Table II. Breakdown of ^{55}Mn Hyperfine Interaction in $Mn(\eta\text{-}C_4H_6)_2PMe_3$ into Isotropic and Anisotropic Parts

axis	^{55}Mn hyperfine interaction, G exptl	isotropic (4s)	anisotropic ($3d_{z^2}$)
x	57.0	87.7	−30.7
y	42.0	87.7	−45.7
z	164.0	87.7	76.3
spin pop.		0.05	0.59

differ from the average of the principal values in frozen 2-methylbutane. In other words, the EPR parameters of $Mn(\eta\text{-}C_4H_6)_2PMe_3$ change slightly at the melting point of the solvent.

Returning to $Mn(\eta\text{-}C_4H_6)_2PMe_3$ in the single crystal matrix, we note that the main differences between it and $Mn(CO)_5$ are (a) an increase in the isotropic ^{55}Mn hyperfine interaction from near zero in $Mn(CO)_5$ to 88 G in $Mn(\eta\text{-}C_4H_6)_2PMe_3$ and (b) the lack of axial symmetry in the spectral parameters of $Mn(\eta\text{-}C_4H_6)_2PMe_3$. Both (a) and (b) are symptomatic of a slightly different wave function for the semioccupied orbital of $Mn(CO)_5$ and $Mn(\eta\text{-}C_4H_6)_2PMe_3$: (a) suggests an increase in Mn 4s spin population from negligible in $Mn(CO)_5$ to 0.05 in $Mn(\eta\text{-}C_4H_6)_2PMe_3$ and (b) indicates spin population not only in $3d_{z^2}$ but also in $3d_{x^2-y^2}$. The breakdown of the orthorhombic ^{55}Mn tensor into isotropic and anisotropic components associated with Mn 4s and $3d_{z^2}$ spin populations[13] is given in Table II. The appreciable departure of both the **g** and ^{55}Mn tensors from axiality is undoubtedly[14] due to configuration interaction between the d_{z^2} and $d_{x^2-y^2}$ components of the a_1 SOMO. With use of McGarvey's expressions for the hyperfine tensor components of a d^7 system, we estimate that the $d_{x^2-y^2}$ contribution to the a_1 orbital is less than 1% of that from d_{z^2}.

At first we thought that free rotation, or lack of it, in the PMe_3 moiety of $Mn(\eta\text{-}C_4H_6)_2PMe_3$ was responsible for the differences between its (solid-) and liquid-phase parameters. Since it appears,[7] however, that the same phenomena occur in $Mn(\eta\text{-}C_4H_6)_2CO$, it must be concluded that it is the butadiene ligands which cause the problem. We surmise that in the solid phase the butadiene ligands are sterically crowded and that in soluton the molecule is free to take up its equilibrium conformation.

We end on a note of caution. The present study has illuminated the pitfalls of a facile interpretation of powder EPR spectra. In our experience, an analysis of such spectra is only reliable if the system is truly axial—$Co(CO)_4$, for example.[15] If the system has orthorhombic **g** and hyperfine tensors, it may be quite impossible (even with the aid of the isotropic spectrum of the same radical) to correctly disentangle three principal values of **g** and **a** from a powder spectrum.

Note Added in Proof. It has now been established that $Fe(\eta\text{-}C_4H_6)_2PMe_3$ crystallizes in the monoclinic system with space group $P2_1/c$. A further report is in progress.

Registry No. $Mn(\eta\text{-}C_4H_6)_2PMe_3$, 82963-75-5; $Fe(\eta\text{-}C_4H_6)_2PMe_3$, 87922-45-0; $Mg(C_4H_6)\cdot 2THF$, 87922-46-1.

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Reactions of the Octachlorodirhenate(III) Anion with Aryl Isocyanides: Homoleptic Isocyanides of Rhenium(I) and Mixed-Ligand Complexes of Rhenium(III)

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The reactions of aryl isocyanides ArNC (Ar = phenyl, *p*-tolyl, 2,6-dimethylphenyl, and 2,4,6-trimethylphenyl) with the quadruply bonded complexes $Re_2(O_2CCH_3)_4Cl_2$ and $(n\text{-}Bu_4N)_2Re_2Cl_8$ in refluxing methanol provide an excellent high-yield synthetic route to the homoleptic rhenium(I) species $[Re(CNAr)_6]PF_6$. When the reactions between ArNC and $(n\text{-}Bu_4N)_2Re_2Cl_8$ are conducted at room temperature, then rhenium(III)-containing intermediates of the types $[Re(CNAr)_6]_2Re_2Cl_8$, $[Re(CNAr)_6][ReCl_4(CNAr)_2]$, and $ReCl_3(CNAr)_3$ can be isolated. These aryl isocyanide complexes all display well-defined electrochemistry (cyclic voltammetry) in 0.2 M TBAH–CH_2Cl_2, the mononuclear rhenium(III) species displaying the redox processes Re(IV) + $e^- \rightleftarrows$ Re(III) and Re(III) + $e^- \rightleftarrows$ Re(II). In the case of $[Re(CNAr)_6]^+$ (Ar = Ph or *p*-tol), oxidation to the dark blue 17-electron cation $[Re(CNAr)_6]^{2+}$ has been accomplished electrochemically (at ca. +1.2 V) and the resulting solutions have been characterized spectroscopically. Characterization of the salts $[Re(CNAr)_6][ReCl_4(CNAr)_2]$ has shown that freshly prepared samples contain the trans anion but the dichloromethane solutions slowly isomerize to the corresponding cis isomer. The ^{1}H NMR spectra of these same salts reveal substantial Knight shifts associated with the paramagnetic d^4 $[ReCl_4(CNAr)_2]^-$ anions.

Introduction

The direct reductive cleavage of multiply bonded dimetal complexes of molybdenum(II) and tungsten(II) by aryl isocyanides (ArNC) constitutes a convenient synthetic strategy for the preparation of the homoleptic isocyanide complexes $M(CNAr)_6$.[1,2] The same is true in the case of the reactions between the quadruply bonded dirhenium-

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(III) carboxylate $Re_2(O_2CCH_3)_4Cl_2$ and alkyl isocyanides in refluxing methanol, whereupon the rhenium(I) cations $[Re(CNR)_6]^+$ (R = C_6H_{11} or CMe_3) are formed in high yield.[3] Interestingly, when the salts $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl or Br) are used in place of $Re_2(O_2CCH_3)_4Cl_2$ and the reaction is carried out at room temperature, these milder conditions are sufficient to permit the isolation of the nonreductive cleavage products $[Re(CNR)_5X_2]PF_6$ (R = CMe_3).[3] Subsequently, we have found that the $[Re(CNR)_6]^+$ cations are formed when more forcing reflux conditions are used.

Although the preceding reactions constitute an excellent synthetic procedure for the isolation of homoleptic isocyanide complexes, we obtained little information on the intermediates that might be formed prior to the reduction step(s),[4] although in the case of the reactions between $(n\text{-}Bu_4N)_2Re_2X_8$ and *tert*-butyl isocyanide,[3] the $[Re(CNR)_5X_2]^+$ species can be viewed as intermediates on the way to $[Re(CNR)_6]^+$. Of further note in this regard is the recent isolation of what is purported to be the ditungsten(I) complex $W_2(\mu\text{-mhp})_2(CN\text{-}t\text{-}Bu)_4$ from the reaction between $W_2(mhp)_4$ (mhp is the monoanion of 2-hydroxy-6-methylpyridine, mhpH) and *tert*-butyl isocyanide, a procedure which gives ultimately $W(CN\text{-}t\text{-}Bu)_6$.[5]

In studying the reactions between various aryl isocyanides and $Re_2(O_2CCH_3)_4Cl_2$ and $(n\text{-}Bu_4N)_2Re_2Cl_8$, we have found that not only are these the best synthetic routes available to $[Re(CNAr)_6]PF_6$ but also that the isolation of several mixed chloride–isocyanide complexes of rhenium(III) provides some insight into the possible mechanism of these reactions. Furthermore, the rhenium(III) species $[ReCl_4(CNAr)_2]^-$ and $ReCl_3(CNAr)_3$ that have been isolated during the course of this work bear an interesting relationship to the analogous isomeric nitrile derivatives that have been produced photochemically from $(n\text{-}Bu_4N)_2Re_2Cl_8$.[6] Details of these studies are described in the present report.

Experimental Section

Starting Materials. Potassium perrhenate was purchased from Pressure Chemical Co. and was used without further purification. The dirhenium(III) complexes $Re_2(O_2CCH_3)_4Cl_2$[7] and $(n\text{-}Bu_4N)_2Re_2Cl_8$[8] were prepared by standard literature procedures. 2,6-Dimethylphenyl isocyanide (xylylNC) was purchased from Fluka AG (Switzerland), while the other isocyanide ligands, phenyl isocyanide (PhNC), *p*-tolyl isocyanide (*p*-tolNC), and 2,4,6-trimethylphenyl isocyanide (mesitylNC), were prepared by using the method described by Weber et al.[9] Dichloromethane-d_2 was purchased from Stohler Isotope Chemicals while potassium hexafluorophosphate was purchased from Alfa Products and recrystallized twice from acetone before use. Solvents were reagent grade and were used as received.

Reactions. All reactions were carried out under an atmosphere of nitrogen in deoxygenated solvents unless otherwise indicated.

A. Reactions of $Re_2(O_2CCH_3)_4Cl_2$. (i) $[Re(CNPh)_6]PF_6$. Phenyl isocyanide (3.0 mL, ~30 mmol) was syringed into a suspension of $Re_2(O_2CCH_3)_4Cl_2$ (0.5 g, 0.74 mmol) in 20 mL of methanol. The solution was stirred under reflux for 2 days.[10] During this time, the orange suspension turned brown and became homogeneous in nature. The mixture was cooled to room temperature and then evaporated under a stream of nitrogen gas to leave a brown residue. A quantity of KPF_6 (0.4 g, 2.2 mmol) dissolved in 40 mL of acetone was added to the residue, and this mixture was stirred for 30 min. The resulting solution was again reduced to dryness, and the $[Re(CNPh)_6]PF_6$ was extracted into dichloromethane and then precipitated with petroleum ether. The white solid was filtered off, washed with petroleum ether, and dried under reduced pressure. Recrystallization from acetone/diethyl ether followed by dichloromethane/petroleum ether was used to obtain the complex as colorless crystals. Yields varied from 62 to 70%. Anal. Calcd for $C_{42}H_{30}F_6N_6PRe$: C, 53.11; H, 3.18. Found: C, 52.95; H, 3.36.

Other complexes of the type $[Re(CNAr)_6]PF_6$ were prepared by a procedure very similar to that described for $[Re(CNPh)_6]PF_6$.

(ii) $[Re(CN\text{-}p\text{-}tol)_6]PF_6$: yield 72%. Anal. Calcd for $C_{48}H_{42}F_6N_6PRe$: C, 55.75; H, 4.09. Found: C, 56.58; H, 4.63.

(iii) $[Re(CNxylyl)_6]PF_6$: yield 65%. Anal. Calcd for $C_{54}H_{54}F_6N_6PRe$: C, 58.00; H, 4.87. Found: C, 57.53; H, 5.32.

(iv) $[Re(CNmesityl)_6]PF_6$: yield 73%. Anal. Calcd for $C_{60}H_{66}F_6N_6PRe$: C, 59.94; H, 5.53. Found: C, 60.41; H, 5.58.

B. Reactions of $(n\text{-}Bu_4N)_2Re_2Cl_8$ with Aryl Isocyanides under Reflux. (i) $[Re(CNPh)_6PF_6$. A solution containing $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.6 g, 0.53 mmol) in 50 mL of methanol was treated with phenyl isocyanide (1.5 mL, ~15 mmol). The solution, which immediately changed from blue to brown, was stirred at room temperature for 4 h and then refluxed for an additional 1 h. After the reaction mixture was cooled to room temperature, the solvent was evaporated under a stream of nitrogen gas. The resulting black tar was treated with 50 mL of acetone containing 0.3 g (1.6 mmol) of KPF_6, the mixture filtered, and the solid residue washed with acetone.[11] The combined filtrate and extracts were reduced to dryness, and the residue was washed with a large volume (~100 mL) of petroleum ether followed by diethyl ether. The resulting $[Re(CNPh)_6]PF_6$ was extracted into 50 mL of dichloromethane and precipitated with petroleum ether. It was necessary to recrystallize this complex with acetone/diethyl ether followed by dichloromethane/petroleum ether; yield 0.57 g (57%). Anal. Calcd for $C_{40}H_{30}F_6N_6PRe$: C, 53.11; H, 3.18. Found: C, 53.22; H, 3.16.

(ii) $[Re(CN\text{-}p\text{-}tol)_6]PF_6$. A procedure similar to that described in B(i) produced this complex in 60% yield. It was identified on the basis of its spectroscopic and electrochemical properties.

C. Reactions of $(n\text{-}Bu_4N)_2Re_2Cl_8$ with Aryl Isocyanides at Room Temperature. (i) $[Re(CNPh)_6]^+[ReCl_4(CNPh)_2]^-$. A solution of 0.6 g of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.53 mmol) in 50 mL of methanol was treated with 1.0 mL of freshly distilled phenyl isocyanide (9.7 mmol). The solution was stirred for 4 h at room temperature and cooled to 0 °C in an ice bath, and the yellow precipitate that formed was filtered off. The yellow solid was washed with 10 mL of cold methanol followed by 50 mL of petroleum ether; yield 0.51 g (72%). Anal. Calcd for $C_{56}H_{40}Cl_4N_8Re_2$: C, 50.23; H, 3.01. Found: C, 50.46; H, 3.21.

The original methanol filtrate, when refluxed and worked up as described in B(i), afforded a small quantity of $[Re(CNPh)_6]PF_6$, yield 0.07 g (7%).

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(4) In the case of the reactions between $Mo_2(O_2CCH_3)_4$ and $W_2(mhp)_4$ (mhp is the monoanion of 2-hydroxy-6-methylpyridine) and phenyl isocyanide, the yields of the final product $M(CNPh)_6$ are quite low and there are clearly considerable quantities of other byproducts that are formed.[1,2] Although $[Re(CNR)_6]^+$ is formed in good yield from the reaction between $Re_2(O_2CCH_3)_4Cl_2$ and RNC,[3] this is a heterogeneous phase reaction because of the insolubility of the rhenium(III) acetate in the reaction solvent methanol. Consequently, it has not proved convenient to monitor spectroscopically the course of these reactions and thereby identify any reaction intermediates.

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(9) Weber, W. P.; Gokel, G. W.; Ugi, I. K.; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 530.

(10) This reaction was carried out at pressures somewhat above atmospheric by using the setup described in ref 8. Reaction times were longer when the reaction was carried out at atmospheric pressure.

(11) The white residue remaining following extraction with acetone appeared to be a mixture of KCl and *N,N'*-dimethylformamidine, $C_6H_5NHCH{=}NPh$. This product could result from a reaction of aniline (the isocyanide is often contaminated with small amounts of the aniline starting material from the preparative method employed[9]) with phenyl isocyanide in the methanol solvent. This compound has been identified by mass spectrometry and IR and ^1H NMR spectroscopy.

(ii) $[Re(CN\text{-}p\text{-}tol)_6]^+[ReCl_4(CN\text{-}p\text{-}tol)_2]^-$. This compound was obtained by using a procedure similar to that described in C(i); yield 67%. Anal. Calcd for $C_{64}H_{56}Cl_4N_8Re_2$: C, 52.96; H, 3.89. Found: C, 52.90; H, 3.88.

A small quantity of $[Re(CN\text{-}p\text{-}tol)_6]PF_6$ was isolated from the reaction filtrate when it was worked up as described in B(i); yield 7%.

(iii) $[Re(CNxylyl)_6]_2[Re_2Cl_8]$ and $[Re(CNxylyl)_6]^+[ReCl_4(CNxylyl)_2]$. Xylyl isocyanide (1.25 g, 9.5 mmol) was added to a solution of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.6 g, 0.53 mmol) in 50 mL of methanol. After the reaction mixture was stirred for 2 h, a blue-green precipitate was filtered off in the air, washed with petroleum ether, and dried under vacuum; yield 0.26 g (38%). Anal. Calcd for $C_{108}H_{108}Cl_8N_{12}Re_4$: C, 49.84; H, 4.18; Cl, 10.90. Found: C, 48.91; H, 4.34; Cl, 11.11.

The methanol reaction filtrate was stirred for an additional 2 h during which time a yellow solid precipitated. This was filtered off, washed with petroleum ether, and dried under vacuum: yield 0.28 g (34%). Anal. Calcd for $C_{72}H_{72}Cl_4N_8Re_2$: C, 55.31; H, 4.64; Cl, 9.07. Found: C, 55.52; H, 5.19; Cl, 9.12.

(iv) $[Re(CNmesityl)_6]^+[ReCl_4(CNmesityl)_2]^-$ and $ReCl_3(CNmesityl)_3$. Following the procedure described in C(i), but using 1.5 g (10.3 mmol) of mesityl isocyanide, a yellow complex was isolated upon stirring the reaction mixture for 4 h; yield 0.24 g (27%). Anal. Calcd for $C_{80}H_{88}Cl_4N_8Re_2$: C, 57.34; H, 5.29. Found: C, 57.33; H, 5.49.

The methanol filtrate was stirred under nitrogen for 1 h, and the insoluble bright green compound was filtered off. This was recrystallized from toluene to afford green needles; yield 0.13 g (17%). Anal. Calcd for $C_{30}H_{33}Cl_3N_3Re$: C, 49.48; H, 4.57; Cl, 14.61. Found: C, 49.91; H, 5.10; Cl, 14.71.

D. Reaction of $[Re(CN\text{-}p\text{-}tol)_6]^+[ReCl_4(CN\text{-}p\text{-}tol)_2]^-$ with p-Tolyl Isocyanide. The mixed-valent p-tolyl salt (0.09 g, 0.06 mmol) was refluxed in 20 mL of methanol for 1 h in the presence of 0.1 g of p-tolyl isocyanide (0.85 mmol). The mixture was cooled to room temperature, and the solvent was evaporated under a stream of nitrogen gas. The residue was stirred for 1 h in 20 mL of acetone containing 0.1 g of KPF_6, and the solid remaining was filtered off and washed with a further 20 mL of acetone. The combined acetone extracts were evaporated to dryness, and the resulting $[Re(CN\text{-}p\text{-}tol)_6]PF_6$ was extracted into dichloromethane. This solution was in turn evaporated to yield the pure product, yield 0.1 g (78%).

E. Reaction of $ReCl_3(CNmesityl)_3$ with Mesityl Isocyanide. A recrystallized sample of $ReCl_3(CNmesityl)_3$ (0.03 g, 0.04 mmol) was refluxed for 12 h in 10 mL of methanol containing (0.1 g, 0.69 mmol) of mesityl isocyanide. The resulting solution was evaporated under a stream of nitrogen gas until dry and then treated with 10 mL of acetone containing 0.05 g of KPF_6 (0.27 mmol). This mixture was stirred in the air for 1 h and then evaporated to dryness. The rhenium-containing compounds were extracted into dichloromethane and the filtrate again taken to dryness. The cyclic voltammogram of this residue (measured in 0.2 M TBAH–CH_2Cl_2) clearly showed the presence of starting material and $[Re(CNmesityl)_6]^+$.

F. Reaction of $Re_2Cl_6(PEtPh_2)_2$ with Phenyl Isocyanide. With use of reaction conditions similar to those described in B(i), but with 0.5 g of $Re_2Cl_6(PEtPh_2)_2$ in place of $(n\text{-}Bu_4N)_2Re_2Cl_8$, a blue solid was isolated. This material was shown to be almost exclusively $[Re(CNPh)_6]PF_6$ by a comparison of its cyclic voltammogram and IR and ^1H NMR spectra to those of an authentic sample; yield 30–40%. All attempts to get this sample completely pure failed.[12]

G. Reaction of $Re_2H_8(PPh_3)_4$ with Phenyl Isocyanide. A test tube was flushed with nitrogen gas and charged with a stirring bar and 0.3 g of $Re_2H_8(PPh_3)_4$ (0.21 mmol) and capped with a rubber stopple. Phenyl isocyanide (3 mL, ~30 mmol) was added, whereupon an exothermic reaction took place. The mixture was stirred for 1 h at room temperature and then at 100 °C for 6 h. The reaction mixture was cooled, and the insoluble material was filtered off and washed with petroleum ether (100 mL) and then with diethyl ether (100 mL). The solid was then stirred with 30 mL of acetone containing 0.2 g of KPF_6 and the mixture filtered. The insoluble residue was washed with a further 30 mL of acetone, and the combined acetone extracts were evaporated to dryness under nitrogen gas. The impure $[Re(CNPh)_6]PF_6$ was dissolved in dichloromethane and reprecipitated by the addition of petroleum ether. Recrystallization was effected as described in A(i); yield 0.10 g (25%). The identity of this complex was confirmed by its electrochemical properties and IR spectrum.

H. Halogen Oxidation of $[Re(CNPh)_6]PF_6$. (i) $[Re(CNPh)_6Cl](PF_6)_2$. Chlorine gas was bubbled slowly through a cooled solution (−10 °C) containing 0.2 g (0.21 mmol) of $[Re(CNPh)_6]PF_6$ in 25 mL of acetone. After 15 min, the chlorine gas was turned off and a small quantity of KPF_6 (0.05 g, 0.27 mmol) was added. The solution was stirred for an additional 15 min and then evaporated to dryness under nitrogen gas. The product was extracted into dichloromethane, precipitated by using petroleum ether, and finally recrystallized from acetone/diethyl ether; yield 0.21 g (88%). Anal. Calcd for $C_{42}H_{30}ClF_{12}N_6P_2Re$: C, 44.63; H, 2.68. Found: C, 44.98; H, 2.81. This complex possesses an IR-active $\nu(C{\equiv}N)$ mode at 2208 (s, br) cm^{-1} that is characteristic of a rhenium(III) isocyanide species.

(ii) $[Re(CNPh)_6Br](PF_6)_2$. Liquid bromine (5 drops) was added to a mixture of $[Re(CNPh)_6]PF_6$ (0.05 g, 0.05 mmol) and KPF_6 (0.1 g, 0.54 mmol) in 20 mL of dichloromethane. The mixture was stirred for 2 h at room temperature under a nitrogen atmosphere and then evaporated to dryness. The residue was extracted into dichloromethane and the filtrate was evaporated to dryness. The resulting yellow powder is believed to be $[Re(CNPh)_6Br](PF_6)_2$, but attempts to purify it by recrystallization from acetone led to its partial decomposition to $[Re(CNPh)_6]PF_6$, as monitored by cyclic voltammetry. The IR spectrum of the impure product showed that the rhenium(III) complex $[Re(CNPh)_6Br](PF_6)_2$ had its $\nu(C{\equiv}N)$ mode at 2194 cm^{-1}.

Physical Measurements. Infrared spectra of Nujol mulls and of dichloromethane solutions were recorded by using a Beckman IR-12 spectrophotometer and Digilab FTS-20B and IBM IR/32 Fourier transform spectrometers. The ^1H NMR spectra were recorded on one of the following instruments: a Perkin-Elmer R32 90-MHz NMR, a Varian XL-200 Fourier transform spectrometer, and a Nicolet NT-470 Fourier transform spectrometer. Samples were dissolved in dichloromethane-d_2, and peak resonances were internally referenced to the residual protons in the solvent. Cyclic voltammetric results were obtained with a BioAnalytical Systems, Inc., Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B x-y recorder. Potential control for coulombic experiments was maintained with a potentiostat purchased from BioAnalytical Systems, Inc. All voltammetric measurements were made by using a platinum bead electrode on dichloromethane solutions containing 0.2 M tetra-n-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. $E_{1/2}$ values (taken as $(E_{p,a} + E_{p,c})/2$) were referenced to the saturated potassium chloride calomel electrode (SCE) at room temperature. A Hewlett-Packard 8450-A diode array spectrophotometer was used to obtain electronic absorption spectra. The Raman spectrum of a solid sample of $[Re(CN\text{-}p\text{-}tol)_6][ReCl_4(CN\text{-}p\text{-}tol)_2]$ was recorded by using 5145-Å radiation with the instrument described previously.[13,14]

Microanalyses were performed by Dr. C. S. Yeh and Dr. H. D. Lee of the Purdue University microanalytical laboratory.

Results and Discussion

(a) Reductive Cleavage of the Dirhenium(III) Quadruple Bond. The reductive cleavage of the quadruply bonded dirhenium(III) species $Re_2(O_2CCH_3)_4Cl_2$ and $[Re_2Cl_8]^{2-}$ by aryl isocyanides provides an excellent route to complexes of the type $[Re(CNAr)_6]PF_6$ when these reactions are carried out in refluxing methanol in the presence of KPF_6. To date, this constitutes the best general synthetic strategy for the homoleptic species $[Re(CNAr)_6]^+$,

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[12] A tetramer of phenyl isocyanide, indigodianil, is known to form spontaneously at room temperature. The blue impurity that is present in this sample of $[Re(CNPh)_6]PF_6$ may be this compound. See: Ugi, I. "Isonitrile Chemistry"; Academic Press: New York, 1971; p 100.

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Table I. Cyclic Voltammetric Data for Dichloromethane Solutions of Isocyanide Complexes of Rhenium(I) and Rhenium(III)[a]

compound	cation $E_{1/2}$(ox)	anion $E_{1/2}$(ox)	anion $E_{1/2}$(red)
$[Re(CNPh)_6]PF_6$	1.18 (75)		
$[Re(CNPh)_6]$[*trans*-$ReCl_4(CNPh)_2$]	1.17 (70)	0.53 (70)	−0.72 (80)
$[Re(CN\text{-}p\text{-}tol)_6]PF_6$	1.06 (100)		
$[Re(CN\text{-}p\text{-}tol)_6]$[*trans*-$ReCl_4(CN\text{-}p\text{-}tol)_2$]	1.09 (75)	0.46 (70)	−0.79 (80)
$[Re(CNxylyl)_6]PF_6$	1.19 (90)		
$[Re(CNxylyl)_6]$[*trans*-$ReCl_4(CNxylyl)_2$]	1.20 (95)	0.42 (95)	−0.88 (100)
$[Re(CNxylyl)_6]$[*cis*-$ReCl_4(CNxylyl)_2$]		0.60[b]	−0.66[b,c]
$[Re(CNxylyl)_6]_2Re_2Cl_8$	1.20 (110)[d]		−0.87 (100)
$[Re(CNmesityl)_6]PF_6$	1.10 (85)		
$[Re(CNmesityl)_6]$[*trans*-$ReCl_4(CNmesityl)_2$]	1.10 (70)	0.38 (70)	−0.90 (80)
$[Re(CNmesityl)_6]$[*cis*-$ReCl_4(CNmesityl)_2$]		0.59[b]	−0.67[b,c]

[a] Values in volts vs. SCE with a Pt bead working electrode and 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte; values of $E_{p,a} - E_{p,c}$ (in mV) recorded at 200 mV s^{-1} are given in parentheses. [b] This value was measured for mixtures of the cis and trans isomers of the anion. [c] Appears to be irreversible with $i_{p,c}/i_{p,a} > 1$; $E_{p,c}$ value given. [d] Coincident couples associated with the cation and the anion.

Table II. Selected Infrared Vibrations for Isocyanide Complexes of Rhenium(I) and Rhenium(III)[a]

compound	ν(C≡N), cm^{-1}	ν(Re—Cl), cm^{-1}
$[Re(CNPh)_6]PF_6$	2080 (s), 2020 (sh)	
$[Re(CNPh)_6]$[*trans*-$ReCl_4(CNPh)_2$]	2120 (sh),[c] 2090 (s), 1995 (sh)	293 (s)
$[Re(CN\text{-}p\text{-}tol)_6]PF_6$	2086 (s), 2036 (m) 2088 (s),[b] 2040 (m)[b]	
$[Re(CN\text{-}p\text{-}tol)_6]$[*trans*-$ReCl_4(CN\text{-}p\text{-}tol)_2$]	2112 (sh),[c] 2081 (s), 2036 (sh) 2113 (s),[b,c] 2077 (s),[b] 2040 (m)[b]	294 (s)
$[Re(CNxylyl)_6]PF_6$	2067 (s), 1998 (m)	
$[Re(CNxylyl)_6]$[*trans*-$ReCl_4(CNxylyl)_2$]	2096 (sh),[c] 2071 (s), 2006 (m)	293 (s)
$[Re(CNxylyl)_6]_2Re_2Cl_8$	2080 (s), 1990 (m)	334 (s)
$[Re(CNmesityl)_6]PF_6$	2070 (s), 1945 (sh) 2078 (s)[b]	
$[Re(CNmesityl)_6]$[*trans*-$ReCl_4(CNmesityl)_2$]	2071 (s, br) 2091 (sh),[b,c] (2076 (s)[b]	296 (s)

[a] Recorded as Nujol mulls on KBr plates unless otherwise stated. Abbreviations are as follows: br, broad, m, medium; s, strong; sh, shoulder. [b] Recroded as dichloromethane solutions in NaCl solution cells. [c] his absorption is assigned to ν(C≡N) of the rhenium(III) anion.

being superior to any of the existing procedures.[15-17] These reactions therefore constitute logical and important extensions of (a) the analogous ones between $Re_2(O_2CCH_3)_4Cl_2$ (or $[Re_2Cl_8]^{2-}$) and alkyl isocyanides (RNC) which provide $[Re(CNR)_6]PF_6$[3,18] in good yield and (b) the reductive cleavage of $Mo_2(O_2CCH_3)_4$ and $W_2(mhp)_4$ (mhp is the monoanion of 2-hydroxy-6-methylpyridine, mhpH) by ArNC to give $M(CNAr)_6$ (M = Mo or W).[1,2] Additionally, we find that the related reactions of phenyl isocyanide with $Re_2Cl_6(PEtPh_2)_2$ and with the hydrido species $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$[19] yield $[Re(CNPh)_6]PF_6$ as the only characterizable rhenium containing species.

Cyclic voltammetric (CV) measurements on 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH)–dichloromethane solutions of $[Re(CNAr)_6]PF_6$ (Table I) show electrochemical behavior similar to that observed for the alkyl isocyanide derivatives $[Re(CNR)_6]PF_6$,[3] namely, a quasi-reversible one-electron oxidation corresponding to the process

$$[Re(CNAr)_6]^+ \xrightarrow{-e^-} [Re(CNAr)_6]^{2+}$$

For these aryl isocyanide derivatives, the $E_{1/2}$ values (Table I) occur in the potential range +1.21 to +1.06 V vs. SCE and are therefore at potentials ~0.3 V more positive than those for $[Re(CNR)_6]PF_6$. This reflects the superior π-accepting properties of ArNC compared to RNC, thereby leading to an increase in the positive charge at the metal center in the case of $[Re(CNAr)_6]PF_6$.

The electronic absorption spectra of dichloromethane solutions of $[Re(CNAr)_6]PF_6$ resemble the spectrum of $[Re(CNCMe_3)_6]PF_6$[20] in exhibiting a shoulder at ~360 nm and bands at 330 ± 5 and 295 ± 5 nm ($\epsilon_{max} = 10^4$–10^5) that are assignable to metal-to-ligand charge-transfer transitions and in turn resemble quite closely the spectrum of isoelectronic $[Mn(CNPh)_6]^+$ in this spectral region.[2] When the bulk electrolysis (at +1.2 V) of a solution of $[Re(CN\text{-}p\text{-}tol)_6]PF_6$ is carried out in 0.2 M TBAH–CH_2Cl_2 (n = 1.0 ± 0.1 by coulometry), an intense blue solution of the dication $[Re(CN\text{-}p\text{-}tol)_6]^{2+}$ was obtained. While we were unable to obtain an ESR spectrum of this species, a CV of the resulting solution showed that the couple at $E_{1/2}$ = +1.06 V vs. SCE now corresponded to a reduction.[21] The IR spectrum of this solution showed ν(C≡N) of $[Re(CN\text{-}p\text{-}tol)_6]^{2+}$ to be at 2130 cm^{-1}, a frequency considerably higher than that for the analogous rhenium(I) cation (Table II). Furthermore, the electronic absorption spectrum of this blue solution revealed absorption bands at 654 and 596 nm ($\epsilon_{max} > 10^3$), resembling the related spectral changes that are observed[2] upon oxidizing $[Mn(CNPh)_6]^+$ to $[Mn(CNPh)_6]^{2+}$. Absorption bands in this spectral region are characteristic of other mononuclear

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(16) Freni, M.; Valenti, V. *Gazz. Chim. Ital.* **1960**, *90*, 1445.

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(18) Girolami, G. S.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2040.

(19) The reaction of PhNC with $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$ is part of a quite general study we are making of the reactivity of this important class of polyhydride complexes. See, for example: Allison, J. D.; Walton, R. A. *J. Chem. Soc., Chem. Commun.* **1983**, 401.

(20) Wood, T. E. Ph.D. Thesis, Purdue University, 1980.

(21) Identical behavior was found for the related phenyl isocyanide system $[Re(CNPh)_6]^{1+,2+}$.

Table III. ^{1}H NMR Chemical Shifts for Isocyanide Complexes of Rhenium(I) and Rhenium(III)[a]

	cation			trans anion					cis anion				
complex	*o*-CH_3	*p*-CH_3	aromatic	*o*-CH_3	*p*-CH_3	*o*-H	*m*-H	*p*-H	*o*-CH_3	*p*-CH_3	*o*-H	*m*-H	*p*-H
$[Re(CNPh)_6]PF_6$			7.45 (m)										
$[Re(CNPh)_6][ReCl_4(CNPh)_2]$			7.44 (m)			7.84 (d)[b]	11.31 (dd)	6.10 (t)			*c*	15.80 (t)	0.94 (t)[d]
$[Re(CN\text{-}p\text{-}tol)_6]PF_6$		2.45 (s)	7.28 (m)										
$[Re(CN\text{-}p\text{-}tol)_6][ReCl_4(CN\text{-}p\text{-}tol)_2]$		2.46 (s)	7.26 (m)		7.16 (s)	7.66 (d)	11.20 (d)						
$[Re(CNxylyl)_6]_2Re_2Cl_8$	2.51 (s)		7.24 (m)										
$[Re(CNxylyl)_6][ReCl_4(CNxylyl)_2]$	2.47 (s)		7.21 (m)	7.92 (s)			11.41 (d)	5.90 (t)	14.51 (s)			16.76 (d)	−1.37 (t)
$[Re(CNmesityl)_6]PF_6$	2.42 (s)	2.33 (s)	6.98 (s)										
$[Re(CNmesityl)_6][ReCl_4(CNmesityl)_2]$	2.42 (s)	2.31 (s)	6.96 (s)	8.20 (s)	7.62 (s)		11.47 (s)		15.24 (s)[b,d]	16.59 (s)[b,d]		17.48 (s)[b]	

[a] The chemical shifts are reported in ppm with reference to the residual protons in CD_2Cl_2 (δ 5.35) at ambient temperature. Spectra recorded at 200 MHz unless otherwise stated. Abbreviations are as follows: s, singlet; d, doublet; dd, doublet of doublets; m, multiplet; t, triplet. [b] Spectrum recorded at 470 MHz. [c] This resonance was not observed. [d] Broadened resonances.

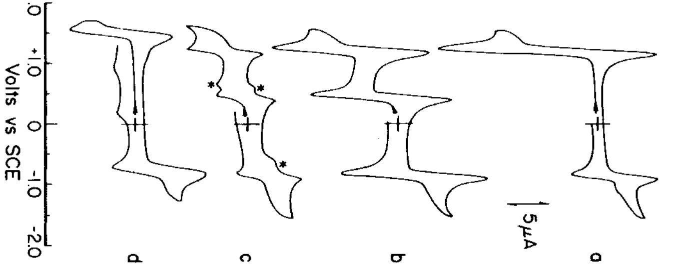

Figure 1. Cyclic voltammograms (at a Pt bead electrode) in 0.2 M tetra-*n*-butylammonium hexafluorophosphate–dichloromethane: (a) $[Re(CNxylyl)_6]_2Re_2Cl_8$ (ν = 200 mV/s); (b) $[Re(CNxylyl)_6][trans\text{-}ReCl_4(CNxylyl)_2]$ (ν = 200 mV/s); (c) solution (b), after being allowed to stand for 7 days, showing the presence of both cis and trans isomers of $[ReCl_4(CNxylyl)_2]^-$; (d) $ReCl_3(CNmesityl)_3$ (ν = 600 mV/s). In c, waves arising from the cis isomer of $[ReCl_4(CNxylyl)_2]^-$ are denoted by an asterisk.

17-electron rhenium(II) isocyanide complexes.[22,23]

The IR and ^{1}H NMR spectral properties of the salts $[Re(CNAr)_6]PF_6$ are unexceptional and will not be discussed here; the appropriate data are listed in Tables II and III.

(b) Nonreductive Cleavage Products from the Reactions of $(n\text{-}Bu_4N)_2Re_2Cl_8$ with Aryl Isocyanides. An important difference between the present results and those found previously for the analogous reactions of alkyl isocyanides with quadruply bonded dirhenium(III) species[3] has proven to be the isolation and characterization of several nonreductive mononuclear rhenium(III) species that can be viewed as intermediates on the way to $[Re(CNAr)_6]^+$.

Whereas the reactions of $(n\text{-}Bu_4N)_2Re_2Cl_8$ with ArNC under reflux conditions give only $[Re(CNAr)_6]^+$, by carrying out these reactions at room temperature and below, we have been able to isolate the following rhenium(III) species: (1) $[Re(CNAr)_6][ReCl_4(CNAr)_2]$, where Ar = Ph, *p*-tol, xylyl, and mesityl, (2) $[Re(CNxylyl)_6]_2Re_2Cl_8$, and (3) $ReCl_3(CNmesityl)_3$.

The complex $[Re(CNxylyl)_6]_2Re_2Cl_8$ is a logical product of this reaction, comprising as it does the stable $[Re(CNxylyl)_6]^+$ cation together with the unreacted $[Re_2Cl_8]^{2-}$ anion. In addition to the characteristic electrochemical and spectroscopic properties of the cation, the low-frequency IR spectrum of this complex shows a ν(Re–Cl) mode at 334 (s) cm^{-1} and the electronic absorption spectrum shows an intense band at 686 nm (assigned to the $\delta \rightarrow \delta^*$ transition) that adequately identify the anion.[24] The cyclic voltammogram of a 0.2 M TBAH–CH_2Cl_2 solution of this complex (Figure 1a) shows a quasi-reversible

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[22] Hertzer, C. A.; Myers, R. E.; Brant, P.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2383.

[23] Allison, J. D.; Walton, R. A., unpublished results.

[24] Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982 and references cited therein.

couple at $E_{1/2}$ = +1.20 V vs. SCE ($E_{p,a} - E_{p,c}$ = 110 mV at ν = 200 mV/s) due to the cation (Table I) together with a characteristic one-electron reduction at $E_{1/2}$ = −0.87 V vs. SCE ($E_{p,a} - E_{p,c}$ = 100 mV at ν = 200 mV/s) due to the process $[Re_2Cl_8]^{2-} + e^- \rightarrow [Re_2Cl_8]^{3-}$. The latter behavior is characteristic of this dirhenium(III) chloroanion[25] and further confirms its presence in this salt. One feature of the CV of this complex that at first puzzled us was the observation that the ratio of currents associated with the couples at +1.20 and −0.87 V was close to 3:1 (see Figure 1a), a result that at first appeared to be inconsistent with the formulation $[Re(CNxylyl)_6]_2Re_2Cl_8$ for which the ratio should be 2:1. The resolution of this problem came with our realization that the $[Re_2Cl_8]^{2-}$ anion (as its n-Bu_4N^+ salt) also possesses a one-electron oxidation which Gray and co-workers[26] have found at $E_{1/2}$ = +1.24 V vs. SCE in CH_3CN and which we find at $E_{1/2}$ = +1.20 V for its solutions in CH_2Cl_2. Thus, for the complex $[Re(CNxylyl)_6]_2Re_2Cl_8$, the oxidation of the anion and the cation occurs at essentially identical potentials, thereby explaining the enhancement in the current associated with the "couple" at +1.20 V.

While we suspect that other salts of the type $[Re(CNAr)_6]_2Re_2Cl_8$ can be isolated, no attempt was made to prepare further examples of such derivatives in the present work.

In all instances, we found that the intermediates $[Re(CNAr)_6][ReCl_4(CNAr)_2]$ could be isolated upon reacting $(n\text{-}Bu_4N)_2Re_2Cl_8$ with ArNC in methanol at room temperature. Further treatment of these complexes with an excess of ArNC results in their conversion to $[Re(CNAr)_6]^+$, as described in the Experimental Section for the p-tolyl isocyanide derivative.[27]

The IR spectra of these salts are, in the ν(C≡N) region, dominated by the absorptions of the cation that swamp the much weaker anion vibrations, thereby making it difficult to identify the latter. However, by resorting to FT-IR difference spectroscopy on dichloromethane solutions of $[Re(CNAr)_6]PF_6$ and $[Re(CNAr)_6][ReCl_4(CNAr)_2]$, we were able to show clearly that the shoulder at ~2100 cm^{-1} in the conventional mull and solution spectra is assignable to ν(C≡N) of the rhenium(III) anion (Table II). Each of the salts $[Re(CNAr)_6][ReCl_4(CNAr)_2]$ possesses a single IR-active ν(Re–Cl) mode of E_u symmetry (Table II). This is in accord with the anions possessing a trans geometry, a conclusion that is supported by Raman spectral results for the p-tolyl isocyanide salt for which the A_{1g} ν(Re–Cl) mode was located at 317 cm^{-1}. The lack of an IR–Raman coincidence for these two ν(Re–Cl) vibrations is expected for a centrosymmetric (i.e., trans) six-coordinate structure.

One of the most striking properties of the salts $[Re(CNAr)_6][ReCl_4(CNAr)_2]$ is the characteristic cyclic voltammograms exhibited by their solutions in 0.2 M TBAH–CH_2Cl_2 (Figure 1b). In addition to the one-electron oxidation associated with the cation, occurring at the same potential as that found for the related hexafluorophosphate salt (Table I), the anion possesses a quasi-reversible one-electron oxidation in the range +0.38 to +0.53 V vs. SCE and a one-electron reduction between −0.72 and −0.90 V vs. SCE. The existence of the electrochemical redox changes $Re(IV) + e^- \rightleftarrows Re(III)$ and $Re(III) + e^- \rightleftarrows Re(II)$ has been recognized for mononuclear rhenium halide species (e.g., $ReCl_3(PR_3)_3$),[28] and the redox chemistry we observe for $[ReCl_4(CNAr)_2]^-$ is consistent with this.

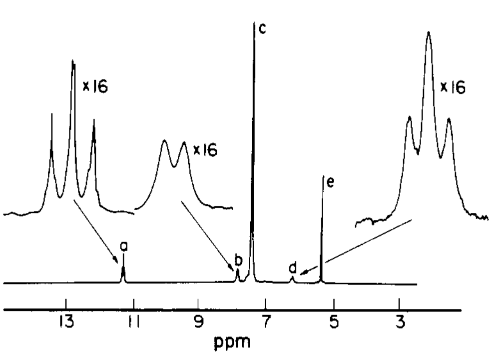

Figure 2. The 200-MHz ^1H NMR spectrum of a CD_2Cl_2 solution of $[Re(CNPh)_6][trans\text{-}ReCl_4(CNPh)_2]$: (a) meta protons of the anion; (b) ortho protons of the anion; (c) cation protons; (d) para proton of the anion; (e) residual protons in the solvent.

In the case of the xylyl and mesityl isocyanide derivatives of the type $[Re(CNAr)_6][ReCl_4(CNAr)_2]$, we found that when their dichloromethane solutions were allowed to stand for several days before these electrochemical measurements were carried out, then the resulting cyclic voltammograms (Figure 1c) showed an additional oxidation ($E_{1/2}$ = +0.60 (±0.01) V vs. SCE) and an additional reduction ($E_{1/2}$ = −0.66 (±0.01) V vs. SCE). These processes occur at potentials ca. 0.2 V more positive than those which characterize the anions $[trans\text{-}ReCl_4(CNAr)_2]^-$ and can be attributable to the formation of $[cis\text{-}ReCl_4(CNAr)_2]^-$. While we have been unable to separate the mixtures of isomers so as to obtain the cis form in a pure state, we can follow this slow isomerization process by ^1H NMR spectroscopy (vide infra).[29]

The ^1H NMR spectra of CD_2Cl_2 solutions of $[Re(CNAr)_6][ReCl_4(CNAr)_2]$ show resonances readily assignable to the $[Re(CNAr)_6]^+$ cations through a comparison with the related spectra of $[Re(CNAr)_6]PF_6$ (Table III). The ^1H NMR spectra of the anions $[trans\text{-}ReCl_4(CNAr)_2]^-$ also exhibit rather sharp and well-defined band shapes (Figure 2), behavior which is consistent with other d^4 systems (including rhenium(III)) which exhibit interpretable ^1H NMR spectra even though they are paramagnetic systems.[30-33] It is perhaps appropriate to refer to these shifts as Knight shifts[33] rather than contact shifts since the latter term implies a particular shift mechanism, whereas, the former does not.[34] When the spectra of the complete series

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[25] Cotton, F. A.; Pedersen, E. *Inorg. Chem.* **1975**, *14*, 383.

[26] Nocera, D. G.; Maverick, A. W.; Winkler, J. R.; Che, C.; Gray, H. B. *ACS Symp. Ser.* **1983**, *No. 211*, 21.

[27] Attempts to carry out cation- and anion-exchange reactions on $[Re(CNAr)_6][ReCl_4(CNAr)_2]$ using KPF_6 and Ph_4AsCl were unsuccessful, perhaps implying a very favorable lattice energy for these salts. Of relevance to these observations is the evidence that their solutions in acetonitrile (10^{-3}–10^{-4} M) are characterized by quite pronounced ion pairing, e.g., for Ar = Ph, Λ_M = 63 Ω^{-1} cm^2 for C_M = 1.10 × 10^{-3} M and Λ_M = 74 Ω^{-1} cm^2 for C_M = 2.21 × 10^{-4}. These Λ_M values are much lower than those which typically characterize 1:1 electrolytes in this solvent; see: Geary, W. J. *Coord. Chem. Rev.* **1971**, 7, 81.

[28] Brant, P.; Salmon, D. J.; Walton, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 4424.

[29] This isomerization was monitored by cyclic voltammetry only in the case of the xylyl and mesityl isocyanide complexes. No attempt was made to do so in the case of the phenyl and p-tolyl isocyanide complexes because of the extreme sluggishness of this isomerization process.

[30] Rossi, R.; Duatti, A.; Magon, L.; Casellato, U.; Graziani, R.; Toniolo, L. *J. Chem. Soc., Dalton Trans.* **1982**, 1949.

[31] Gunz, H. P.; Leigh, G. J. *J. Chem. Soc. A* **1971**, 2229.

[32] Randall, E. W.; Shaw, D. *Mol. Phys.* **1965**, *10*, 41.

[33] Randall, E. W.; Shaw, D. *J. Chem. Soc. A* **1969**, 2867 and references therein.

[34] Randall and Shaw[33] suggest three possible dominant contributions to Knight shifts; these are (a) delocalization of spin density through a π mechanism, (b) delocalization through a σ-constant interaction, and (c) anisotropic effects. From the alternative shift sequence of the aromatic protons of the $[trans\text{-}ReCl_4(CNAr)_2]^-$ anions (i.e., they are shifted to higher and lower parts per million from the homoleptic aromatic protons), it appears that a π delocalization mechanism is the major contributing factor in our systems.

of [*trans*-$ReCl_4(CNAr)_2]^-$ anions are measured, assignments of all the ring and methyl protons were possible (Table III and Figure 2) and these were confirmed by a series of decoupling experiments. Coupling constants for the ring protons were 7.5 ± 0.1 Hz. Measurement of the ^1H NMR spectra of CD_2Cl_2 solutions of $[Re(CNAr)_6][ReCl_4(CNAr)_2]$, after these solutions had been incubated in the dark at room temperature for several days, showed the growth of several new resonances which we attribute to the isomerization of some of the [*trans*-$ReCl_4(CNAr)_2]^-$ to the related cis isomer. This characteristic was observed for the phenyl, xylyl, and mesityl isocyanide derivatives and parallels the electrochemical behavior of such solutions (vide supra). These data, which are also presented in Table III, show that the cis anions exhibit stronger Knight shifts compared to the corresponding trans isomers, a property which probably reflects the effect of increased π backbonding of the unpaired electron density into the π^* orbitals of the pair of mutually *cis*-isocyanide ligands.

The third and final type of rhenium(III) complex to be isolated was the neutral species $ReCl_3(CNmesityl)_3$. While its IR spectrum shows three ν(Re–Cl) modes (323 (s), 293 (s), and 278 (s) cm^{-1}), consistent with a *mer* configuration, there are only two resolvable ν(C≡N) bands (Nujol mull, 2198 (m-s), 2160 (s) cm^{-1}; CH_2Cl_2 solution, 2188 (s), 2163 (s) cm^{-1}). It may be that the more intense band envelope at ca. 2160 cm^{-1} contains two accidentally degenerate vibrations since the *mer* configuration is supported by the ^1H NMR spectrum of this complex (measured at 200 MHz in CD_2Cl_2) which shows a 2:1 ratio of phenyl proton resonances at δ +7.09 and +6.83, and a 4:2:2:1 ratio of methyl proton resonances (δ +2.55, +2.54, +2.41, and +2.28). Although the resonances at δ +2.54 and +2.41 cannot be unequivocally assigned, it seems reasonable to assign the resonance at δ +2.41 to the *p*-CH_3 protons of the two chemically equivalent rings and that at δ +2.54 to the *o*-CH_3 protons to the unique ring. This follows from the chemical shift differences that exist between the *o*- and *p*-CH_3 proton resonances for $[Re(CNmesityl)_6]PF_6$ (Table III). Accordingly, the intensity pattern (relative intensities in parentheses) and assignments are actually *o*-CH_3, δ +2.55 (4), *o'*-CH_3, δ +2.54 (2), *p*-CH_3, δ +2.41 (2), and *p'*-CH_3, δ +2.28 (1), where *o'* and *p'* signify the protons associated with the unique ring. A distinctive feature of the ^1H NMR spectral properties of *mer*-$ReCl_3(CNmesityl)_3$ is that the resonances are not subject to Knight shifting, a surprising result in view of the usual paramagnetism of mononuclear magnetically dilute rhenium(III) complexes.[35] However, the spectroscopic characteristics of this d^4 rhenium(III) complex are consistent with the diamagnetism of its CH_2Cl_2 solutions as measured by the Evans method. This result contrasts with the Knight shifts occurring in the ^1H NMR spectra of the chloro anions $[ReCl_4(CNAr)_2]^-$ (vide supra).

The neutral complex *mer*-$ReCl_3(CNmesityl)_3$ dissolves in acetonitrile to give essentially nonconducting solutions ($\Lambda_M = 5\ \Omega^{-1}\ cm^2$ for $C_M = 1.0 \times 10^3$ M), while cyclic voltammograms of its solutions in 0.2 M TBAH–CH_2Cl_2 (Figure 1d) show a reversible oxidation at +1.55 V vs. SCE and an irreversible reduction at ca. –0.80 V vs. SCE in the scan rate range 50–600 mV/s. The latter reduction process is followed, on the reverse scan, by the formation of chemical product(s), as signaled by the appearance of product waves at $E_{p,a}$ = +0.17 and +0.90 V vs. SCE. At this time, the nature of these products remains uncertain, although we can rule out the formation of either $[Re(CNmesityl)_6]^+$ or $[ReCl_4(CNmesityl)_2]^-$ (see Table I).

(c) Halogenation of $[Re(CNPh)_6]^+$. The homoleptic aryl isocyanide species $[Re(CNAr)_6]^+$ display the same general lack of substitutional lability (e.g., toward phosphine ligands) as do their alkyl isocyanide counterparts.[3] However, like the latter they react with the halogens Cl_2 and Br_2 to produce the salts $[Re(CNAr)_6X](PF_6)_2$ that have been isolated and characterized by IR spectroscopy and electrochemistry in the case of Ar = Ph. Both complexes exhibit ν(C≡N) modes in their IR spectra at frequencies (~2200 cm^{-1}) typical of rhenium(III) species.[3] The cyclic voltammogram of a 0.2 M TBAH–CH_2Cl_2 solution of $[Re(CNPh)_6Cl](PF_6)_2$, like that of its *tert*-butyl isocyanide analogue, is dominated by an irreversible reduction at $E_{p,c}$ = –0.42 V vs. SCE, a potential ca. 0.8 V more positive than that of $[Re(CN\text{-}t\text{-}Bu)_6Cl](PF_6)_2$.[3] This difference reflects the greater π-acceptor capability of PhNC compared to *t*-BuNC and therefore its ability to more effectively stabilize the rhenium(I) oxidation state following this (two-electron) reduction. Electrolysis of a solution of $[Re(CNPh)_6Cl](PF_6)_2$ at a potential of –0.6 V led to the formation of $[Re(CNPh)_6]^+$ as monitored by cyclic voltammetry ($E_{1/2}$ = +1.17 V). In the case of the cyclic voltammogram of $[Re(CNPh)_6Br](PF_6)_2$, the corresponding irreversible reduction is now at –0.10 V vs. SCE, a potential which clearly reflects its ease of reduction to $[Re(CNPh)_6]^+$. Indeed, we have been unable to prepare a pure sample of this bromo derivative since in all instances it was contaminated with $[Re(CNPh)_6]PF_6$.

(d) Mechanistic Considerations. The conversion of the $[Re_2Cl_8]^{2-}$ anion to [*trans*-$ReCl_4(CNAr)_2]^-$ and *mer*-$ReCl_3(CNAr)_3$ bears an interesting relationship to the photochemical cleavage of $[Re_2Cl_8]^{2-}$ in acetonitrile.[6] In this latter reaction, the [*trans*-$ReCl_4(NCCH_3)_2]^-$ anion is the primary photoproduct and is converted to $ReCl_3(NCCH_3)_3$ by a second photolysis. Thus there is a striking similarity between this photochemical reaction[6] and the thermal cleavage of $[Re_2Cl_8]^{2-}$ by aryl isocyanides. We have no evidence that our reactions have a significant photochemical contribution to them, since they proceed in an identical manner in the dark. While there is little doubt that a weak adduct of the type $[Re_2Cl_8(CNAr)_2]^{2-}$ (containing axially bound ArNC ligands) is the initial species to be formed, we have been unable to isolate any intermediates on the way to $[trans\text{-}ReCl_4(CNAr)_2]^-$. However, bearing in mind the well-established reaction chemistry of the $[Re_2Cl_8]^{2-}$ anion,[24] it is not unreasonable that the next step is loss of chloride ion and the formation of $Re_2Cl_6(CNAr)_2$, which may or may not possess a Re–Re quadruple bond. A structure of the type $(ArNC)Cl_2Re(\mu\text{-}Cl)_2ReCl_2(CNAr)$ with an open coordination site on each rhenium trans to the ArNC ligand is feasible. If so, then further reaction with ArNC might be expected to ensue to give $(ArNC)_2Cl_2Re(\mu\text{-}Cl)_2ReCl_2(CNAr)_2$ with mutually trans pairs of isocyanide ligands. This complex could then react with the free chloride ion present, with resulting disruption of the Re–Cl–Re bridges and the formation of the kinetic isomer [*trans*-$ReCl_4(CNAr)_2]^-$. Since both [*trans*-$ReCl_4(CNAr)_2]^-$ and $ReCl_3(CNAr)_3$ are known to react further with an excess of ArNC, with resulting reductive substitution of the rhenium(III) centers to give $[Re(CNAr)_6]^+$, this same reaction course can be expected to occur here. Note that these reactions differ from the photochemical cleavage of $[Re_2Cl_8]^{2-}$ by acetonitrile in that the latter terminate at the stage [*trans*-$ReCl_4(NCCH_3)_2]^-$ or $ReCl_3(NCCH_3)_3$. This is expected since, in contrast to ArNC, acetonitrile is not particularly effective in stabilizing very low oxidation states of the early transition series.

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One of the striking features of this work and previous studies dealing with the cleavage of multiple M–M bonds by isocyanides[3,36] is the rarity of isolable "intermediates" that contain these ligands bound to multiply bonded dimetal units. It seems likely that thermodynamic factors dominate, thereby leading to the electronically saturated 18-electron mononuclear species that are invariably the final products of such reactions. Interestingly, Chisholm and co-workers[37] have recently found that upon reacting the triply bonded $Mo_2(OR)_4(R'COCHCOR')_2$ complexes (R′ = Me or *t*-Bu) with *tert*-butyl isocyanide, the dinuclear species $Mo_2(OR)_2(\mu\text{-}OR)_2(R'COCHCOR')_2(CN\text{-}t\text{-}Bu)_2$ are formed. It may be that the kinetic inertness of these species[37] to cleavage by excess isocyanide is related to the stability of the Mo–(β-diketonate) ring; the absence of metal–ligand dissociation can clearly stabilize these molecules to further reaction with RNC.

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Registry No. $[Re(CNPh)_6]PF_6$, 87829-81-0; $[Re(CNPh)_6][trans\text{-}ReCl_4(CNPh)_2]$, 87829-83-2; $[Re(CN\text{-}p\text{-}tol)_6]PF_6$, 64294-09-3; $[Re(CN\text{-}p\text{-}tol)_6][trans\text{-}ReCl_4(CN\text{-}p\text{-}tol)_2]$, 87829-85-4; $[Re(CNxylyl)_6]PF_6$, 87829-87-6; $[Re(CNxylyl)_6][trans\text{-}ReCl_4(CNxylyl)_2]$, 87829-89-8; $[Re(CNxylyl)_6][cis\text{-}ReCl_4(CNxylyl)_2]$, 87861-08-3; $[Re(CNxylyl)_6]_2Re_2Cl_8$, 87829-90-1; $[Re(CNmesityl)_6]PF_6$, 87829-92-3; $[Re(CNmesityl)_6][trans\text{-}ReCl_4(CNmesityl)_2]$, 87829-94-5; $[Re(CNmesityl)_6][cis\text{-}ReCl_4(CNmesityl)_2]$, 87861-10-7; $Re_2(O_2CCH_3)_4Cl_2$, 14126-96-6; $(n\text{-}Bu_4N)_2Re_2Cl_8$, 14023-10-0; $ReCl_3(CNmesityl)_3$, 87829-95-6; $Re_2Cl_6(PEtPh)_2$, 55661-10-4; $Re_2H_8(PPh_3)_4$, 66984-37-0; $[Re(CNPh)_6Cl](PF_6)_2$, 87829-97-8; $[Re(CNPh)_6Br](PF_6)_2$, 87829-99-0.

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Synthesis and Substitution Reactions of $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$. The Crystal and Molecular Structure of $Mo(\eta^6\text{-}PhPMePh)(CNCMe_3)(PMePh_2)_2$

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The complex $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$, **1**, is readily prepared in one step by reducing a mixture of Mo_2Cl_{10} and 8 mol of $PMePh_2$ in THF with magnesium under argon. There is evidence for molybdenum complexes in oxidation states IV, II, and 0 as intermediates in the high-yield reduction process. Complex **1** reacts with 1 mol of the strongly coordinating ligands L = $P(OMe)_3$, $CNCMe_3$, and CO at 25 °C to give monosubstituted complexes $Mo(\eta^6\text{-}PhPMePh)(L)(PMePh_2)_2$, **2–4**, respectively. Use of excess ligand results in disubstituted products. Only ligands that are sterically smaller than $PMePh_2$ including N_2, PMe_2Ph, PMe_3, and C_2H_2 react with **1**; PPh_3 and $P(C_6H_{11})_3$ do not react. Carbon monoxide uptake kinetics indicate that dissociation of a σ-bonded ligand from **1** is the rate-determining step for these reactions; rate = $k_1[\mathbf{1}]$, $k_1(303\ K) = (1.5 \pm 0.1) \times 10^{-3}\ s^{-1}$, $\Delta H^* = 28.8 \pm 1.6$ kcal mol^{-1}, and $\Delta S^* = 23 \pm 5$ eu. The σ-bonded $PMePh_2$ ligands in **2–4** are diastereotopic and give ABX or AB ^{31}P NMR spectra. The ^{31}P chemical shift of the η^6-PhPMePh ligand is sensitive to the electronic and/or steric properties of the σ-bonded ligands. Compound **3**, $Mo(\eta^6\text{-}PhPMePh)(CNCMe_3)(PMePh_2)_2$, has been studied by X-ray crystallography. It crystallizes in the monoclinic space group $P2_1$ with cell dimensions $a = 9.256$ (3) Å, $b = 11.497$ (3) Å, $c = 18.782$ (10) Å, $\beta = 103.92$ (4)°, $V = 1940$ Å^3, and $D_{calcd} = 1.33$ g cm^{-3} for $Z = 2$. The structure was solved by the heavy-atom method and refined by least-squares and Fourier methods to final residuals $R = 0.0635$ ($R_w = 0.0785$) for 2755 observed ($I > 2\sigma(I)$) reflections. The geometry about the molybdenum is distorted octahedral. Principal dimensions are Mo–P = 2.416 (3) and 2.420 (3) Å, Mo–C(isocyanide) = 1.984 (13) Å, and Mo–C(arene) = 2.24 (1)–2.32 (1) Å. Angles in the $MoP_2(CNCMe_3)$ tripod indicate that the bulky phosphines have moved from ideal octahedral positions toward the $CNCMe_3$ ligand to minimize steric repulsions. The $CNCMe_3$ ligand is nonlinear (C–N–C = 150 (1)°) and is the closest ligand in the tripod to the PMePh group on the η^6 ring.

Introduction

The complex $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ (**1**)[1] is an unusual member of the class of compounds $Mo(\eta^6\text{-}arene)(PR_3)_3$ first synthesized by Green and Silverthorn.[2] Its preparation (eq 1) is the simplest yet described for such

$$Mo_2Cl_{10} + 8PMePh_2 + 5Mg \xrightarrow[THF]{Ar} 2\,\mathbf{1} + 5MgCl_2 \tag{1}$$

complexes,[2,3] and it appears to be unique in containing labile σ-bonded ligands that are substituted by a range of

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