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# Higher coordinate complexes. Part 22. Synthesis and reactions of seven-coordinate technetium and rhenium alkyl isocyanide complexes

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# Synthesis and Reactions of Seven-Coordinate Technetium and Rhenium Alkyl Isocyanide Complexes[1-3]

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Addition of chlorine or bromine to the six-coordinate $[Tc(CNR)_6]^+$ cations produces the seven-coordinate $[Tc(CNR)_6X]^{2+}$ complexes ($R = t\text{-}C_4H_9$, X = Cl, Br; $R = CH_3$, X = Br), which were isolated in 75% yield as their hexafluorophosphate salts. The (*tert*-butyl isocyanide)technetium(III) cations and their rhenium(III) analogues readily dealkylate upon heating in the presence of 2,2′-bipyridine in acetonitrile solution to form the cyanide complexes $[M(CN\text{-}t\text{-}Bu)_5(CN)X]^+$ (M = Tc; X = Cl, Br; M = Re, X = Br). Dealkylation of these and related seven-coordinate Tc(III) and Re(III) alkyl isocyanide complexes was also observed to occur in the gas phase by field desorption mass spectrometry. Attempts to couple the coordinated alkyl isocyanide ligands in the seven-coordinate technetium(III) and rhenium(III) complexes to produce coordinated (RNHC≡CNHR) species, by analogy to known Mo(II) and W(II) chemistry, yielded only reductive elimination to form $[M(CNR)_6]^+$ cations. New complexes were characterized by analysis, $^1H$ NMR and IR spectroscopy, and solution conductivity measurements.

## Introduction

As part of our continuing program to synthesize and study the chemistry of high-coordination transition-metal complexes containing linear ligands,[4] we have been investigating seven-coordinate technetium and rhenium alkyl isocyanide complexes. Recently, one of our groups reported the synthesis of the stable $d^6$ compounds $[Tc(CNR)_6](PF_6)$ ($R = CNCH_3$, $CNC(CH_3)_3$) by reduction of aqueous ammonium pertechnetate.[5] As described here, the desired seven-coordinate complexes $[Tc(CNR)_6X]^{2+}$ are readily accessible by oxidative addition of $X_2$ (X = Cl, Br) to $[Tc(CNR)_6]^+$. Routes to the rhenium(III) analogues have also been developed. These Tc(III) and Re(III) isocyanide complexes are isoelectronic with the well-studied[4] Mo(II) and W(II) systems, and the chemical reactivity of these two classes of compounds, especially dealkylation and reductive coupling reactions, are compared and discussed in this report.

## Experimental Section

**General Procedures.** Technetium was obtained as $NH_4{}^{99}TcO_4$ from New England Nuclear (NEN), Billerica, MA. All manipulations were carried out in laboratories approved for work with low-level radiation using precautions described in detail elsewhere.[6] Sodium perrhenate was purchased from Cleveland Refractory Metals, Solon, OH.

Infrared spectra were recorded in the range 4000–300 $cm^{-1}$ on a Perkin-Elmer PE-180 grating infrared spectrometer using samples mulled in Nujol. Conductivity measurements were performed in acetonitrile with use of a Yellow Springs Model 3403 conductivity cell and a Beckman RC-16C conductivity bridge. $^1H$ NMR spectra were obtained from a JEOL-90X spectrometer with the residual protons of acetonitrile-$d_3$ ($\delta$ 1.93 referenced to $Me_4Si$) as the internal calibrant. Field desorption mass spectra were measured with a Varian MAT 731 instrument described elsewhere.[7] Prior to use, distilled water was passed through a Barnstead Ultrapure D8902 cartridge. Methyl and *tert*-butyl isocyanides were prepared by literature methods.[8,9] The compounds $[Tc(CNR)_6](PF_6)$ ($R = CH_3$, $C(CH_3)_3$), $[Re(CNR)_6](PF_6)$ ($R = CH_3$, $C(CH_3)_3$) and $[Re(CNR)_6Br](PF_6)_2$ ($R = CH_3$, $C(CH_3)_3$) were synthesized as previously described.[6,10] All other chemicals were used without purification, unless otherwise specified. Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, GA.

**$[Tc(CNC(CH_3)_3)_6Cl](PF_6)_2$ (1a).** $[Tc(CNC(CH_3)_3)_6](PF_6)$ (0.201 g, 10.27 mmol) was dissolved in 10 mL of dichloromethane. Chlorine gas was passed through the solution for 10 min. The solution was evaporated to dryness under a stream of nitrogen and redissolved in 10 mL of acetonitrile. $KPF_6$ ( 1 g, 5.4 mmol) in 10 mL of water was added dropwise to this solution to precipitate a yellow solid that was collected on a glass frit by vacuum filtration and washed with 5 mL of water and 5 mL of diethyl ether. The light yellow microcrystalline solid was recrystallized from acetonitrile/water to yield, after recrystallization, 0.183 g (73%) of product. Anal. Calcd for $C_{30}H_{54}ClF_{12}N_6P_2Tc$: C, 39.03; H, 5.90; N, 9.10; Cl, 3.84. Found: C, 39.22; H, 5.98; N, 9.07; Cl, 3.87.

**$[Tc(CNC(CH_3)_3)_6Br](PF_6)_2$ (1b).** Bromine (0.5 mL, 9.7 mmol) was added dropwise to 10 mL of acetonitrile containing $[Tc(CNC(CH_3)_3)_6](PF_6)$ (0.094 g, 0.13 mmol). After the solution sat for 30 min, water was added dropwise to precipitate red crystals. The red crystals were dissolved in 10 mL of acetonitrile, and a filtered solution of $NH_4PF_6$ (0.44 g, 2.7 mmol) in 20 mL of water was added dropwise. The yellow, microcrystalline precipitate was collected by vacuum filtration and washed with water (5 mL) and diethyl ether (5 mL). The yield was 0.105 g (76%). Anal. Calcd for $C_{30}H_{54}BrF_{12}N_6P_2Tc$: C, 37.24; H, 5.63; N, 8.69; Br, 8.26. Found: C, 37.09; H, 5.69; N, 8.66; Br, 8.21.

**$[Tc(CNCH_3)_6Br](PF_6)_2$ (2).** Bromine (0.5 mL, 9.7 mmol) was added to a solution of $[Tc(CNCH_3)_6](PF_6)$ (0.094 g, 0.13 mmol) in 10 mL of acetonitrile. After the mixture sat at room temperature for 10 min, water was added to precipitate a red crystalline solid. The solid was collected and redissolved in 5 mL of acetonitrile, and a yellow solid was precipitated by the dropwise

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(1) Dedicated to the memory of Earl L. Muetterties, a pioneer in the fields of higher coordination and organometallic chemistry.

(2) Part 22 of a continuing series on higher coordinate complexes.

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Table I. Infrared, $^1$H NMR, and Conductivity Data

| compound | $\nu_{C\equiv N}$, cm$^{-1}$ (Nujol mull) | $^1$H NMR, $\delta$ (in CD$_3$CN) | $\Lambda_M$,$^a$ $\Omega^{-1}$ cm$^2$ mol$^{-1}$ |
|---|---|---|---|
| [Tc(CNC(CH$_3$)$_3$)$_6$Cl](PF$_6$)$_2$ (1a) | 2250 m, 2215 s, 2035 w | 1.63 | 292 |
| [Tc(CNC(CH$_3$)$_3$)$_6$Br](PF$_6$)$_2$ (1b) | 2252 m, 2215 s, 2035 w | 1.59 | 303 |
| [Tc(CNCH$_3$)$_6$Br](PF$_6$)$_2$ (2) | 2300 m, 2260 s | 3.68 | 286 |
| [Re(CNC(CH$_3$)$_3$)$_6$Br](PF$_6$)$_2$ | 2250 m, 2215 s, 2050 w | 1.70$^b$ | |
| [Tc(CNC(CH$_3$)$_3$)$_5$(CN)Cl](PF$_6$) (3a) | 2360 vw, 2340 vw, 2233 m, 2192 s, 2120 m | 1.55 | 145 |
| [Tc(CNC(CH$_3$)$_3$)$_5$(CN)Br](PF$_6$) (3b) | 2352 vw, 2328 vw, 2231 m, 2192 s, 2120 m | 1.54 | 156 |
| [Re(CNC(CH$_3$)$_3$)$_5$(CN)Br](PF$_6$) (5) | 2365 vw, 2233 m, 2194 sh, 2184 s, 2120 m | 1.55 | 145 |
| [Re(CNCH$_3$)$_6$Br](PF$_6$)$_2$ (6) | 2295 sh, 2260 s | 3.85 | 267 |
| [Tc(CNC(CH$_3$)$_3$)$_6$](PF$_6$) | 2090 s, 2052 s | 1.43 | 140 |
| [Tc(CNCH$_3$)$_6$](PF$_6$) | 2110 s | 3.39 | 135 |

$^a$ 1 × 10$^{-3}$ M in acetonitrile. $^b$ Acetone-$d_6$, Me$_4$Si reference.

Table II. Summary of Field Desorption Mass Spectrometric Results$^a$

| | [M(CNC(CH$_3$)$_6$X](PF$_6$)$_2$ | | [M(CNCH$_3$)$_6$X](PF$_6$)$_2$ | | [M(CNC(CH$_3$)$_3$)$_5$(CN)X](PF$_6$) | | |
|---|---|---|---|---|---|---|---|
| fragments$^b$ | M = Tc, X = Cl | M = Tc, X = Br | M = Tc, X = Br | M = Re, X = Br | M = Tc, X = Cl | M = Tc, X = Br | M = Re, X = Br |
| ML$_4$X$_2^+$(?) | | | | 21$^d$ | | | |
| ML$_4$(CN)$_2$X$^+$ | 100 | 42 | | | 100 | 100 | 100 |
| ML$_5$X$_2^+$(?) | | | | 25$^d$ | | | |
| ML$_5$(CN)$^+$ | 24 | (100)$^d$ | | | 31 | 43 | 3 |
| ML$_5$(CN)X$^+$ | 62 | 62 | | | 37 | 77 | |
| ML$_6^+$ | 40 | 100 (95$^d$) | 100 | 100$^d$ | 12 | 18 | |
| [ML$_6$X](PF$_6$)$^+$ | | 7 | 100$^c$ | | | | |

$^a$ Numbers in the table refer to the relative abundances of the positive ions in the mass spectrum where 100 is the maximum. Unless otherwise specified, the emitter current is 20-22 mA. $^b$ L = RNC ligand, X = halide. $^c$ 14 mA current. $^d$ 19 mA current.

addition of a filtered aqueous solution of NH$_4$PF$_6$ (0.44 g, 2.7 mmol). The yellow solid was vacuum dried: yield 0.105 g (76%); (+)FD-MS, *m/z* 569 (calcd for C$_{12}$H$_{18}$$^{79}$BrF$_6$N$_6$P$^{99}$Tc 569).

**[Tc(CNC(CH$_3$)$_3$)$_5$(CN)Cl](PF$_6$) (3a).** A solution of [Tc(CNC(CH$_3$)$_3$)$_6$Cl](PF$_6$)$_2$ (0.183 g, 0.2 mmol) and 2,2′-bipyridine (0.155 g, 1 mmol) in 30 mL of acetonitrile was heated on a hot plate for 30 min. The volume was reduced to ca. 5 mL, and diethyl ether was added to precipitate a yellow solid that was collected by vacuum filtration and washed wiith diethyl ether. The solid was redissolved in dichloromethane and filtered to remove a white solid, (bpyH)(PF$_6$), and compound **3a** was precipitated with diethyl ether, washed with 10 mL of water, and vacuum dried; yield 0.122 g (78%). Anal. Calcd for C$_{26}$H$_{45}$ClN$_6$F$_6$PTc: C, 43.31; H, 6.29; N, 11.65; Cl, 4.92. Found: C, 43.17; H, 6.23, 6.24; N, 11.59, 11.61; Cl, 4.88, 4.94.

**[Tc(CNC(CH$_3$)$_3$)$_5$(CN)Br](PF$_6$) (3b).** A solution of [Tc(CNC(CH$_3$)$_3$)$_6$Br](PF$_6$)$_2$ (0.335 g, 0.35 mmol) and 2,2′-bipyridine (0.270 g, 1.7 mmol) in 50 mL of acetonitrile was heated on a hot plate for 30 min. The volume was reduced to 5 mL, and diethyl ether was added dropwise to precipitate a light yellow (sometimes with a pinkish cast) solid that was collected by vacuum filtration and washed with diethyl ether. The solid was redissolved in 5 mL of dichloromethane and filtered to remove a white or light pink solid, (bpyH)(PF$_6$). The title compound was precipitated with diethyl ether, washed with 10 mL of water, and vacuum dried; yield 0.265 g (81%). Anal. Calcd for C$_{26}$H$_{45}$ClN$_6$F$_6$PTc: C, 40.79; H, 5.93; N, 10.98; Br, 10.44. Found: C, 40.84, 40.76; H, 5.85, 5.88; N, 10.89, 10.92; Br, 10.43.

**[Re(CNC(CH$_3$)$_3$)$_5$(CN)Br](PF$_6$) (5).** A solution of [Re(CNC(CH$_3$)$_3$)$_6$Br](PF$_6$)$_2$ (0.225 g, 0.24 mmol) (4) and 2,2′-bipyridine (0.188 g, 1.2 mmol) in 50 mL of acetonitrile was heated on a hot plate for 30 min. The volume was reduced to 5 mL, and diethyl ether was added dropwise to precipitate a light tan solid. The solid was washed with diethyl ether, redissolved in dichloromethane, and filtered to remove a white or pink solid, (bpyH)(PF$_6$). The title compound was precipitated by the addition of diethyl ether, washed with water, and vacuum dried; yield 0.165 g (80%). Anal. Calcd. for C$_{26}$H$_{45}$BrF$_6$N$_6$PRe: C, 36.62; H, 5.32; N, 9.86; Br, 9.37. Found: C, 36.69, 36.72; H, 5.28, 5.29; N, 9.84, 9.78; Br, 9.43, 9.45.

**[Re(CNCH$_3$)$_6$Br](PF$_6$)$_2$ (6).** Bromine (0.5 mL, 9.7 mmol) was added to a solution of [Re(CNCH$_3$)$_6$](PF$_6$) (0.305 g, 0.53 mmol) in 15 mL of acetonitrile. An aqueous solution of KPF$_6$ (1 g, 5.4 mmol) was then added dropwise to precipitate an orange solid. The solid was recrystallized from acetonitrile/diethyl ether: yield after recrystallization 0.4 g (94%); (+)FD-MS, *m/z* 655 (calcd for C$_{12}$H$_{18}$$^{79}$BrF$_6$N$_6$P$^{185}$Re 655).

**Attempted Reductive Coupling Reactions for [M(CNR)$_6$X](PF$_6$)$_2$ (M = Tc, R = C(CH$_3$)$_3$, X = Cl, Br; M = Tc, R = CH$_3$, X = Br; M = Re, R = C(CH$_3$)$_3$, CH$_3$, X = Br).** In a typical reaction, 78.5 mg (0.081 mmol) of [Tc(CNC(CH$_3$)$_3$)$_6$Br](PF$_6$)$_2$, 55 mg (0.84 mmol) of Zn, and 18.32 mg (0.078 mmol) of ZnBr$_2$ in 15 mL of wet THF were refluxed for several hours, during which time the yellow color of the solution disappeared and the IR spectrum (monitored in the 2500–1500 cm$^{-1}$ region) showed only peaks characteristic (Table I) of [Tc(CNC(CH$_3$)$_3$)$_6$](PF$_6$) ($\nu_{C\equiv NR}$ = 2090 and 2045 cm$^{-1}$). Additional heating of the reaction mixture for several days led to no further reaction as judged by infrared spectroscopy.

## Results

**Synthesis and Characterization of [Tc(CNR)$_6$X](PF$_6$)$_2$.** The seven-coordinate Tc(III) complexes [Tc(CNR)$_6$X](PF$_6$)$_2$, where R = C(CH$_3$)$_3$, X = Cl (**1a**), R = C(CH$_3$)$_3$, X = Br (**1b**), and R = CH$_3$, X = Br (**2a**), are readily synthesized by oxidation of the homoleptic Tc(I) isocyanide complexes [Tc(CNR)$_6$](PF$_6$) (R = C(CH$_3$)$_3$, CH$_3$) with halogen followed by precipitation with KPF$_6$. These complexes are light yellow and soluble in acetonitrile and dichloromethane. They have been characterized by elemental analysis, IR and $^1$H NMR spectroscopy, FD-MS, and conductivity measurements (Tables I and II). All the Tc(III) complexes show solution conductance in the range $\Lambda_M \sim 150\ \Omega^{-1}$ cm$^2$ mol$^{-1}$, consistent with their formulation as 2:1 salts.[11] The infrared spectrum of the [Tc(CNR)$_6$X](PF$_6$)$_2$ complexes shows an intense isocyanide stretch at ~2215 (R = C(CH$_3$)$_3$) or ~2260 (R = CH$_3$) cm$^{-1}$. These values are ca. 75 and 100 cm$^{-1}$ higher than in the

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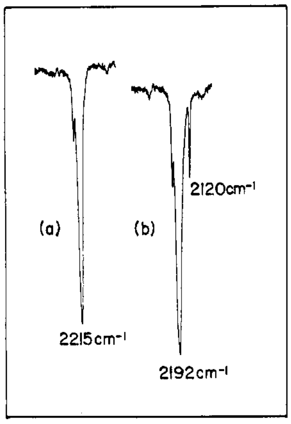

**Figure 1.** Characteristic infrared spectral bands in the $C\equiv N$ stretching frequency region (cf. Table I) for (a) $[Tc(CNC(CH_3)_3)_6Br](PF_6)_2$ (**1b**) and (b) $[Tc(CNC(CH_3)_3)_5(CN)Br](PF_6)$ (**3b**) mulled in Nujol.

respective free ligands, which suggests that $\pi$ back-bonding between the isocyanide ligands and the Tc(III) core is not significant.

The $^1$H NMR spectra of these complexes consist of a single resonance for the alkyl group of the isocyanide ligand, shifted downfield by 0.2 ppm from the value in the Tc(I) complexes. This shift is consistent with oxidation to Tc(III) which deshields the alkyl group protons of the isocyanide. The appearance of a single resonance for the alkyl group of the isocyanides is consistent with the known fluxionality of many seven-coordinate complexes in solution.[4b]

Reaction of 1, 2 or 4 with Zn metal in refluxing wet THF, conditions that lead to reductive coupling of isocyanides in $[MoL_6X]^+$,[4b] results in the reduction of 1, 2, or 4 to the corresponding $[Tc(I)(CNR)_6]^+$ cation, as revealed by $^1$H NMR and IR spectroscopy.

**Dealkylation of Coordinated Isocyanide Ligands. Formation of $[M(CNC(CH_3)_3)_5(CN)X]^+$ Cations.** In an attempt to synthesize 2,2′-bipyridine (bpy) derivatives of $[Tc(CNC(CH_3)_3)_6X](PF_6)_2$, acetonitrile solutions of 1 were refluxed with excess bpy. Over a period of 20 min the yellow solutions became darker and diethyl ether was added to precipitate a light yellow solid.

Elemental analyses (data not given) were in excellent agreement with formulation of the products as 1:1 mixtures of the two salts $[Tc(CNC(CH_3)_3)_5(CN)X](PF_6)$ (**3a**, X = Cl; **3b**, X = Br) and (bpyH)$(PF_6)$. Separation of the salts was accomplished by washing the solid with dichloromethane, which selectively dissolves the technetium complexes, and then precipitating 3 with diethyl ether. The elemental analyses, conductivity, FD-MS, and IR spectra of 3 are consistent with conversion of one isocyanide ligand in 1 into a cyanide ligand in 3. The infrared spectra of 1 and 3 in the $C\equiv N$ stretching region are displayed in Figure 1. A sharp band at 2120 cm$^{-1}$ occurs in 3 assignable to the cyanide $\nu_{CN}$ mode.[12] The isocyanide stretches in 3 occur at ca. 23 cm$^{-1}$ lower in energy than in 1. Conductivity measurements in acetonitrile indicate that these complexes are 1:1 electrolytes (Table I). This result is consistent with the conversion of one neutral isocyanide ligand in 1 into an anionic $CN^-$ ligand in 3, with reduction of the overall charge of the complex from 2+ to 1+. The analogous reaction also occurs for rhenium isocyanide complexes. Refluxing a solution of $[Re(CNC(CH_3)_3)_6Br](PF_6)_2$ (**4**) with excess bpy for 30 min produces upon recrystallization the analytically pure complex $[Re(CNC(CH_3)_3)_5(CN)Br](PF_6)$ (**5**) in high yields.

Base is not necessary to achieve isocyanide dealkylation. Refluxing solutions of 1 and 4 in neat acetonitrile produces the dealkylated products 3 and 5. The $^1$H NMR spectra of the crude solutions, however, show an impurity at ca. 3.9 ppm that is also found in the solution NMR spectra of the isolated solids.

**Field Desorption Mass Spectrometry.** This technique can yield simple spectra for both positively and negatively charged coordination complexes and provides an extremely useful means of obtaining the mass spectra of nonvolatile, inorganic salts.

The fragment ions found over the range *m/z* 300–900 are reported in Table II for compounds **1–5**. The (+)FD-MS spectrum of compound **1b** exhibits a weak peak at *m/z* 821 corresponding to the cluster $[^{99}Tc(CNC(CH_3)_3)_6{}^{79}Br](PF_6)^+$, $(M - A)^+$, obtained from **1b** by loss of an anion. The analogous $(M - A)^+$ peak has not been found in the spectrum of **1a** under similar conditions. Fragment ions corresponding to dealkylation of one or two isocyanides in **1a** and **1b** have also been identified. Thus peaks corresponding to $[Tc(CNC(CH_3)_3)_5(CN)X]^+$ and $[Tc(CNC(CH_3)_3)_4(CN)_2X]^+$ have been found at *m/z* 575 and 518 for X = $^{35}$Cl and *m/z* 619 and 562 for X = $^{79}$Br, respectively. The dealkylation of *tert*-butyl ioscyanide has been observed previously in the electron-impact mass spectrum of transition-metal isocyanide complexes.[13,14] The spectra of the *tert*-butyl isocyanide derivatives **1a** and **1b** show strong signals at *m/z* 597 identified as $[Tc(CNC(CH_3)_3)_6]^+$ and derived from **1a** and **1b** by in situ reduction and loss of halide. Also, a peak corresponding both to a dealkylation and loss of halide, $[Tc(CNC(CH_3)_3)_5(CN)]^+$, is present at *m/z* 540 in the spectra of both **1a** and **1b**.

The methyl isocyanide derivatives **2a** and **2b** exhibit a strikingly different fragment pattern than the *tert*-butyl analogues. At low emitter wire currents (14 mA), the $(M - A)^+$ cluster $[Tc(CNCH_3)_6Br](PF_6)^+$ is observed at *m/z* 569. At higher currents only the Tc(I) species $[Tc(CNCH_3)_6]^+$ is found. No fragments derived from dealkylation of a methyl isocyanide ligand were observed.

The (+)FD-MS spectra of the isolated dealkylated products **3a** and **3b** show fragmentation patterns similar to their precursor complexes **1a** and **1b**, respectively. Compounds **3a** and **3b** exhibit peaks at *m/z* 575 and 619, respectively, corresponding to the parent peak $[Tc(CNC(CH_3)_3)_5(CN)X]^+$. As observed for 1, strong peaks are found for the doubly dealkylated fragment $[Tc(CNC(CH_3)_3)_4(CN)_2X]^+$ (*m/z* 518, X = $Cl^-$; *m/z* 562, X = $Br^-$). The fragment $[Tc(CNC(CH_3)_3)_5(CN)]^+$ is also observed with moderate intensity for both **3a** and **3b**. Surprisingly, the ion $[Tc(CNC(CH_3)_3)_6]^+$ is present in the (+)FD-MS spectra of both **3a** and **3b**. While no evidence for $[Tc(CNC(CH_3)_3)_6]^+$ was found from the IR and $^1$H NMR of **3a** and **3b**, we cannot rule out the possibility that a small quantity of $[Tc(CNC(CH_3)_3)_6](PF_6)$ is present in these samples and is the source of this cation. The (+)FD-MS spectrum of **5** is similar to that of the Tc derivatives in that the fragment derived from a further dealkylation in **5** is quite abundant. The fragment $[Re(CNC(CH_3)_3)_5(CN)]^+$ is present in low intensity, however, and the parent peak $[Re(CNC(CH_3)_3)_5(CN)Br]^+$ is not observed, in contrast to **3a** and **3b**.

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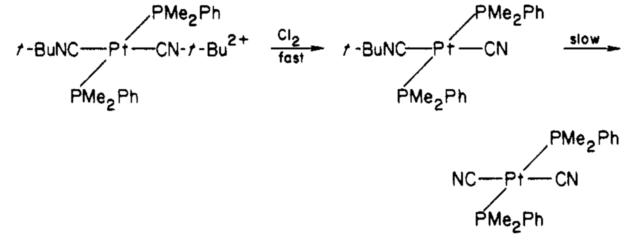
## Discussion

The hexacoordinate complexes $[Tc(CNR)_6](PF_6)$ readily undergo oxidative addition with $X_2$ (X = Cl, Br) to provide the seven-coordinate complexes $[Tc(CNR)_6X](PF_6)_2$. An analogous route has been followed to obtain the rhenium analogues $[Re(CNR)_6X](PF_6)_2$ from $[Re(CNR)_6](PF_6)$.[10] While the solid-state geometries of these complexes are not known, they are fluxional in solution, judging from the single resonance for R = $CH_3$ and R = $C(CH_3)_3$ in the proton NMR spectra. On the basis of the four known geometries for seven-coordinate complexes, we would expect at least two resonances for a static stereochemistry.[15]

The dealkylation of coordinated isocyanide ligands has been observed previously. Dealkylation of methyl isocyanide from $[Pt(R_3P)_2(CNCH_3)X](X)$ (R = Et, X = Cl; R = $C_6H_5$, X = Br) to give $[Pt(R_3P)_2(CN)X]^+$ occurs in refluxing benzene.[16] In another cationic platinum complex, dealkylation of two coordinated isocyanides occurs as shown in eq 1.[17] Recently, dealkylation of a coordinated isocyanide was observed in the seven-coordinate cation $[Mo(CNC(CH_3)_3)_7]^{2+}$, 7.[4c] Refluxing a benzene solution of 7 for 72 h produced the compound $[Mo(CNC(CH_3)_3)_6CN](PF_6)$ in 22% isolated yield. In a similar reaction, refluxing a 1-propanol solution of 7 and 2,2′-bipyridine for 24 h gave the cyanide-bridged complex $\{[Mo(CNC(CH_3)_3)_4(bpy)]_2(\mu\text{-}CN)\}^{3+}$. The seven-coordinate 2,2′-bipyridine adduct $[Mo(CNC(CH_3)_3)_5(bpy)]^{2+}$ was shown to be the precursor to the cyanide-bridged complex.[18] These results, together with those reported here, suggest that an important factor in the dealkylation of coordinated isocyanide is the overall cationic charge on the metal complex. With one recent exception,[19] all known examples of dealkylation of transition-metal isocyanide complexes have occurred from cationic complexes. Dealkylation of coordinated isocyanide reduces the positive charge on the metal complex by conversion of a neutral isocyanide ligand into an anionic cyanide ligand and stabilizes the charged (or neutral) complex.



(1)

Under the conditions in which reductive coupling of isocyanide occurs in $[Mo(CNR)_6X](PF_6)$ the Tc and Re derivatives are readily reduced to the Tc(I) and Re(I) homoleptic isocyanide complexes. This tendency toward reduction rather than "reductive coupling" is a result of the higher charge on the Tc and Re complexes, making them easier to reduce. Thus reductive elimination must be recognized as a major competing pathway to reductive coupling of high-coordinate early transition-metal complexes with linear ligands. In order to achieve reductive coupling of isocyanide ligands in seven-coordinate Tc(III) and Re(III) complexes, it will be necessary to design compounds where formation of six-coordinate Tc(I) and Re(I) species is less favorable.

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**Registry No.** **1a**, 93280-20-7; **1b**, 93280-22-9; **2**, 93280-24-1; **3a**, 93280-26-3; **3b**, 93280-28-5; **4**, 82544-46-5; **5**, 93280-30-9; **6**, 93350-39-1; $[Tc(CNC(CH_3)_3)_6](PF_6)$, 86767-65-9; $[Tc(CNCH_3)_6](PF_6)$, 86767-67-1; $[Re(CNCH_3)_6](PF_6)$, 90999-63-6.

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