

- HClO₄ and either ~2 M 2-propanol (to scavenge ·Cl) or 0.1 M Fe(ClO₄)₃ [to scavenge Co^{II}(N₄)]. Photochemical techniques are described elsewhere.^{15,22}
- (24) If we take $K_0 \sim 0.1 \text{ M}^{-1}$ for the association of the two +2 complexes in solutions 0.1 M in ionic strength, then $\Delta G_{pc} = (\Delta G_0 + \Delta G_w^{\ddagger}) \sim (1.4 + 5) \text{ kcal mol}^{-1}$. In this estimate we have used^{9a,12} $k_w = (KT/h)e^{-\Delta G_w^{\ddagger}/RT} \approx 10^9 \text{ s}^{-1}$ as the rate constant for water loss from $\text{Co}(\text{N}_4)(\text{OH}_2)_2^{2+}$.
- (25) This definition neglects a small entropy change due to solvent compressions on going from the unbound state to the transition state.
- (26) Electron affinities are 0.08 eV for ·CH₃²⁷ compared with 3.56 and ~3.3 eV for ·Cl and ·N₃, respectively.²⁸
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- (30) This description allows stretching of the critical Co–X coordinate toward the homolysis limit, but excludes any perturbation by the reducing center. For simplicity we have neglected the Co^{II}–OH₂ compression. Appropriate functions are $U(r)_h = E_{th}[1 - e^{-r/a}]^2$ and $U(r)_p = E_{th}[1 - e^{-(r-r_e)/a}]^2$. For small displacements, the parameter a is given by $a = (1/\Pi\nu_e)\sqrt{E_{th}/2M}$ (r is the distance along the critical configuration coordinate, ν_e is the vibrational mode associated with this coordinate, M is the reduced mass, and the potential energy minima occur at $r = 0$ and $r = r_e$; see Figure 1). Points along these surfaces correspond to a limiting "valence trapped" situation in which there is no interaction between the metal centers (a and b).
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- (32) Parameters used in this estimate are 224 pm for the Co^{III}–Cl distance,³¹ and a typical Co^{III}–Cl stretching frequency of ~325 cm⁻¹,³² giving $r_e \sim 140 \text{ pm}$ and $\Delta G \sim 14 \text{ kcal mol}^{-1}$. This suggests that $\delta \sim 10 \text{ kcal mol}^{-1}$ for this system. For methyl-bridged case, both ν_e and r_e should be larger.
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Oxidative Addition from a Six-Coordinate to an Eight-Coordinate Complex. Single-Crystal Structures of [Tc(diars)₂Cl₂][ClO₄] and [Tc(diars)₂Cl₄]PF₆

Sir:

In 1960 Fergusson and Nyholm reported¹ that molecular chlorine readily converted the six-coordinate technetium(III) complex [Tc(diars)₂Cl₂]⁺ [diars = *o*-phenylenebis(dimethylarsine)] into the eight-coordinate technetium(V) complex [Tc(diars)₂Cl₄]⁺. However, these researchers worked under severe experimental limitations, having only a total of 15 mg of ⁹⁹Tc available to them, and their assignment of an eight-coordinate product was ultimately based on a single conductivity measurement and analogy to the somewhat better characterized rhenium system.² Moreover, despite intensive interest and research concerning the scope and mechanism(s) of the oxidative addition reaction,^{3,4} no further reports of oxidative addition leading to eight-coordinate complexes have appeared. We therefore thought it worthwhile to reexamine this system, especially in view of the recently expanded interest in technetium chemistry as relevant to the development of new ^{99m}Tc radiopharmaceuticals for use in diagnostic nuclear medicine.^{5–9} While two reports of seven-coordinate technetium complexes have recently appeared,^{10,11} there are no eight-coordinate technetium complexes known.¹² It would therefore be very pertinent to the development of synthetic procedures for new technetium radiopharmaceuticals if eight-coordinate technetium complexes could indeed be generated under the relatively mild oxidative addition conditions described by Fergusson and Nyholm.^{1,2}

The chloride salt of the six-coordinate complex

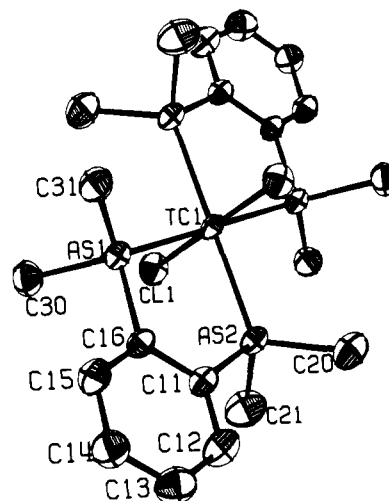
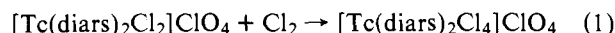


Figure 1. Perspective view of [Tc(diars)₂Cl₂]⁺. The ellipsoids represent 50% probability, and hydrogen atoms have been omitted for clarity. Site symmetry, C₂; approximate symmetry, D_{2h}. Bond lengths: Tc(III)–Cl, 2.348 (8), and 2.288 (7); Tc(III)–As, 2.518 (2), and 2.511 (2) Å. Bond angle: As–Tc–As, 83.50 (4)°.

[Tc(diars)₂Cl₂]⁺ was prepared by the method of Fergusson and Nyholm¹ and then converted into the perchlorate salt by metathesis with HClO₄ in methanol. Single crystals of orange [Tc(diars)₂Cl₂][ClO₄] were grown from ethanol containing 10⁻⁴ M HClO₄ by slow cooling of a warm, saturated solution. These crystals belong to the monoclinic space group C₂, Z = 2, with $a = 13.001 (10)$, $b = 10.409 (3)$, $c = 11.796 (8)$ Å; $\beta = 114.49 (15)^\circ$; $d_{\text{calcd}} = 1.93$, $d_{\text{obsd}} = 1.92 (2) \text{ g cm}^{-3}$. The structure was solved by standard Patterson and Fourier methods using 1474 independent reflections [$I > 2\sigma(I)$, $2\theta < 54^\circ$, Mo K α radiation]. Final least-squares refinement of 181 parameters (overall scale factor, positional and anisotropic temperature parameters for nonhydrogen atoms and fixed hydrogen atoms) converged with a conventional discrepancy index¹³ of 0.027. The structure of the [Tc(diars)₂Cl₂]⁺ cation is shown in Figure 1, the trans octahedral coordination geometry being typical for [M(diars)₂X₂]ⁿ⁺ complexes.¹⁴ Single-crystal X-ray structural analysis of the red chloride salt, [Tc(diars)₂Cl₂]Cl, shows that this material also contains the trans cation; there are only slight differences between the two independent sets of cation structural parameters.

When molecular chlorine is introduced into an alcoholic solution of [Tc(diars)₂Cl₂][ClO₄] at room temperature, the solution rapidly turns deep red in color and a dark brown solid is subsequently deposited. This reaction defines an oxidative addition process with six coordinate, d⁴, Tc(III) being converted into eight coordinate, d², Tc(V) by the addition of Cl₂:



Visible-UV spectrophotometry confirms that the chromophore produced by oxidation of either [Tc(diars)₂Cl₂][ClO₄] or [Tc(diars)₂Cl₂]Cl is the same [maxima at 403 and 275 nm ($\epsilon \approx 3600$ and $9800 \text{ M}^{-1} \text{ cm}^{-1}$), respectively, shoulder at 475 nm ($\epsilon \approx 600 \text{ M}^{-1} \text{ cm}^{-1}$)]. The oxidized chloride salt may be converted into the hexafluorophosphate salt by metathesis with NaPF₆ in nitromethane; visible-UV spectrophotometry again confirms that this PF₆⁻ salt contains the same chromophore.

Single crystals of dark brown [Tc(diars)₂Cl₄]PF₆ were obtained by slow evaporation of the metathesis reaction mixture. These crystals belong to the orthorhombic space group Fddd, Z = 8, with $a = 13.821 (4)$, $b = 21.159 (8)$, $c = 21.227 (18)$ Å; $d_{\text{calcd}} = 2.05$, $d_{\text{obsd}} = 2.05 (2) \text{ g cm}^{-3}$. The structure was solved by standard Patterson and Fourier methods using 986 independent reflections [$I > 2\sigma(I)$, $2\theta < 46^\circ$, Mo K α

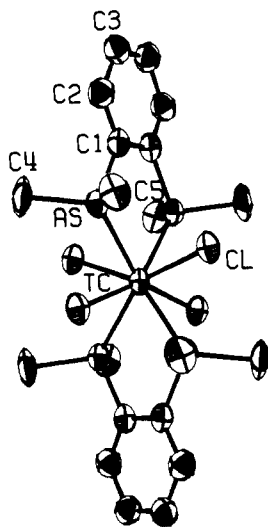


Figure 2. Perspective view of $[\text{Tc}(\text{diars})_2\text{Cl}_4]^+$. The ellipsoids represent 50% probability, and hydrogen atoms have been omitted for clarity. Site symmetry, D_2 ; approximate symmetry, D_{2d} . Bond lengths: Tc(V)–Cl, 2.442 (4); Tc(V)–As, 2.578 (2) Å. Bond angles: As–Tc–As, 129.46 (5), Cl–Tc–Cl, 91.21 (12)°.

radiation]. Final least-squares refinement of 130 parameters (overall scale factor, positional and anisotropic temperature parameters for the nonhydrogen atoms) converged with a conventional discrepancy index¹³ of 0.076. The structure of the $[\text{Tc}(\text{diars})_2\text{Cl}_4]^+$ cation is shown in Figure 2, the D_{2d} dodecahedral coordination geometry being the same as observed^{15–17} in the analogous eight-coordinate titanium(IV) complex $\text{Ti}(\text{diars})_2\text{Cl}_4$. In this geometry the d_{xy} orbital is substantially more stable than any other¹⁸ and therefore it is not surprising that this disposition of ligands can accommodate both a d^0 and a spin-paired d^2 metal center.¹

Single-crystal X-ray confirmation of the proposed coordination geometries of $[\text{Tc}(\text{diars})_2\text{Cl}_2]^+$ and $[\text{Tc}(\text{diars})_2\text{Cl}_4]^+$ establishes reaction 1 as the first known example of oxidative addition from a six-coordinate to an eight-coordinate complex. The stability of the eight-coordinate product undoubtedly results in great part from the presence of the diars ligands which are known to promote high coordination numbers.^{16,17,19–21} However, even for those reactions in which the eight-coordinate products are metastable or unstable, oxidative addition to six-coordinate technetium complexes has great potential as a synthetic route for the interconversion of octahedral technetium complexes and the ultimate synthesis of new technetium radiopharmaceuticals. Likewise, other large octahedral metal centers such as Mo(II) may also undergo oxidative addition reactions, and synthetic routes based on this chemistry may prove profitable. Reaction 1 is also unusual in that it involves a d^4 starting material, whereas most oxidative addition reactions involve d^8 or d^{10} starting materials;³ however, it is consistent with Halpern's generalized formulation of oxidative addition reactions³ in that it involves conversion of an open-shell (16 valence electrons) complex to a closed-shell (18 valence electrons) complex. Studies designed to establish the detailed mechanism of reaction 1 are currently in progress.

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Bond Energy and Conformation of the Molybdenum-to-Molybdenum Triple Bond

Sir:

Recently, thermochemical measurements have been reported for the triply bonded dimers $\text{M}_2(\text{NMe}_2)_6$ ($\text{M} = \text{Mo}$, W).¹ Although the enthalpy of formation for these systems can be accurately measured, it is difficult to determine the actual $\text{M}\equiv\text{M}$ bond energy because it is not obvious what value to use for the $\text{M}-\text{NMe}_2$ bond energy. Thus, a range of $\text{M}\equiv\text{M}$ bond energies from weaker than a carbon-carbon single bond to stronger than a nitrogen-nitrogen triple bond are reported. A value of $592 \pm 196 \text{ kJ mol}^{-1}$ ($141 \pm 47 \text{ kcal mol}^{-1}$) is suggested for the $\text{M}\equiv\text{Mo}$ bond energy.¹

We believe that it would be useful to know this value more precisely. Although it is rare to be able to calculate a dissociation energy more accurately than it can be measured, the large error bars on the experimental value for the $\text{Mo}\equiv\text{Mo}$ bond suggest it would be possible for this case. We have used the generalized molecular orbital (GMO) approach in this study.² The GMO method consists of a multiconfiguration self-consistent-field calculation followed by a configuration interaction (CI) calculation. All of the orbitals are kept doubly occupied except for those involved in the triple bond. For the six electrons in the triple bond, the GMO wave function consists of the dominant single determinant ($\sigma^2\pi_x^2\pi_y^2$) plus all paired double excitations, from these bonding orbitals to their antibonding counterparts ($\sigma^*\pi_x^*\pi_y^*$), weighted equally.² Application of the variation principle yields a set of primary orbitals ($\sigma, \pi_x, \pi_y, \sigma^*, \pi_x^*, \pi_y^*$) in which the weakly occupied ones ($\sigma^*, \pi_x^*, \pi_y^*$) are optimized to correlate the strongly occupied ones (σ, π_x, π_y). The determination of the GMO orbitals is then followed by a full CI calculation in this