Table I. Partial Isotopic Composition of Toluenes and Cycloheptatrienes Produced in the Reaction of Carbon with Benzene[a]

deuterated species	percent of deuterated species in product: cycloheptatriene	toluene	toluene[b]
$C_7D_5H_3$	0 ± 4.1	14.1 ± 8.0	43.3 ± 1.6
$C_7D_6H_2$	25.3 ± 6.2	31.1 ± 5.0	30.6 ± 1.4
C_7D_7H	49.5 ± 3.5	36.9 ± 6.1	19.1 ± 1.0
C_7D_8	25.2 ± 3.7	17.9 ± 4.9	7.0 ± 0.8

[a] Only toluenes and cycloheptatrienes containing five or more deuteriums are reported; quantitative determination of the others was not possible owing to the presence of some of the benzocyclopropenes which were incompletely separated by GC in this experiment. [b] Toluene from reaction of carbon with benzene-d_6 and an equimolar amount of propane.

triene. This observation may be rationalized if one assumes that the reactant is triplet methylene which prefers to abstract hydrogen from propane rather than react with benzene.

The fact that biphenyl is formed is indicative of hydrogen abstractions from benzene to yield phenyl radicals. An analysis of the biphenyl produced in the reaction of carbon with benzene and benzene-d_6 reveals biphenyl-d_0, -d_5, and -d_{10} in a ratio of 1:2:1. Similarly, an analysis of phenylcycloheptatriene reveals an isotope distribution of d_0:d_6:d_{12} of 1:2:1, the ratio expected from the reaction of phenyl carbene with benzene.

In summary, atomic carbon reacts with benzene to produce both carbenes **1** and **3** as primary products. An additional C_7H_6 product is benzocyclopropene which may result from rearrangement of energetic **1** or **2** or by a direct addition of carbon to benzene. A competing process in the reaction of carbon with benzene is a series of hydrogen abstractions to generate methylene and methyl radicals which may react with benzene to produce cycloheptatriene and toluene.

Acknowledgments. We are grateful to Professor W. M. Jones for a generous gift of heptafulvalene. We thank the National Science Foundation for support of this work under Grant CHE 77-24624.

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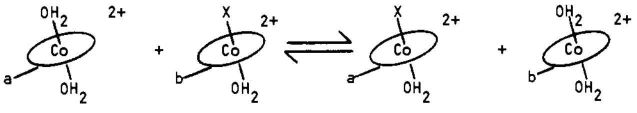
Transition-State Binding Energies and the Nature of the Reaction Coordinate in Inner-Sphere Electron-Transfer Reactions: A Unified Approach to Methyl- and Halogen-Bridged Reactions[1]

Sir:

While cobalt mediated methylations are of considerable biological significance,[2] they present many puzzling mechanistic features. This has even been the case for methyl-transfer reactions between transition metals in aqueous solution.[3,4] These reactions are best described as inner-sphere electron-transfer reactions; yet they are orders of magnitude slower than the halide or pseudohalide analogues. The common mechanistic description of halide and methyl-bridged electron-transfer reactions has been particularly challenging since the coordinated methyl group lacks a nonbonding pair of electrons believed necessary for bonding to the reducing metal in the precursor complex.[5]

Much of the advance in understanding of outer-sphere electron-transfer reactions can be attributed to the systematic separation of "intrinsic", $\Delta G^{\ddagger}{}_{i}$, from free-energy, $\Delta G°$, dependent components of the reactivity.[5-8] A similar level of understanding of inner-sphere electron-transfer reactions has been difficult to achieve in large part because these factors are much more difficult to separate. However, very recent work[9] has shown that intrinsic factors can be systematically examined for inner-sphere electron-transfer reactions in which the metal centers are coordinated to macrocyclic ligands. In such cases an inner sphere self-exchange reaction (a = b) can be investigated (eq 1). Although the inner-sphere self-exchange rate



(1)

constants are ~10^7 times larger (X = Cl, Br, or N_3) than the corresponding outer-sphere self-exchange rate constant (i.e., $\Delta G_i(\text{IS}) \ll \Delta G_i(\text{OS})$), the halide and pseudohalide-bridged reactions still exhibit sensitivity to variations in structural parameters.[9]

We have now used reactions of macrocyclic cobalt complexes (**1**) to isolate the intrinsic reactivity factors for methyl-bridged electron-transfer reactions.[10] We find that for these reactions $\Delta G_i(\text{IS, X} = \text{CH}_3) \gg \Delta G_i(\text{IS, X} = \text{Cl, Br, or N}_3)$; see Table I. The ~$10^6$-fold slower methyl- than halide-bridged self-exchange reactions are not easily rationalized in terms of the simple reorganizational argument presented previously.[9a,11,12]

The reaction coordinate in the inner sphere electron-transfer reactions involves bond breaking and should be described by a potential energy function which takes this into account (e.g., a Morse function). This requires that the Co–X homolysis energy be a factor in the mechanistic analysis. The consideration of homolysis energies in addition to the usual kinetic parameters permits a unified description of methyl- and halide-bridged electron-transfer reactions.

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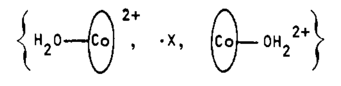
Table I. Kinetic Parameters for the Exchange Reactions[a]

$$\mathrm{Co(N_4)(OH_2)_2^{2+} + Co(N_4')(OH_2)X^{2+} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} Co(N_4)(OH_2)X^{2+} + Co(N_4')(OH_2)_2^{2+}}$$

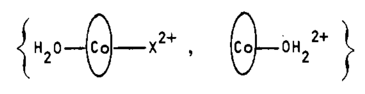
N_4	N_4'	for X = Cl		for X = N_3		for X = CH_3	
		$10^{-3}k_{12}$	$10^{-3}k_{21}$	$10^{-3}k_{12}$	$10^{-3}k_{21}$	k_{12}	k_{21}
Me_4[14]tetraeneN_4	Me_6[14]4,11-dieneN_4	4.2 ± 0.2[b]	1.5 ± 0.1[b]	42 ± 3	26 ± 3	$(8 + 1) \times 10^{-3}$	$<(0.1) \times 10^{-3}$
Me_4[14]tetraeneN_4	Me_2pyo[14]trieneN_4	62 ± 2[b]	160 ± 10[b]	130 ± 10	230 ± 10	31 ± 1	0.15 ± 0.01
Me_2pyo[14]trieneN_4	Me_6[14]4,11-dieneN_4	10 ± 1	27 ± 2	65 ± 3	110 ± 10	$(12 \pm 1) \times 10^{-3}$	$(0.28 \pm 0.03) \times 10^{-3}$
Me_4[14]tetraeneN_4	corrin[c]					1.05 ± 0.08	0.27 ± 0.02
Me_2pyo[14]trieneN_4	corrin[c]					~12[d]	600 ± 50
		For N_4 = Me_4[14]tetraeneN_4					
	$G^{\ddagger}_{exch}$[e]	9 ± (8.6)		7.6 ± 0.8 (8.4)		18	
	E_{th}[f]	46 ± 4		51 ± 2		48 ± 2	
	$(BE)^{\ddagger}$[g]	43 ± 5		49 ± 3		36	

[a] At 25 °C; $\mu = 0.1$ ($NaClO_4$, $HClO_4$), pH 1-2. All rate constants have units $M^{-1}\ s^{-1}$. [b] Reference 4a. [c] Methylcobalamin. [d] Based on $K_{12} \simeq 2 \times 10^{-2}$ and k_{21}. [e] Based on cross reactions: $Co(N_4)(OH_2)X^{2+} + Co(N_4')(OH_2)_2^{2+}$, $Co(N_4)(OH_2)_2^{2+} + Co(N_4')(OH_2)X^{2+}$, and $k_{12} \simeq (k_{11}k_{22}k_{12})^{1/2}$; see ref 10. Numbers in parentheses are based on NMR line-broadening measurements. $\Delta G^{\ddagger}$ values are from $k_{exch} = 10^{11}\ e^{-\Delta G^{\ddagger}/RT}$. [f] Photochemical threshold energy. [g] $(BE)^{\ddagger} = E_{th} + \Delta G_{pc} - \Delta G^{\ddagger}_{exch}$; ΔG_{pc} is the free-energy difference between reactants and the precursor complex as defined in the text.

For an inner-sphere electron-transfer "self-exchange" reaction, it is useful to consider as states of the reacting system: (1) the "ground state" of uncorrelated reactants; (2) a "precursor complex" in which the reactants have been assembled in a solvent cage but are otherwise noninteracting;[12] (3) a "symmetrical transition state" in which the ligand X binds the metals equally and in which the environments and charges of the metal centers are identical; and (4) an "unbound state" of the reacting system composed of two five-coordinate cobalt(II) complexes and the radical ligand, ·X, all contained in close proximity in a solvent cage.



The difference in energy between the



"precursor state" and the unbound state of the system is the Co-X homolysis energy. Recent work has indicated that the minimum photonic energy, E_{th}, required to induce Co-X homolysis is a good measure of the homolytic bond energy[14-20] (see also supplementary material).

In this report we focus primarily on complexes of cobalt containing the equatorially coordinated macrocyclic ligand Me_4[14]tetraeneN_4,[21] and in which X = Cl, N_3, or CH_3. We have previously reported that E_{th} = 48 ± 2 kcal mol^{-1} for the methyl-aquo complex.[22] We have now found that E_{th} = 46 ± 4 and 51 ± 3 kcal mol^{-1} for the chloro- and azido-aquo complexes, respectively.[23]

Values of self-exchange rate constants for reaction 1 with X = Cl or N_3 have been determined both from ^{1}H NMR line broadening and cross reactions (i.e., reactions in which a ≠ b in eq 1) as described previously.[9a] The methyl-bridged reactions are slow (Table I), and this precludes use of the line broadening technique. The relative reactivities of the different combinations of complexes are differently ordered for the methyl-bridged reactions in Table I than for outer-sphere (diaquo) reactions[9c] or the halide-bridged inner-sphere reactions (Table I). The different orders of reactivity are largely a consequence of the larger variations of equilibrium constant for the methyl-bridged than for the halide-bridged reactions. There do appear to be substantial variations in the intrinsic parameters for the methyl-bridged reactions. However, little of this can be expressed in terms of metal-ligand "reorganizational" energy since the Co-OH_2 bond is relatively long and weak in both the methyl and cobalt(II) complexes. Consequently, it is not at all obvious why the methyl-bridged reactions in Table I should be so much slower than the halide-bridged reactions.

The progress of the inner-sphere self-exchange reaction from the precursor complex across the reaction coordinate to the successor complex may be represented as in Figure 1. The axial water molecules of $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{2+}$ are very labile; so we estimate the free-energy difference between the separated reactants and the precursor complex for inner-sphere reactions of Me_4[14]tetraeneN_4 complexes to be $\Delta G_{pc} \sim 6$ kcal mol^{-1}.[24] Since $\Delta G^{\ddagger}_{exch}$ is only 8-10 kcal mol^{-1} for the chloride- and azide-bridged reactions, the difference in energy between the precursor complex and the transition state can obviously be quite small.

The difference in energy between the transition state and the unbound state may be interpreted as a *transition-state binding energy*,[24,25] $(BE)^{\ddagger} = E_{th} + \Delta G_{pc} - \Delta G^{\ddagger}_{exch}$. It follows that the transition states for the inner-sphere self-exchange reactions all have appreciable binding energies (Table I). We may further interpret the transition-state binding in terms of a three-center (Co-X-Co) three-electron bond. The magnitudes of the inferred binding energies are reasonable for such a bonding configuration.

The transition-state binding energy formalism helps rationalize some of the larger variations in reactivity. Thus, the halide- and methyl-bridged reactions are seen to be very similar in principle since both radicals have a singly occupied p_z orbital to bring into the three-center bonding configuration. Furthermore, the smaller value of $(BE)^{\ddagger}$ for the methyl- than halide-bridged interactions is readily attributable to the very small electron affinity of the methyl radical.[26-28] Thus, the relatively slow rates for methyl-bridged, self-exchange reactions are a direct consequence of weaker transition-state binding.

An approximate description of the reaction coordinate can be achieved by reference to the Morse potential energy functions of the reactant (R) and product (P) oxidant species unperturbed by the respective reductants.[29-30] The free energy at the intersection of the unperturbed reactant and product surfaces is given by $\Delta G_i = E_{th}[1 - e^{-r_e/2a}]^2$. A three-center bonding interaction in the transition state would result in an activation barrier ($\Delta G^{\ddagger}_{exch} - \Delta G_{pc}$) smaller than ΔG_i; the difference in these quantities, the interaction energy δ, is determined by the mixing of donor and acceptor orbitals.

The critical vibrational mode, ν_e, would generally be considered to have "inner-sphere" (metal-ligand) and "outer

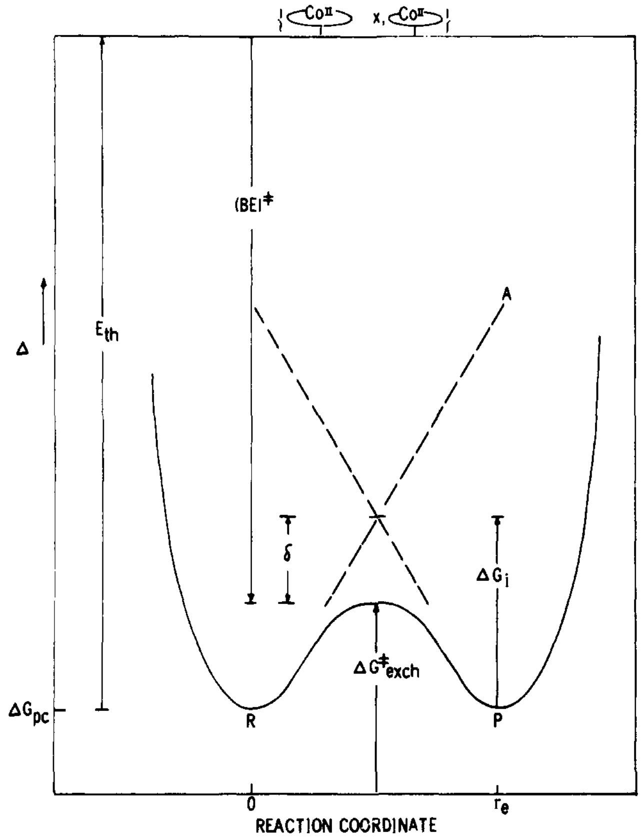
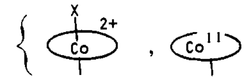


Figure 1. Qualitative representation of reaction coordinate for an inner-sphere electron-transfer reaction. ΔG_i is determined by the intersection of unperturbed reactant (R) and product (P) surfaces as approximated by Morse functions. The zero of energy for the Morse functions is taken as the energy of the precursor complex, as described in the text. The activation barrier for harmonic surfaces would be about twice ΔG_i for the example chosen. The horizontal line indicates the dissociation limit, or the energy of the "unbound state". In general, ΔG_i would be larger than the activation barrier, $\Delta G^{\ddagger}{}_{exch}$, for the self-exchange reaction. The difference, δ, between ΔG_i and $\Delta G^{\ddagger}{}_{exch}$ would depend on the mixing of donor and acceptor orbitals in the transition state.



sphere" (solvent) components.[5,7,31] However, for the inner-sphere reactions considered here, there is no difference in dipole moment between reactants and products and the solvent reorganizational terms can be neglected to a first approximation.[9a] It is possible to make some very approximate estimates of ΔG_i: for the Cl^- bridged case we estimate $\Delta G_i \sim 14$ kcal mol^{-1}, so $\delta \sim 10$ kcal mol; for the methyl bridge we would estimate ΔG_i to be nearly twice as large.

Supplementary Material Available: Thermochemical cycle for determination of E_{th} (calcd) from thermochemical data for $Co(Me_4[14]tetraene\text{-}N_4)(OH_2)Cl^{2+}$ (2 pages). Ordering information is given on any current masthead page.

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(10) The separation of thermodynamic, $\Delta G^{\circ}{}_{ab}$, and intrinsic, $\Delta G^{\ddagger}{}_{i,ab}{}^{(0)}$, parameters using an expression of the type $\Delta G^{\ddagger}{}_{ab} = \alpha\Delta G^{\circ}{}_{ab} + \Delta G^{\ddagger}{}_{i,ab}{}^{(0)}M(\alpha)$ has been discussed for group-transfer reactions by Marcus[7d] and by Levine.[8] For small values of $|\Delta G^{\circ}{}_{ab}|$ this expression reduces to $\Delta G^{\ddagger}{}_{ab} = \frac{1}{2}\Delta G^{\circ}{}_{ab} + \Delta G^{\ddagger}{}_{i,ab}{}^{(0)}$.[7d,8]

(11) We have found that the reactant partners, $Co(N_4)(OH_2)CH_3{}^{2+}$ and $Co(N_4)(OH_2)_2{}^{2+}$, differ much less in axial bond length than the diaquo partners, and (by inference) the $Co(N_4)(OH_2)Cl^{2+}$ and $Co(N_4)(OH_2)_2{}^{2+}$ partners. For example, the $Co^{II}–OH_2$ bond length is 229 pm in $Co(Me_4[14]tetraeneN_4)(OH_2)_2{}^{2+}$,[12] 216 pm in $Co(Me_4[14]tetraeneN_4)(OH_2)CH_3{}^{2+}$ (Butler, W. M.; Endicott, J. F.; Glick, M. D., unpublished work) and 191 pm for $Co(Me_4[14]tetraeneN_4)(OH_2)_2{}^{3+}$: Anderson, T. W.; Glick, M. D.; Durham, B.; Endicott, J. F., unpublished work.

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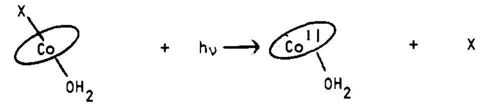
(13) Our definition of a percursor complex differs slightly from the conventional one in that we do not require $Co^{III}–(X^-)–Co^{II}$ bond formation. As a matter of convenience, we consider the labile reactant partner to be coordinatively unsaturated in the precursor complex.

(14) Photohomolyses (2) of coordination complexes have been found to have reasonably well-defined threshold energies, E_{th}.[15] Values of E_{th} have been shown (1) to be determined by the nature of the product species;[15] (2) to be reasonably close to the homolysis energy estimated in thermochemical cycles;[15-17] and (3) to contain information consistent with expectations for Co-X bonding.[18] These observations have led to the proposal that E_{th} values are measures of the homolysis bond energy in the particular solvent medium;[19] i.e., E_{th} can be interpreted as the minimum energy required to break the M-X bond, generating a coordinatively unsaturated, reduced metallo fragment and a radical ·X all thermalized and held in proximity by a "solvent cage". Recent picosecond studies of organocobalamins tend to confirm the thermalization and solvent cage features of this argument.[20]



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(16) The previously described cycles involved, in addition to the usual thermochemical parameters, enthalpies of activation for the (dissociative) hydrolyses of cobalt(III) complexes and some rather primitive assumptions regarding ΔH° values for redox couples. Very recent thermochemical data on redox couples[17] has permitted us to utilize cycles containing relatively well characterized aquo complexes (see supplementary material) to obtain E_{th} (calcd) ~ 51 kcal mol^{-1} compared with E_{th} (obsd) = 46 ± 4 kcal mol^{-1} for $Co(Me_4[14]tetraeneN_4)(OH_2)Cl^{2+}$ and E_{th} (calcd) ~ 65 ± 8 kcal mol^{-1} compared with E_{th} = 74 ± 6 kcal mol^{-1} for $Co(NH_3)_5Cl^{2+}$. This work will be described in detail elsewhere.

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(20) Endicott, J. F.; Netzel, T. L. *J. Am. Chem. Soc.* **1979,** *101,* 4000. This work demonstrates that the excited systems do undergo appreciable thermalization before homolysis and directly documents radical-pair behavior.

(21) Abbreviations for synthetic macrocyclic ligands: $Me_4[14]tetraeneN_4$ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; $Me_2pyo[14]trieneN_4$ = 2,12-dimethyl-3,7,11,17-tetraazabicyclo-[11.3.1]hepta-1(17),2,11,13,15-decane; $Me_6[14]dieneN_4$ = 5,7,7,-12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.

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(23) We have found that the quantum yields for homolysis of $Co(Me_4[14]tetraeneN_4)(OH_2)Cl^{2+}$ increase with excitation energy in the range 254 nm $\leq \lambda <$ 600 nm. The failure to observe an excitation plateau region (i.e., an excitation range for which $\phi \sim$ constant) suggests that the excited states populated by absorption in this complex are not bound and that there is relatively little thermalization of the excited system. In the absence of an excitation plateau, the extrapolation of ϕ to 0 is relatively shallow and there is relatively more uncertainty in E_{th}. Quantum yields were determined from changes of absorbance in deaerated photolyte solutions containing 1 M

HClO$_4$ and either ~2 M 2-propanol (to scavenge ·Cl) or 0.1 M Fe(ClO$_4$)$_3$ [to scavenge Co^{II}(N$_4$)]. Photochemical techniques are described elsewhere.[15,22]

(24) If we take $K_0 \sim 0.1$ M^{-1} for the association of the two +2 complexes in solutions 0.1 M in ionic strength, then $\Delta G_{pc} = (\Delta G_0 + \Delta G_w^{\ddagger}) \sim (1.4 + 5)$ kcal mol^{-1}. In this estimate we have used[9a,12] $k_w = (KT/h)e^{-\Delta G_w^{\ddagger}/RT} \simeq 10^9$ s^{-1} as the rate constant for water loss from Co(N$_4$)(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 ·CH$_3$[27] compared with 3.56 and ~3.3 eV for ·Cl and ·N$_3$, 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}–OH$_2$ compression. Appropriate functions are $U(r)_R = E_{th}[1 - e^{-r/a}]^2$ 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 $r_e \sim 140$ pm and $\Delta G_i \sim 14$ kcal mol^{-1}. This suggests that $\delta \sim 10$ 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)$_2$Cl$_2$]ClO$_4$ and [Tc(diars)$_2$Cl$_4$]PF$_6$

Sir:

In 1960 Fergusson and Nyholm reported[1] that molecular chlorine readily converted the six-coordinate technetium(III) complex [Tc(diars)$_2$Cl$_2$]$^+$ [diars = *o*-phenylenebis(dimethylarsine)] into the eight-coordinate technetium(V) complex [Tc(diars)$_2$Cl$_4$]$^+$. However, these researchers worked under severe experimental limitations, having only a total of 15 mg of ^{99}Tc 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 [Tc(diars)$_2$Cl$_2$]$^+$ was prepared by the method of Fergusson and Nyholm[1] and then converted into the perchlorate salt by metathesis with HClO$_4$ in methanol. Single crystals of orange [Tc(diars)$_2$Cl$_2$]ClO$_4$ were grown from ethanol containing 10^{-4} M HClO$_4$ 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)°; $d_{calcd} = 1.93$, $d_{obsd} = 1.92$ (2) g cm^{-3}. The structure was solved by standard Patterson and Fourier methods using 1474 independent reflections [$I > 2\sigma(I)$, $2\theta < 54°$, Mo Kα 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 index[13] of 0.027. The structure of the [Tc(diars)$_2$Cl$_2$]$^+$ cation is shown in Figure 1, the trans octahedral coordination geometry being typical for [M(diars)$_2$X$_2$]$^{n+}$ complexes.[14] Single-crystal X-ray structural analysis of the red chloride salt, [Tc(diars)$_2$Cl$_2$]Cl, shows that this material also contains the trans cation; there are only slight differences between the two independent sets of cation structural parameters.

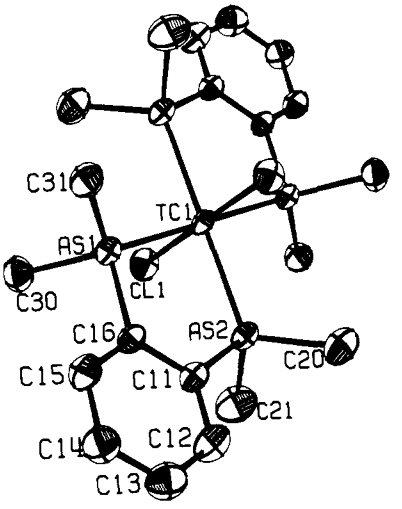

Figure 1. Perspective view of [Tc(diars)$_2$Cl$_2$]$^+$. The ellipsoids represent 50% probability, and hydrogen atoms have been omitted for clarity. Site symmetry, C_2; approximate symmetry, D_{2h}. Bond lengths: Tc(III)–Cl, 2.348 (8), and 2.288 (7); Tc(III)–As, 2.518 (2), and 2.511 (2) Å. Bond angle: As–Tc–As, 83.50 (4)°.

When molecular chlorine is introduced into an alcoholic solution of [Tc(diars)$_2$Cl$_2$]ClO$_4$ 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, d^4, Tc(III) being coverted into eight coordinate, d^2, Tc(V) by the addition of Cl$_2$:

$$\text{[Tc(diars)}_2\text{Cl}_2\text{]ClO}_4 + \text{Cl}_2 \rightarrow \text{[Tc(diars)}_2\text{Cl}_4\text{]ClO}_4 \quad (1)$$

Visible-UV spectrophotometry confirms that the chromophore produced by oxidation of either [Tc(diars)$_2$Cl$_2$]ClO$_4$ or [Tc(diars)$_2$Cl$_2$]Cl is the same [maxima at 403 and 275 nm ($\epsilon \simeq 3600$ and 9800 M^{-1} cm^{-1}), respectively, shoulder at 475 nm ($\epsilon \simeq 600$ M^{-1} cm^{-1})]. The oxidized chloride salt may be converted into the hexafluorophosphate salt by metathesis with NaPF$_6$ in nitromethane; visible-UV spectrophotometry again confirms that this PF$_6^-$ salt contains the same chromophore.

Single crystals of dark brown [Tc(diars)$_2$Cl$_4$]PF$_6$ 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; $d_{calcd} = 2.05$, $d_{obsd} = 2.05$ (2) g cm^{-3}. The structure was solved by standard Patterson and Fourier methods using 986 independent reflections [$I > 2\sigma(I)$, $2\theta < 46°$, Mo Kα

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