appear almost identical, they differing mainly in the values of the metal–halogen stretching frequencies.[7] Moreover, the ligand stretchings appear unaffected by the change in the terminal MX groups (X = O, S), considering that the spectra of the sulfido complexes resemble those of the corresponding oxo analogues except for the lack of the characteristic strong M=O absorptions (in the ranges 890–1020 cm^{-1} for Tc[5] and 910–1000 cm^{-1} for Re[6]). No attempts were made to identify the M=S stretchings, which seem hidden by the ligand bands.[3e,f]

Complexes **1** and **2** are particularly well suited for analysis by mass spectrometry.[7] The mass spectrum of [TcSCl$_2$(HB(pz)$_3$)] shows a cluster of peaks at m/e 414 resulting from the molecular ion M$^+$ and exhibits an isotope distribution pattern that is consistent with a species containing two chlorine atoms. Additionally, the spectrum exhibits other peaks that may be assigned as fragments of the complex resulting from the loss of a monodentate ligand. That is, the doublet at m/e 379 and 381 represents the molecular ion minus a chlorine, the singlet at m/e 344 represents loss of two chlorines, and the singlet at m/e 312 represents loss of two chlorines and the sulfur from the molecular ion.

The parent ion M$^+$, with an isotope distribution pattern characteristic for a rhenium complex containing two chlorine atoms[8] and the same fragmentation behavior found for complex **1**, is observed in the mass spectrum of [ReSCl$_2$(HB(pz)$_3$)].[7]

Faraday measurements showed that the complexes [MSCl$_2$(HB(pz)$_3$)] are diamagnetic in the solid state consistent with a +5 oxidation state for Tc and Re and with the existence of a terminal metal–sulfido multiple bond analogous to the isoelectronic metal–oxo multiple bond.[1b,9]

The present results show the possibility to prepare technetium(V) complexes containing a terminal Tc=S multiple bond; however, the formation and stability of such a group appear strongly dependent upon the nature of the other ancillary ligands coordinated to the metal ion, a factor that must be carefully taken into account for the development of possible technetium(V)–sulfido radiopharmaceuticals.

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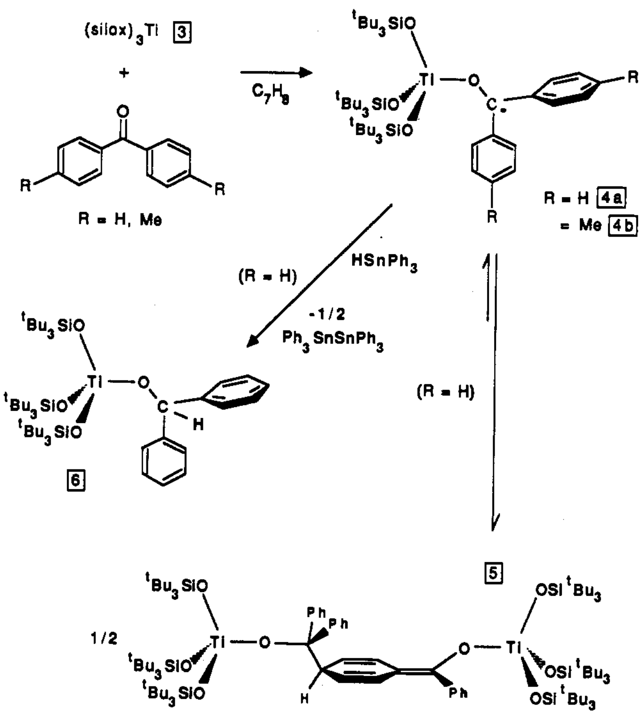
Reversible Dimerization of a Titanium Ketyl: (silox)$_3$TiOCPh$_2^\bullet$ (silox = ^{t}Bu$_3$SiO$^-$)

Inherently reactive organic fragments are often trapped and stabilized by transition metal centers. It has been shown that d^1 complexes, typically those containing Ti(III), promote alkyl cyclizations[1,2] and pinacol-type couplings[3-13] characteristic of carbon-centered radicals. In each instance, it is convenient to view the odd electron as transposed from the metal to a reducible adduct. For example, treatment of CpTiCl$_2$ with acetone[7] leads to [CpCl$_2$Ti]$_2$O$_2$C$_2$(Me)$_4$, the acetone-coupled dimer structurally characterized by Caulton et al.[10] While unhindered dialkyl ketones clearly lead to coupled products, evidence for the reversible coupling of benzophenone,[7] although often cited,[11,12] is far less compelling.[8,9] By employment of the sterically demanding silox (^{t}Bu$_3$SiO$^-$) ligand,[14-16] a reactive fragment may be shielded within

Scheme I



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a hydrocarbon shell. Reported herein is the direct EPR observation of a diphenylcarboxy radical derived from Ti(III) reduction of benzophenone[17] and the reversible C–C bond formation that accompanies its dimerization.

Addition of 3.0 equiv of Na(silox)[15] to $TiCl_4(THF)_2$ in THF resulted in the formation of colorless $(silox)_3TiCl$ (**1**)[18] in 85% yield (eq 1). Reduction of **1** with Na/Hg in DME generated

$$3\text{Na(silox)} + \text{TiCl}_4(\text{THF})_2 \xrightarrow[-3\text{NaCl}]{\text{THF}} \underset{\mathbf{1}}{(\text{silox})_3\text{TiCl}} \tag{1}$$

pale green $(silox)_3Ti(DME)$ (**2**), which was triturated in hexane to afford $(silox)_3Ti$ (**3**).[18] The three-coordinate, monomeric (M_r found 709, calcd 694), d^1 complex was isolated as orange crystals (76%) from hexane solution (eq 2). The visible spectrum of D_{3h}

$$\mathbf{1} \xrightarrow[\text{DME}]{\text{Na/Hg}} \underset{\mathbf{2}}{(\text{silox})_3\text{Ti(DME)}} \xrightarrow{\text{hexane}} \underset{\mathbf{3}}{(\text{silox})_3\text{Ti}} \tag{2}$$

3 consists of a symmetrical absorption at 20 000 cm^{-1} (ϵ = 360 M^{-1} cm^{-1}), assigned to the $^2A_1' \rightarrow {}^2E'$ $((d_{z^2})^1 \rightarrow (d_{x^2-y^2}, d_{xy})^1)$ transition. The lower lying $^2A_1' \rightarrow {}^2E''$ $((d_{z^2})^1 \rightarrow (d_{xz}, d_{yz})^1)$ band, predicted to appear in the near-IR region, could not be identified. Confirmation that the ground electronic state is $^2A_1'$, $(d_{z^2})^1$, was obtained via EPR spectroscopy. The 25 °C EPR spectrum of **3** exhibited a single absorption at g_{iso} = 1.9554 flanked by ^{47}Ti (I = $^5/_2$) and ^{49}Ti (I = $^7/_2$) satellites, with a_{iso} = 155 MHz (~56.7 G). A hyperfine coupling of this magnitude strongly implies that an a_1' orbital (d_{z^2}) is occupied. Furthermore, spectra of **3** in toluene glass at −167 °C revealed $g_\parallel$ = 1.9997 and $g_\perp$ = 1.9323, which theory predicts to be equivalent to $g_e - 6\lambda/\Delta$,[19] where λ is the spin–orbit coupling parameter. Bradley calculated λ for $Ti[N(SiMe_3)_2]_3$ as 108 cm^{-1}, 70% of the free ion value (154 cm^{-1}).[20] Assuming this value to be reasonable for **3**, the $^2A_1' \rightarrow 2E''$ transition is expected to be ~9200 cm^{-1}, and the accompanying crystal field stabilization energy is ~11 700 cm^{-1}.[21,22]

As Scheme I indicates, 1.0 equiv of benzophenone reacted with $(silox)_3Ti$ (**3**) to provide a dimer resulting from the coupling of two $(silox)_3Ti–O(Ph)_2C^\bullet$ (**4a**) units. The C–C bond in $(silox)_3Ti—O(Ph)_2C—(H)\overline{C(CH)_2C(CH{=}}CH){=}C(Ph)O—Ti(silox)_3$ (**5**),[18] formed between the carbonyl and phenyl para carbons of separate Ph_2CO units, is a consequence of the steric influences of the silox groups. This unusual structural feature signifies **5** as an inorganic analogue to hexaphenylethane, reported by Gomberg in 1900.[23] Figure 1 illustrates the distinct set of olefinic resonances denoting the phenyl ring that serves as the bridge. Treatment of **5** with Ph_3SnH immediately produced $(silox)_3Ti–OCHPh_2$ (**6**), providing chemical evidence for the existence of **4a**. Although the equilibrium between the radical (**4a**) and the dimer (**5**) lies heavily toward the latter, sufficient quantities of $(silox)_3Ti–O(Ph)_2C^\bullet$ (**4a**) render it observable by EPR at room temperature. The g value of 2.0005 is representative of a carbon-centered electron and the complexity of the >125-line spectrum, whose hyperfine coupling constants range from 1 to 5 G,[17,24] is best rationalized in terms of inequivalent phenyls. Presumably the peripheral ^tBu groups hinder rotation of the ketone and the individual phenyl rings.[24] Interestingly, the EPR spectrum of **4a**-d_{10}, prepared from **3** and $(C_6D_5)C{=}O$, failed to reveal any titanium hyperfine interactions, consistent with a ligated ketyl (i.e., $(silox)_3Ti^{IV}–O–(Ph)_2C^\bullet$).

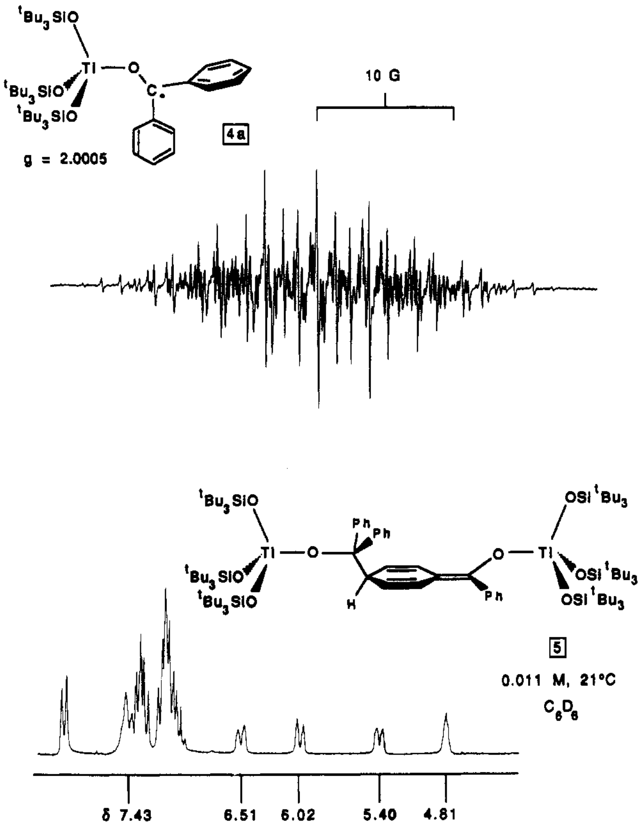

Figure 1. EPR spectrum of **4a** and truncated ^1H NMR spectrum of **5**.

In order to measure the equilibrium constant for [**5**] $\rightleftharpoons$ 2[**4a**], a method for estimating the concentration of **4a** was needed. Exposure of $(silox)_3Ti$ (**3**) to $(p\text{-}MeC_6H_4)_2C{=}O$ generated transiently stable, ink blue $(silox)_3TiO(p\text{-}MeC_6H_4)_2C^\bullet$ (**4b**), analogous to **4a**. Since the para positions of this ketone are capped to prevent dimerization, the complex EPR pattern centered at g = 2.0004 for **4b** was accompanied by an intense visible absorption band at 692 nm (ϵ = 1800 M^{-1} cm^{-1}). A similar band at 646 nm appeared when initially yellow solutions of **5** (4.4 × 10^{-4} to 1.1

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(18) **1**: ^1H NMR (C_6D_6) δ 1.30 (CH_3); $^{13}C\{^1H\}$ δ 23.98 (Si*C*), 30.80 (*C*H_3). Anal. Calcd for $C_{36}H_{81}Si_3O_3TiCl$: C, 59.26; H, 11.19. Found: C, 59.12; H, 11.10. **3**: ^1H NMR (C_6D_6) δ 1.50 (s, CH_3, $\nu_{1/2}$ = 110 Hz). Anal. Calcd for $C_{36}H_{81}Si_3O_3Ti$: C, 62.29; H, 11.76. Found: C, 62.02; H, 11.58. **5**: ^1H NMR (C_6D_6, 0.011 M, 21 °C, tentative assignments) δ 1.25 (CH_3, 162 H), 4.81 ((=CH)$_2$(C*H*)C, m, 1 H), 5.40, 6.02, 6.51, (=CH–, br d (J = 10 Hz), 1 H each), 7.43 (=CH–, br d, 1 H), 6.9–7.6, 7.8–8.0 (Ph, m, 15 H); $^{13}C\{^1H\}$ (THF-d_8, tentative assignments) δ 24.26, 24.16 (Si*C*), 31.66, 31.39 (*C*H_3), 55.09 (allylic), 99.79 (O*C*Ph_2R), 116.93, 124.68, 125.30, 125.42 (olefinic), 127–132 (multiple PH), 137.71, 143.94, 147.08 (C_{ipso}), 163.06, 167.00 (*C*=*C*(Ph)O). The above chemical shifts are concentration and temperature dependent. Anal. Calcd for $C_{98}H_{182}Si_6O_8Ti_2$: C, 67.15; H, 10.47. Found: C, 66.98; H, 10.33. **6**: ^1H NMR (C_6D_6) δ 1.26 (CH_3, s, 81 H), 6.78 (OC*H*Ph_2, s, 1 H) 7.0–7.6, 8.0–8.2 (Ph, m, 10 H); $^{13}C\{^1H\}$ (C_6D_6) δ 23.48 (Si*C*), 30.95 (*C*H_3), 91.47 (O*C*HPh_2), 126.19 (C_{ortho}), 127.57 (C_{para}), 128.60 (C_{meta}), 146.20 (C_{ipso}). Anal. Calcd for $C_{49}H_{92}Si_3O_4Ti$: C, 67.08; H, 10.57. Found: C, 67.02; H, 10.37.

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(24) Attempts at an accurate simulation were frustrated by the complexity of the spectrum. Since two rapidly rotating Ph rings would give rise to a 75-line spectrum, inequivalence of the Ph groups is a plausible explanation. Furthermore, if the latter is true, rotation of each Ph may be slow. While approximately half of the spectrum could be fit reasonably by using six a_H from 1 to 5 G, it became clear that the assigned multiplicities were overestimated, implicating inequivalent hydrogens with very similar coupling constants. As expected, at higher temperatures, the spectrum simplified and broadened as it gained intensity due to a shift in the equilibrium; attempts to model these spectra will be reported in due course.

$\times 10^{-3}$ M) were heated (25–85 °C) in the sample chamber of a UV–visible spectrometer. This temperature-dependent absorption appeared reversibly and was therefore attributed to **4a**. The desired equilibrium constant was estimated by approximating the extinction coefficient of **4a** as 1800 M^{-1} cm^{-1} and calculating its concentration at various temperatures. From van't Hoff plots of three different initial concentrations of **5**, $\Delta H_{diss} = 18$ (1) kcal/mol and $\Delta S = 33$ (3) eu (K_{eq}(25 °C) = $[\mathbf{4a}]^2/[\mathbf{5}] = 7.5 \times 10^{-7}$). Typical ΔH and ΔS values for the dimerization of triarylmethyl radicals are 10 kcal/mol and 20 eu (K_{eq}(25 °C) = 9.2×10^{-4}).[25]

This unique opportunity to spectroscopically observe a reversible C–C bond formation relevant to pinacol coupling is due to three factors: (1) the Ti(III) center in **3** is a potent reductant; (2) the $(silox)_3M$ unit sterically shields the trapped radical; (3) steric factors permit coupling only via the Ph group—loss of its resonance stabilization energy translates into the formation of a weak, reversible C–C bond. Efforts to spectroscopically probe numerous alkoxy and related radicals stabilized by the *tris*-silox coordination sphere are ongoing.

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Articles

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Ion Association and the Reactions of Cobalt(III)–Acido Complexes. 4. Origin of the Products in the Base Hydrolysis of $[Co(NH_3)_5X]^{(3-n)+}$ Complexes

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Reversed-phase high-performance ion-pair chromatography (RP-HPIPC) has been used to accurately determine, or redetermine, under the same experimental conditions (1.0 mol dm^{-3} NaN_3, 25 °C), the amounts of $[Co(NH_3)_5N_3]^{2+}$ (CoN_3^{2+}) formed in the alkaline hydrolysis of a wide range ($k_{OH} = 10^{-2}$ to $>10^6$ dm^3 mol^{-1} s^{-1}) of $[Co(NH_3)_5X]^{(3-n)+}$ ($CoX^{(3-n)+}$) complexes ($X_n^- = SO_4^{2-}$, F^-, $OPO(O^nBu)_2^-$, $OPO(OMe)_2^-$, SCN^-, Cl^-, Br^-, I^-, ONO_2^-, $OSO_2CH_3^-$, $OClO_3^-$, $OSO_2CF_3^-$, $OSMe_2$, $OP(OMe)_3$). For CoX^{2+} there is a trend toward less CoN_3^{2+} production for the more robust systems and a common value for complexes with a rate constant $k_{OH} > 10^2$ dm^3 mol^{-1} s^{-1}. For $CoOSO_3^+$ ~2% less and for CoX^{3+} complexes ~2% more CoN_3^{2+} is formed than with CoX^{2+} systems of similar lability. A similar trend is found for stereochemical change in the $CoOH^{2+}$ products from *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{(3-n)+}$ ($X^{n-} = F^-$, Cl^-, Br^-, ONO_2^-, $OSO_2CF_3^-$, $OSMe_2$, $OP(OMe)_3$). No consistent pattern of stereochemical change is found for the CoN_3^{2+} products. The stereochemistry of $CoOH^{2+}$ and CoN_3^{2+} for a particular leaving group X^- (Br^-) is independent of $[N_3^-]$, but in the absence of N_3^- the stereochemistry of $CoOH^{2+}$ appears to be slightly dependent on the presence, or absence, of other anions (ClO_4^-, $CF_3SO_3^-$, Cl^-, NO_3^-). Hydrolysis of *trans*-$[Co(NH_3)_4(^{15}NH_3)SCN]^{2+}$ gives no stereochemical change in the $CoNCS^{2+}$ product and some 15% more stereochemical change in $CoOH^{2+}$ compared to CoX^{2+} systems that lose X^- entirely but similar absolute amounts of CoN_3^{2+}. These and other observations suggest that all entering groups, and the leaving group X^{n-}, are present in the various transition states leading to products.

Introduction

The two recent papers by Rotzinger in this journal addressing the questions of the compositions and lifetimes of intermediates in the OH^--catalyzed hydrolysis of pentaamminecobalt(III)–acido complexes,[1,2] and the continuing support by the Jackson and Sargeson groups for a common coordinatively unsaturated intermediate for these reactions,[3] prompt us to report some of our observations on this longstanding problem.[4]

Our first set of results concerns the ability of an external ionic species (and we, like others, have used the N_3^- ion) to compete with H_2O from within the solvent cage for the intermediate formed on departure of X^{n-} as this is varied among different $[Co(NH_3)_5X]^{(3-n)+}$ reactants. There is ample evidence[5] to show that neutral leaving groups (i.e. X = Me_2SO, $(NH_2)_2CO$, $(MeO)_3PO$) result in enhanced N_3^- entry (usually reported as an "*R*" value for the products; $R = [CoN_3^{2+}]/[CoOH_2^{3+}][N_3^-]$, with $R \approx 12\%$ for 3+ complexes) when compared to uninegative leaving groups X^- (R = 8.5–10.0%) and to SO_4^{2-} (R = 7.2%,[3] 5.8%[5]), but there is also the possibility that variation might also exist among the uninegative leaving groups. Thus, Rotzinger[2] gives the order Cl^-, $Br^- < FSO_3^-$, $CF_3SO_3^- < SCN^-$, $CH_3SO_3^-$, $I^- < NO_3^-$, ClO_4^- on the basis of a summary of experimental data given by Dixon and co-workers,[5] but the authors of this article themselves view the data as being "superficially the same". However, Jackson and Begbie[6] find an acceptable difference with X = F^- (R = 5.1%) but support the view that this complex could be "mechanistically different from the rest", while Reynolds and Hafezi[7] see their results of $Cl^- < Br^- < NO_3^-$ as being clearly different. Thus, uncertainty remains, and we have taken the view that the variation or uncertainty in the experimental results from the various sources is large enough, and the difference between them for different X^- groups is small enough, to place considerable doubt on the order

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