6032 *Organometallics* **1997,** *16,* 6032−6034

Supramolecular Chemistry of Chiral Rhenium Lewis Acids of the Formula $[(\eta^5\text{-}C_5R_5)Re(NO)(CO)(PPh_3)]^+$: Synthesis and Crystal Structure of a 2:1 Adduct of an Ammonia Complex and 18-Crown-6

Angelo J. Amoroso, Atta M. Arif, and J. A. Gladysz*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Received September 8, 1997⊗

Summary: When ether is added by vapor diffusion to a CH_3CN solution of racemic $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH_3)]^+PF_6^-$ ($\mathbf{1}^+PF_6^-$) and 18-crown-6 (1:2 mol ratio), a 2:1 adduct of composition $\{(\mathbf{1}^+)(\text{18-crown-6})(\mathbf{1}^+)\}2PF_6^-\cdot OEt_2$ crystallizes (94%). A crystal structure shows opposite enantiomers of the cations about a crown-based inversion center, each with three N···H···O hydrogen bonds to complementary sets of ether oxygens—a meso assembly. NMR data also establish binding in solution.

We have had ongoing interest in the synthesis and characterization of compounds in which elemental sp carbon chains span two transition metals.[1] To date, all of our studies have featured at least one chiral rhenium end group of the formula $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)$ (**I**-Me$_5$), which carries 17 valence electrons when neutral.[2] Complexes with chains of up to 20 carbons can be isolated.

We sought to develop the chemistry of these carbon ligands, including the construction of novel supramolecular assemblies. In particular, their wirelike nature would seem to be geometrically well-suited for rotaxanes.[3] However, several exploratory reactions involving crown ethers, cyclophanes, and cyclodextrins were unsuccessful. Hence, we decided to undertake model studies involving other derivatives of **I**-Me$_n$ and previously established types of transition metal based supramolecular species.

Our attention was drawn to adducts of transition metal ammonia complexes and crown ethers.[4−6] These complexes exemplify what is often referred to as "second sphere coordination", an area pioneered by Stoddart. Both 1:1 and 2:1 complexes have been structurally characterized. An example of the latter, derived from a platinum precursor and 18-crown-6, is shown in Figure 1.[5b] In this paper, we report that ammonia complexes of **I**[7] can give analogous solid-state binding motifs, and evidence for similar interactions in solution.

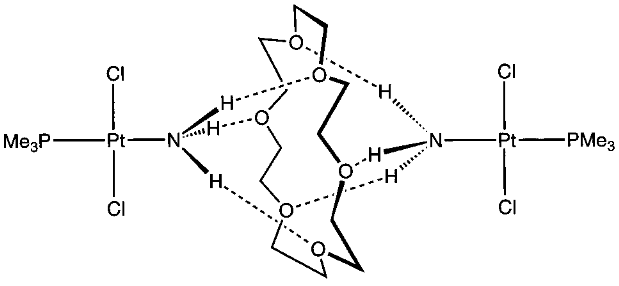
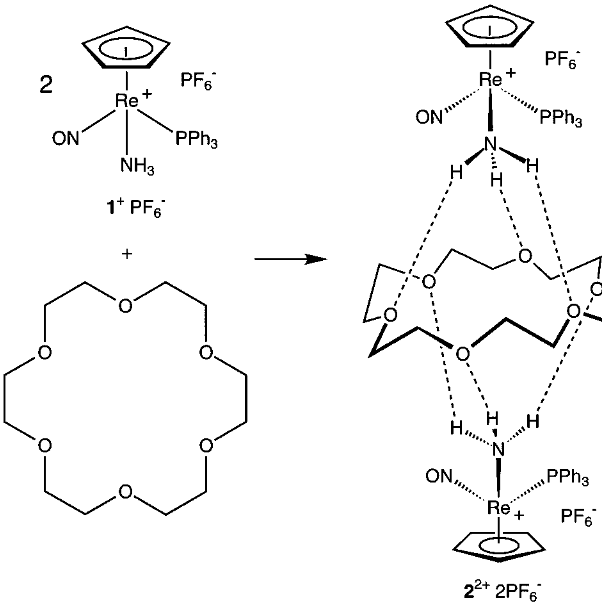


Figure 1. A representative, previously characterized, 2:1 adduct of an ammonia complex and 18-crown-6.

Scheme 1. Synthesis of a 2:1 Adduct of a Rhenium Ammonia Complex and 18-Crown-6



Results and Discussion

As shown in Scheme 1, the cationic ammonia complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH_3)]^+PF_6^-$ ($\mathbf{1}^+PF_6^-$) and 18-crown-6 were combined in CH_3CN in a 1:2 molar ratio. Then ether was slowly added by vapor diffusion. A new species crystallized in 94% yield. Despite the excess of crown ether, the microanalysis was consistent with the

---

⊗ Abstract published in *Advance ACS Abstracts,* December 1, 1997.

[1] (a) Lang, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 547. (b) Bunz, U. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 969.

[2] (a) Brady, M.; Weng, W.; Zhou, Y.; Seyler, J. W.; Amoroso, A. J.; Arif, A. M.; Böhme, M.; Frenking, G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 775. (b) Bartik, T.; Bartik, B.; Brady, M.; Dembinski, R.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 414. (c) Falloon, S. B.; Weng, W.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1997**, *16*, 2008 and references therein.

[3] See the following 1997 papers and reviews cited therein: (a) Asakawa, M.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Bělohradský, M.; Gandolfi, M. T.; Kocian, O.; Prodi, L.; Raymo, F. M.; Stoddart, J. F.; Venturi, M. *J. Am. Chem. Soc.* **1997**, *119*, 302. (b) Cárdenas, D. J.; Gaviña, P.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1997**, *119*, 2656. (c) Whang, D.; Kim, K. *J. Am. Chem. Soc.* **1997**, *119*, 451.

[4] (a) Colquhoun, H. M.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 487. (b) Raymo, F. M.; Stoddart, J. F. *Chem. Ber.* **1996**, *129*, 981.

[5] (a) Colquhoun, H. M.; Stoddart, J. F. *J. Chem. Soc., Chem. Commun.* **1981**, 612. (b) Colquhoun, H. M.; Lewis, D. F.; Stoddard, J. F.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1983**, 607.

[6] Cameron, B. R.; Corrent, S. S.; Loeb, S. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2689.

[7] Dewey, M. A.; Knight, D. A.; Klein, D. P.; Arif, A. M.; Gladysz, J. A. *Inorg. Chem.* **1991**, *30*, 4995.

S0276-7333(97)00792-9 CCC: $14.00

Table 1. Summary of Crystallographic Data for $[\{(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH_3)\}_2\text{-}(18\text{-crown-}6)]^{2+}2PF_6^-\cdot OEt_2$ ($\mathbf{2}^{2+}2PF_6^-\cdot OEt_2$)

formula	$C_{31}H_{40}F_6N_2O_{4.5}P_2Re$
fw	874.79
cryst syst	monoclinic
space group	*P*2/*n*
cell dimens (16 °C)	
a, Å	18.184(6)
b, Å	11.203(3)
c, Å	18.535(3)
β, deg	111.50(2)
V, Å^3	3513(2)
Z	4
d_{calc}, g/cm^3	1.654
d_{found}, g/cm^3	1.622
cryst dimens, mm	0.44 × 0.41 × 0.22
diffractometer	CAD4
radiation, Å	Mo Kα (0.710 73)
data collection method	$\theta-2\theta$
scan speed, deg/min	variable
no. of reflns measd	6384
range/indices (*h*, *k*, *l*)	0−21, 0−13, −22 to 20
2*θ* limit, deg	4.34−49.94
standard reflns check	1 X-ray hour
total no. of unique data	6176
abs coeff, cm^{-1}	36.20
min transmission, %	62.1
max transmission, %	99.90
no. of variables	419
goodness of fit	1.204
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0342
$wR2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4])^{1/2}$	0.1055
Δ/σ (max), e/Å^3	0.000
$\Delta\rho$ (max), e/Å^3	0.971

2:1 adduct $\{(\mathbf{1}^+)(18\text{-crown-}6)(\mathbf{1}^+)\}2PF_6^-\cdot OEt_2$, henceforth denoted as $\mathbf{2}^{2+}2PF_6^-\cdot OEt_2$. When IR spectra were recorded in KBr, two ν_{NO} bands were observed (1711, 1682 cm^{-1}). Under identical conditions, $\mathbf{1}^+PF_6^-$ gave a single band (1682 cm^{-1}). Analogous preparative experiments with the triflate salt $\mathbf{1}^+TfO^-$,[7] which has a much more coordinating anion with the potential for stronger cation interactions, did not precipitate any adducts.

The crystal structure was determined as outlined in Table 1 and described in the Experimental Section. An excerpt is shown in Figure 2 and confirms the formulation proposed above. Selected bond lengths and angles are listed in Table 2, and atomic coordinates are given in Table 3 (Supporting Information). The crown ethers rest on inversion centers, and the ethyl groups of the ether solvates are related by crystallographic 2-fold symmetry axes. As required by the inversion centers, the rhenium cations on opposite sides of the crown ethers are enantiomeric. Thus, $\mathbf{2}^{2+}2PF_6^-\cdot OEt_2$ crystallizes as a *meso* diastereomer. The rhenium−rhenium separation is 8.066 Å, and the ammonia ligands make three N···H···O bonds to complementary 1,3,5 sets of crown ether oxygens.

Stoddart has analyzed in detail the structures of adducts of transition metal ammonia complexes and 18-crown-6 and many related species.[4] Similar features are evident in $\mathbf{2}^{2+}2PF_6^-\cdot OEt_2$. For example, the OH_2C-CH_2O linkages of the crown ether exhibit gauche conformations, in accord with textbook representations. Also, the nitrogen−oxygen distances across the hydrogen bonds (3.10, 3.21, 3.34 Å) are within ranges noted previously for both 1:1 and 2:1 adducts (3.0−3.4 Å).[4] These distances are greater than in 18-crown-6 adducts of organic or main group NH_3 derivatives, such as $[CH_3NH_3]^+$ or BF_3NH_3 (≤2.95 Å). Thus, transition metal amine complexes give a more pronounced "perching".

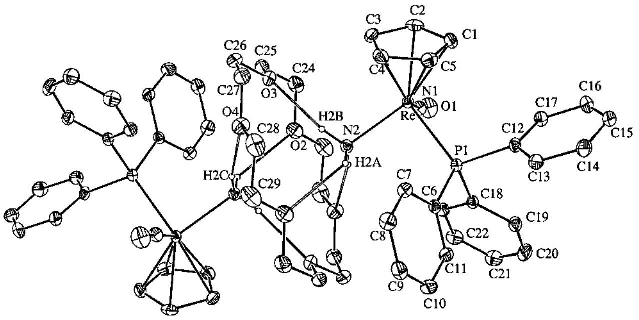


Figure 2. Structure of the dication of $\mathbf{2}^{2+}2PF_6^-\cdot OEt_2$.

Table 2. Key Bond Lengths (Å) and Angles (deg) for $\mathbf{2}^{2+}2PF_6^-\cdot OEt_2$

Re−N(1)	1.755(6)	C(3)−C(4)	1.413(11)
N(1)−O(1)	1.178(7)	C(4)−C(5)	1.380(11)
Re−N(2)	2.200(5)	O(2)−C(24)	1.422(10)
Re−C(1)	2.255(7)	O(2)−C(29)	1.455(11)
Re−C(2)	2.223(7)	O(3)−C(26)^a	1.417(10)
Re−C(3)	2.256(7)	O(3)−C(25)^a	1.426(10)
Re−C(4)	2.309(7)	O(4)−C(27)	1.409(10)
Re−C(5)	2.319(7)	O(4)−C(28)^a	1.419(11)
Re−P(1)	2.387(2)	C(24)−C(25)	1.441(13)
P(1)−C(6)	1.829(7)	C(25)−O(3)^a	1.426(10)
P(1)−C(12)	1.832(6)	C(26)−O(3)^a	1.417(10)
P(1)−C(18)	1.833(7)	C(26)−C(27)	1.48(2)
C(1)−C(2)	1.410(12)	C(28)−O(4)^a	1.419(11)
C(1)−C(5)	1.414(11)	C(28)−C(29)	1.432(14)
C(2)−C(3)	1.416(11)		

N(1)−Re−N(2)	96.9(2)	C(1)−C(2)−C(3)	109.1(7)
N(1)−Re−P(1)	93.6(2)	C(4)−C(3)−C(2)	105.8(7)
N(2)−Re−P(1)	91.7(2)	C(5)−C(4)−C(3)	109.9(7)
Re−N(1)−O(1)	173.5(6)	C(4)−C(5)−C(1)	108.2(7)
C(6)−P(1)−Re	116.7(2)	O(2)−C(24)−C(25)	110.4(7)
C(12)−P(1)−Re	111.6(2)	O(3)^a−C(25)−C(24)	110.7(7)
C(18)−P(1)−Re	116.3(2)	O(3)^a−C(26)−C(27)	108.4(8)
C(24)−O(2)−C(29)	111.8(7)	O(4)−C(27)−C(26)	109.7(7)
C(26)^a−O(3)−C(25)^a	111.3(7)	O(4)^a−C(28)−C(29)	109.0(8)
C(27)−O(4)−C(28)^a	111.4(7)	C(28)−C(29)−O(2)	109.3(7)
C(2)−C(1)−C(5)	107.0(7)		

[a] Symmetry transformations used to generate equivalent atoms: −*x*, −*y*, −*z*.

In this context, $\mathbf{2}^{2+}2PF_6^-\cdot OEt_2$ exhibits tangential van der Waals contacts between the crown ether and the PPh_3 ligand. The N···H···O angles and H···O distances, which cannot be very accurately measured, range from 168° to 136° and 2.2 to 2.5 Å, respectively.

The crystal structure of the related dimethylamine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH(CH_3)_2)]^+TfO^-$ ($\mathbf{3}^+TfO^-$) has been determined.[7] Here, the triflate anion forms a N···H···O hydrogen bond with an oxygen−nitrogen distance of 3.06(5) Å. The Re−NH bond length is not statistically different from that in $\mathbf{2}^{2+}2PF_6^-\cdot OEt_2$ (2.200(5) vs 2.193(4) Å). Other studies have shown that the nitrogen lone pairs in the corresponding neutral amido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}RR')$ are more basic and nucleophilic than those in organic amines.[8] Thus, cationic amine complexes of **I** should be poorer hydrogen-bond donors than organic ammonium salts.

Although 2:1 adducts might seem to be electrostatically disfavored for cationic guests such as $\mathbf{1}^+$, it should be kept in mind that the first binding event orients the crown ether for the second. This in turn raises a number of questions regarding the mechanism of for-

---

(8) Dewey, M. A.; Knight, D. A.; Arif, A. M.; Gladysz, J. A. *Chem. Ber.* **1992**, *125*, 815.

mation of $\mathbf{2}^{2+}2PF_6^-$, for which a dl diastereomer is also possible. To our knowledge, there have been no previous studies of crown ethers and chiral ammonia complexes. In view of the availability of chiral, enantiomerically pure crown ethers, there should be considerable potential for practical resolutions of racemic complexes. Hence, we sought to qualitatively probe for binding between $\mathbf{1}^+X^-$ and 18-crown-6 in solution. Earlier work has shown that the NMR and IR properties of the free amine complex and crown ether can be strongly affected.[5]

Accordingly, a CD_3CN solution of 18-crown-6 was titrated into a CD_3CN solution of $\mathbf{1}^+PF_6^-$. The total volume was kept constant. The chemical shift of the NH_3 signal varied only slightly from 0.00 to 0.75 equiv of crown ether (δ 3.767−3.774) but moved significantly downfield at higher concentrations (δ 3.820, 3.876, 3.898, 3.926, 3.960 at 1.00, 1.50, 1.75, 2.00, 2.50 equiv). The triflate salt $\mathbf{1}^+TfO^-$, which itself has the potential for N···H···O bonding, gave parallel but less-pronounced changes (δ 3.819, 3.825, 3.829, 3.843, 3.845, 3.862, 3.894 at 0.00, 0.25, 0.50, 0.75, 1.00, 1.25, and 1.50 equiv). The cyclopentadienyl signal of $\mathbf{1}^+PF_6^-$ shifted only slightly (δ 5.416−5.417, 0.00−0.75 equiv; 5.433, 2.50 equiv), but the crown ether signal varied somewhat more (δ 3.606, 0.00−0.50 equiv; 3.528, 2.50 equiv). Also, the IR ν_{NO} band of $\mathbf{1}^+PF_6^-$ (1687.8 cm^{-1}, CH_3CN) shifted slightly upon addition of 0.25 equiv of 18-crown-6 but not with further increments (1685.9 cm^{-1}, 0.25−1.50 equiv).

Low-temperature ^1H NMR spectra of a 1:1 mixture of $\mathbf{1}^+TfO^-$ and 18-crown-6 were recorded in CD_2Cl_2. At −40 °C, two broad resonances were observed, corresponding to the NH_3 and crown ether protons (δ 4.11, 3.48; 3:24). Except for very slight chemical shift changes, the former was unaffected by further cooling (δ 4.11−4.09). At −70 °C, the crown ether resonance had decoalesced into two broad overlapping signals (δ 3.57, 3.42; ca. 6:18). Their relative shapes changed upon further cooling (−75 °C δ 3.56, 3.41; −80 °C δ 3.56, 3.45). At −90 °C, four broad crown ether signals were apparent (δ 3.55, 3.50, 3.35, 3.20, ca. 6:8:6:4). Although none of the preceding data can be fully interpreted without extensive further study, it is evident that $\mathbf{1}^+X^-$ and 18-crown-6 exhibit significant binding interactions in solution.

In summary, this model study has established the feasibility of supramolecular complex formation with simple Lewis base derivatives of the chiral rhenium fragment **I**. Our data clearly establish binding between $\mathbf{1}^+X^-$ and 18-crown-6 both in solution and the solid state. Investigations directed at new types of assemblies and motifs are in progress.

Experimental Section

General Data. Instrumental protocols and solvent and reagent purifications were identical to those in earlier papers.[2a] The 18-crown-6 (Aldrich) was stored in a desiccator and used without purification.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH_3)]^+PF_6^-$ ($\mathbf{1}^+PF_6^-$). A flask was charged with a solution of $\mathbf{1}^+TfO^-$ (0.142 g, 0.200 mmol)[7] in acetone (10 mL). Then a solution of $NH_4^+PF_6^-$ (ca. 0.10 g, 0.61 mmol) in methanol (20 mL) was added. Solvent was removed by oil-pump vacuum, and the residue was extracted with acetone (10 mL). Solvent was removed from the extract, and the extraction was repeated twice. Then CH_2Cl_2 was added to precipitate residual $NH_4^+PF_6^-$, and the sample was filtered. Solvent was removed from the filtrate to give $\mathbf{1}^+PF_6^-$ as an orange powder (0.135 g, 0.191 mmol; 96%), mp 199−200 °C. IR (cm^{-1}): KBr, ν_{NO} 1682 (s), ν_{PF} 839 (s); CH_3CN, ν_{NO} 1688 (s). ^1H NMR (δ, CD_3CN): 7.63−7.46 (m), 7.39−7.29 (m), 5.42 (s), 3.77 (br s).

$[\{(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH_3)\}_2(\text{18-crown-6})]^{2+}2PF_6^-\cdot OEt_2$ ($\mathbf{2}^{2+}2PF_6^-\cdot OEt_2$). A flask was charged with $\mathbf{1}^+PF_6^-$ (0.035 g, 0.050 mmol) and CH_3CN (5 mL). Then 18-crown-6 (0.026 g, 0.100 mmol) was slowly added. Ether was slowly added by vapor diffusion to the solution. Over the course of several days, deep red blocks of $\mathbf{2}^{2+}2PF_6^-\cdot OEt_2$ formed, which were collected by filtration and dried under oil-pump vacuum (0.041 g, 0.023 mmol, 94%), mp 176−178 °C. Some colorless crystals of 18-crown-6 also formed and were manually separated. IR (cm^{-1}): KBr, ν_{NO} 1711/1682 (s), ν_{PF} 843 (s); CH_2Cl_2, ν_{NO} 1688 (s); CH_3CN, ν_{NO} 1686 (s). Anal. Calc for $C_{62}H_{80}F_{12}N_4O_9P_4Re_2$: C, 42.56; H, 4.61. Found: C, 42.51; H, 4.57.

Crystallography. Data were collected as outlined in Table 1. Cell constants were obtained from 25 reflections with 22.0° < 2θ < 28.0°. The space group ($P2/n$) was determined from systematic absences ($h0l$ $h+l = 2n$) and subsequent least-squares refinement. Lorentz, polarization, and empirical absorption (Ψ scans) corrections were applied. The structure was solved by standard heavy-atom techniques with the MOLEN/VAX package[9] and refined with SHELXL-93.[10] Non-hydrogen atoms were refined with anisotropic thermal parameters. Most hydrogen-atom positions were calculated, added to the structure factor calculations, and refined (riding model). The NH_3 hydrogens were located with SHELXL instruction AFIX 137, which calculates a difference electron-density synthesis around the circular locus of possible hydrogen positions. The maximum electron density is used as the starting position of the hydrogen atoms (fixed N−H bond lengths and angles). Scattering factors and $\Delta f'$ and $\Delta f''$ values were taken from the literature.[11] Data (excluding structure factors) for have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-100852. Copies of the data can be obtained, free of charge, on application to the director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax +44-(0)1223-336033 or e-mail teched@chemcrys.cam.ac.uk).

Acknowledgment. We thank the NSF for support of this research.

Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates for $\mathbf{2}^{2+}2PF_6^-\cdot OEt_2$ (9 pages). Ordering information is given on any current masthead page.

OM970792E

---

(9) Frenz, B. A. The Enraf-Nonius CAD 4 SDP—A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Determination. In *Computing and Crystallography*; Schenk, H., Olthof-Hazelkamp, R., van Konigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64−71.

(10) Sheldrick, G. M. *SHELXL-93, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1993.

(11) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch: Birmingham, England, 1974; Vol. IV, pp 72−98, 149−150 (Tables 2.2B and 2.3.1).