°C and $[\alpha]_D$ (equilibrium) −37.3° (*c* 1.07, CH_2Cl_2). ^1H NMR ($CDCl_3$; **5b**:**5a** ca. 1.83:1): δ 1.94 (s, 3.9, $AsMe_{5a}$), 2.00 (s, 2.1, $AsMe_{5b}$), 2.28 (br s, 6, $AsMe_{5a,b}$), 2.81 (s, 3.9, SMe_{5a}), 3.28 (s, 2.1, SMe_{5b}), 3.37 (br s, 6, $SMe_{5a,b}$), 7.3–7.7 (m, 14, aromatics). ^{13}C NMR ($CDCl_3$): δ 9.11 (s, $AsMe_{5a}$), 14.80 (s, $AsMe_{5a}$), 10.36 (s, $AsMe_{5b}$), 13.55 (s, $AsMe_{5b}$), 41.85 (s, SMe_{5a}), 45.38 (s, SMe_{5a}), 41.05 (s, SMe_{5b}), 46.57 (s, SMe_{5b}) 128–143 (m, aromatics), 194.76, 195.10 (s, $CO_{5a,5b}$). IR (CH_2Cl_2): 1978 (ν_{co}), 1103 cm^{-1} (ν_{SO}).

The following compounds were prepared similarly. **[*OC*-6-32-(*A*,*C*)-(*RR*,*SS*)]-(RuCl$_2$(CO)(diars)(Me$_2$*S*O-*S*)] (structure 5a and its enantiomorph in the solid state)**: white needles; mp 284–285 °C dec (91% yield); ^1H NMR and IR spectra identical with those of the pure epimer. **[*OC*-6-(34,43)-*A*-(*RS*)]-[RuCl$_2$(CO)(diars)(Me$_2$SO-*S*)] (structure 5c and its enantiomorph)**: white needles; mp 281–282 °C dec (yield 93%); ^1H NMR ($CDCl_3$) δ 2.26 (s, 3, AsMe), 2.29 (s, 3, AsMe), 3.31 (s, 3, SMe), 3.41 (s, 3, SMe), 7.3–7.8 (m, 14, aromatics); IR (CH_2Cl_2) 1983 (ν_{CO}), 1103 cm^{-1} (ν_{SO}). **[*OC*-6-43-*A*-(*SS*)]-[RuCl$_2$(CO)(diphos)(Me$_2$SO-*S*)]**: white needles; mp 238–242 °C (yield 92%); $[\alpha]_D$ (equilibrium) −58.9° (*c* 0.774, CH_2Cl_2); ^1H NMR (CH_2Cl_2; **5b**:**5a** ca. 1.2:1) δ 2.12 (d, J_{PH} = 9.7 Hz, PMe_{5b}), 2.19 (d, J_{PH} = 9.9 Hz, PMe_{5a}), 2.39 (d, J_{PH} = 11.7 Hz, PMe_{5b}), 2.51 (br s, SMe_{5a}), 3.10 (br s, SMe_{5b}), 3.22 (br s, $SMe_{5a,b}$), 7.3–7.8 (br m, aromatics); IR (CH_2Cl_2) 1983 (ν_{CO}), 1102 cm^{-1} (ν_{SO}). **[*OC*-6-43-(*A*,*C*)-(*RR*,*SS*)]-[RuCl$_2$(CO)(diphos)(Me$_2$SO-*S*)]**: white prisms; mp >300 °C (yield 92%); ^1H NMR and IR spectra identical with those of the pure epimer. The sample for X-ray structural analysis was obtained by slow crystallization of this material from a $Me_2SO/MeOH/H_2O$ mixture. **[*OC*-6-(53-*A*-,54-*C*)-(*RS*)]-[RuCl$_2$(CO)(diphos)(Me$_2$SO-S)] (structure 5c and its enantiomorph)**: white needles; mp 250–255 °C (yield 93%); ^1H NMR (CH_2Cl_2) δ 2.36 (d, 3, J_{PH} = 12.0 Hz, PMe), 2.42 (d, 3, J = 11.9 Hz, PMe), 3.17 (s, 3, SMe), 3.30 (s, 3, SMe), 7.3–7.85 (m, 14, aromatic); ^{13}C NMR ($CDCl_3$) δ 12.50 (d, 1, J_{PC} = 40.05 Hz, PMe), 12.55 (d, 1, J_{PC} = 28.61 Hz, PMe), 40.65 (d, 1, J_{PC} = 2.79 Hz, S(O)Me), 45.66 (s, 1, S(O)Me), 128–146 (m, 14, aromatics), 194.63 (t, 1, J_{PC} = 13–16 Hz, CO); IR (CH_2Cl_2) 1991 (ν_{CO}), 1103 cm^{-1} (ν_{SO}).

The Me_2SO derivatives can also be prepared in high yield from the appropriate cis complexes. The Me_2SO-d_6 compounds were prepared from the appropriate dicarbonyl precursors by reacting them with a tenfold excess of Me_2SO-d_6 in boiling 2-methoxypropanol for 3 h. The products were isolated by evaporating the solvent and recrystallizing the residue as described for the non-deuterated compounds.

Acknowledgment. This work was supported by the Australian Research Grants Committee.

Registry No. [*OC*-6-33-(*SS*)]-[RuCl$_2$(CO)$_2$(diars)], 82338-42-9; [*OC*-6-33-(*RR*,*SS*)]-[RuCl$_2$(CO)$_2$(diars)], 82373-33-9; [*OC*-6-13-(*SS*)]-[RuCl$_2$(CO)$_2$(diphos)], 82338-43-0; [*OC*-6-13-(*RR*,*SS*)]-[RuCl$_2$(CO)$_2$(diphos)], 82373-34-0; [*OC*-6-44-(*RS*)]-[RuCl$_2$(CO)$_2$(diars)], 82373-34-0; [*OC*-6-44-(*RS*)]-[RuCl$_2$(CO)$_2$(diars)], 82373-35-1; [*OC*-6-14-(*RS*)]-[RuCl$_2$(CO)$_2$(diphos)], 82373-36-2; [*OC*-6-32-*A*-(*SS*)]-[RuCl$_2$(CO)$_2$(diars)], 82373-37-3; [*OC*-6-32-(*A*,*C*)-(*RR*,*SS*)]-[RuCl$_2$(CO)$_2$(diars)], 82373-38-4; [*OC*-6-32-(*A*,*C*)-(*RR*,*SS*)]-[RuCl$_2$(CO)$_2$(diphos)], 82373-39-5; [*OC*-6-(43,34)-*A*-(*RS*)]-[RuCl$_2$(CO)$_2$(diars)], 82373-40-8; [*OC*-6-23-(*RS*-*SS*)]-[RuCl(CO)$_3$(diphos)]Cl, 82338-44-1; [*OC*-6-(24,34)-(*RS*)]-[RuCl(CO)$_3$(diphos)]Cl, 82373-41-9; *meso*-[((*RR*)-diars)(CO)ClRu(μ-Cl)$_2$RuCl(CO)((*SS*)-diars)], 82338-45-2; *meso*-[((*RR*)-diphos)(CO)ClRu(μ-Cl)$_2$RuCl(CO)((*SS*)-diphos)], 82338-46-3; *anti*-[((*RS*)-diars)(CO)ClRu(μ-Cl)$_2$RuCl(CO)((*RS*)-diars)], 82373-42-0; *anti*-[((*RS*)-diphos)(CO)ClRu(μ-Cl)$_2$RuCl(CO)((*RS*)-diphos)], 82373-43-1; [*OC*-6-32-*C*-(*CS*)]-[RuCl$_2$(CO)(diars)(Me$_2$SO-*S*)], 82373-32-8; [*OC*-6-32-*A*-(*SS*)]-[RuCl$_2$(CO)(diars)(Me$_2$SO-*S*)], 82373-31-7; [*OC*-6-32-(*A*,*C*)-(*RR*,*SS*)]-[RuCl$_2$(CO)(diars)(Me$_2$SO-*S*)], 82338-41-8; [*OC*-6-(34,43)-*A*-(*RS*)]-[RuCl$_2$(CO)(diars)(Me$_2$SO-*S*)], 82398-54-7; [*OC*-6-43-*A*-(*SS*)]-[RuCl$_2$(CO)(diphos)(Me$_2$SO-*S*)], 82373-30-6; [*OC*-6-43-(*A*,*C*)-(*RR*,*SS*)]-[RuCl$_2$(CO)(diphos)(Me$_2$SO-*S*)], 82442-83-9; [*OC*-6-(53-*A*,54-*C*)-(*RS*)]-[RuCl$_2$(CO)(diphos)(Me$_2$SO-*S*)], 82373-29-3; [RuCl$_2$(CO)$_2$]$_n$, 28986-72-3; [RuCl$_2$(CO)$_3$]$_2$, 22594-69-0; [*OC*-6-43-*C*-(SS)]-[RuCl$_2$(CO)(diphos)(Me$_2$SO-*S*)], 82338-40-7.

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Reactions of Alkyl Isocyanides with Polyhydride Complexes of Rhenium and with Binuclear Dirhenium Complexes Containing Quadruple or Triple Bonds: Nonreductive and Reductive Cleavage of Re–Re Multiple Bonds To Afford Mononuclear Isocyanide Complexes of Rhenium(I) and Rhenium(III)

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Received March 2, 1982

Treatment of the dinuclear quadruply bonded complexes $Re_2(O_2CR)_4Cl_2$ (R = CH_3 or C_6H_5) with alkyl isocyanides (RNC; R = CMe_3 or C_6H_{11}) affords solutions from which salts of the $[Re(CNR)_6]^+$ cations can be isolated in good yield. While $[Re(CNR)_6]^+$ is inert to substitution by monodentate tertiary phosphines, routes to species of the type $[Re(CNR)_4(PR_3)_2]^+$ are afforded by (a) the reductive cleavage of the triply bonded complexes $Re_2Cl_4(PR_3)_4$ by RNC ligands or (b) the reductive elimination of H_2 from the polyhydride complexes $ReH_7(PR_3)_2$ and $ReH_5(PR_3)_2L$ in the presence of an excess of RNC. In contrast to the preceding reductive-cleavage reductions, the "halide-rich" salts $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl or Br) react with *tert*-butyl isocyanide to give mononuclear seven-coordinate rhenium(III) species $[Re(CNCMe_3)_5X_2]^+$, which have been isolated as their PF_6^- salts. The mixed isocyanide–halide–phosphine complexes of rhenium(III) $[Re(CNCMe_3)_4(PEtPh_2)Cl_2]PF_6$ and $[Re(CNCMe_3)_3(dppe)Cl_2]PF_6$ (dppe = $Ph_2PCH_2CH_2PPh_2$) are likewise prepared by isocyanide cleavage of quadruply bonded $Re_2Cl_6(PEtPh_2)_2$ and dimeric $Re_2Cl_6(dppe)_2$ (the latter containing $Re(\mu\text{-}Cl)_2Re$ bridges but no Re–Re bond). The spectroscopic and electrochemical properties of these complexes are reported, and the significance of the cleavage reactions by π-acceptor ligands (such as RNC) is discussed in the context of their constituting an important synthetic route to mononuclear transition-metal complexes.

Introduction

While six-coordinate homoleptic rhenium(I) isocyanide species of the type $[Re(CNR)_6]^+$ have been known for many years,[1] little in the way of reaction chemistry or photochemistry of these systems has been developed, particularly when contrasted with the more thoroughly studied manganese systems.[1-3] The synthetic methods available for their preparation include the reactions of alkyl and aryl isocyanides with starting

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materials as varied as Re_3I_9,[4] $ReNI_2(PPh_3)_2$,[5] and $Re(CO)_5X$ (X = Cl or Br).[6] However, the yields of the desired complexes either are very low[6] or have not been reported,[4,5] making it difficult to judge the effectiveness of these procedures.

Perhaps the best characterized rhenium(I) isocyanide complexes are the mixed carbonyl–isocyanide derivatives of the types $Re(CO)_{5-n}(CNR)_nBr$ and $[Re(CO)_{6-n}(CNR)_n]PF_6$, where R = CH_3 or *p*-tolyl, which have been prepared from the pentacarbonyl halides $Re(CO)_5X$ (X = Cl or Br).[1] The mixed halide–isocyanide complexes of rhenium(III) constitute another group of such derivatives. While some synthetic procedures such as the oxidative addition of bromine to $Re(CO)(CNR)_4Br$ to give seven-coordinate $Re(CNR)_4Br_3$[7] and the conversion of the trinuclear rhenium(III) halides Re_3X_9 (X = Cl, Br, or I) to the adducts $Re_3X_9(CNR)_3$[8,9] are perfectly logical, others[8,10] are not. In particular, the reactions between K_2ReX_6 (X = Br or I) and alkyl and aryl isocyanides are dependent on the nature of X, the isocyanide, and the reaction conditions,[8,10] and the various products so obtained remain inadequately characterized.

We have been striving to develop the use of multiply bonded dinuclear complexes as synthetic starting materials for mononuclear complexes, with particular emphasis being placed at present upon reactions with the π-acceptor CO, NO, and alkyl and aryl isocyanide ligands.[11-17] From these studies along with those reported by other groups,[18-22] both reductive and nonreductive cleavage of metal–metal triple and quadruple bonds have been recognized as important reaction pathways. The extension of our studies to include the reactions between alkyl isocyanides and multiply bonded dinuclear complexes of rhenium are reported in the present paper. These reactions constitute an excellent synthetic route to homoleptic isocyanide complexes of rhenium(I) and, depending upon the nature of the dirhenium starting material, also to mixed halide–isocyanide species of rhenium(III). Additionally, we have found that the reactions between RNC ligands and mononuclear polyhydride complexes of rhenium proceed with the reductive elimination of H_2 and the formation, in high yield, of isocyanide complexes of rhenium(I). We have previously reported preliminary information of certain of these reactions,[16,23] and herein we describe the results of these studies in full detail.

Experimental Section

Starting Materials. The following compounds were prepared by standard procedures: $Re_2(O_2CR)_4Cl_2$ (R = CH_3 or C_6H_5),[24] $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl or Br),[25] $Re_2Cl_6(PEtPh_2)_2$,[26] $Re_2Cl_6(Ph_2PCH_2CH_2PPh_2)_2$,[27] $Re_2Cl_4(PR_3)_4$ (R = Et or *n*-Pr),[26] $ReH_7(PR_3)_2$ (PR_3 = PPh_3 or $PEtPh_2$),[28] $ReH_5(PPh_3)_2L$ (L = PPh_3, PEt_2Ph, $C_6H_{11}NH_2$, $C_5H_{10}NH$, or C_5H_5N),[28] and *tert*-butyl and cyclohexyl isocyanides.[29] Tertiary phosphines (including 1,2-bis(diphenylphosphino)ethane, dppe) and all other reagents and solvents were purchased from commercial sources and used as received.

Reaction Procedures. All reactions were carried out under a nitrogen atmosphere, and all solvents were deoxygenated prior to use by purging with nitrogen gas.

A. Reactions of $Re_2(O_2CR)_4Cl_2$. (i) $[Re(CNCMe_3)_6]PF_6$. A quantity of *tert*-butyl isocyanide (0.60 mL, 5.7 mmol) was syringed into a stirred suspension of $Re_2(O_2CCH_3)_4Cl_2$ (0.456 g, 0.67 mmol) in 20 mL of methanol. The reaction mixture was refluxed for 6 h, during which time the orange suspension dissolved and a brown solution formed. The solution was taken to dryness, 20 mL of a saturated solution of KPF_6 in acetone was added, and the mixture was stirred for 1 h. The solution was again taken to dryness and the residue redissolved in 2-propanol. Diethyl ether was added dropwise until the solution clouded. The solution was chilled and then filtered, yielding 0.67 g of tan crystals, which were washed with diethyl ether and dried in vacuo. Anal. Calcd for $C_{30}H_{54}F_6N_6PRe$: C, 43.42; H, 6.56; N, 10.13. Found: C, 43.14; H, 6.53; N, 11.15. The yield was 60%. IR (Nujol mull): $\nu(C{\equiv}N)$ 2100 (s), 2060 (s) cm^{-1}.

When this same procedure was used for the benzoate complex $Re_2(O_2CPh)_4Cl_2$, the reaction proceeded much more rapidly than for the acetate possibly due to the much greater solubility of this complex in the reaction solvent. The tetraphenylborate salt $[Re(CNCMe_3)_6]BPh_4$ can be produced by substituting a $NaBPh_4$-saturated solution of methanol for the acetone solution of KPF_6 in the above procedure. This complex was identified on the basis of its spectroscopic (IR and ^1H NMR) properties.

(ii) $[Re(CNC_6H_{11})_6]PF_6$. A procedure similar to that in A(i) but with 1 mL (7.8 mmol) of cyclohexyl isocyanide and a 10:1 diethyl ether–petroleum ether reaction solvent yielded a pink product. Anal. Calcd for $C_{42}H_{66}F_6N_6PRe$: C, 51.16; H, 6.69. Found: C, 50.64; H, 6.63. The yield was 55%. Its spectroscopic and electrochemical properties were in accord with this formulation. IR (Nujol mull): $\nu(C{\equiv}N)$ 2085 (s), 2048 (sh) cm^{-1}.

B. Reactions of $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl or Br). (i) $[Re(CNCMe_3)_5Cl_2]PF_6\cdot{}^1/_2CH_2Cl_2$. A mixture of *tert*-butyl isocyanide (0.65 mL, 6.2 mmol) and $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.383 g, 0.336 mmol) in 25 mL of methanol was stirred for 2 days. The initial blue color gave way to a red-brown solution during this period. The solution was reduced in volume under a stream of nitrogen, and 0.23 g of KPF_6 dissolved in 15 mL of acetone was added. The resulting mixture was stirred for 15 min and taken to dryness under nitrogen. The residue was stirred with dichloromethane and filtered to remove excess KPF_6. A creamy white product was obtained by the addition of a 1:1 diethyl ether–hexane mixture to the filtrate. Anal. Calcd for $C_{25.5}H_{46}Cl_3F_6N_5PRe$: C, 35.61; H, 5.40. Found: C, 35.52; H, 5.66. The yield was 60%. IR (Nujol mull): $\nu(C{\equiv}N)$ 2258 (m), 2205 (s), 2055 (w) cm^{-1}; $\nu(C\text{-}Cl)$ of lattice CH_2Cl_2 740 (m-w) cm^{-1}.

(ii) $[Re(CNC(CH_3)_3)_5Br_2]PF_6\cdot(CH_3)_2CO$. A cream-colored product was obtained by a procedure analogous to that in B(i) above using

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$(n\text{-}Bu_4N)_2Re_2Br_8$. The product was purified by recrystallization from acetone–diethyl ether (3:1). Anal. Calcd for $C_{27}H_{51}Br_2F_6N_5PRe$: C, 35.02; H, 5.44. Found: C, 34.86; H, 5.33. The yield was 60%. IR (Nujol mull): ν(C≡N) 2250 (m), 2200 (s), 2060 (w) cm^{-1}; ν(C═O) of lattice acetone 1710 (m) cm^{-1}.

C. Reaction of $Re_2Cl_6(PEtPh_2)_2$. $[Re(CNCMe_3)_4(PEtPh_2)Cl_2]PF_6$. *tert*-Butyl isocyanide (0.60 mL, 5.7 mmol) was syringed into a solution of 0.2 g of $Re_2Cl_6(PEtPh_2)_2$ in 15 mL of methanol. The reaction mixture was stirred and warmed gently for 1 h. After this period the solution was taken to dryness under a stream of nitrogen, 0.05 g of KPF_6 in 10 mL of acetone was added to the remaining solid, and the solution was stirred for an additional 10 min. A yellow solid was then obtained upon the slow addition of a 1:1 diethyl ether–hexane mixture. The product was recrystallized from a dichloromethane–diethyl ether mixture. Anal. Calcd for $C_{34}H_{51}F_6Cl_2N_4P_2Re$: C, 43.03; H, 5.42. Found: C, 42.50; H, 5.40. The yield was 70%. IR (Nujol mull): ν(C≡N), 2233 (m), 2200 (sh), 2180 (s), 2151 (s) cm^{-1}.

D. Reactions of $Re_2Cl_4(PR_3)_4$ (R = Et or *n*-Pr). (i) $[Re(CNCMe_3)_4(P\text{-}n\text{-}Pr_3)_2]PF_6$. A suspension of $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ (0.2 g, 0.17 mmol) in 10 mL of acetone was treated with an excess of *tert*-butyl isocyanide (1.0 mL, 9.5 mmol), and the mixture was stirred for 1 h and then treated with solid KPF_6 (0.05 g). The reaction solution was evaporated to dryness, the residue treated with dichloromethane (20 mL), and the mixture filtered. An equal volume of diethyl ether was added to the filtrate, which upon cooling to −40 °C afforded a pink microcrystalline product. Anal. Calcd for $C_{38}H_{78}F_6N_4P_3Re$: C, 46.37; H, 7.99. Found: 47.18; H, 8.29. The yield was 69%. IR (Nujol mull): ν(C≡N) 2085 (sh), 2035 (s) cm^{-1}.

(ii) $[Re(CNCMe_3)_4(PEt_3)_2]PF_6$. This complex was prepared in 49% yield with use of a procedure analogous to that in D(i) with $Re_2Cl_4(PEt_3)_4$ as the starting material. The identity of the product was confirmed by its spectroscopic and electrochemical properties. IR (Nujol mull): ν(C≡N) 2085 (sh), 2035 (s) cm^{-1}.

E. Reaction of $Re_2Cl_6(dppe)_2$. $[Re(CNCMe_3)_3(dppe)Cl_2]PF_6\cdot{}^1/_2CH_2Cl_2$. A suspension of $Re_2Cl_6(dppe)_2$ (0.2 g, 0.15 mmol) in acetone (10 mL) was treated with *tert*-butyl isocyanide (1 mL, 9.5 mmol). When the reaction mixture was refluxed, the red suspension dissolved slowly to give a clear yellow solution. After 24 h this solution was treated with solid KPF_6 (0.05 g), stirred, and then taken to dryness. The residue was extracted with dichloromethane, the solution was filtered, and diethyl ether added dropwise to the filtrate to precipitate the desired yellow complex. Anal. Calcd for $C_{41.5}H_{52}Cl_3F_6N_3P_3Re$: C, 45.62; H, 4.80. Found: C, 45.36; H, 5.19. IR (Nujol mull): ν(C≡N) 2205 (m), 2160 (s) cm^{-1}. The ^1H NMR spectrum of a solution of this complex in $CDCl_3$ exhibited a resonance at δ 5.25 arising from the CH_2Cl_2 solvent of crystallization in addition to the normal Me_3CNC and dppe resonances.

F. Halogenation Reactions of $[Re(CNCMe_3)_6]PF_6$. (i) $[Re(CNCMe_3)_6Cl](PF_6)_2$. Chlorine gas was bubbled into a stirred solution of $[Re(CNCMe_3)_6]PF_6$ (0.139 g, 0.167 mmol) and KPF_6 (0.03 g, 0.17 mmol) in 20 mL of dichloromethane. After 10 min the chlorine gas flow was shut off and the system purged with nitrogen gas, and the resulting white solid that separated was filtered off, washed with 2-propanol and diethyl ether, and dried in vacuo. The product was purified by recrystallization from a dichloromethane–hexane–diethyl ether mixture (3:1:1). Anal. Calcd for $C_{30}H_{54}ClF_{12}N_6P_2Re$: C, 35.66; H, 5.39; N, 8.32. Found: C, 35.38; H, 5.46; N, 8.61. The yield was 89%.

(ii) $[Re(CNCMe_3)_6Br](PF_6)_2\cdot1^1/_2CH_2Cl_2$. Liquid bromine (0.50 mL, 9.2 mmol) was added to a stirred solution of $[Re(CNCMe_3)_6]PF_6$ (0.136 g, 0.164 mmol) and KPF_6 (0.03 g, 0.17 mmol) in 20 mL of dichloromethane. A pale yellow precipitate formed immediately. The solution was stirred an additional 15 min, and the solid was separated by filtration, washed with water, 2-propanol, and diethyl ether, and dried in vacuo. The pale yellow product was recrystallized from a dichloromethane–2-propanol mixture (2:1). The yellow color fades with successive recrystallizations. Anal. Calcd for $C_{31.5}H_{57}BrCl_3F_{12}N_6P_2Re$: C, 32.00; H, 5.00. Found: C, 32.00; H, 4.86. The yield was 85%. The presence of lattice CH_2Cl_2 was in accord with the ^1H NMR (δ 5.25) and IR (ν(C–Cl) at 745 cm^{-1}) spectral properties of this complex.

(iii) $[Re(CNCMe_3)_6I](PF_6)_2$. A mixture of iodine (0.317 g, 1.25 mmol), $[Re(CNCMe_3)_6]PF_6$ (0.302 g, 0.363 mmol), and KPF_6 (0.070 g, 0.38 mmol) in 20 mL of chloroform was refluxed for 5 min. The solution was reduced to dryness under nitrogen, a copious amount of benzene was added to the residue, and the mixture was stirred for 15 min. Filtration yielded a brown product, which was repeatedly washed with benzene and diethyl ether and dried in vacuo; yield 93%. This product was identified on the basis of its spectroscopic properties.

G. Reactions of $ReH_7(PR_3)_2$ (PR_3 = PPh_3 or $PEtPh_2$). (i) $[Re(CNCMe_3)_4(PPh_3)_2]PF_6$. A slurry of $ReH_7(PPh_3)_2$ (0.18 g, 0.25 mmol) in 10 mL of MeOH was treated with an excess of *tert*-butyl isocyanide (0.3 mL, 2.6 mmol). The reaction mixture was refluxed for 3 h, the solvent removed under reduced pressure, and the residue treated with 30 mL of KPF_6-saturated acetone and stirred for 2 h. The resulting mixture was filtered, the filtrate was evaporated, and the residue was washed with water and then diethyl ether and dried under vacuum. Anal. Calcd for $C_{56}H_{66}F_6N_4P_3Re$: C, 56.60; H, 5.60; N, 4.71. Found: C, 56.44; H, 5.88; N, 4.70. The yield was 0.25 g (85%). IR (Nujol mull): 2090 (s), 2050 (s) cm^{-1}.

(ii) $[Re(CNC_6H_{11})_4(PPh_3)_2]PF_6$. This complex was prepared in a manner similar to that described in G(i). Anal. Calcd for $C_{64}H_{74}F_6N_4P_3Re$: C, 59.47; H, 5.77. Found: C, 59.57; H, 5.74. The yield was 79%. IR (Nujol mull): 2172 (s); 2080 (s) cm^{-1}.

(iii) $[Re(CNCMe_3)_4(PEtPh_2)_2]PF_6$. This complex was prepared in a manner similar to that described in G(i). Anal. Calcd for $C_{48}H_{66}F_6N_4P_3Re$: C, 52.78; H, 6.09. Found: C, 52.84; H, 6.10. The yield was 81%. IR (Nujol mull): 2080 (s); 2040 (s) cm^{-1}.

H. Reactions of $ReH_5(PPh_3)_2L$ (L = PPh_3 or $C_6H_{11}NH_2$). (i) $[Re(CNCMe_3)_4(PPh_3)_2]PF_6$. A solution containing 0.3 g of $ReH_5(PPh_3)_2L$ and 0.5 mL of *tert*-butyl isocyanide in 25 mL of tetrahydrofuran was refluxed for a period of 4 days. The solvent was evaporated under reduced pressure, and the residue was stirred with a KPF_6–ethanol slurry for 3 h. Upon slow evaporation of the filtrate, yellow crystals separated, which were washed with water and then with diethyl ether and dried in vacuo; yield 55%. This product had spectroscopic properties identical with those of samples prepared by procedure G(i).

(ii) $[Re(CNC_6H_{11})_4(PPh_3)_2]PF_6$. This light yellow complex was synthesized with use of a procedure analogous to that in H(i); yield 45%.

Physical Measurements. Infrared spectra of Nujol mulls and dichloromethane solutions were recorded in the region 4000–200 cm^{-1} with a Beckman IR-12 spectrophotometer and a Digilab FTS 20B spectrometer. Electronic absorption spectra were recorded with a Varian Series 634 spectrophotometer. A Perkin-Elmer R-32 NMR spectrometer was used to obtain the ^1H NMR spectra. Samples were dissolved in acetone-d_6, chloroform-d_1, or dichloromethane-d_2, and peak resonances were internally referenced to Me_4Si. X-ray photoelectron spectra were obtained with a Hewlett-Packard 5950A ESCA spectrometer. Further experimental details are described elsewhere.[30] Cyclic voltammetric results were obtained with a Bioanalytical Systems Inc. CV-1A instrument with a platinum-bead electrode at 23 °C.[31]

Results and Discussion

(1) Dinuclear Multiply Bonded Dirhenium Complexes. (a) $Re_2(O_2CR)_4Cl_2$ (R = CH_3 or Ph). Reactions of an excess of *tert*-butyl isocyanide or cyclohexyl isocyanide with quadruply bonded $Re_2(O_2CR)_4Cl_2$, where R = CH_3 or C_6H_5, in refluxing methanol produce solutions of the $[Re(CNR)_6]^+$ cations, which we have isolated in good yield as their PF_6^- salts. The adaptation of this procedure to include other isocyanide ligands has been demonstrated[32] by our isolation of the phenyl isocyanide complex $[Re(CNPh)_6]PF_6$ (obtained in greater than 60% yield). In a study by Girolami and Anderson,[20] it was claimed (in a preliminary report) that the addition of *tert*-butyl isocyanide to $Re_2(O_2CCH_3)_4Cl_2$ produces mononuclear $Re(CNCMe_3)_5Cl$ in high yield. However, a later reinterpretation of these results,[21] subsequent to our own initial communication on this subject,[16] demonstrated that this product was in reality $[Re(CNCMe_3)_6]Cl$, a result which is in accord with our findings.

The observation that isocyanide ligands cleave the quadruple bond of $Re_2(O_2CR)_4Cl_2$ complexes is expected in view of our observations concerning the cleavage reactions of the iso-

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[30] Hamer, A. D.; Walton, R. A. *Inorg. Chem.* **1974**, *13*, 1446.

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

[32] Cameron, C.; Walton, R. A., unpublished work.

Table I. ^1H NMR and Infrared Spectral Data for Isocyanide Complexes of Rhenium(I) and Rhenium(III)

complex	^1H chem shifts, δ^a phosphine	^1H chem shifts, δ^a isocyanide	IR abs^b $\nu(C\equiv N)$, cm^{-1}
$[Re(CNCMe_3)_6]PF_6$		1.50 s	2100 s, 2060 s
$[Re(CNC_6H_{11})_6]PF_6$		3.90 m, 1.76 m, 1.49 m	2085 s, 2048 sh
$[Re(CNCMe_3)_5Cl_2]PF_6\cdot{}^1/_2CH_2Cl_2$		1.64 s	2258 m, 2205 s, 2055 w
$[Re(CNCMe_3)_5Br_2]PF_6\cdot(CH_3)_2CO$		1.64 s	2250 m, 2200 s, 2060 w
$[Re(CNCMe_3)_4(PEtPh_2)Cl_2]PF_6$	7.75 br, 7.55 br	1.43 s	2233 m, 2200 sh, 2180 s, 2151 s
$[Re(CNCMe_3)_4(P\text{-}n\text{-}Pr_3)_2]PF_6$	1.70 t, 1.10 m, 1.02 t	1.40 s	2085 sh, 2035 s
$[Re(CNCMe_3)_4(PEt_3)_2]PF_6$			2085 sh, 2035 s
$[Re(CNCMe_3)_3(dppe)Cl_2]PF_6\cdot{}^1/_2CH_2Cl_2$	7.55 br, 2.45 br, 2.30 br	1.10 s	2205 m, 2160 s
$[Re(CNCMe_3)_6Cl](PF_6)_2$		1.68 s	2260 sh, 2210 s
$[Re(CNCMe_3)_6Br](PF_6)_2\cdot1.5CH_2Cl_2$		1.70 s	2250 m, 2215 s, 2050 w
$[Re(CNCMe_3)_6I](PF_6)_2$		1.51 s	2255 m, 2205 s, 2050 w
$[Re(CNCMe_3)_4(PPh_3)_2]PF_6$	7.50 m, 7.30 m	0.85 s	2090 s, 2050 s
$[Re(CNC_6H_{11})_4(PPh_3)_2]PF_6$	7.70 m, 7.50 m	3.45 m, 1.35 br, 1.20 br	2172 s, 2080 s
$[Re(CNCMe_3)_4(PEtPh_2)_2]PF_6$	7.52 br, 7.40 br, 2.50 m, ~1.00 m	1.08 s	2080 s, 2040 s

[a] All ^1H NMR data are internally referenced to Me_4Si. Abbreviations are as follows: br = broad, m = multiplet, t = triplet, s = singlet. [b] IR data recorded as Nujol mulls.

Table II. XPS Core Electron Binding Energies for Isocyanide Complexes of Rhenium^a

compd	Re $4f_{5/2,7/2}$	N 1s
$[Re(CNCMe_3)_6]PF_6$	42.7, 40.3	*b*
$[Re(CNCMe_3)_6Cl](PF_6)_2$	45.2, 42.9	400.4
$[Re(CNCMe_3)_6Br](PF_6)_2$	45.1, 42.7	400.3
$[Re(CNCMe_3)_5Cl_2]PF_6$	44.7, 42.4	400.0
$[Re(CNCMe_3)_5Br_2]PF_6$	44.8, 42.5	400.0
$[Re(CNCMe_3)_4(PEtPh_2)Cl_2]PF_6$^{c}	44.3, 42.4	400.0

[a] All binding energies (in eV) are referenced to a C 1s binding energy of 285.0 eV. [b] Not recorded. [c] Other binding energies for this complex are as follows: Cl $2p_{3/2}$, 198.3 eV; P $2p(PF_6^-)$, 136.2 eV; P $2p(PEtPh_2)$, 131.4 eV.

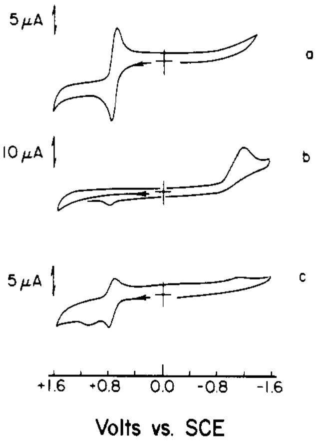

Figure 1. Cyclic voltammograms in 0.2 M tetra-*n*-butylammonium hexafluorophosphate–dichloromethane solutions of (a) $[Re(CNCMe_3)_6]PF_6$ and (b) $[Re(CNCMe_3)_6Cl](PF_6)_2$ and (c) a solution of (b) following reduction at −1.25 V.

electronic quadruply bonded dimolybdenum and ditungsten species.[16] Where the reactions with dirhenium(III) carboxylates differ is in that *reductive* cleavage takes place. However, the formation of the homoleptic 18-electron rhenium(I) cation $[Re(CNR)_6]^+$ is not unexpected since the alternative seven-coordinate species $[Re(CNR)_7]^{3+}$ are unknown and $[Re(CNR)_6]^+$, like the manganese(I) analogues $[Mn(CNR)_6]^+$,[6] are very stable species.

These reactions of the dirhenium(III) carboxylates $Re_2(O_2CR)_4Cl_2$ with RNC ligands must proceed initially by the dissociation of a terminally bound chloride ligand (i.e., $Re_2(O_2CR)_4Cl_2 + RNC \rightarrow [Re_2(O_2CR)_4Cl(CNR)]^+ + Cl^-$) or through attack of RNC at an equatorial position with concomitant opening of a carboxylate bridge. While we have been unable to isolate any intermediates from the reaction mixtures and cannot, therefore, distinguish between these two pathways, both are known to occur in the chemistry of multiply bonded dimetal complexes.[33]

While many of the spectroscopic and other characterizations of $[Re(CNR)_6]PF_6$ are quite routine (Tables I and II) and will not be discussed in detail here,[34] a couple of features are worth noting. First, in the X-ray photoelectron spectrum (XPS) of $[Re(CNCMe_3)_6]PF_6$ (Table II), we find that the Re $4f_{5/2,7/2}$ binding energies (42.7 and 40.3 eV) are, as expected, much lower than those of isocyanide complexes of rhenium(III) and, indeed, of other rhenium complexes possessing oxidation states of +2 or greater.[35,36] Second, the IR mull spectrum of $[Re(CNCMe_3)_6]PF_6$ (Table I) exhibits a split $\nu(C\equiv N)$ band (2100 s and 2060 s cm^{-1}), a feature which is also displayed by dichloromethane solutions of this complex. This result is in accord with previous results for the IR spectra of $[Re(CNCMe_3)_6]Cl$,[21] $[Re(CNPh)_6]PF_6$,[32] and $[Re(CNtol)_6]PF_6$,[6] but whether it reflects a distortion of these cations from O_h symmetry must await an X-ray structure determination on one of these salts.

In addition to exploring the electrochemical redox behavior of the $[Re(CNCMe_3)_6]^+$ cation (vide infra), we have also carried out some studies of its chemical reactivity. The complex $[Re(CNCMe_3)_6]PF_6$ failed to undergo any noticeable degree of reaction upon refluxing its suspension in methanol with monodentate tertiary phosphines or the bidentates of the type $Ph_2P(CH_2)_nPPh_2$ (n = 1 or 2). This kinetic inertness to substitution by phosphines is in contrast to the rapid oxidation of this cation by the halogens (Cl_2, Br_2, and I_2). Dichloromethane solutions react with X_2 in the presence of 1 equiv of KPF_6 with the almost quantitative formation of $[Re(CNCMe_3)_6X](PF_6)_2$ (X = Cl, Br, or I). An acetonitrile solution of the bromide complex (9.6×10^{-4} M) exhibited a conductivity (260 Ω^{-1} cm^2 mol^{-1}) that is consistent with it being a 1:2 electrolyte,[37] while the Re $4f_{5/2,7/2}$ binding energies in the XPS of the chloride and bromide complexes (Table II)

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(33) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley-Interscience: New York, 1982.

(34) In addition to the IR and X-ray photoelectron spectroscopic properties of $[Re(CNCMe_3)_6]PF_6$, which are discussed in the text, this complex has a ^1H NMR spectrum (δ 1.50 in acetone-d_6) and a conductivity in acetonitrile (124 Ω^{-1} cm^2 mol^{-1} for a 0.82×10^{-3} M solution) that closely parallel the related properties of $[Re(CNCMe_3)_6]Cl$.[21] For the cyclohexyl isocyanide derivative $[Re(CNC_6H_{11})_6]PF_6$, the ^1H NMR spectrum of a $CDCl_3$ solution shows multiplets at δ 3.90, 1.76, and 1.49 (Table I).

(35) Tisley, D. G.; Walton, R. A. *J. Mol. Struct.* **1973**, *17*, 401.

(36) Ebner, J. R.; Walton, R. A. *Inorg. Chem.* **1975**, *14*, 2289.

(37) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81 and references therein.

Table III. Voltammetric Half-Wave Potentials ($E_{1/2}$) for Isocyanide Complexes of Rhenium(I)[a]

compd	$E_{1/2}$(ox)	($E_{pa} - E_{pc}$)[b]
$[Re(CNCMe_3)_6]PF_6$	+0.74[c]	80
$[Re(CNC_6H_{11})_6]PF_6$	+0.79	90
$[Re(CNCMe_3)_4(PEt_3)_2]PF_6$	+0.63	100
$[Re(CNCMe_3)_4(P\text{-}n\text{-}Pr_3)_2]PF_6$	+0.62[d]	100
$[Re(CNCMe_3)_4(PPh_3)_2]PF_6$	+0.81	80
$[Re(CNC_6H_{11})_4(PPh_3)_2]PF_6$	+0.76	80
$[Re(CNCMe_3)_4(PEtPh_2)_2]PF_6$	+0.78	85

[a] In volts vs. SCE with a Pt-bead working electrode and 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. [b] In millivolts; recorded at $\nu = 200$ mV s^{-1}. [c] $n = 0.93$ as determined by exhaustive electrolysis; for the reduction of $[Re(CNCMe_3)_6]^{2+}$ back to $[Re(CNCMe_3)_6]^+$ we found an n value of 0.91. [d] $n = 1.06$ as determined by exhaustive electrolysis; for the reduction of $[Re(CNCMe_3)_4(P\text{-}n\text{-}Pr_3)_2]^{2+}$ back to $[Re(CNCMe_3)_4(P\text{-}n\text{-}Pr_3)_2]^+$ we found an n value of 0.99.

support the formulation of these complexes as rhenium(III) derivatives.[35,36] In contrast to the XPS results for the chloride and the bromide, the iodide $[Re(CNCMe_3)_6I](PF_6)_2$ had Re $4f_{5/2,7/2}$ energies of 42.5 and 40.2 eV, values which indicate that X-ray-induced surface reduction (Re(III) → Re(I)) has occurred. As indicated in Table I, all three complexes exhibit a single sharp resonance in their ^1H NMR spectra,[38] behavior which resembles that exhibited by the isoelectronic stereochemically nonrigid molybdenum and tungsten species $[M(CNCMe_3)_6X]^+$.[39] The ν(C≡N) absorptions in the IR spectra of these complexes (Table I) are, as expected, shifted to higher energies relative to those of $[Re(CNR)_6]^+$, in accord with the occurrence of less Re → (CNR) π back-bonding in the case of the rhenium(III) complexes.

Cyclic voltammetric (CV) measurements on 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH)–dichloromethane solutions of $[Re(CNCMe_3)_6]PF_6$ show a couple at +0.74 V vs. SCE (Figure 1), while in acetonitrile the $E_{1/2}$ value is +0.72 V (Table III). The oxidation at ~+0.7 V corresponds to a one-electron process:

$$[Re(CNCMe_3)_6]^+ \xrightarrow{-e^-} [Re(CNCMe_3)_6]^{2+}$$

The peak current ratio $i_{pc}/i_{pa} \approx 1$ and values of $i_{pa}/v^{1/2}$ were essentially constant for scan rates (v) from 50 to 400 mV s^{-1}. The electrochemical properties of $[Re(CNC_6H_{11})_6]PF_6$, with $E_{1/2} = 0.79$ V vs. SCE, were very similar to those of the *tert*-butyl isocyanide derivative. The electrochemical oxidation of $[Re(CNCMe_3)_6]PF_6$ at a potential of +0.8 V produced solutions that appeared to be fairly stable as monitored by CV, but attempts to obtain a resonance in the X-band ESR spectrum of a dichloromethane glass (−160 °C) were unsuccessful. Our failure to obtain a signal may be due to fast spin–lattice relaxations at the temperature used. Under experimental conditions comparable to those used by us, Treichel and Williams[6] measured $E_{1/2}$ values of +1.20 and +1.10 V vs. SCE for the aryl isocyanide derivatives $[Re(CNtol)_6]PF_6$ and $[Re(CNC_6H_4OMe)_6]PF_6$, respectively. This trend reflects the better σ-donor properties of alkyl isocyanides relative to aryl isocyanides and hence the greater ease of oxidizing complexes containing the former ligands.[6,40] The shift of the E_{pa} value to a more positive potential for $[Mo(CNR)_7]^{2+} \rightarrow [Mo(CNR)_7]^{3+} + e^-$ (and for the analogous tungsten system)[14,15] relative to isoelectronic $[Re(CNR)_6]^+ \rightarrow [Re(CNR)_6]^{2+} + e^-$, is consistent with the higher ionic charge on the molybdenum and tungsten species.

In the CV of a 0.2 M TBAH–CH_2Cl_2 solution of $[Re(CNCMe_3)_6Cl](PF_6)_2$ the only identifiable process (between +1.4 and −1.6 V) is an irreversible reduction at $E_{pc} = -1.18$ V vs. SCE. This reduction is followed by the generation of $[Re(CNCMe_3)_6]^+$ as shown by the appearance of an oxidation at $E_{pa} = +0.78$ V on a *second sweep* in the CV (Figure 1). This was confirmed by electrolyzing a solution of $[Re(CNCMe_3)_6Cl](PF_6)_2$ at −1.25 V and measuring the CV of the resulting solution. Both $[Re(CNCMe_3)_6]^+$ ($E_{1/2} = +0.72$ V) and Cl^- ($E_{pa} \simeq +1.16$ V)[41] were readily identified as the products that form following the reduction (Figure 1).

(b) $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl or Br) and $Re_2Cl_6(PEtPh_2)_2$. In contrast to the reactions between $Re_2(O_2CR)_4Cl_2$ and RNC in which reductive cleavage of the $Re \overset{4}{-} Re$ bond occurs, the salts $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl or Br) react with *tert*-butyl isocyanide to form the rhenium(III) complexes $[Re(CNCMe_3)_5X_2]PF_6$ as the principal products (60% yield). The only previous report of a reaction between $[Re_2Cl_8]^{2-}$ and an RNC ligand is that involving $(n\text{-}Bu_4N)_2Re_2Cl_8$ and methyl isocyanide.[42] With methanol as the reaction solvent, the green rhenium(IV) complex $(n\text{-}Bu_4N)ReCl_5(CNCH_3)$ was produced in low yield, but the nature of the oxidant, the identity of the "reduction product", and the fate of the major proportion of the rhenium remain unknown in this interesting reaction. Our isolation of $[Re(CNR)_5X_2]PF_6$ and $[Re(CNR)_6X](PF_6)_2$ in the present work, taken in conjunction with the previously characterized $Re(CNR)_4Br_3$,[7] demonstrates the existence of an extensive group of seven-coordinate mixed halide–isocyanide complexes of rhenium(III). It appears that only in the presence of a deficiency of halide ligand in the starting material (viz., $Re_2(O_2CR)_4Cl_2$) is reduction to rhenium(I) favored, since "excess" halide (as with the $[Re_2X_8]^{2-}$ anions) favors the retention of the rhenium(III) oxidation state.

In a recent paper, Girolami and Andersen,[21] in questioning the generality of the bond-cleavage reaction, found that singly bonded $Rh_2(O_2CCH_3)_4$ (possessing the $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2(\pi^*)^4$ configuration)[33] reacted with *tert*-butyl isocyanide to produce the adduct $Rh_2(O_2CH_3)_4(CNCMe_3)_2$. Fission of the Rh–Rh bond was found not to occur.[21] While this result was in accord with the expectation that good π acceptors should strengthen the Rh–Rh bond,[43] thereby explaining why such an adduct of Rh_2^{4+} can be stable, the experimental results of Girolami and Andersen[21] are not fully in accord with our own observations. While we agree that the initial product of the room-temperature reaction between $Rh_2(O_2CCH_3)_4$ and *tert*-butyl isocyanide is the orange 1:2 adduct, we find that refluxing the reaction mixture produces solutions from which the reductive-cleavage product $[Rh(CNCMe_3)_4]PF_6$ can be isolated.[44] Thus $Rh_2(O_2CCH_3)_4$ is *not* an exception to the observation that isocyanide ligands cleave the metal–metal bond of dinuclear complexes that either possess multiple bonds or have single bonds with an electronic configuration closely related thereto.

The Re $4f_{5/2,7/2}$ core electron binding energies of the chloride and bromide complexes $[Re(CNCMe_3)_5X_2]PF_6$ are somewhat less than those of $[Re(CNCMe_3)_6X](PF_6)_2$ (Table II) but are still indicative of rhenium(III). These complexes form solutions in acetonitrile whose conductivities (146 (X = Cl) and 161 (X = Br) Ω^{-1} cm^2 mol^{-1} for $c = 1.03 \times 10^{-3}$ M) are consistent with[37] their formulation as 1:1 electrolytes. The ^1H NMR spectra of solutions of $[Re(CNCMe_3)_5X_2]PF_6$ (in

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(38) These spectra were recorded in dichloromethane-d_2 (X = Cl), acetone-d_6 (X = Br), and chloroform-d_1 (X = I).

(39) Lam, C. T.; Novotny, M.; Lewis, D. L.; Lippard, S. J. *Inorg. Chem.* **1978**, *17*, 2127.

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(43) Christoph, G. G.; Koh, Y.-B. *J. Am. Chem. Soc.* **1979**, *101*, 1422.

(44) Mialki, W. S. Ph.D. Thesis, Purdue University, 1981.

CD_2Cl_2 for X = Cl and $(CD_3)_2CO$ for X = Br) show a single sharp resonance at δ 1.64 (Table I), similar in position to the related resonance in the ^1H NMR of $[Re(CNCMe_3)_6X](PF_6)_2$. At ambient temperatures solutions containing mixtures of the $[Re(CNCMe_3)_5X_2]PF_6$–$[Re(CNCMe_3)_6X](PF_6)_2$ pairs display separate signals corresponding to each of the components (Table I), there being no evidence for exchange.

In the CV of $[Re(CNCMe_3)_5Cl_2]PF_6$ (in 0.2 M TBAH–CH_2Cl_2) an irreversible reduction at $E_{pc} = -1.54$ V vs. SCE is shifted to more negative potentials relative to that in the CV of $[Re(CNCMe_3)_6Cl](PF_6)_2$ (vide supra). Controlled-potential electrolysis of such a solution (at −1.6 V) led to decomposition, there being no identifiable rhenium-containing product formed.

When the dirhenium(III) complex $Re_2Cl_6(PEtPh_2)_2$, containing both chloride and phosphine ligands, was reacted with *tert*-butyl isocyanide, the resultant product was again a mononuclear derivative of rhenium(III), viz., $[Re(CNCMe_3)_4(PEtPh_2)Cl_2]PF_6$. In this reaction the phosphine ligands are clearly quite inert to substitution and the reactions proceed in a fashion analogous to that observed with $[Re_2Cl_8]^{2-}$. The ^1H NMR spectrum of a $CDCl_3$ solution of this complex (Table I) was fully in accord with this formulation (δ 1.43 ($CNCMe_3$), 7.55 and 7.75 br (PEt*Ph*$_2$)), and the XPS supported its being a derivative of rhenium(III) (Table II).

While the bis(μ-chloro) complex $Re_2Cl_6(dppe)_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) does not contain a Re–Re bond,[27] it reacts with *tert*-butyl isocyanide in a fashion rather similar to that described for quadruply bonded $Re_2Cl_6(PEtPh_2)_2$. However, in this instance it is the $[Re_2Cl_2]$ bridge unit that is broken, rather than the Re–Re bond, to afford mononuclear fragments. The bidentate phosphine ligand is retained, but again (as with $Re_2Cl_6(PEtPh_2)_2$) one chloride ligand is replaced upon coordination of the isocyanide ligands to give $[Re(CNCMe_3)_3(dppe)Cl_2]PF_6$.

(c) $Re_2Cl_4(PR_3)_4$ (R = Et or *n*-Pr). With triply bonded complexes of the type $Re_2Cl_4(PR_3)_4$, which are derived from the Re_2^{4+} core, fission of the $Re\equiv Re$ bond occurs as expected. However, unlike the situation with mixed halide–phosphine complexes of Re_2^{6+}, reduction to rhenium(I) is the predominant pathway and the complexes $[Re(CNCMe_3)_4(PR_3)_2]PF_6$ result (R = Et or *n*-Pr). The IR-active $\nu(C\equiv N)$ modes of these complexes occur at frequencies characteristic of rhenium(I) (Table I), and their electrochemical properties resemble those of homoleptic $[Re(CNCMe_3)_6]PF_6$ (Table III). Like the latter complex, 0.2 M TBAH–CH_2Cl_2 solutions of $[Re(CNCMe_3)_4(PR_3)_2]PF_6$ possess an oxidation close to +0.6 V. An alternative route to mixed isocyanide–phosphine complexes of rhenium(I) is provided by the reactions of isocyanides with mononuclear polyhydrides of the types $ReH_7(PR_3)_2$ and $ReH_5(PR_3)_2L$ (vide infra).

(2) Mononuclear Polyhydrides of Rhenium. Thermal reactions of heptahydride complexes of the type $ReH_7(PR_3)_2$ ($PR_3 = PPh_3$ or PEt_2Ph) with unsaturated organics have recently been documented, in which hydrogenation of the latter occurs and the metal-containing residue contains a ReH_x fragment (*x* = 3 or 2).[45,46] Additionally, in the presence of 3,3-dimethylbut-1-ene as a hydrogen acceptor, $ReH_7(PR_3)_2$ activates the C–H bonds of cyclopentane under very mild conditions to produce $(\eta^5\text{-}C_5H_5)ReH_2(PR_3)_2$.[47] A further pathway for the reaction of $ReH_7(PR_3)_2$ with organic substrates is demonstrated in our study of the reactions between the heptahydrides ($PR_3 = PPh_3$ or $PEtPh_2$) and alkyl isocyanides RNC (R = CMe_3 or C_6H_{11}), namely, the release of dihydrogen, the concomitant formal 6-electron reduction of the metal center, and its stabilization in the form $[Re(CNR)_4(PR_3)_2]^+$ by the coordination of the RNC π-acceptor ligands. The evolution of H_2 was confirmed by mass spectral analysis of the vapor above the reaction solution in a closed reaction vessel. The amount of H_2 released was ca. 85% of that expected on the basis of the reduction from Re(VII) to Re(I), i.e., $ReH_7(PR_3)_2 + 4RNC \rightarrow [Re(CNR)_4(PR_3)_2]^+ + \text{"}H^-\text{"} + 3H_2$. The fate of the remaining hydridic hydrogen is unknown, although it may be released as H_2 through reaction with trace amounts of water upon the subsequent treatment of the reaction mixture containing $[Re(CNR)_4(PR_3)_2]^+$ with acetone solutions of KPF_6. The ^1H NMR and IR spectra of these complexes (Table I) appear normal for rhenium(I) species.[48]

A characteristic thermal reaction of $ReH_7(PR_3)_2$ is that in which an excess of a phosphine or tertiary amine produces a complex of the type $ReH_5(PR_3)_2L$.[28] We have attempted to prepare $ReH_5(PR_3)_2(CNR)$ by the reaction of $ReH_7(PR_3)_2$ with equimolar quantities of RNC. However, under these conditions we isolate only $[Re(CNR)_4(PR_3)_2]^+$ and unreacted $ReH_7(PR_3)_2$ so, apparently, coordination of CNR so activates the molecule to further attack by RNC that the intermediate $ReH_5(PR_3)_2(CNR)$, if it indeed forms, is extremely unstable. This behavior contrasts with the relative kinetic inertness of preformed $ReH_5(PPh_3)_2L$, where L is a phosphine or tertiary amine, toward further reaction with σ donors and π acceptors since vigorous reaction conditions are necessary for these latter reactions to proceed.[28,49,50] In accord with such observations we find that the thermal reactions of RNC with $ReH_5(PPh_3)_2L$ proceed very slowly. For L = PPh_3 or $C_6H_{11}NH_2$, reflux with an excess of RNC (R = CMe_3 or C_6H_{11}) in tetrahydrofuran for 4 days is necessary in order to get reasonable yields (~50%) of product. In all instances, the complexes $[Re(CNR)_4(PPh_3)_2]PF_6$ were the major (if not the exclusive) products of these reactions. Preliminary experiments with other complexes of the type $ReH_5(PPh_3)_2L$ (L = PEt_2Ph, C_5H_5N, or $C_5H_{11}NH$) showed that they also react with RNC extremely slowly. The necessity of using very long reaction times in these reactions presumably reflects the extremely slow ligand (L) loss in $ReH_5(PPh_3)_2L$ to form the reactive intermediate $ReH_5(PPh_3)_2(CNR)$.

Electrochemical measurements on 0.2 M TBAH–CH_2Cl_2 solutions of $[Re(CNR)_4(PPh_3)_2]PF_6$ and $[Re(CNR)_4(PEtPh_2)_2]PF_6$ (Table III) reveal the presence of an oxidation at an $E_{1/2}$ of ca. +0.8 V vs. SCE, behavior similar to that which characterizes the electrochemistry of $[Re(CNR)_6]PF_6$ and $[Re(CNCMe_3)_4(PR_3)_2]PF_6$ (R = Et or *n*-Pr). Note that, for the trialkylphosphine complexes of this type, the $E_{1/2}$ values are ca. 0.2 V more negative than for the PPh_3 and $PEtPh_2$ derivatives. This correlates with the increased basicity of the trialkylphosphines and their ability therefore to better stabilize the oxidized species $[Re(CNR)_4(PR_3)_2]^{2+}$.

Acknowledgment. We thank the National Science Foundation (Grant CHE79-09233) for support of this research.

Registry No. $[Re(CNCMe_3)_6]PF_6$, 81625-51-6; $[Re(CNC_6H_{11})_6]PF_6$, 82554-80-1; $[Re(CNCMe_3)_5Cl_2]PF_6$, 82544-32-9; $[Re(CNC(CH_3)_3)_5Br_2]PF_6$, 82544-34-1; $[Re(CNCMe_3)_4(PEtPh_2)Cl_2]PF_6$, 82544-36-3; $[Re(CNCMe_3)_4(P\text{-}n\text{-}Pr_3)_2]PF_6$, 82544-38-5; $[Re(CNCMe_3)_4(PEt_3)_2]PF_6$, 82544-40-9; $[Re(CNCMe_3)_3(dppe)Cl_2]PF_6$,

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Inductive, Steric, and Environmental Effects in the Nonaqueous Electrochemistry of Hexakis(aryl isocyanide)chromium Complexes

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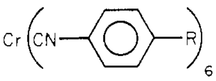
Received January 22, 1982

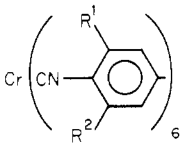
The electrochemical behavior of a series of hexakis(aryl isocyanide)chromium(I) complexes has been studied by cyclic voltammetry. The inductive effects of para substituents on $E^{\circ\prime}$ for the (0 ↔ 1+), (1+ ↔ 2+), and (2+ ↔ 3+) couples have been found to give linear correlations with the Hammett σ_p parameter. Solvent and supporting-electrolyte effects have also been investigated and are discussed in terms of donor/acceptor theory and ion-pairing effects, respectively. The introduction of bulky ortho substituents on the aryl isocyanide ring was found to dramatically influence both the $E^{\circ\prime}_{3+/2+}$ and the substitutional lability of the Cr(CNR)$_6^{3+}$ complexes. These effects are attributed to significant weakening of the Cr$^{\text{III}}$–C bonds in the ortho-substituted complexes relative to the para-substituted complexes due to steric interactions among the ortho substituents.

Introduction

The photochemistry and electrochemistry of hexakis(aryl and alkyl isocyanide)metal complexes have been an area of increasing interest in recent years, with contributions arising from several groups.[1-10] Our intended utilization of these compounds Cr(CNR)$_6$ in photoelectrochemical systems required that we carefully characterize their electrochemical behavior. Previous studies[5,6,8,10] had shown that these compounds undergo a series of three reversible one-electron-transfer reactions at solid electrodes:



R = H, Cl, OCH$_3$, CH$_3$, N(CH$_3$)$_2$



R^1, R^2 = H, CH$_3$; CH$_3$, CH$_3$; CH(CH$_3$)$_2$, CH(CH$_3$)$_2$

$$\mathrm{Cr(CNR)_6^+ + e^- \rightleftharpoons Cr(CNR)_6} \quad E^{\circ\prime}_{1+/0} \qquad (1)$$

$$\mathrm{Cr(CNR)_6^{2+} + e^- \rightleftharpoons Cr(CNR)_6^+} \quad E^{\circ\prime}_{2+/1+} \qquad (2)$$

$$\mathrm{Cr(CNR)_6^{3+} + e^- \rightleftharpoons Cr(CNR)_6^{2+}} \quad E^{\circ\prime}_{3+/2+} \qquad (3)$$

However, junction potential effects and solvent/electrolyte effects had not been extensively investigated. Additionally, we wished to assess the effect of ortho ring substituents on the $E^{\circ\prime}$ values of the complexes, because their photochemical[3] and spectroscopic[2] behaviors differ markedly from those exhibited by para-substituted complexes.

This paper reports the results of electrochemical studies which show that inductive, environmental, and steric effects are all important in influencing not only the formal potentials for the processes described in eq 1–3 but also the substitutional lability of the complexes.

Experimental Section

All electrochemical measurements were performed *in the dark* at 20 ± 2 °C with a PAR Model 170 electrochemistry system. A three-electrode configuration was used, employing a platinum flag or platinum disk working electrode, a platinum spiral auxiliary electrode, and a AgCl/Ag reference electrode. The reference electrode (1.0 M KCl, saturated with AgCl) was connected to the working electrode compartment via a salt bridge terminating in a modified Luggin capillary. The salt bridge contained 0.5 M supporting electrolyte. The electrolysis solution was 0.1 M in supporting electrolyte and generally 0.5 mM in complex. Methylene chloride, acetonitrile (UV grade), and propylene carbonate were used directly as received from Burdick and Jackson without further purification. Tetra-n-butylammonium perchlorate (TBAP) and tetra-n-butylammonium hexafluorophosphate (TBAH) (electrometric grade, Southwestern Analytical Chemicals, Inc.) were used as supporting electrolytes without further recrystallization.

Ferrocene was used as an internal reference system to correct for the junction potential.[12-14] This correction employed an $E^{\circ\prime}$ value for FeCp$_2^+$/FeCp$_2$ of 0.400 V vs. NHE,[14] which was assumed to be independent of the medium. *All* potentials reported here are reported vs. *corrected* AgCl/Ag(aq). Ferrocene appeared at varying potentials, depending on the solvent/supporting electrolyte system used: CH$_3$CN/TBAH, $E^{\circ\prime}_{\mathrm{FeCp_2^+/FeCp_2}}$ = 0.41 V; CH$_3$CN/TBAP, $E^{\circ\prime}$ = 0.43 V; CH$_2$Cl$_2$/TBAH, $E^{\circ\prime}$ = 0.48 V; CH$_2$Cl$_2$/TBAP, $E^{\circ\prime}$ = 0.49 V; propylene carbonate/TBAP, $E^{\circ\prime}$ = 0.39 V. No iR compensation was used in any of the electrochemical studies.[12]

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