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Synthetic and Reactivity Studies on $(C_5H_5)_2Ti(\mu\text{-}SH)_2Mo(CO)_4$ and Related Compounds

Charles J. Ruffing and Thomas B. Rauchfuss*

School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

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The compounds $(RCp)_2Ti(SH)_2$ ($RCp = \eta^5\text{-}C_5H_4R$; **1a**, R = H; **1b**, R = CH_3) react with $C_7H_8M(CO)_4$ (M = Mo, W) to form the dimers $(RCp)_2Ti(\mu\text{-}SH)_2M(CO)_4$ (**2a**, R = H, M = Mo; **2b**, R = CH_3, M = Mo; **3**, R = H, M = W) which were characterized analytically and spectroscopically. The reactivity of **2a,b** differs sharply with that observed for **1a,b**. While **1a,b** show little nucleophilicity at sulfur, compounds **2a,b** react with Ph_2E_2 (E = S, Se), S_8, $(RCp)_2TiS_5$, and $CH_2{=}CHCO_2Me$ to give $(RCp)_2Ti(EPh)_2$, $(RCp)_2TiS_5$, 1,4-$[(RCp)_2Ti]_2S_4$, and $(RCp)_2Ti(SCH_2CH_2CO_2Me)_2Mo(CO)_4$, respectively. ^1H NMR studies show that the bimetallic compounds prepared in this study exist as a mixture of syn and anti isomers which differ in the relative orientation of the hydrogen substituent on the sulfur. Through DNMR studies it was shown that interconversion of these isomers occurs with $\Delta G^{\ddagger} \approx 72$ kJ/mol which is comparable to the barriers found for other SR-bridged 34-electron dimers. While the facility of the isomerization process is unaffected by acid, catalytic quantities of triethylamine has an accelerating effect. Reaction of **2a,b** with strong bases gives the highly reactive dianions which were isolated in pure form using bulky counterions.

Introduction

Metal complexes containing the SH ligand are of current interest and are of probable relevance to the chemistry underlying certain types of industrial[1] and biological catalysis.[2] Studies on a number of complexes containing terminal and bridging SH moieties have revealed a rich chemistry deriving from the ability of the SH functionality to add to a variety of substrates (Scheme I).[3,4] While this prior work has been valuable in defining the scope of metallothiol chemistry, little information exists that bears on the crucial issue of how this reactivity is influenced by the electronic configuration of the metal center. This report describes such a study.

Previously we reported that $Cp_2W(SH)_2$ resembles an organic thiol insofar as it is readily alkylated under mild conditions and adds to coordinated isocyanides.[4] We have since examined the chemistry of $Cp_2Ti(SH)_2$,[5] and these results, which are described in this paper, differ strongly from those for the tungsten analogue. Furthermore, we have prepared and characterized the reactivity of its derivative $Cp_2Ti(\mu\text{-}SH)_2Mo(CO)_4$ whose rich chemistry provides possible insights into the bimetallic effect[6] in certain types of heterogeneous metal sulfide catalysis.

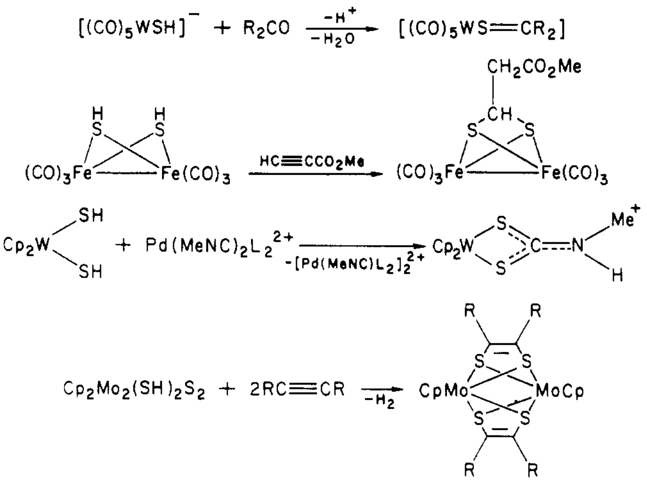
Results and Discussion

The compound $Cp_2Ti(SH)_2$ (**1a**, Cp = C_5H_5) was first reported in 1965 by Köpf and Schmidt[5] and its synthesis from Cp_2TiCl_2 was substantially improved upon by McCall and Shaver.[7] We have found that the analogous methylcyclopentadienyl complex **1b** is particularly attractive for experimental studies since it is more easily obtained in crystalline form and is highly soluble. The S*H* ligand in **1b** undergoes rapid H–D exchange with MeOD. Compound **1b** does not form an observable dianion with NaOMe although treatment with $LiN(i\text{-}Pr)_2$ at −78 °C followed by methyl iodide afforded $(MeCp)_2Ti(SMe)_2$. Attempts to isolate the dianion were unsuccessful; for example, treatment of **1a** with KH at low temperatures, followed by warming, gave an insoluble solid which did not react with methyl iodide. The product of the KH reaction reacted with anhydrous HCl giving $CpTiCl_3$, indicating that $[Cp_2TiS_2]^{2-}$, if it formed at all, is unstable with respect to loss of a cyclopentadienyl group[8] (eq 1). For comparison, **1b** reacts cleanly with an excess of HCl to give $(MeCp)_2TiCl_2$. Attempts to alkylate **1b** using more conventional procedures failed,[9] and **1** is sufficiently nonnucleophilic to withstand dissolution in neat benzyl chloride. Taken collectively, these studies indicate that the reactivity of the SH ligand in **1a,b** is substantially influenced by the 16-electron titanium(IV) center.

$$Cp_2Ti(SH)_2 \xrightarrow[\text{(2) HCl (excess)}]{\text{(1) 2KH}} CpTiCl_3 \qquad (1)$$

Compounds **1a** and **1b** react readily with equimolar quantities of Mo(norbornadiene)$(CO)_4$ to give the free

Scheme I



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(9) Köpf has reported alkylation of **1a** using dimethyl sulfate.[5]

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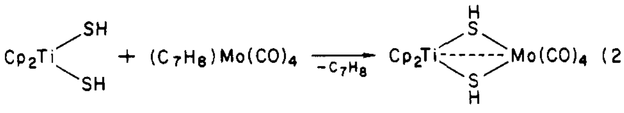
Table I. Rate Constants and Thermodynamic Parameters for Syn to Anti Isomerization of $Cp_2Ti(SH)_2W(CO)_4$

T, K	k_1, s^{-1}	k_{-1}, s^{-1}	$\Delta G_1^{\ddagger}$, kJ	$\Delta G_{-1}^{\ddagger}$, kJ	ΔG, kJ	K_{eq}
303	4.6	7.02	70.4	69.3	1.1	0.65
339	24.2	33.3	74.4	73.5	0.9	0.73
357	57.2	46.0	75.9	76.6	−0.7	1.25

diene concomitant with the formation of deep blue solutions of $(RCp)_2Ti(SH)_2Mo(CO)_4$, **2a** and **2b** (eq 2). These



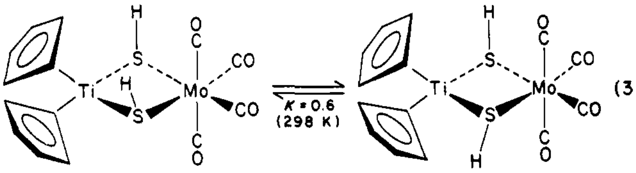
$$Cp_2Ti(SH)_2 + (C_7H_8)Mo(CO)_4 \xrightarrow[-C_7H_8]{} Cp_2Ti(\mu\text{-}SH)_2Mo(CO)_4 \quad (2)$$

compounds were isolated as analytically pure crystals which are soluble in a variety of solvents, giving intensely blue, air-sensitive solutions. The analogous tungsten compounds could be prepared from either $W(C_7H_8)(CO)_4$ or, more conveniently, $W(CH_3CH_2CN)_3(CO)_3$. The spectroscopic properties and reactivity characteristics of the molybdenum and tungsten compounds were very similar, and most of our studies focused on $Cp_2Ti(SH)_2Mo(CO)_4$, **2a**.

The formulation of **2a**,**b** follows from microanalytical data, solution molecular weight measurements, and field desorption mass spectrometry. The deep colors of **2a**,**b** and its relatives contrasts with their precursors but are characteristic of this specific class of polar 34-electron dimers.[10] The spectroscopic properties of **2a**,**b** closely match those reported for $Cp_2Ti(SR)_2Mo(CO)_4$ (R = Ph, Me).[10b] The solution IR spectrum of **2a** does show two weak ν_{SH} bands in the 2500 cm^{-1} region as found for **1** and more conventional organic thiols.[11]

The 90-MHz ^1H NMR spectrum of **2a** consists of singlets at 5.3 and 2.1 ppm in a 5:1 intensity ratio; the smaller peak undergoes facile H–D exchange with CH_3OD. In comparison with the data for **1a**, the C_5H_5 and SH resonances are shifted upfield by 0.4 and 1 ppm, respectively. The latter shift is in the opposite direction expected if simple deshielding effects were operating; for comparison conversion of $W(CO)_5(SH)^-$ to $W_2(CO)_{10}(\mu\text{-}SH)^-$ induces a 1.2 ppm shift to lower field.[3a] The SH chemical shifts for $Cp_2Mo(SH)_2$[12] and $Cp_2Mo_2(SH)_2(S)_2$[3b] are centered at −2.36 and −1.47 ppm, respectively.

At 360 MHz, the ^1H NMR spectrum of **2a** consists of three comparably intense Cp resonances although the S*H* absorption remains a single line. This data indicate the presence of a 2:1 mixture of the syn and anti isomers of **2a**, the isomerism arising from the relative orientation of the substituents on sulfur (eq 3). The interconversion of



(3)

these isomers was studied by DNMR (Figure 1). Complete band shape analysis of the spectra obtained at various temperatures yielded rate constants and activation parameters for the isomerization process. At coalescence (85 °C) the equilibrium constant relating the two isomers of $Cp_2Ti(SH)_2W(CO)_4$ was nearly unity and with this information the activation energies were calculated to be 76 ± 0.8 kJ/mol (Table I). This value is comparable with those reported for inversion of the bridging SR groups in $Fe_2(\mu\text{-}S\text{-}t\text{-}Bu)_2(CO)_6$[13] (77 kJ/mol) and $[W_2O_2Cl_4(\mu\text{-}Cl)(\mu\text{-}S\text{-}t\text{-}Bu)_2]^-$[15] (75 kJ/mol). These experiments show that the dynamic behavior of the μ-SH ligand is very similar to that for a μ-SR and that inversion is probably not occurring by proton exchange. We investigated the effect of acid and base on the syn–anti isomerization rates in compound **2a** as monitored by ^1H NMR spectroscopy. The addition of 10 mol % trifluoroacetic acid to CD_2Cl_2 solutions of **2a** was found to have *no* effect on the coalescence temperature. On the other hand, 10 mol % of triethylamine lowered the coalescence temperature from 85 to below −90 °C. This *catalytic* amount of triethylamine effectively more than halves the activation energy for the isomerization processes. These results strongly suggest that there are *two* isomerization mechanisms for $(\mu\text{-}SH)_2$ complexes: complexes, a unimolecular pyramidal inversion pathway that resembles that for other M–SR species and a potentially very facile base-catalyzed pathway. The base-catalyzed pathway is proposed to involve a deprotonation–reprotonation sequence, the facility of which is related to the dramatic effect of base on the *reactivity* of **2a**.

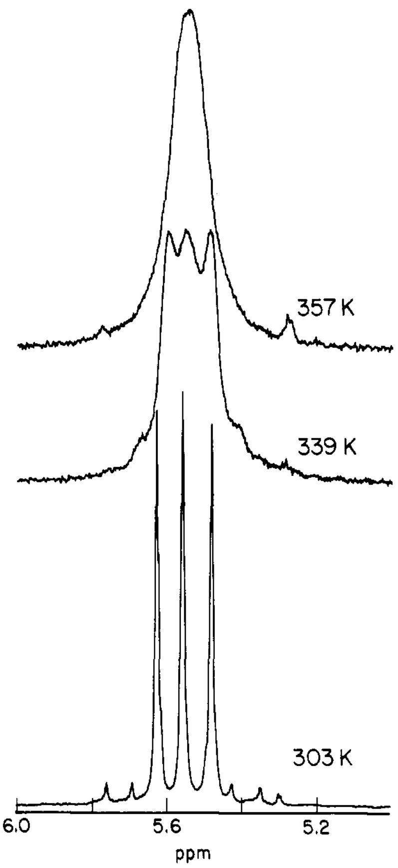


Figure 1. ^1H NMR spectra (360 MHz) of cyclopentadienyl region of $Cp_2Ti(\mu\text{-}SH)_2W(CO)_4$.

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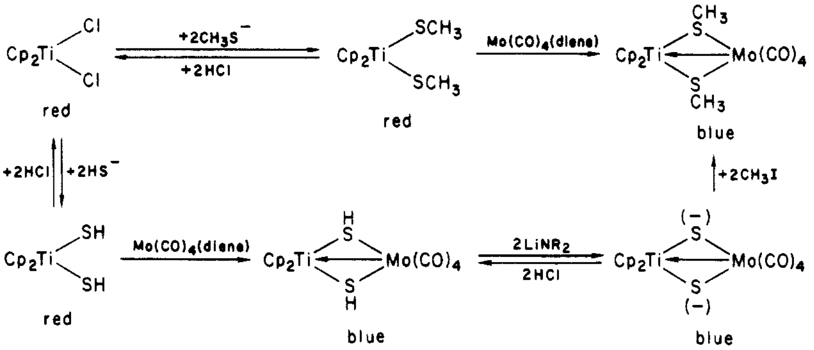
(16) We thank M. L. H. Green for this suggestion.

Scheme II



The SH-localized reactivity of **2** differs dramatically from that for **1**. In the presence of weak bases, compound **2a** is readily alkylated under mild conditions (eq 4). The

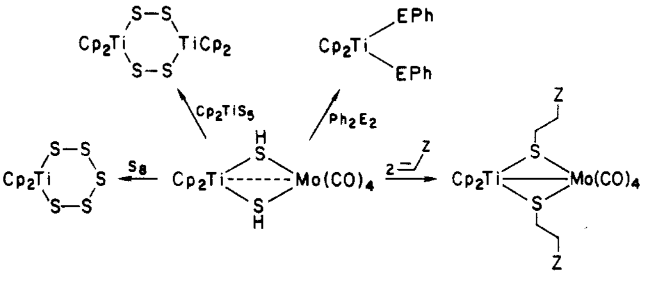
$$Cp_2Ti(SH)_2Mo(CO)_4 + 2RX + 2Et_3N \rightarrow Cp_2Ti(SR)_2Mo(CO)_4 + 2Et_3NHX \quad (4)$$

alkylated products are isolated in high yield and in analytically pure form. The stability of **2a**,**b** toward excess acids is striking, and in fact **2a**,**b** can be recovered from solutions saturated with HCl(g). As already mentioned, **1b** reacts with 2 equiv of HCl to quantitatively regenerate $(MeCp)_2TiCl_2$. This effect is attributable to the fact that protonation and metalation (e.g., by $Mo(CO)_4$) compete for the same reactive sites on **1**. We have found that THF solutions of **2a** react with a variety of bases at low-temperature including $LiNPr_2$, NaOMe, NaH, and KH to give dark red, air-sensitive compound tentatively formulated as $[Cp_2TiS_2Mo(CO)_4]^{2-}$. The red dianion reacts at low temperature with MeI or anhydrous HCl to afford blue $Cp_2Ti(SMe)_2Mo(CO)_4$ or **2a**, respectively, in quantitative yield (Scheme II). In the presence of large cations such as K(18-crown-6)$^+$ or PPN$^+$, red air-sensitive solids were isolated and characterized by analysis and IR spectroscopy. However, alkylation or protonation of the isolated solids proceeded with significant reduction in yield. In fact, after storage under N_2 at room temperature for several hours the isolated PPN$^+$ and K(18-crown-6)$^+$ salts of $[Cp_2TiS_2Mo(CO)_4]^{2-}$ did not react with MeI or HCl(g). The carbonyl IR spectra for the freshly isolated K(18-crown-6) dianion exhibit the same pattern observed for **2a** except that all of the bands are shifted 35 cm^{-1} to lower frequency.

Compound **2a** is reactive toward a variety of substrates via processes attributable to the considerable nucleophilicity of its sulfhydryl ligand. In the presence of catalytic amounts of Et_3N, **2a** reacts vigorously with elemental sulfur affording Cp_2TiS_5.[17] With $(MeCp)_2TiS_5$, **2b** reacts to give moderate yields of 1,4-$[(MeCp)_2Ti]_2S_4$.[18] While **2a** displays no noticeable reactivity toward PhS$^-$, it does undergo rapid base-catalyzed reactions with Ph_2E_2 to produce $Cp_2Ti(EPh)_2$ (E = S, Se).[19,20] Such reactions (Scheme III) proceed with the evolution of CO and the precipitation of an X-ray amorphous molybdenum sulfide.

In keeping with their nucleophilicity, the SH moieties in **2a** readily add to methyl acrylate to give the conjugate addition product. This derivative was isolated in pure form as blue-violet, low-melting crystals and was thoroughly characterized spectroscopically. In contrast, **1a**,**b** were found to be unreactive toward neat methyl acrylate and reacted only sluggishly with dimethyl acetylenedicarboxylate.

Scheme III



E = S, Se; Cp = C_5H_5; Z = CO_2CH_3

Conclusions

The spectroscopic data for **2a** and its analogue provides convincing evidence that they are structurally similar to known examples of this type which are derived from the dicyclopentadienyltitanium dimercaptides.[10] In previous work, the presence of a metal–metal interaction in this class of polar 34-electron dimers was inferred from the structural data on $Cp_2Ti(SMe)_2Mo(CO)_4$ which revealed an unusually expanded S–Ti–S angle of 99.5°, acute Ti–S–Mo angles of 82.8°, and an ambiguous Ti–Mo distance of 3.32 Å.[21] Furthermore, the optical spectroscopic characteristics for this Ti(μ-SR)$_2$Mo compound are distinctly different from those for $Cp_2W(SPh)_2M(CO)_4$ (M = Cr, Mo, and W) and $Mo(MeSCH_2CH_2SMe)(CO)_4$.[22]

In the present work we have shown that the reactivity of the SH ligand is substantially affected by its coordination to the $Mo(CO)_4$ moiety. The bridging SH ligand in the 34-electron dimer was found to be a considerably better nucleophile than a terminal SH moiety in a closely related 16-electron complex. This contrasts with the results observed in studies of $W(CO)_5SH^-$ and $[W(CO)_5]_2SH^-$, where the reactivity of the thiol group is significantly reduced upon coordination to a second metal.[23] This result indicates that the nucleophilicity of the SH moiety, which may be tempered by S to Ti π-bonding in its monometallic precursor $Cp_2Ti(SH)_2$,[24] is enhanced by the rehybridization which occurs upon formation of the bi-

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metallic derivative. Related 34-electron dimers that have been studied recently include $Mo_2(\mu\text{-}SR)_2(CO)_8^{2-}$,[25] $Fe_2S_2(NO)_4^{2-}$,[26] and $Fe_2(SH)_2(CO)_6$;[3c] however, in the present work we have been able to compare the chemistry of related pairs of both electron-deficient mono- and bimetallic SH complexes.

π-Rich metals such as Co(II) and Ni(II) are well-known to enhance the activity of molybdenum or tungsten sulfide hydrodesulfurization catalysts.[6] The results presented in this paper are suggestive of how this effect could arise.

Experimental Section

Materials and Methods. All preparative reactions were performed under an atmosphere of purified nitrogen, and unless otherwise noted, workups were done aerobically in an efficient hood. Tetrahydrofuran (THF), toluene, and hexanes were obtained as reagent grade solvents and were distilled from sodium benzophenone ketyl. CH_2Cl_2 was obtained as a reagent grade solvent and was distilled from P_4O_{10}. $Cp_2Ti(SH)_2$,[7] Cp_2TiS_5,[17] $C_7H_8Mo(CO)_4$,[27] $C_7H_8W(CO)_4$,[27] and $(C_2H_5CN)_3W(CO)_3$[28] were prepared by published procedures. All other chemicals were purchased from commercial sources and used without further purification.

The following instruments were used in this work: Nicolet MX-5 and Nicolet 7199 (IR); Varian Cary 219 (UV–vis); Varian EM-390 with internal frequency lock (^{1}H NMR); Nicolet NT 360 (variable-temperature ^{1}H NMR). Field desorption mass spectra were measured as a service on a Varian 731 spectrometer at the University of Illinois Mass Spectrometry Laboratory. Analyses were performed by the University of Illinois Microanalytical Laboratory.

$(MeCp)_2Ti(SH)_2$ (1b). A 5.00-g sample $(MeCp)_2TiCl_2$ (18 mmol) was slurried in 150 mL of THF and 5 mL of Et_3N (36 mmol). H_2S was passed through the solution for 1 h after which the solution was stirred for an additional 2 h. The mixture was filtered, and the precipitated Et_3NHCl was washed with THF. After removal of the solvent, the solid was recrystallized from CH_2Cl_2/Et_2O to afford 3.0 g of red needles (60%). ^{1}H NMR ($CDCl_3$): δ 6.0 (m, 8 H), 3.1 (s, 2 H), 2.3 (s, 6 H). IR (HCBD): 2545 (w), 2562 cm^{-1} (w). Anal. Calcd for $C_{12}H_{16}TiS_2$: C, 52.93; H, 5.92; Ti, 17.58. Found: C, 52.85; H, 5.81; Ti, 17.51.

$(RCp)_2Ti(SH)_2Mo(CO)_4$ (2a,b). A 300-mg (1-mmol) sample of solid $C_7H_8Mo(CO)_4$ was added to a solution of 244 mg (1 mmol) of **1a** in 15 mL of toluene. After 3 h GLC analysis of the solution established the presence of 1 equiv of norbornadiene; the product was precipitated with hexane from the concentrated solution as dark blue crystals, yield 375 mg (82%) of **2a**. ^{1}H NMR ($CDCl_3$): δ 5.6 (s, 5 H), 2.1 (s, 1 H). IR (mineral oil mull): 2014 (s), 1903 (br) cm^{-1} (ν_{CO}), 2556 (w), 2522 (w) cm^{-1} (ν_{SH}). Anal. Calcd for $C_{14}H_{12}O_4MoTiS_2$: C, 37.42; H, 2.65; Ti, 10.62; M_r, 454. Found: C, 37.17; H, 2.83; Ti, 10.84; M_r, 442. IR (mineral oil mull): 2010, 1920, 1870 cm^{-1} (ν_{CO}). Compound **2b** was prepared similarly. ^{1}H NMR ($CDCl_3$) δ 5.0–5.5 (m, 4 H), 2.25 (s, 3 H), 1.95 (s, 2 H). Anal. Calcd for $C_{16}H_{16}O_4MoTiS_2$: C, 40.00; H, 3.33; Ti, 9.99. Found: C, 39.96; H, 3.48; Ti, 9.97.

The tungsten compound $Cp_2Ti(SH)_2W(CO)_4$ (**3**) may be made by an analogous procedure (yield 30% after 20 h) or by reacting 1.3 equiv. of $(C_2H_5CN)_3W(CO)_3$ with 1 equiv of $Cp_2Ti(SH)_2$ for 12 h (25%). ^{1}H NMR ($CDCl_3$) δ 5.5 (s, 5 H), 2.05 (s, 1 H). IR (mineral oil mull): 2001 (s), 1874, 1864 (br) cm^{-1} (ν_{CO}), 2517 (w), 2550 (w) cm^{-1} (ν_{SH}). FDMS: *m/e* 540 (M$^+$). Anal. Calcd for $C_{14}H_{12}O_4TiWS_2$: C, 31.11; H, 2.22; Ti, 8.88. Found: C, 31.32; H, 2.19; Ti, 8.51.

Alkylation of 2. Method a. A solution of 100 mg (0.22 mmol) of **2a** was treated with 61.5 μL (0.44 mmol) of Et_3N and 30 μL (0.47 mmol) of CH_3I. After 1 h, the solvent was removed under vacuum, and the residue was extracted with CH_2Cl_2. The CH_2Cl_2 extract was filtered through silica gel, concentrated, and diluted with hexane to afford a blue solid (100 mg, 92%) which was identified as $Cp_2Ti(SMe)_2Mo(CO)_4$ by NMR.

Method b. A 452-mg (1-mmol) sample of **2a** was dissolved in 20 mL of THF. The solution was cooled to −78 °C and treated with a solution of 214 mg (2 mmol) of lithium diisopropylamide in 5 mL of THF. An immediate color change from blue to red was noted. Addition of 130 μL of CH_3I (2.01 mmol) restored the blue color; the resultant solutions were worked up as above affording $Cp_2Ti(SMe)_2Mo(CO)_4$ (400 mg, 83%). Treatment of the red solutions of $Li_2[Cp_2TiS_2Mo(CO)_4]$ with anhydrous HCl regenerated **2a** in quantitative yield.

Method c. A solution 100 mg (0.22 mmol) of **2a** in 5 mL of $CH_2{=}CHCO_2CH_3$ was treated with 6 μL (0.04 mmol) of Et_3N. After 30 min, the solvent was removed and the residue washed with hexane. Recrystallization from CH_2Cl_2/hexane afforded 97 mg (71%) of $Cp_2Ti(SCH_2CH_2CO_2CH_3)_2Mo(CO)_4$ as violet crystals. ^{1}H NMR (C_6D_6): δ 5.0 (s, 5 H), 3.35 (s, 3 H), 3.0 (m, 4 H). IR (mineral oil mull) 2013, 1900 (br), 1734 cm^{-1} (ν_{CO}). FDMS: *m/e* 626 (M$^+$). Anal. Calcd for $C_{22}H_{24}MoO_8TiS_2$: C, 42.30; H, 3.84; Ti, 7.69. Found: C, 42.30; H, 4.16; Ti, 7.62.

Alkylation of 1. Compound **1a** may be alkylated by method b (above) affording a 60% yield of $Cp_2Ti(SMe)_2$. Compound **1a** is unreactive under the conditions outlined in methods a and c.

Reaction of 1a with KH. Compound **1a** was treated with KH in the manner described for **2a**. These solutions did not react with CH_3I to form any isolable Ti species. Treatment of the solutions with anhydrous HCl afforded a yellow heterogeneous mixture. The mixture was filtered, the solvent was removed, and $CpTiCl_3$ was isolated in 68% yield by extraction with hexane, removal of solvent, and sublimation. The product was identified by NMR and by its reaction with $Na_2[S_2C_2(CN)_2]$ to form purple $CpTi[S_2C_2(CN)_2]_2^-$.

$(PPN)_2[(MeCp)_2TiS_2Mo(CO)_4]$. A 100-mg (0.21-mmol) sample of $(MeCp)_2Ti(SH)_2Mo(CO)_4$ in 10 mL of THF was treated with 20 mg of 40% NaH dispersion in mineral oil at 0 °C. The resulting red solution was filtered under nitrogen into a solution of 250 mg PPNCl in 5 mL CH_2Cl_2. After removal of the solvent, the residue was extracted with CH_2Cl_2 and filtered; the desired product precipitated by the addition of hexane as a dichloromethane solvate. Anal. Calcd for $C_{88}H_{44}MoN_2O_4P_4S_2Ti\cdot 2CH_2Cl_2$: C, 62.70; H, 4.44; Ti, 2.78. Found: C, 62.96; H, 4.65; Ti, 2.70.

Reactions of 2a with Chalcogen Compounds. With Ph_2S_2. To a stirred solution of 100 mg of **2a** (0.22 mmol) in 10 mL of THF was added 61 μL of Et_3N and 50 mg (0.23 mmol) of Ph_2S_2. After being stirred overnight, the reaction mixture was filtered through silica gel, and the solvent removed to afford a 48% yield of violet crystals of $Cp_2Ti(SPh)_2$ which was identified by NMR.[19] **With Ph_2Se_2.** Treatment of **2a** with 1 equiv of Ph_2Se_2 as described above gave $Cp_2Ti(SePh)_2$ as a green solid in 40% yield. The product was identified by NMR.[19] **With S_8.** To a stirred solution of 100 mg (0.22 mmol) of **2a** was added 61 μL (0.44 mmol) of Et_3N followed by 40 mg (0.15 mmol) of S_8. Gas evolution is seen accompanied by a color change from blue to red. The solution is filtered and the solvent removed to yield 63 mg (85%) of Cp_2TiS_5 as identified by NMR.[17] **With $(MeCp)_2TiS_5$.** **2b** was treated with 1 equiv of $(MeCp)_2TiS_5$ in the manner described above. After 3 h, flash chromatography on silica gel afforded 1,4-$[(MeCp)_2Ti]_2S_4$ in 25% yield. The identification followed from TLC and NMR comparisons with authentic samples.

Variable-Temperature NMR Studies. Spectra were recorded at 5 °C intervals from room temperature to coalescence (60 °C for **2a** and 84 °C for **3**). Probe temperatures were measured by a Doric Trendicator 400A. Following the experiment the integrity of the samples was rechecked at ambient temperatures. Individual spectra were hand digitalized at intervals of 4 Hz and used as input in DNMR3 IT2,[29] a program for calculating exchange broadened NMR spectra. Rate constants were calculated by the program with final differences in the calculated from the observed spectra in the range of 10%. Activation parameters were calculated from these rate constants using the equation[30]

$$\Delta G^\ddagger = aT[10.319 + \log T/k]$$

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Rate constants accurate to ±10% yield activation values accurate to ±0.5 kJ.

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Registry No. **1a**, 12170-34-2; **1b**, 79816-63-0; **2a**, 94161-38-3; **2b**, 94161-39-4; **3**, 94161-40-7; $Cp_2Ti(SMe)_2Mo(CO)_4$, 94234-84-1; $Li_2[Cp_2TiS_2Mo(CO)_4]$, 94161-41-8; $Cp_2Ti(SCH_2CH_2CO_2CH_3)_2Mo(CO)_4$, 94161-42-9; $Cp_2Ti(SMe)_2$, 12089-78-0; $CpTiCl_3$, 1270-98-0; $CpTi[S_2C_2(CN)_2]_2^-$, 94161-43-0; $(PPN)_2[(MeCp)_2TiS_2Mo(CO)_4]$, 94202-27-4; $Cp_2Ti(SPh)_2$, 1292-47-3; $Cp_2Ti(SePh)_2$, 12290-57-2; Cp_2TiS_5, 12116-82-4; 14-$[(MeCp)_2Ti]_2S_4$, 79816-62-9; $(MeCp)_2TiCl_2$, 1282-40-2; H_2S, 7783-06-4; $C_7H_8Mo(CO)_4$ (C_7H_8 = norbornadiene), 12146-37-1; $C_7H_8W(CO)_4$ (C_7H_8 = norbornadiene), 12129-25-8; $(C_2H_5CN)_3W(CO)_3$, 84580-21-2; $CH_2{=}CHCO_2CH_3$, 96-33-3; $Na_2[S_2C_2(CN)_2]$, 18820-77-4; Ph_2S_2, 882-33-7; Ph_2Se_2, 1666-13-3; S_8, 10544-50-0; $(MeCp)_2TiS_5$, 78614-86-5.

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Electronic Structure and Photochemistry of the $(\eta^5\text{-}C_5H_5)_2TiI_2$ Complex

Mitchell R. M. Bruce and David R. Tyler*

Department of Chemistry, Columbia University, New York, New York 10027

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The photochemistry of the Cp_2TiI_2 (Cp = η^5-C_5H_5) complex can be interpreted in terms of a low-energy I → Ti charge-transfer excited state. Low-energy irradiation ($\lambda > 600$ nm) of unpurged solutions of Cp_2TiI_2 in benzene produces $(Cp_2TiI)_2$ and 0.5 mol of I_2/mol of Cp_2TiI_2 photolyzed. Under similar conditions, photolysis of Cp_2TiI_2 in CCl_4 produces $Cp_2Ti(I)Cl$. In inert-gas-purged solutions, titanocene is formed as well as 1 mol of I_2/mol of Cp_2TiI_2 photolyzed. Under no conditions were nitrosodurene spin-trapped Cp radicals observed by ESR. These results are interpreted in terms of a mechanism involving stepwise loss of I· from the Cp_2TiI_2 complex to produce $(Cp_2TiI)_2$. Further irradiation of this dimer then forms titanocene and more I_2. The electronic spectrum of the Cp_2TiI_2 complex is reported. Previously reported spectra were complicated by the following equilibrium: $Cp_2TiI_2 + nS \rightleftharpoons [(Cp_2Ti(I_{2-n})S_n)^{n+}(nI^-)^{n-}]$ (S = solvent = CH_2Cl_2 or CH_3CN). In benzene, the equilibrium above does not occur to any appreciable extent, while in CH_2Cl_2 $n = 1$ and the equilibrium constant is $K = 3 \times 10^{-3}$ and in CH_3CN $n = 2$ and $K = 2.5 \times 10^{-3}$.

We are interested in the photochemistry of ligand-to-metal charge-transfer excited states as a way of photoreducing organometallic complexes. One aspect of our work involves the study of halide → metal charge-transfer excited states. For that reason, we have been investigating the Cp_2TiX_2 (X = F, Cl, Br, I; Cp = η^5-C_5H_5) complexes. We recently reported the results of self-consistent-field–Xα–scattered-wave (SCF–Xα–SW) molecular orbital calculations on these complexes.[1] Of interest to the photochemistry of these complexes is the calculational result that the lowest energy excited states in the fluoride, chloride, and bromide complexes are Cp → Ti charge-transfer excited states rather than halide → Ti charge transfer. These calculational results are consistent with the known photochemistry: Cp–Ti bond cleavage occurs when the chloride and bromide complexes are irradiated.[2] The calculation could not be used to definitively assign the lowest energy excited state in the Cp_2TiI_2 complex because the Cp → Ti and I → Ti CT transitions have nearly equal energies (within the accuracy of the calculation) in this complex.

A study of the photochemistry of Cp_2TiI_2 seemed worthwhile for three reasons. First, it is likely that the photochemistry would result from the desired halide → Ti charge-transfer excited state. Second, with proper caution we could use the photochemical results to suggest assignments for the low energy excited states of the complex. And third, the close proximity of the I → Ti and Cp → Ti charge-transfer bands might lead to some interesting wavelength dependent photochemistry. This paper reports the results of our photochemical study of the Cp_2TiI_2 complex.

Experimental Section

All manipulations were carried out under argon on a Schlenk line, in a Vacuum Atmospheres glovebox or in a glove bag. Acetonitrile (spectrograde, Kodak), benzene (spectranalyzed, Fisher), carbon tetrachloride (certified, Fisher), chloroform (Amend), methylene chloride (certified, Fisher), and toluene (certified, Fisher) were dried,[3] distilled under nitrogen, and degassed before use. Thallium hexafluorophosphate (Strem Chemicals, Inc.) and C_6D_6 (99.5 atom % D, Aldrich) were used as received. Nitrosodurene was synthesized by a published procedure.[4]

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