} m^{-1}. Circular dichroism (CD) spectra were recorded on a Jasco UV/5 ORD instrument fitted with a Sproul Scientific SS20 CD modification. The $\Delta\epsilon$ values for the CD spectra are quoted in units of M^{-1} cm^{-1}. The instrument was calibrated against a solution of $(+)_D$-$[Co(en)_3]_2Cl_6 \cdot NaCl \cdot 6H_2O$ ($\Delta\epsilon = 1.80$ at 484 nm).[6] A Pharmacia K 50/100 chromatography column was used for the resolution of the dimeric complexes into their optical isomers.

Synthesis of the Meso and Racemic Diastereomers of $\{[Co(en)_2(\mu\text{-}O_3POC_6H_5)]_2\}X_2$ ($X = Cl^-, CF_3SO_3^-$). *cis*-$[Co(en)_2Cl_2]ClO_4$ (20 g) was dissolved in vigorously stirred Me_2SO (100 mL, 4A molecular-sieve dried) at 80 °C (the flask contained several small glass beads to assist in the fragmentation of the starting materials). Powdered anhydrous $Ag_2O_3POC_6H_5$ (24 g) was added in 2-g lots over a period of 5 min. Stirring was continued for a further 70 min at 80 °C, after which time the mixture was allowed to cool to room temperature. The mixture was then poured into ice-cold water (300 mL). Sodium iodide solution was added to ensure that all residual Ag^+ had precipitated. The silver salts were removed, and the filtrate was diluted to 15 L. The reaction products were sorbed on Sephadex C-25 resin (Na^+ form, 12 × 8.5 cm). Elution with 0.2 M NaCl gave rise to several bands. The first two (blue and red, respectively) were minor ones and were discarded. The third (major) band was intense red-violet and contained the desired product. Evaporation of this fraction to 250 mL resulted in the formation of red-violet crystals of the chloride salt. After the solution was cooled at 0 °C for 4 h, the product was collected and washed with ice-cold LiCl solution (20 ml, 3 M), methanol (20 mL), and diethyl ether (4 × 10 mL). It was then dried in air (yield 18 g). Anal. Calcd for $\{[Co(C_4H_{16}N_4)(\mu\text{-}O_3POC_6H_5)]_2\}Cl_2 \cdot 2H_2O$: C, 30.36; H, 5.60; N, 14.16. Found: C, 30.7; H, 5.5; N, 14.1. The ^1H NMR spectrum of a saturated solution of the chloride salt of the complex in 1 mL of D_2O containing one drop of concentrated DCl gave the following chemical shifts in ppm (relative peak areas and multiplicities in parentheses). Ethylenediamine: CH_2, 2.29 (4, br); CH_2, 2.76 (4, br); NH_2 3.48 and 3.90 (total 4, overlapping br); NH_2

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(5) The kinetics and mechanism of base hydrolysis of the nitrophenyl phosphate analogue of the dimeric species reported in this paper will be presented in a contemporary publication.

0020-1669/82/1321-4155$01.25/0 © 1982 American Chemical Society