Contribution from the Department of Chemistry,
University of Utah, Salt Lake City, Utah 84112

Synthesis and Properties of Chiral Rhenium Ether Complexes of the Formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OR_2)]^+X^-$

Sênamê K. Agbossou, Jesús M. Fernández, and J. A. Gladysz*

Received June 16, 1989

Reaction of the dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ ($2^+BF_4^-$; in CH_2Cl_2) and tetrahydrofuran gives $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(THF)]^+BF_4^-$ ($5^+BF_4^-$; 91% after workup). Reaction of $2^+BF_4^-$ and methyl ether gives $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OMe_2)]^+BF_4^-$ ($4^+BF_4^-$, characterized in situ). Ethyl ether and $2^+BF_4^-$ react to give $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OEt_2)]^+BF_4^-$ ($3^+BF_4^-$), but not under preparatively useful conditions. Reaction of the hydride complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (**6**), $Ph_3C^+PF_6^-$, and tetrahydrofuran gives $5^+PF_6^-$ (90%). Reaction of **6**, $Ph_3C^+PF_6^-$, and ethyl ether gives $3^+PF_6^-$ (93%). Reactions of alkoxide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OR)$ and oxonium salts $R_3O^+X^-$ (R = Et, Me) in CH_2Cl_2 give ethers R_2O and ether complexes $3^+X^-/4^+X^-$ in quantitative NMR yields. These and other data show that tetrahydrofuran, methyl ether, and ethyl ether have higher thermodynamic binding affinities than dichloromethane for the metal fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ and that the oxygen lone-pair basicity in $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OR)$ is greater than that in R_2O.

Introduction

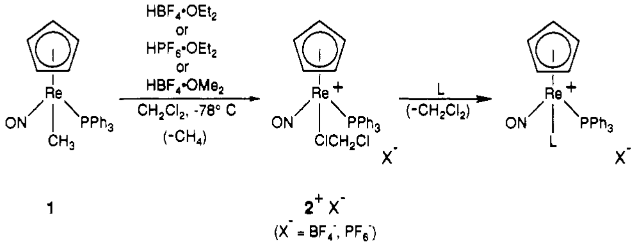
We recently reported that the reaction of the chiral methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**1**) and $HBF_4{\cdot}OEt_2$, $HPF_6{\cdot}OEt_2$, or $HBF_4{\cdot}OMe_2$ in CH_2Cl_2 at -78 °C gives the dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+X^-$ (2^+X^-), as shown in Scheme I.[1,2] Complex 2^+X^- decomposes above -20 °C, and has not yet proved isolable in spectroscopically pure form. However, it is a particularly useful synthetic intermediate. For example, 2^+X^- reacts with a variety of neutral donor ligands L at -50 °C to -30 °C to give substitution products $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+X^-$, with overall retention of configuration at rhenium from **1**.[1,3]

Ethers are much stronger bases than alkyl halides in the gas phase toward both H^+ and Li^+.[4] A variety of experimental data indicate an identical basicity order in solution.[5] Hence, we were surprised that the reaction of methyl complex **1** and $HBF_4{\cdot}OEt_2$ or $HPF_6{\cdot}OEt_2$ (Scheme I) did not give the ethyl ether complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OEt_2)]^+X^-$ (3^+X^-), and that the reaction of **1** and $HBF_4{\cdot}OMe_2$ did not give the methyl ether complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OMe_2)]^+BF_4^-$ ($4^+BF_4^-$). In fact, $2^+BF_4^-$ still formed cleanly in the presence of 20-25 equiv of ethyl ether![1] Consequently, we sought to probe whether the preferential formation of 2^+X^- over 3^+X^- and 4^+X^- in Scheme I was indicative of a kinetic effect, a thermodynamic effect, or both. This objective required the independent generation of authentic samples of ether complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OR_2)]^+X^-$. In this paper, we (1) describe several complementary syntheses of this class of ether complexes, some of which are chemically novel, and (2) establish that simple aliphatic ethers are in fact stronger bases than dichloromethane toward the 16-valence-electron Lewis acid fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I).

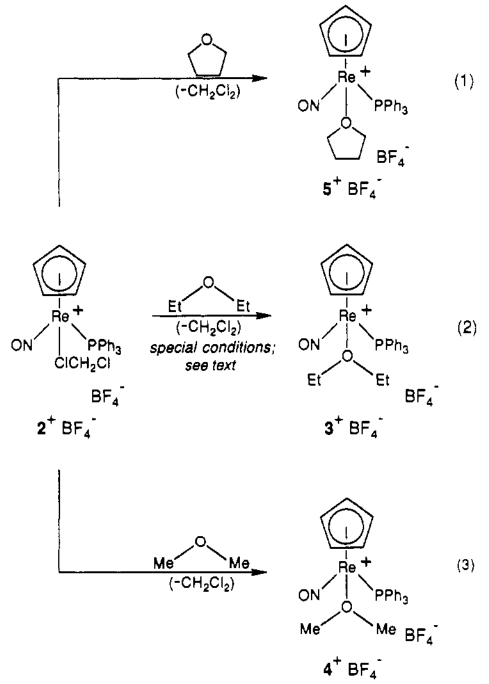
Results

1. Syntheses of Ether Complexes from Dichloromethane Complexes. Since we were uncertain of the stability of the target ethyl ether complex 3^+X^-, initial efforts were directed at the synthesis of the tetrahydrofuran complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(THF)]^+X^-$ (5^+X^-). Tetrahydrofuran is less bulky than ethyl ether and is a stronger Brønsted base in aqueous sulfuric acid.[6] Hence, it might be expected to have a higher binding constant to the rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$

Scheme I. Synthesis and Substitution Reactions of the Dichloromethane Complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+X^-$ (2^+X^-)



Scheme II. Syntheses of Ether Complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OR_2)]^+BF_4^-$ from the Dichloromethane Complex $2^+BF_4^-$



---

(1) Fernández, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207.

(2) See also: Winter, C. H.; Gladysz, J. A. *J. Organomet. Chem.* **1988**, *354*, C33.

(3) (a) Fernández, J. M.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 8268. (b) Fernández, J. M.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1988**, 37. (d) Bodner, G. S.; Fernández, J. M.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 4082. (e) Winter, C. H.; Veal, W. R.; Garner, C. M.; Arif, A. M.; Gladysz, J. A. *Ibid.* **1989**, *111*, 4766.

(4) (a) Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 5920. (b) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695. (c) McMahon, T. B.; Heinis, T.; Nicol, G.; Hovey, J. K.; Kebarle, P. *J. Am. Chem. Soc.* **1988**, *110*, 7591.

(5) For example, oxonium salts $R_3O^+X^-$ are stable in CH_2Cl_2. Since these are kinetically fast alkyl-transfer reagents, ethers R_2O must be much stronger bases toward "R^+" than CH_2Cl_2. See: Perst, H. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1976; Vol. 5; pp 1961-2047.

(6) (a) pK_a (conjugate acid, H_2SO_4): OMe_2 (-3.83) > OEt_2 (-3.59) > THF (-2.08): Arnett, E. M.; Wu, C. Y. *J. Am. Chem. Soc.* **1960**, *82*, 4999. (b) Gas phase proton basicities: OEt_2 > THF ≫ OMe_2.[4b]

0020-1669/90/1329-0476$02.50/0

(I). Accordingly, the dichloromethane complex 2^+BF_4 was generated in CH_2Cl_2 (10 mL) at −78 °C as described previously (Scheme I)[1] and then flooded with tetrahydrofuran (20 mL) at −42 °C (Scheme II, eq 1). Workup gave tetrahydrofuran complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(THF)]^+BF_4^-$ ($5^+BF_4^-$) in 91% yield as an analytically pure pink powder. Solid $5^+BF_4^-$ was air-stable and could be stored for several months at −10 °C without significant decomposition. However, $5^+BF_4^-$ slowly decomposed above −30 °C in CH_2Cl_2 or $CDCl_3$. The rate of decomposition in $CDCl_3$ was monitored at 10.2 °C and was found to be first-order: $k_{obs} = 1.68 \times 10^{-4}\ s^{-1}$; $t_{1/2} = 1.1$ h.

Complex $5^+BF_4^-$ was characterized by IR and low-temperature NMR (^1H, ^{13}C, $^{31}P\{^1H\}$) spectroscopy (Experimental Section). The IR ν_{NO} and cyclopentadienyl ^1H and ^{13}C NMR chemical shifts were characteristic of those found previously for cationic complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+X^-$. Only one set of ^{13}C NMR resonances was observed for the diastereotopic tetrahydrofuran carbons at −70 °C.

The deuteriodichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCD_2Cl)]^+BF_4^-$ ($2\text{-}d_2{}^+BF_4^-$) was generated at −78 °C in CD_2Cl_2 (0.6 mL) in a NMR tube and then treated with 5 equiv (0.39 mmol) of tetrahydrofuran. The reaction was monitored by ^{31}P and ^1H NMR spectroscopy as the tube was gradually warmed. No reaction occurred below −50 °C. Over the course of 1 h at −40 °C, ca. 80% of the $2^+BF_4^-$ converted to the tetrahydrofuran complex $5^+BF_4^-$. The probe was warmed to 0 °C, and conversion to $5^+BF_4^-$ was ≥90% complete. This sample of $5^+BF_4^-$ was more stable than isolated $5^+BF_4^-$ that had been redissolved in CH_2Cl_2, presumably due to the presence of excess tetrahydrofuran. These data bound K_{eq} for eq 1 of Scheme II as $>2 \times 10^2$.

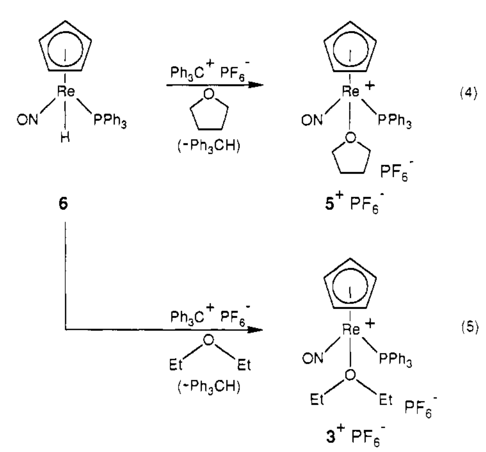
An NMR experiment analogous to the preceding one but utilizing the hexafluorophosphate salt $2^+PF_6^-$ cleanly gave tetrahydrofuran complex $5^+PF_6^-$. However, in corresponding preparative experiments, we were unable to isolate $5^+PF_6^-$ in analytically pure form.

Similar low-temperature NMR experiments were conducted with $2^+BF_4^-$ and 25 equiv of ethyl ether and $2^+PF_6^-$ and 35 equiv of ethyl ether. However, no evidence was found for the formation of ethyl ether complex 3^+X^-. Above −20 °C, 2^+X^- independently decomposed.[7] Next, a sample of $2^+BF_4^-$ in CH_2Cl_2 (0.3 mL, −78 °C) was flooded with three volumes of ethyl ether (1.0:1.8 mol ratio). A considerable amount of material precipitated. The mixture was warmed to −40 °C, and a ^{31}P NMR spectrum was recorded. One product accounted for >65% of the total area of all PPh_3 resonances. The chemical shift (18.7 ppm) corresponded to that of ethyl ether complex $3^+BF_4^-$, the isolation of which is described below. Hence, eq 2 of Scheme II can at least to some extent proceed in the forward direction.

To further probe the direction of this equilibrium, the reaction of methyl complex **1** and $HBF_4{\cdot}OEt_2$ (Scheme I) was repeated in 50:50 (v/v) CH_2Cl_2/ethyl ether (1.0:0.6 mol ratio). A large amount of material precipitated upon the addition of acid, and the sample was transferred to a −40 °C NMR probe. A ^{31}P NMR spectrum was immediately recorded and showed dichloromethane complex $2^+BF_4^-$, ethyl ether complex $3^+BF_4^-$ ((64 ± 2):(36 ± 2) PPh_3 resonance area ratio), and lesser amounts of byproducts. A spectrum recorded 10 min later showed a substantial decrease in the concentration of $2^+BF_4^-$ and a corresponding increase in the concentration of $3^+BF_4^-$ ((13 ± 2):(87 ± 2) area ratio), as judged from reference peaks among the byproducts. This experiment, although not under optimal conditions (e.g., inhomogeneous), strongly suggests that K_{eq} for eq 2 of Scheme II is greater than 1.

Finally, the deuteriodichloromethane complex $2\text{-}d_2{}^+BF_4^-$ was generated at −78 °C in CD_2Cl_2 (0.6 mL) in an NMR tube, and an excess of liquified methyl ether (0.1–0.2 mL, ca. 100 equiv) was added by cannula. The reaction was monitored by ^1H and ^{31}P NMR as the tube was warmed (Scheme II, eq 3). At −40 °C, resonances attributed to the methyl ether complex $4^+BF_4^-$ slowly appeared (Experimental Section) as those of $2\text{-}d_2{}^+BF_4^-$ diminished. After 4 h, conversion to $4^+BF_4^-$ was ca. 90% complete. Only one ^1H NMR resonance was observed for the diastereotopic methyl groups, and the excess *free* methyl ether exhibited a separate resonance. These data (assuming the density of methyl ether to be comparable to that of ethyl ether) bound K_{eq} for eq 3 of Scheme II as $>2 \times 10^1$.

Scheme III. Syntheses of Ether Complexes $[(\eta^5\text{-}C_6H_5)Re(NO)(PPh_3)(OR_2)]^+PF_6^-$ from the Hydride Complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (**6**)



In corresponding preparative experiments, we were unable to isolated $4^+BF_4^-$ in analytically pure form. However, the structural assignment was supported by an independent synthesis described below.

2. Syntheses of Ether Complexes from Hydride and Alkoxide Complexes. The trityl cation, Ph_3C^+, has previously been shown to abstract hydride ligands from metal hydride complexes.[8] Hence, the hydride complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (**6**)[9] was suspended in tetrahydrofuran at −15 °C and treated with a CH_2Cl_2 solution of $Ph_3C^+PF_6^-$ (Scheme III, eq 4). Workup gave the solvate $5^+PF_6^-{\cdot}0.75THF$ in 90% yield as an analytically pure brown powder, which was characterized by a method analogous to that use for $5^+BF_4^-$ above. The ^1H NMR spectrum showed separate resonances for the coordinated and free (solvated) tetrahydrofuran. Byproduct Ph_3CH was also isolated in 80–85% yields by chromatography. Complex $5^+PF_6^-$ appeared to decompose at a slightly slower rate than $5^+BF_4^-$ in $CDCl_3$ at 10.2 °C: $k_{obs} = 1.78 \times 10^{-5}\ s^{-1}$; $t_{1/2} = 10.8$ h.

A similar reaction was conducted with hydride complex **6** and $Ph_3C^+PF_6^-$ in ethyl ether (Scheme III, eq 5). A transient deep yellow precipitate was observed,[10] and workup gave the ethyl ether complex $3^+PF_6^-$ in 93% yield as an analytically pure brown

---

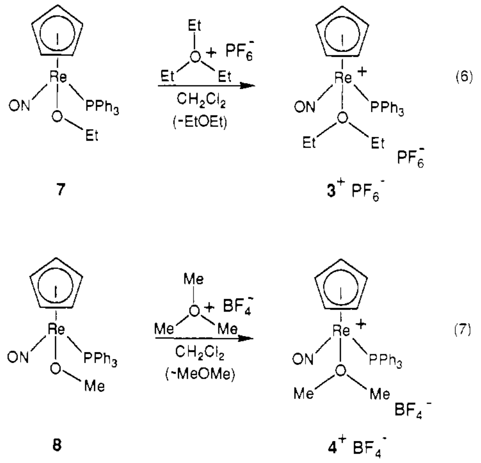
(7) Workup of corresponding preparative reactions gave brown powders that were slightly soluble in CH_2Cl_2 and exhibited several ^{31}P NMR resonances between 24 and 15 ppm (−70 °C). The predominant resonance (20.4 ppm) matched that of an intermediate previously observed in reactions of $2^+BF_4^-$ and less reactive donor ligands L (Scheme I), such as certain alkyl iodides.[3e]

(8) (a) Sweet, J. R.; Graham, W. A. G. *J. Organomet. Chem.* **1981**, *217*, C37. (b) Sweet, J. R.; Graham, W. A. G. *Organometallics* **1982**, *1*, 982. (c) Sweet, J. R.; Graham, W. A. G. *Ibid.* **1983**, *2*, 135.

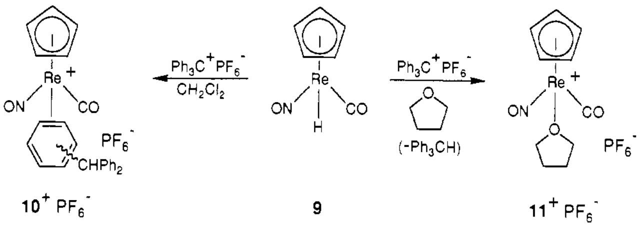
(9) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6110.

(10) The precipitate was isolated by cold filtration in a separate experiment. (a) NMR (CD_2Cl_2, −80 °C): ^1H (δ) C_5H_5 at 5.61 (major), 5.16 (minor); ^{31}P (ppm) 20.3 (major), 8.8 (minor). No evidence for a hydride ligand was noted. (b) When the NMR sample was warmed to −40 °C, the 20.3 ppm ^{31}P NMR resonance decreased as a new resonance at 12.5 ppm and the existing resonance at 8.8 ppm increased. Further warming gave a multitude of products. (c) A sample was dissolved in 1:3 (v/v) CH_2Cl_2/tetrahydrofuran (1.0:2.6 mol ratio) at −78 °C, and a ^{31}P NMR spectrum was immediately recorded at −30 °C. Tetrahydrofuran complex $5^+PF_6^-$ had formed in >90% spectroscopic yield. (d) An identical experiment was conducted with 1:3 (v/v) CH_2Cl_2/ethyl ether (1.0:1.9 mol ratio). The ^{31}P NMR spectrum showed dichloromethane complex $2^+PF_6^-$, ethyl ether complex $3^+PF_6^-$ ((65 ± 2):(35 ± 2) PPh_3 resonance area ratio), and other minor byproducts. The sample was warmed to 0 °C, and the $2^+PF_6^-$ PPh_3 resonance diminished (vs the PF_6^- resonance) as the PPh_3 resonances of 3^+ PF_6^- and the by-products intensified. Some $3^+PF_6^-$ precipitated, and the 2^+ $PF_6^-/3^+PF_6^-$ ratio in solution was (30 ± 2):(70 ± 2). Further conversion of $2^+PF_6^-$ to $3^+PF_6^-$ occurred with additional time or warming.

Scheme IV. Syntheses of Ether Complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OR_2)]^+X^-$ from Alkoxide Complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OR)$



Scheme V. Previously Reported Reactions of the Carbonyl-Substituted Hydride Complex **9**



powder. Complex $\mathbf{3}^+PF_6^-$ was characterized in a manner analogous to that used for tetrahydrofuran complexes $\mathbf{5}^+X^-$ (Experimental Section). The diastereotopic ether ligand carbons exhibited a single set of ^{13}C NMR resonances at −70 °C, and only one methyl ^1H NMR resonance was observed. The solution and solid-state stability of $\mathbf{3}^+PF_6^-$ was comparable to that of $\mathbf{5}^+BF_4^-$ (decomposition rate in $CDCl_3$ at 10.2 °C: $k_{obs} = 1.65 \times 10^{-4}\ s^{-1}$; $t_{1/2} = 1.2$ h). Attempts to analogously prepare methyl ether complex $\mathbf{4}^+PF_6^-$ were unsuccessful.

With authentic samples of ether complexes $\mathbf{3}^+X^-$–$\mathbf{5}^+X^-$ in hand, other synthetic approaches could easily be evaluated. A CD_2Cl_2 solution of the ethoxide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OCH_2CH_3)$ (**7**)[3a,11] was treated with the oxonium salt $Et_3O^+PF_6^-$ at −78 °C (Scheme IV, eq 6). The reaction was slowly warmed and monitored by ^1H and ^{31}P NMR. Clean ethyl group transfer occurred over the temperature range −30 to 0 °C to give the ethyl ether complex $\mathbf{3}^+PF_6^-$ and ethyl ether. Similarly, reaction of the methoxide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OCH_3)$ (**8**)[12] and $Me_3O^+BF_4^-$ occurred between −78 and −60 °C to give the methyl ether complex $\mathbf{4}^+BF_4^-$ and methyl ether in quantitative NMR yields. However, the ether complexes generated by this route slowly decomposed in situ above −20 °C, and isolation attempts have to date been unsuccessful. No appreciable quantities (<5%) of dichloromethane complexes $\mathbf{2}^+X^-$ built up during the decompositions.

Discussion

The preceding reactions allow several conclusions regarding the bonding of oxygenated ligands to the rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I). First, the displacement of dichloromethane (also the solvent) from $\mathbf{2}^+BF_4^-$ by tetrahydrofuran (5 equiv) as shown in eq 1 of Scheme II establishes that the thermodynamic binding constant of tetrahydrofuran to I is much greater than that of dichloromethane. Second, the similar displacement of dichloromethane from $\mathbf{2}^+BF_4^-$ by methyl ether (16–33 vol%) as shown in eq 3 of Scheme II indicates that the binding constant of methyl ether is also greater than that of dichloromethane.

Although the conversion of the dichloromethane complex $\mathbf{2}^+BF_4^-$ to the ethyl ether complex $\mathbf{3}^+BF_4^-$ (eq 2, Scheme II) can be observed in solution, reaction conditions are heterogeneous and thus far from ideal for equilibrium measurements. Still, the data strongly suggest that the binding constant of ethyl ether to I is greater than that of dichloromethane. Further, the experiments in CH_2Cl_2/ethyl ether solvent mixtures unequivocally show (at least for the reactions studied)[10d] that ethyl ether is a poorer nucleophile than dichloromethane. This may be steric in origin, as there are two substituents attached to an ether oxygen but only one attached to a dichloromethane chlorine. Interestingly, there is good evidence that coordinatively unsaturated metal species such as $Cr(CO)_5$ initially bind to the carbon–hydrogen bonds of ethers and then rearrange to oxygen-ligated products,[13]

Ether complexes $\mathbf{3}^+X^-$–$\mathbf{5}^+X^-$ do not react with dichloromethane between −78 and −40 °C. Hence, the formation of the dichloromethane complex $\mathbf{2}^+X^-$ in Scheme I must be under kinetic control, possibly due to the steric factors noted above. There is the hypothetical question as to what the product distribution might be under thermodynamic control. Typical CH_2Cl_2/ether mole ratios under the conditions of Scheme I are 120–235. This may provide sufficient mass action to reverse to some extent eq 2 and 3 in Scheme II. Unfortunately, the K_{eq} values that can be extracted from our data are not sufficiently quantitative to address this point. However, note that if Scheme I were to be under thermodynamic control, detectable quantities of ether complexes should form in reactions run in the presence of 20–25 equiv of ether. We are currently attempting to isolate $\mathbf{2}^+PF_6^-$, which might be more stable and amenable to equilibrium experiments in purified form.

Equations 6 and 7 in Scheme IV establish that the rhenium fragment I enhances the (carbon) basicity of –ÖR lone pairs over those in the corresponding ethers $\ddot{O}R_2$. Thus, despite the fact that the alkoxide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OR)$ are bulkier than ethers, alkyl groups are cleanly transferred from oxonium salts. This trend likely has its origin in rhenium d orbital/oxygen lone-pair repulsive interactions.[14] As expected from steric considerations, the transfer of methyl to the methoxide complex **8** is faster than the transfer of ethyl to the ethoxide complex **7**.

We have previously shown that phosphido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{P}R_2)$ are more reactive toward electrophiles than the corresponding phosphines $\ddot{P}R_3$.[14] Hence, oxygen nucleophilicity is likely enhanced in the alkoxide complexes as well. We have also found that the carbon basicities of the β-sulfur atoms in (α-thioalkyl)alkyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2\ddot{S}R)$ are enhanced relative to those in the corresponding sulfides.[15]

Brynzda has reported that the d^8, coordinatively unsaturated platinum(II) methoxide complex $(dppe)Pt(CH_3)(OCH_3)$ reacts with methyl iodide to give $(dppe)Pt(CH_3)(I)$ and *free* methyl ether.[16] On the basis of deuterium labeling experiments, initial methylation of the methoxide oxygen was proposed. Interestingly, the related iridium(I) methoxide complex *trans*-$(Ph_3P)_2Ir(CO)(OCH_3)$ reacts with methyl iodide to give an oxidative-addition product, which does not extrude methyl ether upon heating.[17]

The synthesis of the tetrahydrofuran complex $\mathbf{5}^+PF_6^-$ shown in eq 4 of Scheme III is based upon earlier findings of Graham and co-workers.[8] They reported that reaction of the *carbonyl*-substituted rhenium hydride complex $(\eta^5\text{-}C_5H_5)Re(NO)(CO)(H)$ (**9**) and $Ph_3C^+PF_6^-$ in dichloromethane at −78 °C precipitated

---

(11) Garner, C. M.; Quirós Méndez, N. I.; Kowalczyk, J. J.; Fernández, J. M.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. Submitted for publication.

(12) Buhro, W. E.; Georgiou, S.; Fernández, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1986**, *5*, 956.

(13) Xie, X.; Simon, J. D. *J. Phys. Chem.* **1989**, *93*, 4401 and references therein.

(14) Buhro, W. E.; Zwick, B. D.; Georgiou, S.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 2427.

(15) McCormick, F. B.; Gleason, W. B.; Zhao, X.; Heah, P. C.; Gladysz, J. A. *Organometallics* **1986**, *5*, 1778.

(16) (a) Brynzda, H. E.; Calabrese, J. C.; Wreford, S. S. *Organometallics* **1984**, *3*, 1603. (b) Brynzda, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163.

(17) Bernard, K. A.; Atwood, J. D. *Organometallics* **1987**, *6*, 1133.

an analytically pure mixture of cationic η^2-triphenylmethane complexes $\mathbf{10}^+PF_6^-$, as shown in Scheme V. Complex $\mathbf{10}^+PF_6^-$ rapidly decomposed in dichloromethane above −40 °C. The η^2-triphenylmethane ligand was readily displaced by a variety of neutral donor ligands. When the reaction of **9** and $Ph_3C^+PF_6^-$ was carried out in the presence of tetrahydrofuran, $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)(THF)]^+PF_6^-$ ($\mathbf{11}^+PF_6^-$) was isolated in high yield.

We likewise find that reactions of the hydride complex **6**, $Ph_3C^+X^-$, and donor ligands L can be used to prepare a variety of cationic complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+X^-$.[18] Our observations are consistent with a similar mechanism, with the yellow precipitate noted above[10] likely an analogue of $\mathbf{10}^+PF_6^-$. The carbonyl-substituted rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)]^+$ is a stronger Lewis acid than **I**[19] and is less sterically encumbered. Hence, the binding constants of ethers should be greater. However, we prepared a sample of $\mathbf{11}^+PF_6^-$ and found its *kinetic* stability to be comparable to that of $\mathbf{5}^+PF_6^-$ ($CDCl_3$, 10.2 °C: $k_{obs} = 1.72 \times 10^{-5}\ s^{-1}$; $t_{1/2} = 11.2$ h). A variety of chiral and achiral cationic cyclopentadienyliron ether complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)(OR_2)]^+X^-$ have also been isolated,[20] as well as related molybdenum complexes.[21]

Structurally, ether complexes $\mathbf{3}^+X^-$–$\mathbf{5}^+X^-$ should resemble the neutral phosphido complexes[14] $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PR_2)$ and the cationic sulfide complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SR_2)]^+X^-$,[22] in which the ligating heteroatoms are pyramidal. Extremely low phosphorus and sulfur atom inversion barriers have been found in both types of compounds (11–15 kcal/mol). Importantly, the ether ligands in $\mathbf{3}^+X^-$–$\mathbf{5}^+X^-$ do not exchange with free ethers on the ^1H NMR time scale. Hence, the absence of distinct NMR resonances for diastereotopic groups in the ether ligands can similarly be ascribed to low oxygen inversion barriers.

Finally, we have sometimes observed that reactions of the dichloromethane complex $\mathbf{2}^+BF_4^-$ with kinetically less reactive donor ligands L (see Scheme I) afford substitution products $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+BF_4^-$ by two pathways: by a direct pathway and via a transient (up to ca. 10%) that slowly converts to product at higher temperatures.[1,3e] On the basis of the above NMR data for $\mathbf{3}^+X^-$, it may be concluded that this transient is not an ethyl ether complex. Attempts to generate other possible candidates for this species are in progress.[23]

In summary, we have devised protocols for the isolation of labile ether complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OR_2)]^+\ X^-$ in high yields and shown that aliphatic ethers are stronger bases than dichloromethane toward the rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**). Future reports will describe additional mechanistic experiments associated with questions noted above and the synthesis of the related *alcohol* complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ROH)]^+X^-$.[23]

Experimental Section

General Data. All reactions were carried out under a dry N_2 atmosphere. FT-IR spectra were recorded on Perkin-Elmer 1500 and Mattson Polaris spectrometers. NMR spectra were recorded on Varian XL-300 spectrometers: ^{31}P NMR, referenced to external 85% H_3PO_4; ^1H NMR, referenced to $CDHCl_2$ at δ 5.32 or $CHCl_3$ at δ 7.24; ^{13}C NMR, referenced to CD_2Cl_2 at 53.8 ppm or $CDCl_3$ at 77.0 ppm. Microanalyses were conducted by Atlantic Microlab. Melting points were determined in evacuated capillaries and were not corrected.

Solvents and reagents were purified as follows: CH_2Cl_2, distilled from P_2O_5; tetrahydrofuran, ethyl ether, methyl ether, and benzene, distilled from Na/benzophenone; hexane, distilled from sodium; $CDCl_3$ and CD_2Cl_2, vacuum transferred from CaH_2; $HBF_4\cdot OEt_2$ (Aldrich), standardized as previously described;[1] $Ph_3C^+PF_6^-$ (Columbia), dissolved in a minimum of CH_2Cl_2, precipitated with ethyl acetate, and washed with hexane; $Et_3O^+PF_6^-$ and $Me_3O^+BF_4^-$ (Alfa), used as received.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(THF)]^+BF_4^-$ ($\mathbf{5}^+BF_4^-$). A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**1**; 0.224 g, 0.40 mmol),[24] CH_2Cl_2 (10 mL), and a stir bar and was cooled to −78 °C. Then $HBF_4\cdot OEt_2$ (0.052 mL, 0.40 mmol) was added to generate $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ ($\mathbf{2}^+BF_4^-$).[1] The solution was stirred for 10 min, and the flask was then transferred to a −42 °C bath. After 10 min, tetrahydrofuran (20 mL) was added. The reaction was slowly allowed to warm to room temperature while solvents were removed under oil pump vacuum. Then tetrahydrofuran (20 mL) was added to the resulting brown precipitate. Hexane was added to the resulting brown suspension, and the precipitate was collected by filtration and dried under vacuum to give $\mathbf{5}^+BF_4^-$ (0.255 g, 0.36 mmol, 91%) as a pink powder, mp 154–156 °C dec. IR (cm^{-1}, KBr): ν_{NO} 1692 s. ^1H NMR (δ, CD_2Cl_2, −70 °C): 7.60–7.10 (m, 3 C_6H_5), 5.52 (s, C_5H_5), 3.88 (m, 2 OCH), 3.47 (m, 2 OCH′), 1.70 (m, OCCH), 1.54 (m, OCCH′). ^{13}C NMR (ppm, CD_2Cl_2, −70 °C): $P(C_6H_5)$ at 133.1 (d, $J_{CP} = 11$ Hz), 131.7 (d, $J_{CP} = 55$ Hz, *ipso*), 131.4 (s, *p*), 129.1 (d, $J_{CP} = 11$ Hz); 91.5 (s, C_5H_5), 86.3 (s, OC), 26.9 (s, OCC). ^{31}P NMR (ppm, CD_2Cl_2, −70 °C): 18.1 s. Anal. Calcd for $C_{27}H_{28}BF_4NO_2PRe$: C, 46.16; H, 4.02. Found: C, 46.10; H, 4.02.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(THF)]^+PF_6^-$ ($\mathbf{5}^+PF_6^-$). A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (**6**;[8] 0.427 g, 0.78 mmol), tetrahydrofuran (50 mL), and a stir bar and was cooled to −15 °C. To this suspension was slowly added a solution of $Ph_3C^+PF_6^-$ (0.304 g, 0.78 mmol) in CH_2Cl_2 (6 mL). A deep brown solution resulted. More tetrahydrofuran (30 mL) was added, and the solution was allowed to warm to room temperature. Then hexane (50 mL) was added, and the reaction was stirred for an additional hour. The resulting brown precipitate was collected by filtration, washed with hexane (3 × 15 mL), and dried under vacuum to give $\mathbf{5}^+PF_6^-\cdot 0.75THF$ (0.570 g, 0.70 mmol, 90%), mp 131–132 °C dec. IR (cm^{-1}, KBr): ν_{NO} 1700 s. ^1H NMR (δ, CD_2Cl_2, −70 °C): 7.50–7.15 (m, 3 C_6H_5), 5.50 (s, C_5H_5), 3.86 (m, 2 OCH), 3.47 (m, 2 OCH′), 1.72 (m, OCCH), 1.55 (m, OCCH′); THF of solvation at 3.62 (m, OCH), 1.77 (m, OCCH). ^{13}C NMR (ppm, CD_2Cl_2, −70 °C): $P(C_6H_5)$ at 133.1 (d, $J_{CP} = 11$ Hz), 131.6 (d, $J_{CP} = 56$ Hz, *ipso*), 131.4 (s, *p*), 129.1 (d, $J_{CP} = 11$ Hz); 91.4 (s, C_5H_5), 86.2 (s, OC), 26.8 (s, OCC); THF of solvation at 67.5 (s, OC), 25.2 (s, OCC). ^{31}P NMR (ppm, CD_2Cl_2, −70 °C): 18.1 (s, PPh_3), −143.7 (sept, $J_{PF} = 708$ Hz, PF_6^-). Anal. Calcd for $C_{27}H_{28}BF_4NO_2PRe\cdot 0.75C_4H_8O$: C, 44.22; H, 4.21. Found: C, 44.18; H, 4.23.

Solvent was removed from the filtrate by rotary evaporation. The residue was dissolved in CH_2Cl_2 and chromatographed on a silica gel column with CH_2Cl_2. The appropriate fractions were concentrated to a white powder, which was dried under vacuum to give Ph_3CH (0.161 g, 0.66 mmol, 85%). The R_f and ^1H NMR spectrum were identical with those of an authentic sample.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OEt_2)]^+PF_6^-$ ($\mathbf{3}^+PF_6^-$). A Schlenk flask was charged with **6** (0.430 g, 0.79 mmol), ethyl ether (50 mL), and a stir bar and was cooled to −15 °C. To this suspension was slowly added a solution of $Ph_3C^+PF_6^-$ (0.309 g, 0.79 mmol) in CH_2Cl_2 (6 mL). A deep yellow precipitate formed,[9] and the mixture was stirred for 10 min at −15 °C. The flask was removed from the cold bath and stirred for 1.5 h, during which time a deep brown precipitate formed. Then hexane (50 mL) was added, and the reaction was vigorously stirred for an additional hour. The precipitate was collected by filtration, washed with hexane (3 × 15 mL), and dried under vacuum to give $\mathbf{3}^+PF_6^-$ (0.559 g, 0.73 mmol, 93%) as a brown powder, mp 127–128 °C dec. IR (cm^{-1}, KBr): ν_{NO} 1692 s. ^1H NMR (δ, CD_2Cl_2, −70 °C): 7.76–7.01 (m, 3 C_6H_5), 5.50 (s, C_5H_5), 3.94 (dq, $J_{H(\alpha)H(\alpha')} = 12.2$ Hz, $J_{H(\alpha)H(\beta)} = 6.9$ Hz, 2 OCH), 3.70 (dq, $J_{H(\alpha')H(\alpha)} = 6.9$ Hz, $J_{H(\alpha')H(\beta)} = 12.4$ Hz, 2 OCH′), 0.84 (t_{pseudo}, $J_{H(\beta)H(\alpha,\alpha')} = 6.1$ Hz, 2 CH_3). ^{13}C NMR (ppm, CD_2Cl_2, −70 °C): $P(C_6H_5)$ at 133.1 (br d, $J_{CP} = 8$ Hz), 131.6 (d, $J_{CP} = 56$ Hz, *ipso*), 131.4 (s, *p*), 129.1 (d, $J_{CP} = 11$ Hz), 91.5 (s, C_5H_5), 90.7 (s, OC), 13.3 (s, OCC). ^{31}P NMR (ppm, CD_2Cl_2, −70 °C): 17.4 s. Anal. Calcd for $C_{27}H_{30}F_6NO_2P_2Re$: C, 42.52; H, 3.96. Found: C, 42.36; H, 3.95. Byproduct Ph_3CH was isolated as described in the preceding experiment (0.158 g, 0.65 mmol, 82%).

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OMe_2)]^+BF_4^-$ ($\mathbf{4}^+BF_4^-$). The following procedures are representative of the low temperature, NMR-monitored experiments in this paper. Further detail has been given elsewhere.[1,3e,9]

Reaction A. A 5-mm NMR tube was charged with **1** (0.053 g, 0.095 mmol), capped with a septum, evacuated, filled with nitrogen, and cooled to −78 °C. Then CD_2Cl_2 (0.6 mL) and $HBF_4\cdot OEt_2$ (0.012 mL, 0.095 mmol) were added by syringe. The tube was shaken and transferred to a −70 °C NMR probe, and ^1H and ^{31}P NMR spectra showed the for-

---

(18) Fernández, J. M. Unpublished results, University of Utah.

(19) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592.

(20) See: Cutler, A. R.; Todaro, A. B. *Organometallics* **1988**, *7*, 1782, and references therein.

(21) (a) Schloter, K.; Beck, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 985. (b) Sünkel, K.; Urban, G.; Beck, W. *J. Organomet. Chem.* **1985**, *290*, 231.

(22) Quirós Méndez, N. I. Unpublished results, University of Utah.

(23) Agbossou, S. Unpublished results, University of Utah.

(24) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

mation of **2**-$d_2{}^+BF_4^-$. The tube was cooled to −78 °C, and liquified Me_2O (ca. 0.2 mL) was added by cannula. The tube was shaken and again placed in a −70 °C NMR probe. No reaction had occurred. The probe was warmed to −40 °C, and ^1H and ^{31}P NMR spectra were recorded over the course of 4 h, after which time conversion to $\mathbf{4}^+BF_4^-$ was ca. 90% complete. ^1H NMR (δ): 7.50–7.56 (m, 3 C_6H_5), 5.63 (s, C_5H_5), 3.72 (s, 2 CH_3); 3.23 (free Me_2O). ^{31}P NMR (ppm): 18.1 s.

Reaction B. This reaction is representative of those in Scheme IV. A 5 mm NMR tube was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OCH_3)$ (**8**;[11,12] 0.051 g, 0.060 mmol) and $Me_3O^+BF_4^-$ (0.089 g, 0.60 mmol), capped with a septum, evacuated, filled with nitrogen, and cooled to −78 °C. Then CD_2Cl_2 was slowly added by syringe. The heterogeneous reaction mixture was transferred to a −60 °C NMR probe. Spectra showed **8** to be consumed, and the clean formation of $\mathbf{4}^+BF_4^-$. ^1H NMR (δ): 5.61, 3.72. ^{31}P NMR (ppm): 18.7. The $\mathbf{4}^+BF_4^-$ was warmed in 20 °C increments, and additional ^1H and ^{31}P NMR spectra were recorded. Complex $\mathbf{4}^+BF_4^-$ slowly decomposed. ^1H NMR (δ, 20 °C): C_5H_5 (s) at 5.60 ($\mathbf{4}^+BF_4^-$), 5.52, 5.48; free Me_2O at 3.28. ^{31}P NMR (ppm, 20 °C): 18.2 ($\mathbf{4}^+BF_4^-$), 19.6, 22.8.

Acknowledgment. We thank the Department of Energy for support of this research.

Contribution from the Department of Chemistry,
Bowling Green State University, Bowling Green, Ohio 43403

Synthesis and Spectroscopic Characterization of (Triethylphosphine)gold(I) Complexes $AuX(PEt_3)$ (X = Cl, Br, CN, SCN), $[AuL(PEt_3)^+]$ (L = SMe_2, $SC(NH_2)_2$, H_2O), and $(\mu\text{-}S)[Au(PEt_3)]_2$

M. M. El-Etri and W. M. Scovell*

Received April 18, 1989

Neutral complexes of the type $AuX(PEt_3)$ (X = Br, CN, SCN) were prepared and characterized by infrared and Raman spectroscopy, with the major emphasis on the assignment of the gold–ligand vibrations and discerning the mode of bonding for the ambidentate ligands. The photosensitive cationic complexes $[(Au(SMe_2)(PEt_3)]PF_6$ and $\{Au[SC(NH_2)_2](PEt_3)\}Cl$ in addition to $[Au(OH_2)(PEt_3)]NO_3$ and $(\mu\text{-}S)[(PEt_3)Au]_2$ were also prepared and characterized by infrared and NMR spectroscopy. In both cases in which the ambidentate ligands SCN^- and $SC(NH_2)_2$ were complexed with Au(I), the sulfur atom coordinates to the metal, providing evidence for a symbiotic relationship in these complexes.

Introduction

Interest in the characterization of Au(I) complexes for the type $AuL(PEt_3)$ has been rekindled by reports that indicated oral administration of chloro(triethylphosphine)gold(I) in rats revealed its potential in the treatment of arthritis.[1,2] Subsequent studies have shown that a number of gold(I) complexes of the type $Au(SR)(PEt_3)$ also display activity in the treatment of rheumatoid arthritis,[3–6] in addition to in vivo antitumor activity.[7] Auranofin, a Au(I) compound containing triethylphosphine and tetraacetylthioglucose ligands, is currently being used clinically in the treatment of arthritis.[6]

The linear geometry of $AuL(PEt_3)$ about a heavy metal provides an especially attractive system for characterization by vibrational spectroscopy, in that vibrational frequencies can be readily assigned for the M–L vibrational modes in complexes containing other complex ligands. In addition, these complexes are ideal for studying the mode of bonding of ambidentate ligands in terms of their electronic control and in the absence of steric factors, in addition to serving as excellent models for further exploring the symbiotic or antisymbiotic trans influence.[8,9] Relatively few reports have appeared in the literature on the metal–ligand vibrations in gold(I) complexes of the type $AuL(PEt_3)$. A factor partially responsible for this is that Au(I) compounds are often unstable, many being especially photosensitive. In this report, we have synthesized a number of neutral and cationic Au(I) complexes and characterized them with infrared, Raman, and proton NMR spectroscopy. In addition to the Au–P vibrations, assignments for the Au–L vibrations and those diagnostic of the mode of binding for ambidentate ligands are presented and compared to the relevant literature.

Experimental Section

General Data. The elemental analysis was performed by Galbraith Microanalytical Laboratories, Knoxville, TN. The $AuCl(PEt_3)$ was kindly provided by Smith, Kline and French Laboratories, Philadelphia, PA.

$AuBr(PEt_3)$. An ethanolic solution of $AuCl(PEt_3)$ (0.20 g, 0.57 mmol in 3 mL of ethanol) was mixed with an aqueous solution of $AgNO_3$ (0.09 g, 0.51 mmol in 2 mL of H_2O) and the precipitated AgCl removed by filtration. The colorless, aqueous solution of $[Au(OH_2)(PEt_3)]NO_3$ was treated with aqueous NaBr solution (0.23 g, 2.0 mmol in 2 mL of H_2O) to give immediate white crystals of $AuBr(PEt_3)$. These were filtered out and washed with H_2O. The product was recrystallized from hot ethanol: yield 89% (0.18 g); mp 88–89 °C (lit.[10,11] mp 88–89 °C).

$Au(CN)(PEt_3)$. An aqueous solution of $[Au(OH_2)(PEt_3)]NO_3$ (1 mmol) was treated with an aqueous solution of KCN (0.07 g, 1.0 mmol in 3 mL of H_2O). The solution mixture initially turned white and then became colorless upon further addition of the KCN. The solution was stirred for 5 min at room temperature and then cooled in an ice bath to give white needle-shaped crystals of $Au(CN)(PEt_3)$. These were filtered out, washed with H_2O, and then dried over P_4O_{10} under vacuum: yield

---

(1) Walz, D. T.; DiMartino, M. J.; Sutton, B. M.; Misher, A. *J. Pharm. Exp. Ther.* **1972**, *181*, 292.

(2) Weinstock, J.; Sutton, B. M.; Kuo, G. Y.; Walz, D. T.; DiMartino, M. J. *J. Med. Chem.* **1974**, *17*, 139.

(3) Finkelstein, A. E.; Walz, D. T.; Batista, V.; Mizraj, M.; Rosiman, F.; Misher, A. *Ann. Rheum. Dis.* **1976**, *35*, 251.

(4) Berglof, F. E.; Berglof, K.; Walz, D. T. *J. Rheumatol.* **1978**, *5*, 68.

(5) Sutton, B. M. In *Platinum, Gold and Other Metal Chemotherapeutic Agents*; Lippard, S. J., Ed.; ACS Symposium Series 209; American Chemical Society: Washington, DC, 1983; pp 355–371 and other articles in section titled Gold Antiarthritic Drugs: Biochemistry and Chemistry.

(6) Crooke, S. T.; Snyder, R. M.; Butt, T. R.; Ecker, F. J.; Allaudeen, H. S.; Monia, B.; Mirabelli, C. K. *Biochem. Pharmacol.* **1980**, *35*, 3423.

(7) Mirabelli, C. K.; Johnson, R. K.; Hill, D. T.; Faucette, L. F.; Girard, G. R.; Kuo, G. Y.; Sung, C. M.; Crooke, S. T. *J. Med. Chem.* **1986**, *29*, 218.

(8) Melpolder, J. B.; Burmeister, J. L. *Inorg. Chim. Acta* **1981**, *49*, 115.

(9) Pearson, R. G. *Inorg. Chem.* **1973**, *12*, 712.

(10) Coates, G. E.; Kowala, C.; Swan, J. M. *Aust. J. Chem.* **1966**, *19*, 539.

(11) Mann, F. G.; Purdie, G. T. *J. Chem. Soc.* **1940**, 1235.

0020-1669/90/1329-0480$02.50/0 © 1990 American Chemical Society