Metal−Metal Multiply-Bonded Complexes of Technetium. 4.[1] Photodissociation of the Tc≡Tc Triple Bond in $[Tc_2(CH_3CN)_{10}][BF_4]_4$

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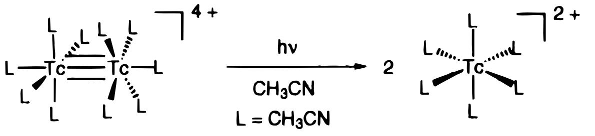
Photodissociation of metal−metal single bonds such as those in $M_2(CO)_{10}$ (M = Mn, Re),[2] $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ (M = Mo, W),[2] $Co_2(CO)_8$[2], and the $[Hg_2]^{2+}$ ion[2f] is well-known. It is not surprising that for a single σ bond, photoexcitation from the σ^2 (bonded) ground state to a state derived from the $\sigma\sigma^*$ configuration (nonbonded) should trigger M−M bond scission. On the other hand, efficient (i.e., essentially quantitative) photolysis of multiple bonds, including metal−metal multiple bonds,[3] neither is to be generally expected nor has been observed, with the sole exception of photocleavage of the quadruple bond in $[Re_2Cl_8]^{2-}$, which occurs in acetonitrile and affords $ReCl_3(CH_3CN)_3$ as the final product.[4] We report here a striking example of such a process, wherein the $[(CH_3CN)_5Tc{\equiv}Tc(CH_3CN)_5]^{4+}$ ion[5] is photolyzed in CH_3CN to give two $[Tc(CH_3CN)_6]^{2+}$ ions in nearly quantitative isolated yield (eq 1).



1 **2** (1)

Acetonitrile solutions of $[Tc_2(CH_3CN)_{10}][BF_4]_4$ (**1**) when exposed to room light over a period of several days gradually lose their intense blue color and become colorless. Workup of the colorless solution by addition of diethyl ether gives a salmon-colored precipitate that was identified as the mononuclear complex $[Tc(CH_3CN)_6][BF_4]_2$ (**2**). Using a 300 W tungsten lamp, the conversion of **1** to **2** occurs over a period of 12−24 h. For preparative scale reactions, a 1000 W Hg vapor lamp was used. After only 90 min of irradiation with the Hg lamp, the mononuclear species was isolated in 95% yield by careful addition of diethyl ether.[6]

An X-ray diffraction study of **2** revealed that the Tc center is ligated by six acetonitrile ligands in an octahedral arrangement (Figure 1).[7] A slight distortion of the N−Tc−N angles from 90° results in the lowering of the idealized molecular symmetry from O_h symmetry to the crystallographically imposed C_i symmetry. The three crystallographically independent Tc−N bond distances of 2.062(4), 2.062(3), and 2.062(4) Å are only slightly longer than those reported for $[Ru(CH_3CN)_6]^{2+}$ (2.013−2.032 Å)[8] and are similar to those found for the equatorial acetonitrile ligands of $[Tc_2(CH_3CN)_8(O_3SCF_3)_2][BF_4]_2$ ($Tc{-}N_{avg}$ = 2.08(1) Å).[1b] The dimensions of the coordinated acetonitrile ligands fall within the expected ranges. No $[Tc(NCR)_6]^{n+}$ ion has previously been reported.

A solid state IR spectrum of $[Tc(CH_3CN)_6][BF_4]_2$ displays C≡N vibrational modes at 2319 and 2280 cm^{-1}. The presence of the $[BF_4]^-$ counterion was evidenced by the observation of a strong band at 1065 cm^{-1}.[9] The electronic spectrum of $[Tc(CH_3CN)_6][BF_4]_2$ in acetonitrile exhibits no observable absorption bands in the visible region, accounting for the nearly colorless appearance of **2** in solution. The lowest energy transition appears at 330 nm and tails slightly into the visible region, giving concentrated solutions of **2** a faint yellow color. The effective magnetic moment of **2** in solution, 2.1 μ_B, investigated by the Evans method,[10] is consistent with an $S = {}^1/_2$ ground state. In spite of the paramagnetism of the Tc(II) cation, a ^1H NMR spectrum in CD_3CN was obtained. A broad and highly shifted resonance corresponding to the coordinated acetonitrile ligands appears at 70.3 ppm ($\Delta\nu_{1/2} \approx 110$ Hz). The expected $^2T_{2g}$ ground state configuration for an octahedral Tc(II) ion allows sufficiently rapid electronic relaxation for the observation of relatively narrow NMR line widths.[11] Over the course of several hours, the coordinated nitrile ligands exchange with the deuterated solvent and only a resonance at 1.95 ppm corresponding to uncoordinated CH_3CN is observed. The demonstrated lability of the acetonitrile ligands could potentially be exploited to make **2** a versatile starting material for the further investigation of Tc(II) coordination chemistry. For the same reason that a ^1H NMR spectrum could be obtained, we were unable to observe a well-defined EPR signal at temperatures as low as 15 K. A cyclic voltammogram of $[Tc(CH_3CN)_6][BF_4]_2$ in acetonitrile exhibits a reversible reduction at −0.81 V *vs* Cp_2Fe corresponding to the Tc(I)/Tc(II) redox couple and a quasi-reversible oxidation at + 0.72 V *vs* Cp_2Fe consistent with a Tc(II)/Tc(III) couple.[12] The reduction process occurs at a slightly less negative potential than that of the metal−metal bonded species **1** ($E_{1/2,red}$ = −0.82 V *vs* Cp_2Fe).[1b] The presence

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(5) As reported in ref 1b, this cation, structurally characterized as a mixed $[O_3SCF_3]^-/[BF_4]^-$ salt, has a Tc≡Tc triple bond, based on a $\sigma^2\pi^4\delta^2\delta^{*2}$ electronic configuration.

(6) Anal. Calcd for $C_{12}H_{18}N_6B_2F_8Tc$: C, 27.83; H, 3.51; N, 16.23. Found: C, 28.51; H, 2.94; N, 16.18.

(7) Crystal data for **2**: $C_{12}H_{18}B_2F_8N_6Tc$, MW = 518.94, monoclinic, $P2_1/c$ with unit cell parameters a = 8.1750(9) Å, b = 8.3775(7) Å, c = 16.256(2) Å, β = 92.058(5)°, V = 1112.6(2) Å^3, Z = 2, ρ_{calcd} = 1.546 g/cm^3, μ(Mo Kα) = 7.21 cm^{-1}, λ = 0.71073 Å. Data were collected on an Enraf-Nonius CAD-4 diffractometer at 22(2) °C using the $\omega{-}2\theta$ scan technique ($2\theta \le 50°$). Of 2091 reflections, 1622 with $I > 2.0\sigma(I)$ were used in refinement. Refinement of 133 variables (SHELXL-93) converged with residuals of R = 0.050 and R_w = 0.134 (based on F_o^2). The largest remaining peak of electron density was 0.9(1) e/Å^3.

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(12) Measurements were performed at room temperature in acetonitrile using 0.1 M [n-Bu_4N][PF_6] as a supporting electrolyte. A platinum disk working electrode and a platinum wire counter electrode were used in conjuction with a silver wire quasi-reference electrode that was separated from the bulk solution by a fine porosity glass frit.

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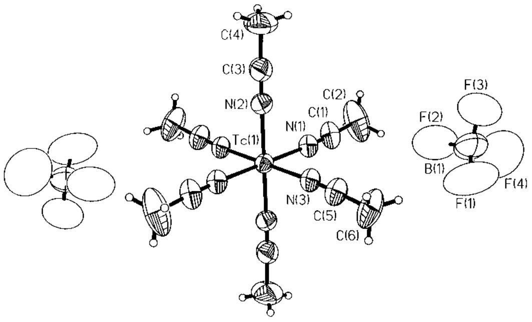

Figure 1. [Tc(CH$_3$CN)$_6$]$^{2+}$ ion, viewed down a pseudo-3-fold axis, and its accompanying [BF$_4$]$^-$ ions. It approximates closely to having O_h symmetry with the following mean bond lengths (Å): Tc−N, 2.062(4); N−C, 1.124(3); C−C, 1.46(1). The N−Tc−N angles are in the range 88.8−91.2°.

of the oxidation couple is noteworthy since such a process does not occur for **1** and was not reported in the cyclic voltammogram of [Ru(CH$_3$CN)$_6$]$^{2+}$.[8a]

Preliminary results indicate that under similar conditions, neither the Re−Re triple bond in [Re$_2$(CH$_3$CN)$_{10}$][BF$_4$]$_4$[13] nor the Mo−Mo quadruple bond in [Mo$_2$(CH$_3$CN)$_8$][BF$_4$]$_4$[14] undergoes metal−metal bond photolytic homolysis. Also, solutions of [Tc$_2$(CH$_3$CN)$_{10}$][BF$_4$]$_4$ are stable with respect to thermal metal−metal bond cleavage in refluxing acetonitrile. In fact, **1** is prepared under refluxing conditions from either Tc$_2$Cl$_4$(PR$_3$)$_4$ (PR$_3$ = PEt$_3$, PMe$_2$Ph, or PMePh$_2$) or [Bu$_4$N]$_2$[TcCl$_6$] thus demonstrating the thermal stability of the Tc≡Tc bond.[1b]

Irradiation into the broad absorption band at 616 nm appears to be responsible for the observed photochemistry. This is indicated by the fact that while broad-band irradiation, in Pyrex, covers both the low-energy tail of the UV absorption and the entire 616 nm band, an argon laser (514.5 nm) catches only the higher energy tail of the 616 nm band, and we have found that the argon laser bleaches the original blue solution. We tentatively assign the 616 nm band in the [Tc$_2$(CH$_3$CN)$_{10}$]$^{4+}$ spectrum to a δ^* to π^* transition on the basis of comparisons with other Re$_2$$^{4+}$ and Tc$_2$$^{4+}$ complexes.[1a,3,13] The cleavage process is irreversible as there is no evidence for an equilibrium existing between **1** and **2**. Attempts to thermally labilize one of the coordinated nitrile ligands in an effort to reform the metal−metal bond in the solid state resulted in decomposition of the complex.

Monitoring the photolysis by electronic spectroscopy (Figure 2) reveals that metal−metal bond cleavage of **1** is not a simple process but instead involves the formation of at least two intermediates prior to formation of [Tc(CH$_3$CN)$_6$]$^{2+}$. After 5 min of irradiation with a Hg lamp, a broad transition appears at 1100 nm together with two lower energy bands at 490 and 405 nm. Furthermore, the band at 616 nm undergoes a slight blue shift and a slight increase in intensity. As the reaction progresses, these bands disappear leaving the nearly featureless spectrum of **2**. Irradiation of **1** with a 300 W incandescent tungsten lamp results in the formation of the same absorption bands, but the 490 nm band does not decrease in intensity at the same rate as the 1100 and 405 nm bands, thus demonstrating that the 490 nm chromophore is a separate chemical entity.

The low-energy band at 1100 nm is reminiscent of the low-energy $\delta-\delta^*$ transitions found for many Tc$_2$(II,III) and Re$_2$(II,III) complexes[1c,15] and may implicate the intermediacy of a mixed valent dinuclear species that then decomposes into mononuclear fragments. Such an intermediate is plausible assuming that irradiation of **1** produces a long-lived excited state species, [Tc$_2$]$^{4+*}$, which then participates in an electron transfer process to form a mixed-valent complex. Similar photoinduced redox processes are well-established for quadruply-bonded dimolybdenum and dirhenium compounds.[16] For example, the $^1\delta\delta^*$ excited state of [Re$_2$Cl$_8$]$^{2-}$ was determined to be a powerful one-electron oxidant and a moderately strong one-electron reductant. Photoexcitation of [Re$_2$Cl$_8$]$^{2-}$ in the presence of various electron donors and acceptors resulted in generation of the mixed-valence species [Re$_2$Cl$_8$]$^{3-}$ and [Re$_2$Cl$_8$]$^-$. Gray and co-workers demonstrated that back electron transfer could be prevented by further reaction of [Re$_2$Cl$_8$]$^-$ with chloride ion.[17] Initially we believed that by analogy, back electron transfer of the photogenerated Tc species may be averted by chemical decomposition of either the donor or acceptor, thereby allowing the dinuclear metal species to ultimately undergo metal−metal bond cleavage to produce **2**. However, solution and solid state emission studies of **1** failed to demonstrate the existence of a long-lived excited state species capable of undergoing intermolecular electron transfer.

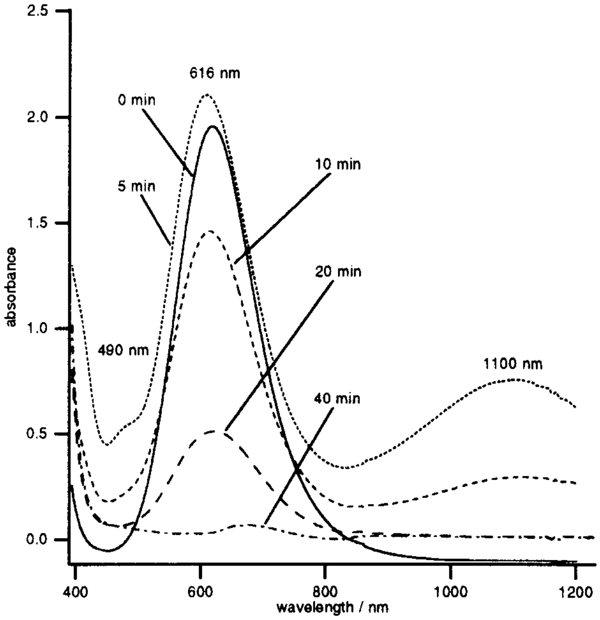

Figure 2. Visible spectra during photolysis of [Tc$_2$(CH$_3$CN)$_{10}$][BF$_4$]$_4$ in CH$_3$CN as a function of time.

A plausible idea (admittedly not yet supported experimentally) is that photoexcitation produces a mixed-valent, charge-separated Tc(I)−Tc(III) complex that undergoes metal−metal bond cleavage to produce mononuclear Tc(I) and Tc(III) nitrile complexes. These mononuclear species could then undergo a comproportionation reaction to yield **2** consistent with the observed electrochemical potentials of the Tc(I)/Tc(II) and Tc(II)/Tc(III) redox couples (*vide supra*). Admittedly, the chemical identities of the photogenerated intermediates are presently unknown, and elucidation of the photochemical pathway will require further investigation into the complex photochemistry.

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Supporting Information Available: Crystallographic data, positional parameters, anisotropic displacement parameters, and bond lengths and angles for **2** (5 pages). Ordering information is given on any current masthead page.

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