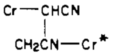
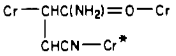
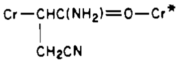
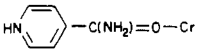
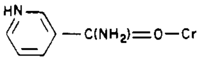
Table VI. Aquation Rates of Pentaaquochromium(III) Complexes (25 °C)

complex[a]	rate constant, s^{-1}
Cr–NCCH$_3$	4.3×10^{-4} [b]
 $Cr{-}CHCN$ / $CH_2CN{-}Cr^*$	3.6×10^{-4}
 $Cr{-}CHC(NH_2){=}O{-}Cr$ / $CHCN{-}Cr^*$	2×10^{-4}
Cr–NCCH=CHCN	$1.19 \times 10^{-2} + 4.14 \times 10^{-4}[H^+]^{-1}$
Cr–NC–C$_6$H$_4$CN	1.7×10^{-2} [c]
 $Cr{-}CHC(NH_2){=}O{-}Cr^*$ / CH_2CN	3.6×10^{-5}
	6.5×10^{-5} [d]
	5×10^{-5} [d]

[a] An asterisk indicates the site of aquation in cases of ambiguity. [b] Reference 7. [c] Balahura, R. J., private communication In 0.1 M HClO$_4$. [d] Taube, H.; Nordmeyer, F. *J. Am. Chem. Soc.* 1968, *90*, 1162.

(iv) It has been proposed that the nitrile group is activated toward carboxamide formation by the neighboring chromium(III) atoms in the $(H_2O)_5Cr{-}CH{-}C{\equiv}N{-}Cr(OH_2)_5$ system. This explains the formation of V in both systems studied here (Schemes I and II).

There have been varying observations on the rate law for chromium(II) reductions analogous to those studied here. Under conditions of [substrate] > [Cr(II)], it has been concluded that fumaric and maleic acids[4,5] are reduced with a rate law first order in each reactant. On the other hand, diethyl fumarate[18] has an overall third-order rate law when [Cr(II)] > [diethyl fumarate], analogous to that reported here (eq 5). The observations of Castro et al.[18] on the secondary reaction are also analogous to those reported here, indicating Cr(II)-catalyzed aquation of the initial organochromium(III) product. Preliminary results[19] with fumaric and maleic acids, with [Cr(II)] > [substrate], show a third-order rate law with rate constants of 2.6 $M^{-2}\ s^{-1}$ and 79 $M^{-2}\ s^{-1}$, respectively. It is not clear at present if the rate law really changes with the relative reagent concentrations or if the original[4,5] evaluation of the rate law on the basis of the linearity of the appropriate plots is in error. If the general mechanism is

$$Cr^{2+} + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{CrL\}^{2+} \xrightarrow[H^+]{k_2[Cr^{2+}]} \text{products}$$

and a steady state is assumed for the intermediate, then rate $\propto k_1k_2[Cr^{2+}]^2[L](k_{-1} + k_2[Cr^{2+}])^{-1}$. This does not predict that the order with respect to $[Cr^{2+}]$ should change from first to second as $[Cr^{2+}]$ is increased.

The fact that free fumaronitrile is reduced about 10^3 times more slowly than its chromium(III) complex may be attributed to the affect of coordination on the reducibility of the ligand. However, this type of rate enhancement seems not to apply to fumarate[16] and maleate[17] coordinated to chromium(III) since previous studies on these systems in the presence of chromium(II) do not appear to be complicated by ligand reduction. Possibly the comparison is not justified, because a proton in the acid has been replaced by $(L)_5Cr^{3+}$ in the complex. The proton may enhance reducibility more than L_5Cr^{3+}. The fumaronitrile system is free from this ambiguity.

The rate constant for the chromium(II) reduction of the $(NH_3)_5Co^{3+}$ complex of fumaronitrile is $\sim 10^7$ times larger than that of succinonitrile.[1] This is a particularly dramatic example of the large effect of a simple change in ligand structure on the electron-transfer rate. Of course the mechanism has also changed from outer sphere with succinonitrile to inner sphere with fumaronitrile. Although the lead-in and remote groups are the same, the –C=C– bond in fumaronitrile greatly affects the ligand reducibility and facilitates electron transfer between the two metal centers.

It might be surprising that the rate constant for reduction of the $(NH_3)_5Co^{3+}$ complex of 1,4-dicyanobenzene (0.92 $M^{-1}\ s^{-1}$)[2] is so much smaller than that of the fumaronitrile complex (1.9 × 10^5 $M^{-1}\ s^{-1}$). This may be due to the difference in ligand reducibility. The polarographic half-wave potentials (DMF vs. SCE) are −1.35 and −1.57 V for fumaronitrile[20] and 1,4-dicyanobenzene,[21] respectively. This observation implicates a chemical reduction mechanism at least for the fumaronitrile complex.

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Registry No. I, 97633-49-3; III, 97633-50-6; IV, 97633-51-7; VII, 97633-52-8; $[(NH_3)_5CoNCCH{=}CHCN](ClO_4)_3$, 80679-82-9; $(H_2O)_5CrNCCH{=}CHCN^{3+}$, 97633-48-2; Cr, 7440-47-3; (*E*)-NCCH=CHCN, 764-42-1.

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[18] Castro, C. E.; Stephens, R. D.; Mojé, S. *J. Am. Chem. Soc.* **1966**, *88*, 4964.

[19] Jordan, R. B., unpublished results. For fumaric acid the reaction was monitored at 580 nm in 0.90 M HClO$_4$ with [fumaric acid] = 7.0 × 10^{-4} M and $[Cr^{2+}]$ between 1.90 × 10^{-2} and 4.70 × 10^{-2} M. With maleic acid the reaction was monitored at 410 and 580 nm in 0.93 M HClO$_4$, with [maleic acid] = 5.5 × 10^{-4} M and $[Cr^{2+}]$ between 0.79 × 10^{-2} and 2.37 × 10^{-2} M.

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Homoleptic Isocyanide Complexes of Ruthenium(II) and Osmium(II)

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The diruthenium(II,III) and diosmium(III) acetates $Ru_2(O_2CCH_3)_4Cl$ and $Os_2(O_2CCH_3)_4Cl_2$ react with alkyl isocyanides RNC (R = $CHMe_2$, CMe_3, or C_6H_{11}) to give the homoleptic metal(II) complexes $[M(CNR)_6](PF_6)_2$ (M = Ru or Os). This is the first general synthetic route to these complexes and is an important further illustration of the use that can be made of the cleavage of multiple metal–metal bonds by π-acceptor ligands such as isocyanides. The *tert*-butyl isocyanide complexes readily undergo a dealkylation reaction to give the cyano derivatives $[M(CNCMe_3)_5CN]PF_6$. The spectroscopic (IR and ^1H and ^{13}C NMR) and electrochemical properties of these complexes have been measured.

Introduction

Homoleptic isocyanide complexes of ruthenium and osmium are rare. Reduction of *trans*-$Ru(CNR)_4Cl_2$ (R = CMe_3 or $CHMe_2$) with sodium amalgam in the presence of excess isocyanide has been used to prepare $Ru(CNCMe_3)_5$ and $Ru_2(CNCHMe_2)_9$.[1,2] The only zerovalent osmium complex of this type that has been reported to date is $Os(CNxylyl)_5$, which is described as being formed by reduction of *trans*-$Os(CNxylyl)_4Cl_2$.[3] The cationic species $[Ru(CNCH_3)_6]^{2+}$[4] and $[Os(CNCH_3)_6]^{2+}$[5] can be prepared by methylation of the hexacyanometalate anions with dimethyl sulfate and methyl fluorosulfate, respectively, but other simple cations of this type have not been isolated although the reactions of $[M(CN)_6]^{4-}$ with triethyloxonium tetrafluoroborate in the presence of ketones lead to the formation of homoleptic isocyanides of the type $[M(CNC(R^1R^2)CHR^3COR^4)_6]^{2+}$[6] (M = Fe, Ru, or Os). Dinuclear complexes of the type $[M_2(CNxylyl)_{10}](PF_6)_2$ (M = Ru or Os)[3] and $[Ru_2(L_2)_4](PF_6)_2$ (L_2 = 2,5-dimethyl-2,5-diisocyanohexane)[7] have also been reported.

Our own efforts to synthesize homoleptic isocyanide complexes of the type $[Os(CNR)_6]^{2+}$ by reacting $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2X_4(PPh_3)_2$ or $OsO_2X_2(PPh_3)_2$ (X = Cl or Br) with an excess of alkyl isocyanide in toluene were unsuccessful and led instead to an excellent method for preparing *trans*-$Os(CNR)_4X_2$.[8] An alternative approach to the synthesis of the $[M(CNR)_6]^{2+}$ (M = Ru or Os) complexes is based upon the observation that multiply bonded dimetal complexes of molybdenum, tungsten, and rhenium react with isocyanide ligands to yield the corresponding homoleptics in high yield.[9-13] Previous work by Girolami and Andersen[13] has shown that $Ru_2(O_2CCH_3)_4Cl$ reacts with *tert*-butyl isocyanide to yield *trans*-$Ru(CNCMe_3)_4(O_2CCH_3)_2$. Under similar conditions, the triply bonded diosmium(III) complex $Os_2(O_2CCH_3)_4Cl_2$ yields a mononuclear osmium(III) complex.[14] We have now developed these reactions to afford a convenient method for preparing $[M(CNR)_6]^{2+}$ (R = $CHMe_2$, CMe_3, or C_6H_{11}), thereby providing the first general route to such homoleptic isocyanide complexes for M = Ru or Os.

Experimental Section

The diruthenium(II,III) and diosmium(III) acetates $Ru_2(O_2CCH_3)_4Cl$ and $Os_2(O_2CCH_3)_4Cl_2$ were prepared as described in the literature.[14,15] The isocyanide ligands used were all prepared by the method of Weber et al.[16] Potassium hexafluorophosphate was purchased from Alfa Products and recrystallized from water before use. All other reagents were purchased from commercial sources and used without subsequent purification. Solvents were reagent grade and were deoxygenated prior to use. All reactions were carried out under an atmosphere of nitrogen unless otherwise noted.

A. Reactions of $Ru_2(O_2CCH_3)_4Cl$. (i) *trans*-$Ru(CNCHMe_2)_4(O_2CCH_3)_2\cdot 4H_2O$. Isopropyl isocyanide (1.0 mL, ~11 mmol) was added to a suspension of $Ru_2(O_2CCH_3)_4Cl$ (0.241 g, 0.509 mmol) in 20 mL of a 1/1 (v/v) diethyl ether/methanol solution. The mixture was stirred at room temperature for 24 h to give a yellow solution. The solvent was removed in vacuo, and the resulting yellow residue was extracted with diethyl ether. Filtration produced a yellow filtrate, which was then reduced to low volume and refrigerated at −20 °C overnight. The pale yellow precipitate of *trans*-$Ru(CNCHMe_2)_4(O_2CCH_3)_2\cdot 4H_2O$ was removed by filtration, washed with cold diethyl ether, and vacuum dried for 1 h; yield 0.27 g (47%). Anal. Calcd for $C_{20}H_{42}N_4O_8Ru$: C, 42.32; H, 7.46. Found: C, 43.14; H, 8.04. The presence of water in this complex was inferred from the appearance of a broad absorption at 3400 cm^{-1} in the IR spectrum, and the amount of water was determined by ^1H NMR spectroscopy.

(ii) $[Ru(CNCMe_3)_6](PF_6)_2$ and $[Ru(CNCMe_3)_5CN]PF_6$. To 10 mL of methanol were added $Ru_2(O_2CCH_3)_4Cl$ (0.308 g, 0.650 mmol), KPF_6 (0.6 g), and *tert*-butyl isocyanide (1.5 mL, ~14 mmol). The mixture was refluxed for 12 h, the resulting pale yellow solution was cooled to room temperature, and the solvent was removed in vacuo. The residue was then extracted with dichloromethane and filtered to remove potassium salts of acetate, chloride, and hexafluorophosphate. The pale yellow filtrate was taken to dryness and then stirred in 10 mL of ethanol for a few minutes. Filtration yielded crude $[Ru(CNCMe_3)_6](PF_6)_2$ as a white solid, and a pale yellow filtrate that contained $[Ru(CNCMe_3)_5CN]PF_6$. The homoleptic complex $[Ru(CNCMe_3)_6](PF_6)_2$ was purified by dissolving the crude product in a small volume of dichloromethane and filtering this into diethyl ether with stirring. The white solid that precipitated was filtered off, washed with ethanol and diethyl ether, and vacuum dried for 1 h; yield 0.50 g (44%). Anal. Calcd for $C_{30}H_{54}F_{12}N_6P_2Ru$: C, 40.49; H, 6.12. Found: C, 40.73; H, 6.60.

The filtrate that remained following removal of the crude $[Ru(CNCMe_3)_6](PF_6)_2$ was reduced in volume to about 5 mL. Diethyl ether was added (25 mL), and this solution was refrigerated overnight. The white, crystalline product was removed by filtration, washed with diethyl ether, and vacuum dried; yield 0.213 g (24%). Anal. Calcd for $C_{26}H_{45}F_6N_6PRu$: C, 45.41; H, 6.60; N, 12.22. Found: C, 46.04; H, 7.41; N, 11.94.

Other complexes of the type $[Ru(CNR)_6](PF_6)_2$ (R = $CHMe_2$ or C_6H_{11}) were prepared by a method similar to that described above for $[Ru(CNCMe_3)_6](PF_6)_2$.

(iii) $[Ru(CNCHMe_2)_6](PF_6)_2$. Yield: 95%. Anal. Calcd for $C_{24}H_{42}F_{12}N_6P_2Ru$: C, 35.77; H, 5.26. Found: C, 36.24; H, 5.61.

(iv) $[Ru(CNC_6H_{11})_6](PF_6)_2$. Yield: 60%. Anal. Calcd for $C_{42}H_{66}F_{12}N_6P_2Ru$: C, 48.22; H, 6.37. Found: C, 48.52; H, 6.79.

B. Reactions of *trans*-$Ru(CNR)_4(O_2CCH_3)_2$ (R = CMe_3, $CHMe_2$) with Isocyanides. (i) $[Ru(CNCMe_3)_6](PF_6)_2$. A sample of *trans*-$Ru(CNCMe_3)_4(O_2CCH_3)_2$ (0.162 g, 0.293 mmol), prepared by the method of Girolami and Andersen,[13] was refluxed in 10 mL of methanol, which contained 0.2 g of KPF_6 and 0.2 mL of *tert*-butyl isocyanide, for 24 h. The solvent was removed in vacuo, and the residue was dissolved in dichloromethane and filtered. The pale yellow filtrate was taken to a small volume (ca. 5 mL) and diethyl ether was added to precipitate $[Ru(CNCMe_3)_6](PF_6)_2$. This white solid was washed with ethanol and diethyl ether and vacuum dried; yield 0.157 g (60%). The spectroscopic properties of $[Ru(CNCMe_3)_6](PF_6)_2$ synthesized in this manner were identical with those of the sample synthesized directly from $Ru_2(O_2CCH_3)_4Cl$ (see section A(ii)).

(ii) $[Ru(CNCHMe_2)_6](PF_6)_2$. As in method B(i), *trans*-$Ru(CNCHMe_2)_4(O_2CCH_3)_2\cdot 4H_2O$ (0.070 g, 0.123 mmol) was converted to $[Ru(CNCHMe_2)_6](PF_6)_2$; yield 0.087 g (88%).

C. Dealkylation of $[Ru(CNCMe_3)_6](PF_6)_2$ to $[Ru(CNCMe_3)_5CN]PF_6$. To 15 mL of *n*-propanol was added $[Ru(CNCMe_3)_6](PF_6)_2$ (0.316 g, 0.355 mmol). This mixture was refluxed for 12 h by which time a clear solution had resulted. The solution was cooled and then filtered to remove any unreacted starting material, and the filtrate was evaporated to dryness. The pale yellow residue was dissolved in a small volume of ethanol, and diethyl ether was added. The solution was refrigerated overnight to yield $[Ru(CNCMe_3)_5CN]PF_6$ as white crystals, which were removed by filtration, washed with cold diethyl ether, and vacuum dried; yield 0.160 g (66%).

D. Reactions of $Os_2(O_2CCH_3)_4Cl_2$ with Alkyl Isocyanides. (i) $[Os(CNCMe_3)_6](PF_6)_2$ and $[Os(CNCMe_3)_5CN]PF_6$. A quantity of $Os_2(O_2CCH_3)_4Cl_2$ (0.244 g, 0.335 mmol) was admixed with lead(II) nitrate (0.128 g, 0.386 mmol) and KPF_6 (0.4 g). Ethanol (10 mL) and *tert*-butyl isocyanide (1.5 mL, ~14.2 mmol) were added, and this mixture was then refluxed 24 h. After this period, the reaction mixture was cooled and filtered, and the resulting solid was washed several times with acetone and dichloromethane. The orange filtrate and washings were combined and taken to dryness. This orange residue was dissolved in dichloromethane and filtered to remove the excess of KPF_6. The dichloromethane filtrate was evaporated to dryness, and ethanol was added to the residue.

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Filtration afforded an orange filtrate and a small amount of brown solid. The brown solid was dissolved in dichloromethane and filtered, and diethyl ether was added. The solution was refrigerated overnight to produce white crystals of $[Os(CNCMe_3)_6](PF_6)_2$, which were removed by filtration, washed with diethyl ether, and vacuum dried for 1 h; yield 0.044 g (6%). Anal. Calcd for $C_{30}H_{54}F_{12}N_6OsP_2$: C, 36.81; H, 5.56. Found: C, 35.97; H, 5.66.

The final orange ethanol filtrate was evaporated to dryness. The residue was redissolved in dichloromethane (3 mL), whereupon diethyl ether (6 mL) and hexanes (6 mL) were added, and this mixture was refrigerated overnight. White crystals of $[Os(CNCMe_3)_5CN]PF_6$ were filtered off, washed with hexanes, and vacuum dried for 2 h; yield 0.121 g (23%). Anal. Calcd for $C_{26}H_{45}F_6N_6OsP$: C, 40.20; H, 5.84. Found: C, 39.69, H, 5.91.

Other complexes of the type $[Os(CNR)_6](PF_6)_2$ (R = $CHMe_2$ or C_6H_{11}) were prepared by a method similar to that described above for $[Os(CNCMe_3)_6](PF_6)_2$.

(ii) $[Os(CNCHMe_2)_6](PF_6)_2$. Yield: 17%. Anal. Calcd for $C_{24}H_{42}F_{12}N_6OsP_2$: C, 32.22; H, 4.73. Found: C, 31.98; H, 4.78.

(iii) $[Os(CNC_6H_{11})_6](PF_6)_2$. Yield: 33%. Anal. Calcd for $C_{42}H_{66}F_{12}N_6OsP_2$: C, 44.44; H, 5.86. Found: C, 44.72; H, 5.77.

Physical Measurements. Infrared spectra of Nujol mulls and of dichloromethane solutions were recorded on an IBM Instruments IR/32 spectrometer. Cyclic voltammetric results were obtained as previously described[17] for dichloromethane solutions containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) or for acetonitrile solutions containing 0.1 M TBAH. Potentials were referenced to the silver/silver chloride electrode at room temperature. ^1H NMR spectra were recorded at 90 MHz with a Perkin-Elmer R32 spectrometer or at 200 MHz with a Varian XL-200 spectrometer. $^{13}C\{^1H\}$ NMR spectra were recorded at 50.29 MHz on a Varian XL-200 spectrometer. GC studies were carried out as described previously.[18] Fast atom bombardment (FAB) spectra were obtained on a Kratos MSCC instrument in the Department of Medicinal Chemistry, Purdue University. Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Results and Discussion

The synthesis of $[Ru(CNR)_6](PF_6)_2$ (R = $CHMe_2$, CMe_3, or C_6H_{11}) from the reaction of $Ru_2(O_2CCH_3)_4Cl$ with RNC under reflux occurs readily and in high yield. In the synthesis of $[Ru(CNCMe_3)_6]^{2+}$, an appreciable amount of the dealkylation product $[Ru(CNCMe_3)_5CN]PF_6$ is produced (see Experimental Section). The present results, along with the previous work of Girolami and Andersen,[13] indicate that the formation of these homoleptic ruthenium complexes proceeds through the intermediacy of *trans*-$Ru(CNR)_4(O_2CCH_3)_2$. The complexes *trans*-$Ru(CNR)_4(O_2CCH_3)_2$ (R = $CHMe_2$ or CMe_3) can be isolated by using mild reaction conditions and are therefore identified as the initial products of multiple bond cleavage. They may in turn be converted to $[Ru(CNR)_6](PF_6)_2$ by reaction with an excess of RNC under reflux in the presence of KPF_6.

Although the corresponding reactions of $Os_2(O_2CCH_3)_4Cl_2$ with RNC led to mixtures of products, we were unable to isolate any identifiable products in reasonable yield. However, in the presence of lead(II) nitrate, the homoleptic osmium(II) salts $[Os(CNR)_6](PF_6)_2$ (R = $CHMe_2$, CMe_3, or C_6H_{11}) were isolable, albeit in rather low yield (<35%). The role of $Pb(NO_3)_2$ seems to be in the labilization of the osmium–chlorine and/or osmium–acetate bonds, thereby allowing for attack by RNC at a rate which is competitive with other reaction pathways that apparently lead to undesirable products and therefore to a drastically reduced yield of $[Os(CNR)_6]^{2+}$. We note that $Pb(NO_3)_2$ has been previously employed in the conversion of dimolybdenum(II) acetate to $[Mo(CNR)_7]^{2+}$ (R = CH_3, CMe_3, or C_6H_{11}).[19]

Table I. Properties of $[M(CNR)_6]^{2+}$ and $[M(CNCMe_3)_5CN]^+$ (M = Ru or Os)

complex	Λ_m,[a] Ω^{-1} cm^2 mol^{-1}	IR $\nu(C{\equiv}N)$, cm^{-1}
$[Ru(CNCHMe_2)_6](PF_6)_2$	258	2211 vs. 2035 vw[b] 2207 vs[c]
$[Ru(CNCMe_3)_6](PF_6)_2$	262	2197 vs, 2041 vw[b] 2199 vs, 2040 vw[c]
$[Ru(CNC_6H_{11})_6](PF_6)_2$	239	2207 vs, 2037 vw[b]
$[Os(CNCHMe_2)_6](PF_6)_2$	267	2205 vs, 2037 vw[b]
$[Os(CNCMe_3)_6](PF_6)_2$	259	2188 vs, 2044 vw[b]
$[Os(CNC_6H_{11})_6](PF_6)_2$	246	2201 vs, 2041 vw[b]
$[Ru(CNCMe_3)_5CN]PF_6$	120	2242 w, 2184 s, 2130 m[b] 2236 w, 2184 vs, 2130 m[c]
$[Os(CNCMe_3)_5CN]PF_6$	125	2242 w, 2176 s, 2132 m[b] 2240 w, 2175 vs, 2131 m[c]

[a] 1×10^{-3} M solutions in acetonitrile. [b] Nujol mull. [c] Dichloromethane solution.

While the yields of $[Os(CNR)_6](PF_6)_2$ are lower than hoped for; nonetheless, this procedure is the only one which is currently available that offers promise of being of general applicability. In the case of $[Os(CNCMe_3)_6](PF_6)_2$, the yield is still further reduced by its dealkylation to give $[Os(CNCMe_3)_5CN]PF_6$ in a fashion reminiscent of the conversion of $[Ru(CNCMe_3)_6](PF_6)_2$ to $[Ru(CNCMe_3)_5CN]PF_6$ (see Experimental Section). Previous work on transition-metal complexes containing alkyl isocyanide ligands has shown that dealkylation of the isocyanide ligands can occur, yielding transition-metal cyano complexes.[20-24] Attempts were made to determine the fate of the C_4H_9 species lost upon dealkylation by GC analysis of the gases above the reaction. However, no butane or butene was detected. Previously, Floriani and co-workers[23] detected the presence of cyclohexane when $(C_5Me_5)_2V$ was reacted with excess cyclohexyl isocyanide to form $(C_5Me_5)_2V(CNC_6H_{11})(CN)$. These authors concluded that cyclohexyl isocyanide decomposes by a free-radical process in which homolytic cleavage of the C_6H_{11}–NC bond occurs.

Solutions of the complexes $[M(CNR)_6](PF_6)_2$ and $[M(CNCMe_3)_5CN]PF_6$ (M = Ru or Os) in acetonitrile possess conductivities typical of 1:2 and 1:1 electrolytes, respectively,[25] viz., Λ_m = 235–265 and 120–125 Ω^{-1} mol^{-1} cm^2 (Table I). In the case of $[Ru(CNCMe_3)_5CN]PF_6$, a fast atom bombardment (FAB) spectrum showed a peak at *m/z* 543 due to the $[^{102}Ru(CNCMe_3)_5CN]^+$ cation (the correct isotopic pattern for Ru was observed).[26]

The IR spectra of the $[M(CNR)_6]^{2+}$ complexes reveal an intense $\nu(C{\equiv}N)$ mode at ~2200 cm^{-1} and a weak feature at ~2040 cm^{-1} (Table I). Similar features in the $\nu(C{\equiv}N)$ region have been observed for other six-coordinate homoleptic isocyanide complexes of the type $[M(CNR)_6]^{n+}$; the intense band is attributed to the IR-active T_{1u} mode expected for six-coordinate complexes having O_h symmetry, while the weak feature reflects some lowering in symmetry due to the slight deviation from linearity of some of the $M{-}C{\equiv}N{-}C$ units.[11,27,28] The nonlinearity of the $M{-}C{\equiv}N{-}C$ axis may arise (in part) from back-donation of electron density from the metal center to the ligand. Back-donation of electron density from ruthenium(II) or osmium(II) in these $[M(CNR)_6]^{2+}$ complexes can be expected to be smaller than back-donation from rhenium(I) in $[Re(CNR)_6]^+$,[11] because of the greater nuclear charge present in the ruthenium and osmium

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Table II. NMR Spectra of $[M(CNR)_6]^{2+}$ and $[M(CNCMe_3)_5CN]^+$ (M = Ru or Os)

complex	^{1}H, δ[a]	^{13}C{^{1}H}, δ[a]
$[Ru(CNCHMe_2)_6](PF_6)_2$	1.51 (d of t, CH_3, ^3J(H–H) = 6.7 Hz, ^3J(^{14}N–H) = 2.4 Hz), 4.30 (h, CH, ^2J(H–H) = 6.7 Hz)[b]	23.0 (s, CH_3), 50.9 (s, CH), 132.5 (t, $C\equiv N$, $J(^{13}C-^{14}N)$ = 21.6 Hz)[d]
$[Ru(CNCMe_3)_6](PF_6)_2$	1.55 (br, CH_3)[c]	30.3 (s, CH_3), 60.7 (s, C), 132.1 (t, $C\equiv N$, $J(^{13}C-^{14}N)$ = 20.4 Hz)[d]
$[Ru(CNC_6H_{11})_6](PF_6)_2$	~1.75 (m, CH_2), 4.22 (t of t, CH, ^3J(H–H) = 7.3 and 3.7 Hz)[c]	22.8 (s, 3,5-CH_2), 25.3 (s, 4-CH_2), 32.1 (s, 2,6-CH_2), 56.3 (s, CH), 133.4 (t, $C\equiv N$, $J(^{13}C-^{14}N)$ = 22 Hz)[d]
$[Os(CNCHMe_2)_6](PF_6)_2$	1.51 (d of t, CH_3, ^3J(H–H) = 7 Hz, ^3J(^{14}N–H) = 2 Hz), 4.47 (h, CH, ^3J(H–H) = 7 Hz)[b]	23.3 (s, CH_3), 50.9 (s, CH), 113.4 (t, $C\equiv N$, $J(^{13}C-^{14}N)$ = 23.7 Hz)[d]
$[Os(CNCMe_3)_6](PF_6)_2$	1.65 (t, CH_3, ^3J(^{14}N–H) = 2 Hz)[b]	
$[Os(CNC_6H_{11})_6](PF_6)_2$	1.75 (m, CH_2), 4.45 (br, CH)[b]	23.0 (s, 3,5-CH_2), 25.5 (s, 4-CH_2), 32.5 (s, 2,6-CH_2), 56.3 (s, CH), 113.9 (t, $C\equiv N$, $J(^{13}C-^{14}N)$ = 23.8 Hz)[d]
$[Ru(CNCMe_3)_5CN]PF_6$	1.58 (s)[b]	30.4 (s, CH_3), 59.4 (s, C), 137.5 (t, $C\equiv N$(eq), $J(^{13}C-^{14}N)$ = 18.6 Hz), 138.8 (t, $C\equiv N$(ax), $J(^{13}C-^{14}N)$ = 38 Hz)[d]
$[Os(CNCMe_3)_5CN]PF_6$	1.60 (s)[b]	30.1 (s, CH_3), 59.0 (s, C)8 118.8 (br, $C\equiv N$(eq)), 127.4 (br, $C\equiv N$(ax))[e]

[a] s = singlet, t = triplet, h = heptet, m = multiplet, d of t = doublet of triplets, t of t = triplet of triplets. [b] Measured in acetone-d_6. [c] Measured in $CDCl_3$. [d] Measured in acetonitrile-d_3 containing 0.05 M $Cr(acac)_3$. [e] Measured in $CDCl_3$ containing 0.05 M $Cr(acac)_3$.

complexes. Such an effect is apparent in the $\nu(C\equiv N)$ region of these complexes since the osmium and ruthenium complexes display a barely discernible feature at ca. 2040 cm^{-1} (Table I), while the spectra of $[Re(CNR)_6]^+$ show[11,28] a noticeably more intense band in this spectral region. Also, the higher nuclear charge in the case of the ruthenium and osmium homoleptics relative to that of $[Re(CNR)_6]^+$ leads to the T_{1u} $\nu(C\equiv N)$ mode occurring at a higher energy (~2200 cm^{-1} vs. ~2100 cm^{-1}) for the ruthenium and osmium complexes. The increase in the complexity of the IR spectra of $[M(CNCMe_3)_5CN]PF_6$ relative to those of $[M(CNR)_6](PF_6)_2$ (Table I) reflects the lower symmetry (C_{4v}) of the former. Only three of the four IR-active $\nu(C\equiv N)$ modes (3 A_1 + E) were observed; this may indicate that one of the A_1 modes is of very low intensity or that the spectra are simplified by the occurrence of accidental degeneracies.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of the homoleptic cations are quite simple and, accordingly, need not be discussed in any detail (see Table II). Due to the linearity, or close approach to linearity , of the $M-C\equiv N-C$ units, the electronic symmetry is high, thereby leading to a small zero-field gradient about the ^{14}N nucleus.[29] Consequently, quadrupolar relaxation of the ^{14}N nucleus is slowed, and $^1J(^{13}C-^{14}N)$ and $^3J(^{14}N-H)$ couplings are seen for the isocyanide ligands. Previously, $^1J(^{13}C-^{14}N)$ coupling has been observed for certain other transition-metal isocyanide complexes.[30-32]

The 90-MHz ^{1}H NMR spectra of the $[M(CNCMe_3)_5CN]^+$ complexes show only one resonance due to the methyl groups of the isocyanide ligands (Table II). The methyl groups of the equatorial and axial isocyanide ligands apparently have very similar ^{1}H NMR chemical shifts. A similar effect was noted by Doonan and Balch[4] for the methyl isocyanide resonances in $[(CH_3NC)_5Ru(C(NHCH_3)_2)](PF_6)_2$ and $[(CH_3NC)_5Fe(C(NHCH_3)NH_2)](PF_6)_2$. The ^{13}C{^{1}H} NMR spectra of these same $[M(CNCMe_3)_5CN]^+$ derivatives show only one resonance for the methyl carbons and one resonance for the carbon atom bound to the methyl groups. Two isocyanide signals, $\delta(C\equiv N)$, are observed (at 137.5 and 138.8 ppm for M = Ru, and 118.8 and 127.4 ppm for M = Os), the higher field resonance being assigned to the equatorial carbon atoms on account of its much higher intensity. Both signals show $^1J(^{13}C-^{14}N)$ coupling, just as is the case for $[M(CNR)_6]^{2+}$; this implies that the isocyanide ligands are close to being linear. The resonance due to the single cyano group in each complex was not detected in these measurements.

Electrochemical studies on the mixed halide/isocyanide complexes *trans*-$OsX_2(CNR)_4$ (X = Cl or Br) have shown[8a] that they are oxidized to the corresponding osmium(III) monocations at ca. +0.7 V vs. SCE. Cyclic voltammetric measurements on solutions of *trans*-$Ru(CNR)_4(O_2CCH_3)_2$ (R = $CHMe_2$ or CMe_3) in 0.2 M $TBAH/CH_2Cl_2$ show a reversible one-electron oxidation at +0.9 V vs. Ag/AgCl. In the case of $[M(CNR)_6]^{2+}$ (M = Ru or Os), we observed no significant electrochemical response in the potential range +2.0 to −2.0 V vs. Ag/AgCl in either 0.2 M $TBAH/CH_2Cl_2$ or 0.1 M $TBAH/CH_3CN$. This accords with the previous report[4] that $[Ru(CNCH_3)_6]^{2+}$ displays no redox activity from +3 to −2 V in CH_3CN. Apparently, the substitution of two halide or two acetate ligands by RNC shifts the oxidation to much higher positive potentials; this presumably reflects the superior electron-withdrawing ability of isocyanide.

Replacement of a π acceptor such as isocyanide with a σ donor like cyanide should lead[33] to the M(III)/M(II) couple occurring at a less positive potential while any metal-based reduction should occur at an even more negative potential. While we observed no electrochemistry for $[Ru(CNCMe_3)_5CN]PF_6$ in acetonitrile out to +2.3 V, an irreversible oxidation occurs at $E_{p,a}$ = +2.0 V vs. Ag/AgCl for solutions of $[Os(CNCMe_3)_5CN]PF_6$ in 0.1 M $TBAH/CH_3CN$.

Concluding Remarks. The cleavage of the metal–metal multiple bonds of $Ru_2(O_2CCH_3)_4Cl$ and $Os_2(O_2CCH_3)_4Cl_2$ by alkyl isocyanide ligands provides the first general synthetic route to the homoleptic cations $[Ru(CNR)_6]^{2+}$ and $[Os(CNR)_6]^{2+}$. This provides a further important illustration of the synthetic utility of multiply bonded dimetal complexes in their reactions with π-acceptor ligands.[34] The thermal dealkylation of $[M(CNCMe_3)_6](PF_6)_2$ to give $[M(CNCMe_3)_5CN]PF_6$ accords with the notion[24] that such dealkylation reactions in isocyanide complexes are most likely to be encountered where it is accompanied by a reduction in the cationic charge.

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Registry No. $[Ru(CNCHMe_2)_6](PF_6)_2$, 97877-36-6; $[Ru(CNCMe_3)_6](PF_6)_2$, 97877-38-8; $[Ru(CNC_6H_{11})_6](PF_6)_2$, 97877-40-2; $[Os(CNCHMe_2)_6](PF_6)_2$, 97877-42-4; $[Os(CNCMe_3)_6](PF_6)_2$, 97877-44-6; $[Os(CNC_6H_{11})_6](PF_6)_2$, 97889-62-8; $[Ru(CNCMe_3)_5]PF_6$, 97889-64-0; $[Os(CNCMe_3)_5]PF_6$, 97877-46-8; *trans*-$Ru(CNCHMe_2)_4(O_2CCH_3)_2$, 97877-47-9; *trans*-$Ru(CNCMe_3)_4(O_2CCH_3)_2$, 77136-40-4; $Ru_2(O_2CCH_3)_4Cl$, 38833-34-0; $Os_2(O_2CCH_3)_4Cl_2$, 81519-41-7; $CNCMe_3$, 7188-38-7; lead(II) nitrate, 10099-74-8.

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