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THE REACTIONS OF K_2ReX_6 (X = Br OR I) AND Re_3X_9 (X = Cl, Br OR I) WITH ALKYL AND ARYL ISOCYANIDES

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Summary

The reactions of alkyl isocyanides (RNC) and aryl isocyanides (ArNC) with the rhenium halides K_2ReX_6 (X = Br or I) and Re_3X_9 (X = Cl, Br or I) have been investigated. When the K_2ReX_6 salts are treated with neat isocyanide at room temperature, or with isocyanide ligands in polar solvents under reflux conditions, then the homoleptic isocyanide cations $[Re(CNR)_6]^+$ or $[Re(CNAr)_6]^+$, are isolated. Under less forcing conditions, various rhenium(III) and rhenium(I) species, e.g. $[Re(CNCMe_3)_5I_2]^+$ and $Re(CNAr)_5I$, which may be considered as intermediates on the way to the formation of the homoleptic species, can be obtained. The rhenium(I) complexes $Re(CNAr)_5I_3$, which are believed to contain the coordinated triiodide ligand, have also been isolated and characterized. One route to these complexes is through the reaction of $Re(CNAr)_5I$ with I_2. Reactions of the trinuclear halides Re_3X_9 (X = Cl, Br or I) with alkyl isocyanides at room temperature are found, in all instances, to provide adducts of the type $Re_3X_9(CNR)_3$. Under reflux conditions, Re_3Cl_9 and $Re_3Cl_9(PEtPh_2)_3$ react with Me_3CNC to form products of cluster disruption, viz. $[Re(CNCMe_3)_6]^+$ and $[Re(CNCMe_3)_4(PEtPh_2)_2]^+$, respectively. The spectroscopic and electrochemical properties of complexes derived in this study are reported. These results are compared with those reported previously by Freni et al.

Introduction

Cleavage of the metal–metal multiple bonds of dinuclear complexes of molybdenum, tungsten and rhenium by alkyl and aryl isocyanide ligands [1–8], has provided a convenient entry into the chemistry of mononuclear isocyanide complexes of these elements. This work, along with related studies by Treichel [9,10], has led to a fairly thorough understanding of the nature of the isocyanide complexes of

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rhenium(I) and rhenium(III). In addition to the existence of several well characterized mixed carbonyl-isocyanide complexes [6], species of the types $[Re(CNR)_6]^+$, $[Re(CNAr)_6]^+$, $[Re(CNR)_5X_2]^+$, $[Re(CNR)_6X]^{2+}$, $[Re(CNAr)_6X]^{2+}$, $Re(CNAr)_4X_3$, $[Re(CNAr)_2X_4]^-$ and $Re(CNAr)_3X_3$, where R = alkyl, Ar = aryl and X = halide, have now been isolated and characterized [1,3,7,9,10].

While carrying out these investigations we had cause to consider the earlier work of Freni and co-workers [11,12] in which the reactions between the cyclohexyl and *p*-tolyl isocyanide ligands and the halides K_2ReX_6 (X = Br or I) and Re_3I_9 were investigated. We felt that several of the products had formulations that were inconsistent with the known reaction chemistry of the parent halides and our own studies of rhenium isocyanide complexes [1,3,7]. Recent investigations by ourselves of the reactions between K_2ReX_6 (X = Br or I) and cyclohexyl, t-butyl, phenyl, *p*-tolyl and xylyl isocyanides, and between Re_3X_9 (X = Cl, Br or I) and methyl, iso-propyl, cyclohexyl, n-butyl and t-butyl isocyanides provide further insights into the results of Freni [11,12]. The details of this work is described herein.

Experimental section

Starting materials

The following rhenium halides were prepared by standard literature procedures: K_2ReBr_6 [13,14], K_2ReI_6 [15], Re_3Cl_9 [16,17], Re_3Br_9 [16,17], and Re_3I_9 [17,18]. The tertiary phosphine complex $Re_3Cl_9(PEtPh_2)_3$, was prepared from the direct reaction of Re_3Cl_9 with the phosphine ligand in ethanol [19]. The isocyanide ligands, phenyl isocyanide (PhNC), *p*-tolyl isocyanide (*p*-tolNC), 2,6-dimethylphenyl isocyanide (xylylNC), methyl isocyanide (CH_3NC), cyclohexyl isocyanide ($C_6H_{11}NC$), n-butyl isocyanide (C_4H_9NC) and t-butyl isocyanide (Me_3CNC) were prepared by the method described by Weber et al. [20]. Potassium perrhenate was purchased from Pressure Chemical Company and was used without further purification. All other reagents and solvents were obtained from commercial sources and were used as received.

Reaction procedure

All reactions were carried out under an atmosphere of dry nitrogen, and solvents were deoxygenated prior to use by purging with N_2 gas.

A. Reactions of K_2ReX_6 (X = Br or I)

(i) $[Re(CNCMe_3)_6]I_3$. Neat t-butyl isocyanide (1.5 ml, 14.2 mmol) was added to solid K_2ReI_6 (0.41 g, 0.40 mmol) in a stoppered test tube. The mixture turned purple immediately and then brown. After 72 h the reaction mixture was filtered, thereby removing a small amount of green solid (which was discarded), and 5 ml of a 1/1 isopropyl alcohol/diethyl ether mixture was added to the filtrate. This solution was taken to small volume, and the deep red-brown solid that separated was filtered off and washed with a 2/3 mixture of diethyl ether/hexane, and dried in vacuo. Yield 0.34 g (80%). Anal. Found: C, 32.71; H, 5.06. $C_{30}H_{54}I_3N_6Re$ calcd.: C, 33.81; H, 5.11%. The IR spectrum of this complex is identical to that of $[Re(CNCMe_3)_6]PF_6$ [1] with the exception of the anion vibrations. The ν_3 mode of the octahedral PF_6^- anion (840s cm^{-1}) was replaced by the ν_3 mode of the linear I_3^- anion at 140 cm^{-1} [21].

An alternative procedure used to obtain this complex was as follows. An excess of t-butyl isocyanide (1.0 ml, 9.5 mmol) was syringed into a suspension of K_2ReI_6 (0.47 g, 0.46 mmol) in 20 ml of ethanol. The reaction mixture was refluxed overnight and the resulting solution cooled and then reduced in volume. The addition of hexane produced a dark red brown solid that was separated by filtration, washed with hexane and dried in vacuo. Yield 0.44 g (90%). The product was shown by IR and ^1H NMR spectroscopy to be identical to the product obtained using neat isocyanide. The I_3^- anion in this complex can be selectively reduced using a dilute ethanolic solution of $NaBH_4$. This affords the iodide salt $[Re(CNCMe_3)_6]I$ whose IR is unchanged from that of $[Re(CNCMe_3)_6]I_3$, except for the disappearance of the I_3^- vibration at 140 cm^{-1}.

(ii) $[Re(CNCMe_3)_6]PF_6$. An excess of t-butyl isocyanide (1.3 ml, 12.0 mmol) was syringed into a stirred suspension of K_2ReBr_6 (0.89 g, 1.20 mmol) in 30 ml of ethanol. This mixture was refluxed for 48 h, cooled, and then filtered to yield a small amount of white material that was discarded. The filtrate was taken to dryness and admixed with 0.4 g of KPF_6. The mixture was redissolved in 50 ml of acetone, filtered, and the filtrate then taken to small volume to produce a cream colored solid. The resulting filtrate was taken to dryness and redissolved in a small volume of isopropyl alcohol. The addition of diethyl ether and subsequent cooling produced an additional quantity of cream colored solid. Yield 0.50 g (50%). Both solids were identified as $[Re(CNCMe_3)_6]PF_6$ by ^1H NMR and IR spectroscopy.

(iii) $[Re(CNCMe_3)_5I_2]I_3$. t-Butyl isocyanide (0.50 ml, 4.8 mmol) was syringed into a mixture of K_2ReI_6 (0.82 g, 0.80 mmol) and 25 ml of ethanol. The solution darkened immediately and reaction mixture was stirred for 1 h. The reaction mixture was then filtered to yield a brown material that was repeatedly washed with methylene chloride. The washings were collected, reduced in volume, and a small volume of hexane was added. This solution was chilled and then filtered to yield a crop of golden brown crystals. These were washed with hexane and dried in vacuo. Yield 0.32 g (32%). Anal. Found: C, 24.41; H, 3.67. $C_{25}H_{45}I_5N_5Re$ calcd.: C, 24.29; H, 3.67%.

A small quantity of $[Re(CNCMe_3)_6]I_3$ could be isolated upon refluxing the original ethanol reaction filtrate following the removal of the initial insoluble brown reaction product. Work-up followed the procedure described in A(i).

(iv) $Re(CNPh)_5I$. A mixture of K_2ReI_6 (0.60 g, 0.58 mmol) and phenyl isocyanide (0.6 ml) was added to 20 ml of acetone. This was stirred at room temperature for 1 h and then evaporated to half volume under a stream of nitrogen. A 50% aqueous ethanol solution (20 ml) was added to the brown colored solution and the resulting light brown solid filtered off and dried. It was then dissolved in 200 ml of diethyl ether, the solution filtered and the filtrate allowed to evaporate slowly. This afforded bright yellow needles of the complex. Yield 0.13 g (27%). Anal. Found: C, 50.92; H, 3.30. $C_{35}H_{25}IN_5Re$ calcd.: C, 50.73; H, 3.04%.

(v) $Re(CNxylyl)_5I$. This complex was obtained as green-yellow crystals using a procedure analogous to A(iv). Yield 32%. Anal. Found: C, 55.01; H, 4.10 $C_{45}H_{45}IN_5Re$ calcd.: C, 55.78; H, 4.68%.

(vi) $Re(CNPh)_5I_3$. Phenyl isocyanide (0.4 ml) was added to a suspension of K_2ReI_6 (1.0 g, 0.97 mmol) in 20 ml of ethanol. The mixture was stirred at room temperature for 1 h, cooled, and filtered. The resulting red-brown crystals were dissolved in 20 ml of dichloromethane, and this solution treated with 4 drops of

hexane and allowed to evaporate slowly to afford the complex as dark red crystals. Yield 0.32 g (30%). Anal. Found: C, 39.08; H, 2.48; I, 35.11. $C_{35}H_{25}I_3N_5Re$ calcd.: C, 38.83; H, 2.33; I, 35.17%. This complex is soluble in chlorinated solvents but insoluble in hexanes and diethyl ether.

An alternative means of obtaining this complex involves the reaction between $Re(CNPh)_5I$ (0.1 g, 0.12 mmol) and a large excess of I_2 (0.3 g, 1.18 mmol) in 30 ml of carbon tetrachloride. This solution was stirred in the air for 1 h, evaporated under a nitrogen gas stream, and the residue extracted with a large volume of hexanes (15 × 100 ml). This extraction procedure dissolves the excess I_2. The remaining red solid was dissolved in the minimum volume of dichloromethane (about 5–10 ml) and allowed to recrystallize. Yield 0.11 g (84%). The spectroscopic and electrochemical properties of this product are identical to those of the samples prepared by the other procedure.

(vii) The conversion of $Re(CNPh)_5I_3$ to $Re(CNPh)_5I$. When $Re(CNPh)_5I_3$ (0.1 g, 0.09 mmol) was treated with bis(diphenylphosphino)methane (0.3 g, 0.78 mmol) in 20 ml of acetone, the solution changed color from red to yellow. This solution was then evaporated to dryness under a stream of gaseous nitrogen and the solid residue extracted with diethyl ether. The extract was filtered and the filtrate allowed to evaporate slowly to afford $Re(CNPh)_5I$ as yellow crystals. Yield 0.06 g (78%). The spectroscopic and electrochemical properties of this product are identical to those exhibited by samples of this complex prepared as described in A(iv).

(viii) $Re(CNxylyl)_5I_3$. This complex was prepared from the reaction between $Re(CNxylyl)_5I$ and I_2 in dichloromethane using the procedure describe in A(vi). The identity of this red-brown crystalline product was based upon the similarity of its spectroscopic and electrochemical properties to those of $Re(CNPh)_5I_3$.

(ix) $[Re(CNPh)_6]I_3$. An exothermic reaction occurred upon adding neat phenyl isocyanide (2.0 ml) to K_2ReI_6 (0.6 g, 0.58 mmol). After stirring the reaction mixture at room temperature for 4 h, it was filtered and the solid washed with petroleum ether. The remaining yellow solid was dissolved in dichloromethane, the solution filtered, and petroleum ether added to the filtrate to precipitate the complex. Yield 0.65 g (94%). Anal. Found: C, 43.10; H, 2.47. $C_{42}H_{30}I_3N_6Re$ calcd.: C, 42.55; H, 2.55%.

(x) $[Re(CNPh)_6]PF_6$. An anion exchange reaction to convert $[Re(CNPh)_6]I_3$ into $[Re(CNPh)_6]PF_6$ can be accomplished by adding KPF_6 (0.4 g, 2.17 mmol) to a solution of $[Re(CNPh)_6]I_3$ (0.2 g, 0.17 mmol) in 30 ml of acetone. The resulting solution was stirred for 1 h in air, filtered and the filtrate evaporated to dryness. The residue was dissolved in dichloromethane and pure $[Re(CNPh)_6]PF_6$ precipitated by the addition of petroleum ether. Yield 0.15 g (94%). Anal. Found: C, 52.95; H, 3.36. $C_{42}H_{30}F_6N_6PRe$ calcd.: C, 53.11; H, 3.18%.

(xi) $ReBr_3(CN\text{-}p\text{-}tol)_3$. A complex of this stoichiometry was claimed to be formed [11] by the reaction of K_2ReBr_6 with *p*-tolNC in aqueous ethanol. However, since the preparative details were so meagre [11], we give full details of the procedure that we used to isolate this material. A mixture of K_2ReBr_6 (1.0 g, 1.3 mmol) and *p*-tolyl isocyanide (1.0 g, 8.5 mmol) in 20 ml of ethanol was stirred at room temperature for 24 h. Up to this point no reaction appeared to have taken place. Water was then added (10 ml) and the resulting solution stirred for 30 min; during this time, the solution turned from orange to a brown-green color. The reaction mixture was filtered in air, and the green solid was washed with 10 ml of 90%

ethanol, followed by acetone and then dichloromethane. The dichloromethane washings were set aside and worked-up separately. The dark green solid remaining on the filter (yield 0.20 g (19%)) had microanalyses consistent with the formulation previously ascribed to it by Freni and Romiti [11]. Anal. Found: C, 36.91; H, 3.38. $C_{24}H_{21}Br_3N_3Re$ calcd.: C, 37.08; H, 2.71%.

The dichloromethane washings were evaporated to dryness under a stream of nitrogen gas to afford a dark green solid that appeared to be the *p*-tolyl amine complex $ReBr_3(NH_2\text{-}p\text{-tol})_3$. Yield 0.14 g (14%). Anal. Found: C, 33.76; H, 3.45. $C_{21}H_{27}Br_3N_3Re$ calcd.: C, 33.75; H, 3.64%. The IR spectrum of this complex (Nujol mull) showed the absence of any $\nu(C{\equiv}N)$ vibrations, but instead exhibited bands at ~ 3220 and ~ 3190 cm^{-1}, assigned to $\nu(N\text{–}H)$, and $\nu(Re\text{–}Br)$ at 211s cm^{-1}. We attribute the formation of this complex to the presence of a small amount of *p*-tolNH$_2$ contaminant in the *p*-tolNC; it appears that not all of the amine had been removed upon distilling the isocyanide during its final purification.

B. Reactions of Re_3X_9 (X = Cl, Br or I)

(i) $Re_3Cl_9(CNCH_3)_3$. Methyl isocyanide (0.2 ml, 3.6 mmol) was syringed into a stirred solution of Re_3Cl_9 (0.40 g, 0.45 mmol) in 20 ml of methanol. The purple colored solution immediately thickened. After a reaction time of 5 min the reaction mixture was filtered yielding a purple product which was washed with methanol and dried in vacuo. Yield 0.40 g (88%). Anal. Found: C, 6.96; H, 1.06; N, 4.51. $C_6H_9Cl_9N_3Re_3$ calcd.: C, 7.20; H, 0.91; N, 4.20%.

(ii) $Re_3Cl_9(CNCHMe_2)_3$. This dark purple compound was obtained by a procedure similar to that described in B(i). Yield 54%. The spectroscopic and electrochemical properties of this compound confirmed its identity.

(iii) $Re_3Cl_9(CNC_6H_{11})_3$. A dark red-purple solid was isolated using a procedure analogous to B(i). The identity of this complex was confirmed by the similarity of its spectroscopic and electrochemical properties to those of $Re_3Cl_9(CNCH_3)_3$.

(iv) $Re_3Cl_9(CNCMe_3)_3$. A shiny purple product was produced upon following a procedure analogous to B(i). This product had similar spectroscopic and electrochemical properties to those of $Re_3Cl_9(CNCH_3)_3$.

(v) $[Re(CNCMe_3)_6]PF_6$. A quantity of Re_3Cl_9 (0.30 g, 0.34 mmol) was refluxed with 0.3 ml (2.9 mmol) of t-butyl isocyanide in 20 ml of methanol for 6 h. The resulting clear, yellow-brown solution was taken to dryness and the residue was then dissolved in acetone to which 0.03 g of KPF_6 was added. Following the dropwise addition of diethyl ether, a tan solid separated. This solid was recrystallized from dichloromethane/diethyl ether. Yield 0.51 g (60%). This product was identified as $[Re(CNCMe_3)_6]PF_6$ on the basis of its IR spectrum and the cyclic voltammogram of its solution in 0.2 *M* tetra-n-butylammonium hexafluorophosphate-dichloromethane [1].

(vi) $Re_3Br_9(CNMe)_3$. This dark red-brown complex was prepared using a procedure analogous to that described for its chloride analogue in B(i), using ethanol as the solvent and reaction time of 1 h; yield 93%. Anal. Found: C, 4.89; H, 0.68. $C_6H_9Br_9N_3Re_3$ calcd.: C, 5.14; H, 0.65%.

(vii) $Re_3Br_9(CNCHMe_2)_3$. A procedure analogous to that described in B(vi), afforded red-brown crystals of this complex in 90% yield. This compound was identified by its spectroscopic and electrochemical properties.

(viii) $Re_3Br_9(CNCMe_3)_3$. This complex was synthesized by an analogous proce-

dure to that described in B(vi); yield 80%. This product had similar spectroscopic and electrochemical properties to the other bromide analogs.

(ix) $Re_3Br_9(CNC_6H_{11})_3$. Dark red crystals of this compound were formed using a procedure similar to that described in B(vi); yield 88%. The identity of this complex was established from its spectroscopic and electrochemical properties.

(x) $Re_3I_9(CNCH_3)_3$. This purple-black complex was obtained using a procedure analogous to that described for the chloride analogue $Re_3Cl_9(CNCH_3)_3$ in B(i). Anal. Found: C, 4.23; H, 0.49; I, 63.00. $C_6H_9I_9N_3Re_3$ calcd.: C, 3.95; H, 0.50; I, 62.62%.

(xi) $Re_3I_9(CNCHMe_2)_3$. A procedure analogous to that described in B(vi), but using methanol in place of ethanol, led to formation of dark purple crystals of this complex; yield 83%. The identity of this complex was established by its spectroscopic properties.

(xii) $Re_3I_9(CNCMe_3)_3$. This compound was prepared using a procedure similar to that described in B(xi). Yield 52%.

(xiii) $Re_3I_9(CNC_4H_9)_3$. The reaction at room temperature between Re_3I_9 and n-butyl isocyanide in ethanol led to the precipitation of $Re_3I_9(CNC_4H_9)_3$ as a dark purple-black solid. Anal. Found: C, 9.13; H, 1.60; I, 59.00; N, 2.15. $C_{15}H_{27}I_9N_3Re_3$ calcd.: C, 9.24; H, 1.40; I, 58.57; N, 2.15%.

(xiv) $Re_3I_9(CNC_6H_{11})_3$. This complex was prepared using a procedure similar to that described in B(xi). Anal. Found: I, 56.81. $C_{21}H_{33}I_9N_3Re_3$ calcd.: I, 56.31%.

C. Reaction of $Re_3Cl_9(PEtPh_2)_3$ with t-butyl isocyanide

A quantity of $Re_3Cl_9(PEtPh_2)_3$ (0.25 g, 0.16 mmol) was refluxed with 0.4 ml (3.6 mmol) of t-butyl isocyanide in 20 ml of acetone for 2 h. To the resulting yellow solution was added 0.03 g of KPF_6. Diethyl ether was then added dropwise until the solution clouded, at which point the mixture was chilled to 0°C. The resulting yellow solid was shown to be $[Re(CNCMe_3)_4(PEtPh_2)_2]PF_6$ on the basis of its IR spectrum and the cyclic voltammogram of a solution in dichloromethane-0.2 *M* tetra-n-butylammonium hexafluorophosphate [1].

Physical measurements

Infrared spectra of Nujol mulls were recorded in the region 4000–200 cm^{-1} with a Beckman IR-12 spectrophotometer and from 500 to 50 cm^{-1} on a Digilab FTS-20B spectrometer, using KBr and polyethylene plates. Cyclic voltammetry experiments were performed on dichloromethane solutions of the complexes containing 0.2 *M* tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. All measurements were made in a single-chambered cell and were taken at a platinum bead electrode. Voltammetric measurements were taken with a Bioanalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B x-y recorder. $E_{1/2}$ values were referenced to the saturated potassium chloride calomel electrode (SCE) at room temperature. X-ray photoelectron spectra were recorded with a Hewlett-Packard Model 5950A ESCA spectrometer using our standard procedure [22]. Microanalyses were performed by Dr. C.S. Yeh and Dr. H.D. Lee of the Purdue University microanalytical laboratory.

Results and discussion

Reactions of K_2ReX_6 (X = Br or I) with aryl isocyanides

The six coordinate mononuclear rhenium(I) complex $Re(CNPh)_5I$ can be obtained as bright yellow needles upon reacting K_2ReI_6 with PhNC in acetone for 1 h at room temperature. In this regard, the reaction resembles that between K_2ReI_6 and *p*-tolNC which, as reported by Freni and Romiti [11], yields Re(CN-*p*-tol)$_5$I. Noteworthy features in the IR Nujol mull spectrum of $Re(CNPh)_5I$ are: (i) ν(C≡N) modes at ~ 2100sh, 2056s, ~ 2000sh,br and 1892m,br cm^{-1}, and (ii) an intense band at 216 cm^{-1} tentatively assigned to ν(Re–C). The related reaction between K_2ReI_6 and xylylNC affords Re(CNxylyl)$_5$I, which exhibits similar spectroscopic properties to $Re(CNPh)_5I$ viz., ν(C≡N) at 2080sh, 2052s, 2007m, 1965m and 1918m cm^{-1}, and ν(Re–C) at 190 cm^{-1}.

When the reaction between K_2ReI_6 and PhNC is carried out in ethanol instead of acetone (again for 1 h at room temperature), dark red crystals of the complex $Re(CNPh)_5I_3$ are isolated rather than $Re(CNPh)_5I$. Under these same conditions, Freni and Romiti [11] claimed that the interaction of K_2ReI_6 with *p*-tolNC afforded the rhenium(III) complex Re(CN-*p*-tol)$_4$I$_3$, a stoichiometry clearly differing from that which we obtained for the product from the PhNC reaction. The PhNC derivative $Re(CNPh)_5I_3$, like Re(CN-*p*-tol)$_4$I$_3$ [11], exhibits four ν(C≡N) vibrations in its IR spectrum (recorded both as a KBr pellet and a Nujol mull). For $Re(CNPh)_5I_3$ these absorptions are at 2170w, ~ 2100sh, 2075s and 1984s cm^{-1}, whereas Re(CN-*p*-tol)$_4$I$_3$ is purported [11] to have ν(C≡N) at 2180m, 2140s, 2100s and 2020m cm^{-1}, although the medium in which this measurement was carried out was never specified. In contrast to these spectroscopic results [11], Treichel et al. [10] report only a single intense ν(C≡N) absorption in the region 2190–2150 cm^{-1} for authentic complexes of the type $Re(CNR)_4Br_3$, where R = CH_3 or *p*-tol. Thus the IR spectrum reported for "Re(CN-*p*-tol)$_4$I$_3$" [11] is in actuality more consistent with a complex of stoichiometry Re(CN-*p*-tol)$_5$I$_3$. Additional spectral features of note for $Re(CNPh)_5I_3$ are an intense absorption at 213 cm^{-1}, very similar to the related vibration for $Re(CNPh)_5I$, and the characteristic "triiodide" vibration at 148s cm^{-1} [21].

We believe that $Re(CNPh)_5I_3$ is not a complex of rhenium(III) but instead contains rhenium(I) and coordinated triiodide. Interestingly, it has reasonable thermal stability and does not decompose until 137–139°C. It can also be formed from $Re(CNPh)_5I$ by the reaction of the latter with an excess of I_2 in carbon tetrachloride and can, in turn, be converted back to the monoiodide by reaction with an excess of a phosphine ligand ($Ph_2PCH_2PPh_2$ was chosen for this purpose).

Furthermore, the electrochemical properties of these two complexes, as measured using the cyclic voltammetric technique (CV), reveal some important similarities. The CV of a 0.2 *M* TBAH/CH_2Cl_2 solution of $Re(CNPh)_5I$ (Fig. 1a) shows an electrochemically irreversible oxidation at +1.26 V vs. SCE, the value of which is similar to $E_{1/2}$ for the reversible $[Re(CNPh)_6]^{+,2+}$ couple (vide infra) and which is therefore more than likely associated with a metal-based oxidation. Additionally, there is a couple at $E_{1/2} = +0.52$ V ($i_{p,a}/i_{p,c} \sim 1$ and ΔE_p 85 mV at ν 200 mV s^{-1}) which we attribute to a redox process occurring at the coordinated iodide ligand. A minor feature at $E_{p,c} \sim +0.7$ V is due to very small amounts of free iodide released following the oxidations at +0.56 and +1.26 V. In comparing the CV of $Re(CNPh)_5I$

with that of Re(CNPh)$_5$I$_3$ (Fig. 1b), it is apparent that the most striking similarity is the oxidation at +1.26 V. However, the presence of free iodide/iodine in the latter system is signified by oxidations at +0.34 and +0.74 V and their coupled reduction waves at −0.08 and +0.60 V. The current associated with the iodide/iodine couple at +0.67 V (Fig. 1b) is enhanced because of its close coincidence with another couple (ca. +0.55 V) that is characteristic of the coordinated iodide ligand (Fig. 1a). Thus we can explain the electrochemical behavior of dilute solutions of Re(CNPh)$_5$I$_3$ in 0.2 *M* TBAH/CH$_2$Cl$_2$ as arising through loss of iodine from the coordinated triiodide ligand, according to the equilibrium Re(CNPh)$_5$I$_3$ $\rightleftharpoons$ Re(CNPh)$_5$I + I$_2$, a process which must lie far to the right. Re(CNxylyl)$_5$I can be converted to Re(CNxylyl)$_5$I$_3$ by I$_2$ in a similar fashion to the conversion of Re(CNPh)$_5$I to Re(CNPh)$_5$I$_3$. The complex Re(CNxylyl)$_5$I$_3$ has spectroscopic properties that are very similar to those of Re(CNPh)$_5$I$_3$, and the electrochemical properties of Re(CNxylyl)$_5$I and Re(CNxylyl)$_5$I$_3$ bear such a striking correspondence to those of their PhNC analogues that these pairs of complexes must bear a close structural relationship to one another *.

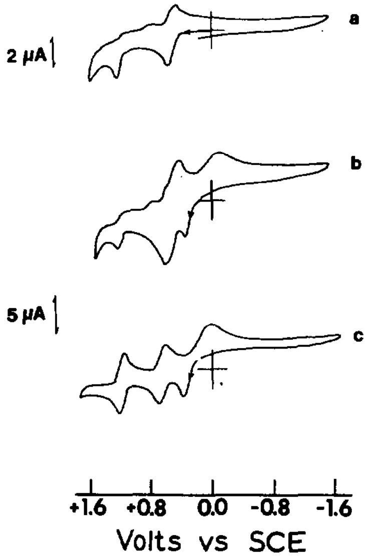

Fig. 1. Cyclic voltammograms (scan rate 200 mV s^{-1} at a Pt-bead electrode) in 0.2 *M* tetra-n-butylammonium hexafluorophosphate-dichloromethane: (a) Re(CNPh)$_5$I; (b) Re(CNPh)$_5$I$_3$; (c) [Re(CNPh)$_6$]I$_3$.

The reactions between K$_2$ReI$_6$ and ArNC (Ar = Ph or xylyl) in acetone or ethanol that we have described above should be contrasted with that between K$_2$ReI$_6$ and the neat PhNC ligand. In the latter instance, the homoleptic species [Re(CNPh)$_6$]I$_3$ is formed in 90% yield. In its IR spectrum, the ν(C≡N), and ν(I$_3^-$)

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* A few cases of coordinated triiodide have recently been reported. See for example: (a) F. Calderazzo, F. Marchetti, R. Poli, D. Vitali and P.F. Zanazzi, J. Chem. Soc., Dalton Trans., (1982) 1665; (b) D. Petridis, A. Kostikas, A. Simopoulos and D. Niarchos, Inorg. Chem., 21 (1982) 766.

modes are at 2078s and 140vs cm^{-1}, respectively. The presence of I_3^- is further confirmed both by CV measurements (Fig. 1c), and anion exchange experiments using KPF_6. The latter reaction gives $[Re(CNPh)_6]PF_6$, characterized by its IR active $\nu(C{\equiv}N)$ mode at 2088s cm^{-1}. The CV's of $[Re(CNPh)_6]X$, where $X = I_3$ or PF_6, show the $[Re(CNPh)_6]^{+,2+}$ couple to be at + 1.20 V vs. SCE; $n = 1.0 \pm 0.1$ from controlled potential electrolysis experiments. This $E_{1/2}$ value is in excellent agreement with comparable data for the *p*-tolNC derivative $[Re(CN\text{-}p\text{-}tol)_6]PF_6$ reported by Treichel and Williams [9].

In the reaction between K_2ReI_6 and *p*-tolNC in EtOH which Freni and Romiti [11] claim produces $Re(CN\text{-}p\text{-}tol)_4I_3$, and which we have suggested is the rhenium(I) complex $Re(CN\text{-}p\text{-}tol)_5I_3$ (vide supra), addition of water to the mother liquor (following isolation of this complex) was said [11] to afford black crystals of $Re(CN\text{-}p\text{-}tol)_3I_3$. The analogous green crystalline bromide complex $Re(CN\text{-}p\text{-}tol)_3Br_3$ was described as the sole product when K_2ReBr_6 was reacted with *p*-tolNC in ethanol [11]. We have attempted to isolate $Re(CN\text{-}p\text{-}tol)_3Br_3$ using the recipe described by Freni and Romiti [11], and have succeeded in obtaining the requisite green solid (albeit in low yield) upon adding water to the reaction solution (see Experimental section). Microanalytical data and IR spectroscopy ($\nu(C{\equiv}N)$ at 2203s cm^{-1}) support this formulation; the value of $\nu(C{\equiv}N)$ is in accord with this being a rhenium(III) species [1,10]. However, since we have recently succeeded in isolating a better defined complex of this type, namely $ReCl_3(CNmesityl)_3$ [7] *, we have not pursued further the complete characterization of $ReBr_3(CN\text{-}p\text{-}tol)_3$.

Reactions of K_2ReX_6 ($X = Br$ or I) with alkyl isocyanides

The reaction at room temperature of K_2ReI_6 with neat t-butyl isocyanide resembles that with neat PhNC in that the homoleptic species $[Re(CNR)_6]I_3$ ($R = CMe_3$) is obtained. This complex has the expected spectroscopic properties (see Experimental section). This same complex was obtained when the reaction was carried out in refluxing ethanol for 12 h. However, reaction in ethanol at room temperature for 1 h gave the intermediate rhenium(III) complex $[Re(CNCMe_3)_5I_2]I_3$. This molecule has spectroscopic properties that are very similar to those of the previously described salts $[Re(CNCMe_3)_5X_2]PF_6$ ($X = Cl$ or Br) [1], i.e., IR (Nujol mull), $\nu(C{\equiv}N)$ 2240m, 2200s and 2050w cm^{-1} and $\nu(I_3^-)$ 145s cm^{-1}; ^{1}H NMR ($CDCl_3$), δ 1.61 ppm; XPS Re $4f_{5/2,7/2}$ binding energies, 44.0 and 41.6 eV. The latter reaction was carried out under conditions that were essentially identical to those that Romiti et al. [12] used in the reaction of K_2ReI_6 with $C_6H_{11}NC$ and which they claimed afforded violet crystalline "trinuclear" $Re_3I_6(CNC_6H_{11})_6$. Our attempts to repeat this latter preparation were not successful. The violet solid we isolated did not analyze for a complex with this stoichiometry **. While its IR spectrum compares quite well with that reported by Romiti et al. [12], we find this material to be diamagnetic (by the Evans method) while they describe it as possessing a magnetic moment of 3.27 BM (Gouy Method) based upon the tri-

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* IR (Nujol (mull): $\nu(C{\equiv}N)$ 2195m-s, 2160s cm^{-1}, IR(CH_2Cl_2): $\nu(C{\equiv}N)$ 2188s, 2163 s cm^{-1}; CV in 0.2 *M* TBAH/CH_2Cl_2: $E_{1/2}$(ox)+ 1.55 and $E_{p,c}$ −0.80 V vs. SCE.

** Found: C, 13.10; H, 2.25; I, 53.30%. Romiti et al. [12] report the following microanalytical data: C, 25.35; H, 3.20; N, 4.23%.

nuclear formulation $Re_3I_6(CNC_6H_{11})_6$. The identity of this material remains unknown, although its XPS spectrum (Re $4f_{5/2,7/2}$ binding energies at 44.4 and 42.1 eV) and IR spectrum (Nujol mull, $\nu(C\equiv N)$ 2230m-s and 2200sh cm^{-1}) are certainly in accord with it being a rhenium(III) species. In any event, since an excess of isocyanide ligand eventually leads to a disruption of the Re_3X_9 clusters to give mononuclear species (vide infra), it seems unlikely that a trinuclear cluster $Re_3I_6(CNC_6H_{11})_6$ would be formed from a mononuclear starting material, i.e. K_2ReI_6.

K_2ReBr_6, like K_2ReI_6, reacts with Me_3CNC in refluxing ethanol to give the homoleptic rhenium(I) cation $[Re(CNCMe_3)_6]^+$, which in this instance we isolated as its PF_6^- salt.

Reactions of Re_3X_9 (X = Cl, Br, or I) with alkyl isocyanides

The reactions at room temperature between the trinuclear halides Re_3X_9 (X = Cl, Br or I) and alkyl isocyanides lead to the formation of the adducts $Re_3X_9(CNR)_3$ (see Table 1). This is a well established mode of reactivity of the rhenium(III) halides towards monodentate donors [19,23,24]. While Freni and co-workers [12,25] have previously shown that Re_3Cl_9 and Re_3I_9 react with *p*-tolyl isocyanide and cyclohexyl isocyanide to form $Re_3X_9(CN\text{-}p\text{-tol})_3$ (X = Cl or I) [25] and $Re_3I_9(CNC_6H_{11})_3$ [12], the present study demonstrates for the first time the generality of this reaction course for all three halides and a variety of alkyl isocyanides. The isolation of the series of iodide complexes $Re_3I_9(CNR)_3$ provides the only examples of coordination complexes of Re_3I_9 [26].

When reactions are performed under more forcing conditions, viz. in refluxing alcohol, cluster disruption occurs and the thermodynamically stable $[Re(CNR)_6]^+$ cation, isolated as its PF_6^- salt, is formed. This reaction is easily extended to the phosphine adduct $Re_3Cl_9(PEtPh_2)_3$ which, upon reaction with Me_3CNC and KPF_6 in refluxing acetone, yields $[Re(CNCMe_3)_4(PEtPh_2)_2]PF_6$. Similar cluster disruption was observed by Freni and Valenti [27] upon reaction of Re_3I_9 with neat RNC ($R = C_2H_5$ or *p*-tolyl) to form the homoleptic complexes $[Re(CNR)_6]I_3$ and is to be expected in view of the ease with which π-acceptor ligands can instigate cleavage of multiple metal–metal bonds [3] *.

The IR spectra of these cluster complexes (Table 1) are unexceptional. The $\nu(C\equiv N)$ modes are in a region characteristic of the binding of isocyanide to rhenium(III) centers [1]. Furthermore, the low frequency IR spectra are characterized by intense bands in the region 360–310 cm^{-1} for the chlorides, 260–200 cm^{-1} for the bromides, and 200–150 cm^{-1} for the iodides. For the chloride series, the values compare very closely with the $\nu(Re\text{–}Cl)$ modes of other $Re_3Cl_9L_3$ compounds (where L = pyridine, PPh_3, pyrazine, etc.) [24]. Electronic absorption spectra of dichloromethane solutions of representative cluster complexes are reported in Table 1. In the case of the chloride and bromide complexes, these spectra compare very well with spectra reported for other complexes of the type $Re_3X_9L_3$ [23,24,28]. The spectra of the cluster compounds synthesized in the present study, and those reported previously [23,24,28] are strikingly similar in the low energy

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* The Re_3X_9 clusters contain Re–Re double bonds; see F.A. Cotton and R.A. Walton, Multiple Bonds Between Metal Atoms, J. Wiley and Sons, 1982; p. 265.

TABLE 1

INFRARED AND ELECTRONIC ABSORPTION SPECTRA OF $Re_3X_9(CNR)_3$ COMPOUNDS

Compound	ν(C≡N) [a] (cm^{-1})	λ (nm) (ε (M^{-1} cm^{-1})) [b]
$Re_3Cl_9(CNMe)_3$	2253	792 (0.47), 532 (1.52), 415sh, 325sh, 311 (11.5)
$Re_3Cl_9(CNCHMe_2)_3$	2222	800 (0.68), 532 (1.97), 413sh, 326sh, 311 (13.0)
$Re_3Cl_9(CNCMe_3)_3$	2221	798 (0.35), 530 (0.92), 417sh, 325sh, 310 (5.5)
$Re_3Cl_9(CNC_6H_{11})_3$	2228sh, 2222	802 (0.65), 532 (2.26), 410sh, 326sh, 312 (14.9)
$Re_3Br_9(CNMe)_3$	2245	790 (0.70), 553 (1.73), 445sh, 391 (9.9), 339sh, 314 (7.6)
$Re_3Br_9(CNCHMe_2)_3$	2220	[c]
$Re_3Br_9(CNCMe_3)_3$	2218	801 (0.90), 549 (2.18), 450 (4.86), 390 (11.4), 363sh, 318 (8.1)
$Re_3Br_9(CNC_6H_{11})_3$	2218	800 (0.65), 553sh, 452sh, 400sh, 369 (9.1)
$Re_3I_9(CNMe)_3$	2229, 2207	[c]
$Re_3I_9(CNCHMe_2)_3$	2212sh, 2198	[c]
$Re_3I_9(CNCMe_3)_3$	2185	~ 850sh, 770 (2.70), 695sh, ~ 640sh, 530 (8.2), 454 (7.9), ~ 390sh
$Re_3I_9(CNC_6H_{11})_3$	2213	825sh, ~ 800sh, ~ 750sh, 700 (3.80), ~ 630sh, 534 (10.0), 470 (8.9), ~ 400sh, ~ 360sh

[a] Recorded as Nujol mulls; all bands are of medium-strong intensity. [b] Recorded as CH_2Cl_2 solution; molar extinction coefficient in parentheses (× 10^{-3}). [c] Not measured.

region. In particular, bands occurring near 800 and 540 nm are diagnostic of the retention of the trirhenium cluster structure. This consistency in spectral properties throughout the series has been attributed [23,24] to transitions that are localized on the Re_3 core. In the case of $Re_3I_9(CNR)_3$ clusters, the spectra are complicated by the onset of intense $I(\pi) \rightarrow Re$ charge transfer transitions that encroach upon the visible region. Despite these additional bands, the Re_3 "core transitions" can be seen in the 700–800 and 530–540 nm regions suggesting, once again, that the Re_3 cluster has remained intact. The aforementioned spectral data, along with the microanalytical data, support the notion that these complexes are uniformly of the type $Re_3X_9L_3$.

The electrochemical properties of these cluster compounds are noteworthy. The cyclic voltammogram of $Re_3Br_9(CNMe)_3$, a representative of this cluster series, is shown in Fig. 2a and voltammetric data for all the complexes are reported in Table 2. For the chloride and bromide compounds, a quasi-reversible [29,30] one-electron oxidation [31] is observed in the potential range $+1.7$ to $+1.5$ V vs. SCE. Following an irreversible reduction at ~ -0.13 V ($i_{p,c} \gg i_{p,a}$), a chemical process occurs to yield a new species characterized by two couples (labeled "Product Waves" in Table 2). Solutions containing this chemical product may be generated by bulk electrolyses at potentials more negative than that of the first reduction ($E_{p,c}$(red(1)) in Table 2) but positive of the first product wave ($E_{1/2}$(red) in Table 2), a process which yields a solution devoid of starting complex and characterized by the two product waves. The cyclic voltammogram of a solution of $Re_3Br_9(CNMe)_3$, following exhaustive electrolysis at -0.20 V, is shown in Fig. 2b. The potentials that characterize this product are reminiscent of those observed for complexes containing the Re_2^{5+} core [32] and might signal the formation of a dinuclear complex of this type. These chemical and electrochemical reductions and the nature of the chemical product(s) are currently the subject of further study.

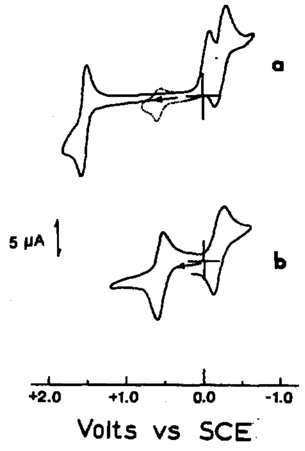

Fig. 2. Cyclic voltammogram (scan rate 200 mV s^{-1} at a Pt-bead electrode) in 0.2 *M* tetra-n-butylammonium hexafluorophosphate-dichloromethane; (a) $Re_3Br_9(CNMe)_3$; (b) solution in (a) following exhaustive electrolysis at -0.20 V. In (a) switching potentials of $+1.8$ and -0.7 V were used and a second scan is indicated by a dotted line. A second irreversible reduction occurs to more negative potentials but is not shown on this scan (see Table 2).

TABLE 2

CYCLIC VOLTAMMETRIC DATA FOR DICHLOROMETHANE SOLUTIONS OF $Re_3X_9(CNR)_3$ [a]

Compound	$E_{1/2}$(ox)	$E_{p,c}$(red(1)) [b]	$E_{p,c}$(red(2)) [b]	Product waves	
				$E_{1/2}$(ox)	$E_{1/2}$(red)
$Re_3Cl_9(CNMe)_3$	+1.70 (90)	−0.11	−1.18	+0.63 (80)	−0.25 (140)
$Re_3Cl_9(CNCHMe_2)_3$	+1.70 (85)	−0.14	−1.26	+0.59 (75)	−0.31 (120)
$Re_3Cl_9(CNCMe_3)_3$	+1.70 (100)	−0.15	−1.50	+0.55 (90)	−0.34 (115)
$Re_3Cl_9(CNC_6H_{11})_3$	+1.71 (95)	−0.15	−1.30	+0.57 (90)	−0.31 (130)
$Re_3Br_9(CNMe)_3$	+1.57 (85)	−0.10	−1.06	+0.58 (65)	−0.23 (155)
$Re_3Br_9(CNCHMe_2)_3$	+1.56 (95)	−0.13	−1.18	+0.52 (70)	−0.31 (180)
$Re_3Br_9(CNCMe_3)_3$	+1.56 (80)	−0.14	−1.26	+0.50 (65)	−0.33 (145)
$Re_3Br_9(CNC_6H_{11})_3$	+1.57 (95)	−0.13	−1.24	+0.51 (75)	−0.32 (195)

[a] Values in volts vs. SCE with a Pt-bead electrode and 0.2 *M* tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte; values of $E_{p,a} - E_{p,c}$ (mV) at a sweep rate of 200 mV s^{-1} are given in parentheses. [b] Irreversible, $i_{p,c}/i_{p,a} \gg 1$.

A second, irreversible reduction wave is observed for the chloride and bromide cluster compounds $Re_3X_9(CNR)_3$ at potentials within the range −1.1 to −1.5 V (Table 2). The reverse (positive) scan, following this reduction, revealed several irreversible, ill-defined processes, and indicated that cluster disruption had occurred, accompanied by the formation of several chemical products. This irreversible reduction and the accompanying product waves are not shown in the scan displayed in Fig. 2a.

The electrochemistry of the iodide clusters is characterized by several ill-defined irreversible redox processes. This increased complexity of the electrochemistry no doubt results from the presence of iodide ligands in the complex, since both metal- and ligand-based redox processes occur leading to the formation of free iodide/iodine in the system. No well-defined electrochemical processes corresponding to those of the analogous chloride or bromide complexes could be discerned from the voltammograms.

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