The unpolarized single-crystal spectra exhibit two bands at 8000 and 18 500 cm^{-1}, which are tentatively assigned to the $^2B_1 \rightarrow {}^2A_1$ and $^2B_1 \rightarrow {}^2A_2$ transitions, respectively. The lower energy band has not been observed before, while the second band appears at about 22 000 cm^{-1} for O_3^--doped solids and in solution. The large shift of about 3500 cm^{-1} for the higher energy band is very surprising, because the O–O bond length and O(3)–O(1)–O(2) bond angles of the O_3^- centers in $KClO_3$ (128 pm and 120 ± 6°, as estimated from CNDO calculations[6] on the basis of the EPR results) are very close to those found for the MO_3 compounds. Possibly strong matrix strains in case of the O_3^--doped host structures and solvent effects in liquid ammonia produce the considerable energy changes with respect to the MO_3 compounds, in which the O_3^- radicals are in a more or less unstrained state.

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Disulfanido Ligands:[1] Preparation and Reactions of $Cp_2Ti(SSR)X$, Where X = SR, Phthalimido, and Cl and R = Alkyl and Aryl Groups

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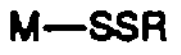
The complex $Cp_2Ti(CO)_2$ oxidatively adds RSSX to give the complexes $Cp_2Ti(X)(SSR)$, where X = SR and R = $CHMe_2$, CMe_3, CH_3Ph, and 4-C_6H_4Me; X = phthalimido and R = $CHMe_2$, CMe_3, CH_2Ph, and 4-C_6H_4Me; and X = Cl and R = CPh_3. The complexes $Cp_2Ti(SR)(SSR)$ reacted with $PhCH_2Br$ to give $CpTiBr_2$, $PhCH_2SR$, and $PhCH_2SSR$, confirming the presence of the disulfanido ligand. These complexes desulfurized slowly in solution and rapidly in the presence of PPh_3 to give $Cp_2Ti(SR)_2$ and $SPPh_3$. The complexes for which X = phthalimido undergo alcoholysis to give the species where X = OET.

Introduction

While organic disulfides are common and are of industrial and biological importance, complexes containing terminal disulfanido ligands of the type RSS^- are rare and their chemistry relatively unknown. Nevertheless, a handful of such species have recently appeared. An (alkyldisulfanido)copper(II) species[3] was isolated from model studies of copper(II) enzymes (type A[3-8]). Model studies of molybdenum dimers by Nobel and co-workers[9a] gave complexes containing bridging disulfanido ligands (type B[9-12]). Similar bridging systems have also been observed in the anion[10] $[Fe_2S(SS\text{-}t\text{-}Bu)(CO)_6]^-$ and in the complexes $Cp_2Ti(\mu\text{-}SR)(\mu\text{-}SSR)Mo(CO)_4$, where R = $CHMe_2$ and CMe_3.[12] The complex $CpW(NO)(CH_2SiMe_3)(\eta^2\text{-}SSCH_2SiMe_3)$, which results from insertion of sulfur atoms[13] into the tungsten carbon bond, has a "side-on" bonding mode,[13c] which has also been observed in other systems (type C[13-15]). We have prepared the complexes $CpW(CO)_2SSR$[5,6] and *cis*-$(PPh_3)_2Pt(phth)SSR$,[5,7] where phth = phthalimido, which have simple terminal disulfanido ligands. The former spontaneously desulfurized in solution to give the corresponding thiolate while the latter was very stable. The complexes $Cp_2Ti(SSR)_2$, where R = aryl, rearrange to give $Cp_2Ti(SR)(SSSR)$; one of the first examples of a trisulfanido ligand.[8] The complexes $Cp_2Mo(SSR)_2$ extrude[16] the disulfide RSSR to give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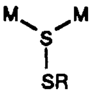
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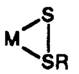
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Table I. Products of Oxidative Addition of RSSSR to $Cp_2Ti(CO)_2$[a]

R	% product		
	$Cp_2Ti(SSR)(SR)$	$Cp_2Ti(SR)(SR)$	$Cp_2Ti(SSR)(SSR)$
4-C_6H_4Me	84	16	0
$CHMe_2$	93	3	4
CMe_3	96	4	0
CH_2Ph	81	14	5

[a] Percentage, based on NMR integration of the peaks due to Cp and/or R groups at the point in the reaction when all $Cp_2Ti(CO)_2$ was consumed, as determined by IR.

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Cp_2MoS_2. The factors that affect the stability of disulfanido ligands with respect to loss or gain of sulfur are not understood.

The complex $Cp_2Ti(CO)_2$ (**1**) oxidatively adds disulfides[17] to give the bis(thiolato) complexes $Cp_2Ti(SR)_2$ and adds sulfur[18] to give Cp_2TiS_5. We report the reactions of **1** with organic trisulfides and disulfides of the type RSSX, where X = phth or Cl, as a route to complexes of the type $Cp_2Ti(X)(SSR)$, which contain a disulfanido ligand.

Results

$Cp_2Ti(CO)_2$ + RSSSR at Low Temperature. The reactions between $Cp_2Ti(CO)_2$ (**1**) and trisulfides in toluene were monitored by observing the decrease in intensity of the CO bands due to **1** in the infrared spectrum. The products consisted of a mixture (Table I) of the new complexes $Cp_2Ti(SR)(SSR)$ (**2a–d**) and the dithiolates $Cp_2Ti(SR)_2$ (**3a–d**), as determined from NMR spectra of the crude products (eq 1). The relative amounts of the two

$$\underset{\mathbf{1}}{\mathrm{Cp_2Ti(CO)_2}} + \mathrm{RSSR} \rightarrow \underset{\substack{\mathbf{2a},\ \mathrm{4\text{-}C_6H_4Me}\\ \mathbf{2b},\ \mathrm{CHMe_2}\\ \mathbf{2c},\ \mathrm{CMe_3}\\ \mathbf{2d},\ \mathrm{CH_2Ph}}}{\mathrm{Cp_2Ti(SR)SSR}} + \mathrm{2CO} \tag{1}$$

products depended upon the R group and the reaction temperature. In general, lower temperatures favored **2a–d** with the ratio **2**:**3** being as follows: **a**, 5.3 (−20 °C); **b**, 31 (20 °C); **c**, 24 (20 °C); **d**, 5.8 (12 °C). The solubility and chromatographic properties of **2** and **3** are very similar, making separation difficult; however, pure samples of **2a** and **2c** were isolated. Attempts to grow crystallographic grade crystals of **2a–d** were unsuccessful possibly due to their instability in solution and the usual presence of small amounts of RS_xR, which tend to cause oils.[19] Complexes **2a**, **2b**, and **2d** are deep purple while **2c** is an intense emerald green. The dithiolates are red.

$Cp_2Ti(CO)_2$ + RSSSR at 120 °C. The reaction of $Cp_2Ti(CO)_2$ and trisulfide in refluxing toluene gave **3a**, **3b**, and **3d** as the major products with the ratio of **2**:**3** being as follows: **a**, 0.04 (5.5 h); **b**, 0.09 (74 h), **d**, 0.14 (15 h). In the case of $Me_3CSSSCMe_3$, only traces of **2c** and **3c** were detected in the NMR spectrum of the crude product; however, a very broad band appeared in the Cp region between 7 and 5 ppm together with strong peaks due to $Me_3CSSCMe_3$ and $Me_3CSSSCMe_3$. Significant amounts of the appropriate starting trisulfides were also detected in the reactions producing **3a**, **3b**, and **3d**. When **1** and $PhCH_2SSSCH_2Ph$ were reacted at 80 °C in C_6D_6 for 48 h, a similar broad band in the Cp region was detected in addition to bands due to **2d** and **3d**. The crude product from the latter reaction run on a preparative scale was chromatographed on a column capable of separating a standard sample consisting of **3d** and sulfur. While **3d** was isolated, no sulfur was observed nor was sulfur detected in any of the above reactions when sensitive TLC techniques previously developed for this purpose were used.[6] The complex(es) responsible for the broad band in the Cp region did not survive the chromatography.

When **1** and $4\text{-}MeC_6H_4SSS\text{-}4\text{-}C_6H_4Me$ were refluxed for 64 h in toluene, an insoluble material was obtained, the elemental analysis of which gave the empirical formula $C_{10}H_{10}S_{1.50}Ti_{0.80}$. In another reaction wherein **2a** was treated with **1**, a fairly soluble product was isolated that exhibited the characteristic broad band of resonances in the Cp region of the NMR spectrum. Elemental analysis of this material was consistent with the empirical formula $C_{10}H_{10}S_{0.78}Ti_{1.34}$. Purification via recrystallization was unsuccessful.

$Cp_2Ti(SR)(SSR) \rightarrow Cp_2Ti(SR)_2$ in C_6D_6. The NMR spectra of C_6D_6 solutions of samples of **2a–d**, which contained the appropriate amounts of **3a–d** as a result of the preparation but no residual **1**, were monitored. For **2a** and **2d**, peaks due to **3a** and **3d**, respectively, grew in intensity at the expense of those of the starting complexes until the ratio of **2**:**3** was as follows: **a**, 2.0 (1 day); **d**, 1.7 (3 days). The presence of approximately 1 equiv of PPh_3 in fresh solutions accelerated the loss of sulfur such that only **3a** and **3d**, respectively, were detected after the same times. Peaks due to Ph_3PS were detected. The complex **3d** and Ph_3PS were subsequently isolated from a preparative scale reaction in 61% and 72% yields, respectively.

Table II. Products of the Reaction of $Cp_2Ti(SR)(SSR)$ with $PhCH_2Br$

R	$PhCH_2SR$:$PhCH_2SSR$	
	calcd[a]	found
$4\text{-}C_6H_4Me$	1.38	1.83
$CHMe_2$	0.98	0.74
CMe_3	1.08	0.61
CH_2Ph	1.20	1.50

[a] The calculated ratio is corrected for the presence of $Cp_2Ti(SR)_2$ and $Cp_2Ti(SSR)_2$ formed in the preparation of $Cp_2Ti(SR)(SSR)$, Table I.

In the cases of **2b** and **2c** in C_6D_6, the spectral changes in the NMR spectra were dominated by the growth of a broad band in the Cp region. In the case of **2c**, this band accounted for 77% of the integrated intensity in the Cp region after 11 days, with minor peaks due to **2c** and **3c** also present. In the case of **2b**, the broad band accounted for 50% of the Cp intensity accompanied by the peak for **2b** (40%) and a minor peak assigned to $Cp_2Ti(SSCHMe_2)_2$;[8] no **3b** was detected. In both these cases involving **2b** and **2c**, peaks due to RS_xR, where $x = 2$ and 3, were detected. When PPh_3 was present, **2c** was undetectable after 11 days while **3c** accounted for 22% of the integrated intensity in the Cp region and the broad band made up the remainder. Addition of PPh_3 to **2b** led to the detection of peaks due to **2b**, **3b**, and the broad band in the relative intensities 1:1:2, respectively, after 3 days. For both **2b** and **2c**, peaks due to Ph_3PS and RS_xR, where x = 2 and 3, were also observed.

$Cp_2Ti(CO)_2$ + RSSX (X = phth, Cl). The reactions of **1** with RSS(phth) in toluene lead to the precipitation of $Cp_2Ti(phth)(SSR)$ (**4a–d**) (eq 2). These reactions are clean; however,

$$\mathrm{Cp_2Ti(CO)_2 + RSS(phth) \rightarrow Cp_2Ti(phth)SSR + 2CO} \tag{2}$$

products **4a–d** are only slightly soluble in toluene and dissolved with decomposition in CH_2Cl_2. They steadily decompose in toluene and even in the solid state under nitrogen. If the reactions of **1** with RSS(phth) are run to completion and then EtOH is added, high yields of $Cp_2Ti(OEt)(SSR)$ (**5a–d**) are obtained (eq 3).

$$\mathrm{Cp_2Ti(phth)SSR + EtOH \rightarrow Cp_2Ti(OEt)SSR + Hphth} \tag{3}$$

Treatment of **1** with Ph_3CSSCl gave $Cp_2Ti(Cl)(SSCPh_3)$ (**6**). Triphenylphosphine does not react with **5c** but partially desulfurized **5a** over 5 days to give $Cp_2Ti(OEt)(S\text{-}4\text{-}C_6H_4Me)$ and Ph_3PS.

Treatment of **2a–d** with $PhCH_2Br$ in refluxing toluene gave Cp_2TiBr_2 and the appropriate sulfides ($PhCH_2SR$) and disulfides ($PhCH_2SSR$) in approximately the expected ratio (eq 4) as de-

$$\mathrm{Cp_2Ti(SR)(SSR) + 2PhCH_2Br \rightarrow Cp_2TiBr_2 + PhCH_2SSR + PhCH_2SR} \tag{4}$$

termined by NMR and GC (Table II). The ratios found for **2a** and **2d** are too high (i.e. rich in sulfide) probably due to the high temperature of the reaction which would accelerate their conversion to **3a** and **3d** as shown above. The complexes **2b** and **2c** are more thermally resistant; however the ratios found here are too low (i.e. poor in sulfide) possible due to loss of the more volatile sulfides $PhCH_2SCHMe_2$ and $PhCH_2SCMe_3$, respectively during the concentration step of the workup.

Discussion

The presence of the TiSSR linkage in **2a–d** is consistent with their physical and chemical properties. The complexes display

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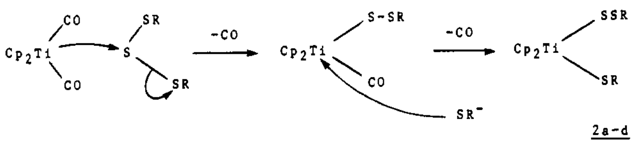
Scheme I



NMR spectra that are in accordance with their unsymmetrical nature with respect to the number and relative intensities of the peaks due to the Cp ligands and the two R groups. The NMR signals observed at high field for one of the R groups are similar in chemical shift to those observed for RS_xR, where $x \geq 1$, while the signals for the other R groups are similar to those observed for **3a–d**. It seems reasonable to assume that the R groups of the disulfanido ligand account for the higher field peaks. The rate of oxidative addition of RSSSR to **1** decreases in the order p-C_6H_4Me > CH_2Ph > $CHMe_2$ > CMe_3. Since arenethiolate anions are better leaving groups than alkanethiolates,[20] the observed order is consistent with a mechanism in which the stability of an intermediate thiolate anion plays an important role (Scheme I). This has previously been proposed by Floriani et al. for the reaction of **1** with disulfides, RSSR.[17a] The rate of oxidation of **1** may also be retarded by steric hinderance when the R group is large. In addition, the titanium–sulfur bond strength may be weakened by sterically demanding thiolate ligands.[21] The qualitative order of the rate of S loss from **2a–d** under thermal conditions, or in the presence of Ph_3P, is similar to that observed for the rates of oxidative addition of the parent trisulfides.

When complex **1** reacts with RSS(phth), it could oxidatively add either the S–S bond or the S–N bond. The complex $(PPh_3)_2Pt(C_2H_4)$ adds the latter to give the disulfanido compounds *cis*-$(PPh_3)_2Pt(phth)(SSR)$.[7] Complex **1** also adds the S–N bond to give $Cp_2Ti(phth)(SSR)$ (**4a–d**), which precipitate from toluene. This insolubility renders these preparations much cleaner than those of **2a–d**; however, the complexes are quite unstable in solution. The assignment of **4a–d** as disulfanido complexes rather than the dithiolates $Cp_2Ti(Sphth)(SR)$ is based on three pieces of evidence. The NMR chemical shifts of the R groups are closer to those of the disulfanido ligands in **2a–d** than to those of the thiolato ligands in **2a–d** and **3a–d**. The $\nu(CO)$ stretching frequencies in the infrared spectra of **4a–d** are closer to those observed for *cis*-$(PPh_3)_2Pt(phth)SSR$, which contain Pt–phth bonds, than those assigned to the Pt–S(phth) species in *cis*-$(PPh_3)_2Pt(phth)S(phth)$.[7] Finally **4a–d** react very smoothly with ethanol to give $Cp_2Ti(OEt)(SSR)$ (**5a–d**) and phthalimide.

The spontaneous and PPh_3-promoted loss of sulfur by **2a–d** to give **3a–d** is similar to that observed for $CpW(CO)_3SSR$.[6] While some organosulfur compounds exhibit spontaneous loss of sulfur,[22] most organic disulfides are quite resistant even in the presence of PPh_3. It is interesting that the disulfanido ligands in *cis*-$(PPh_3)_2Pt(phth)(SSR)$[7] and in $CpRu(PPh_3)(CO)SSR$[23] are also very resistant to spontaneous loss of sulfur. Metallodisulfanes, therefore, exhibit a broad range of activity with respect to sulfur loss. If PPh_3 is present, complexes **2a–d** lose sulfur to give **3a–d** and Ph_3PS. If PPh_3 is not present, loss of sulfur gives **2a–d** plus other products including polysulfides RS_xR, where $x = 2$ and 3, and Cp_xTi species, which are responsible for broad bands in the Cp region of the NMR spectrum, where x could be 1 or 2. The broad band and the signals due to RS_xR were more intense than those of **3** when bulkier R groups were present. Elemental sulfur was never detected as a product of spontaneous desulfurization, in contrast to the case of $CpW(CO)_3SSR$.[6]

The reaction of **1** with 4-MeC_6H_4SSS-4-C_6H_4Me or **2a** in refluxing toluene produced insoluble and soluble products, respectively. Elemental analyses and physical properties of the products indicate that both species contain C_5H_5 moieties and that the titanium and sulfur ratios vary from 1.5:0.8 (insoluble material) to 0.78:1.34 (soluble material). The soluble material exhibited the typical broad band in the Cp region. Apparently, **1** abstracts a sulfur atom from the disulfanido linkage in **2a** to form **3a** and the soluble material. Since the latter does not analyze for "Cp_2TiS", Cp exchange and perhaps rearrangement of Cp and S ligands has occurred. Similar transformations might also occur to give the insoluble product in the reaction of **1** with 4-MeC_6H_4SSS-4-C_6H_4Me. The structures of both species (or mixtures of species) are not known. However, the possibility of attack by sulfur on the Cp ring[24] and the presence of Ti–S–Ti linkages[25] cannot be excluded even in the sulfur-deficient material. The similarity of the NMR spectrum of the soluble product to that of the broad bands obtained in the NMR spectra of the products of other reactions of **2a–d** suggests that similar species are present.

The complex $Cp_2Ti(CO)_2$ is a strong oxophile.[26] The ability of the complex to abstract sulfur from sulfur,[18] disulfides,[17] trisulfides, and the disulfanido complexes **2a–d** and to retain the sulfur in titanium-containing species demonstrates considerable "thiaphilicity". This reactivity and the inherent instability of **2a–d**, even in the absence of **1**, complicates the synthesis of the former.

The reaction of $PhCH_2Br$ with **2a–d** to give the appropriate sulfides and disulfides (**3a–d** gave only sulfides[27]) is a convenient diagnostic test for the presence of the disulfano ligand. Other metal sulfide and thiolate complexes have been used as precursors to organosulfur compounds in other reactions.[17a,28,29]

Experimental Section

General Procedures. All reactions and manipulations were conducted by using standard inert-atmosphere techniques[30] under an atmosphere of prepurified nitrogen (Union Carbide), in appropriate-sized three-necked round-bottom flasks, one neck of which was always equipped with a gas inlet. NMR spectra were measured on a Varian XL-200 spectrometer, and all data are reported in ppm relative to TMS as an internal standard. Infrared spectra were measured on a Perkin-Elmer 457 or 297 spectrometer calibrated by using the 1601-cm^{-1} band of polystyrene and are reported in cm^{-1}. Melting points were determined in air, unless otherwise stated, on a Thomas-Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI. Gas chromatography was performed on a Shimadzu GC-8APF instrument equipped with a flame-ionization detector. The silica capillary column (30 M × 0.25 mm i.d.) was coated with a film (1 M) of poly[methyl(5% phenyl) siloxane] (Coating A). The temperature was raised at the rate of 20 °C/min from 100 to 260 °C with an N_2 flow rate of 0.5 mL/min. GC–mass spectrometry was conducted on a Finnigan Model 700 ion trap detector coupled to a Varian 3500 gas chromatograph with a column identical with that above or on a Hewlett-Packard 5984 A spectrometer with a 6% OV101 Chromosorb W/HP column (2M × 2 mm i.d.). Simple mass spectra (70 ev) were obtained via direct inlet on a Hewlett-Packard 5984A or on a DuPont 21-492B spectrometer using ion sources at 210 or 250 °C respectively.

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The solvents tetrahydrofuran, hexanes (boiling range 68–70 °C), diethyl ether, and toluene were refluxed over sodium/benzophenone; CH_2Cl_2 was refluxed over P_2O_5 while methanol and ethanol were both refluxed over magnesium turnings. All solvents were freshly distilled under N_2 just prior to use. The NMR solvents C_6D_6 and $CDCl_3$ were dried over molecular sieves (Linde 4A). Thin-layer chromatography was performed using BDH 150F254 aluminum sheets. Benzyl bromide (Kodak) was distilled before use; the fraction boiling in the range 100–107 °C (41 mmHg) was retained. The chemicals bis(2-propyl) sulfide, dibenzyl sulfide, dibenzyl disulfide, bis(*p*-tolyl) disulfide, and dibenzyl trisulfide (Aldrich) and bis(2-propyl) disulfide (Fairfield) were used as received. The following compounds were prepared by literature methods: bis(2-propyl) trisulfide,[31] bis(4-methylphenyl) trisulfide,[31] phenylmethyl 2-propyl sulfide,[32] phenylmethyl 4-methylphenyl sulfide,[32] *N*-(2-propyl)bis(thiophthalimide),[33] *N*-(phenylmethyl)bis(thiophthalimide),[33] *N*-(4-methylphenyl)bis(thiophalimide),[33] (triphenylmethyl)-chlorotrisulfane,[34] and the complexes Cp_2TiL_2, where L = $SCHMe_2$,[35] SCH_2Ph,[36] S-4-C_6H_4Me,[36] and CO.[37] The following compounds, prepared by literature methods,[38] were kindly supplied by others: *N*-(*tert*-butyl)bis(thiophthalimide) (D. Ryan), *N*-(2-propyl)thiophthalimide (B. Soo Lum), *N*-(phenylmethyl)thiophthalimide (R. Turrin), and *N*-(4-methylphenyl)thiophthalimide (P.-Y. Plouffe). Reaction products were identified in the following ways: organic sulfides, by means of comparison of GC parameters and NMR spectral data to those of authentic samples and, where appropriate, by means of their GC–mass spectra; disulfides, by their GC–mass spectra; triphenylsulfide, by comparison of the NMR spectrum and TLC to that of an authentic sample.

Bis(η-cyclopentadienyl)(4-methylbenzenethiolato)((4-methylphenyl)-disulfanido)titanium(IV), $Cp_2Ti(S\text{-}4\text{-}C_6H_4Me)(SS\text{-}4\text{-}C_6H_4Me)$ (2a). The procedure used to prepare the complex is typical of that used throughout and thus is described in detail. To a red-brown solution of $Cp_2Ti(CO)_2$ (0.22 g, 0.93 mmol) in toluene (20 mL) at −20 °C was added $(4\text{-}C_6H_4Me)_2S_3$ (0.26 g, 0.93 mmol). The progress of the reaction was monitored by following the decrease in intensity of the characteristic CO bands of $Cp_2Ti(CO)_2$ in the infrared spectrum of the reaction solution. The solution was stirred at −20 °C for 9 h and then warmed to 5 °C and stirred for a further 12 h. The deep purple solution was stripped at room temperature and the residue extracted with CS_2 (25 mL) at 0 °C. The solution was filtered through a Celite pad on a sintered glass frit into an ice-cold receiving flask. The solvent was stripped at 0 °C and the residue recrystallized from ether (40 mL) at −30 °C to give dark purple microcrystals of the product (yield 0.07 g, 16%; mp 136–138 °C). Anal. Calcd for $C_{24}H_{24}S_3Ti$: C, 63.14; H, 5.30; S, 21.07. Found: C, 62.83; H, 5.50; S, 20.84. ^1H NMR (C_6D_6): δ 7.64–6.98 (m, 8 H, C_6H_4), 5.77 (s, 10 H, Cp), 2.11 (s, 3 H, S-4-C_6H_4*Me*) 2.03 (s, 3 H, SS-4-C_6H_4*Me*).

$Cp_2Ti(SCHMe_2)(SSCHMe_2)$ (2b). The reaction was conducted at 20 °C for 16 h. Spectroscopically pure samples (NMR) could not be obtained due to persistent contamination by $Cp_2Ti(SCHMe_2)_2$[35] and $Cp_2Ti(SSCHMe_2)_2$[8] present in 3% and 4%, respectively, as determined by integration of the Cp region of the spectrum. ^1H NMR (C_6D_6): δ 5.81 (s, 10 H, Cp), 3.76 (septet, 1 H, J(H–H) = 6.6 Hz, SC*H*Me_2), 3.11 (septet, 1 H, J(H–H) = 6.8 Hz, SSC*H*Me_2), 1.46 (d, 6 H, SCHMe_2), 1.34 (d, 6 H, SSCHMe_2).

$Cp_2Ti(SCMe_3)(SSCMe_3)$ (2c). The reaction was conducted at 22 °C for 45 h and the product recrystallized from hexanes at −78 °C to give green microcrystals (yield 5.3 g, 60%; mp 85–87 °C dec). Anal. Calcd for $C_{18}H_{28}TiS_3$: C, 55.65; H, 7.26; S, 24.76. Found: C, 55.71; H, 7.37; S, 24.72. Mass spectrum (chemical ionization using NH_3), m/z (relative intensity): M + H^+; 389 (13.7). Visible spectrum: maximum (CH_2Cl_2) 570 nm (ϵ 3.3 × 10^3 L mol^{-1} cm^{-1}). ^1H NMR (C_6D_6): δ 5.91 (s, 10 H, Cp), 1.66 (s, 9 H, $SCMe_3$), 1.42 (s, 9 H, $SSCMe_3$).

$(MeCp)_2Ti(SCMe_3)(SSCMe_3)$. This complex was recrystallized at −78 °C from hexanes to give a green powder that melted at room temperature (yield 2.45 g, 77%). Anal. Calcd for $C_{20}H_{32}S_3Ti$: C, 57.67; H, 7.74; S, 23.09. Found: C, 57.60; H, 7.76; S, 23.16. ^1H NMR (C_6D_6): δ 6.13 (m, 2 H, C_5H_4), 6.06 (m, 2 H, C_5H_4), 5.96 (m, 2 H, C_5H_4), 5.70 (m, 2 H, C_5H_4), 1.90 (s, 6 H, $C_5H_4CH_3$), 1.70 (s, 9 H, $SCMe_3$), 1.44 (s, 9 H, $SSCMe_3$).[39]

$Cp_2Ti(SCH_2Ph)(SSCH_2Ph)$ (2d). The reaction was stirred at 12 °C for 40 h. The crude product was contaminated by $Cp_2Ti(SCH_2Ph)_2$[36] and $Cp_2Ti(SSCH_2Ph)_2$ (^1H NMR (C_6D_6): δ 5.72 (S, 10 H, Cp), 3.97 (S, 4 H, CH_2),, phenyl region obscured) present in 14% and 5%, respectively, as determined by integration of the Cp region of the NMR spectrum. ^1H NMR (C_6D_6) for **2d**: δ 7.44–7.03 (m, C_6H_5), 5.71 (s, 10 H, Cp), 4.39 (s, 2 H, SCH_2Ph), 3.94 (s, 2 H, SSCH_2Ph).

Reaction of $Cp_2Ti(SR)(SSR)$ with Benzyl Bromide. Toluene solutions of **2a–c**, prepared as described above, were treated with 2 equiv of $PhCH_2Br$ and then refluxed for 4 h to give orange-red solutions. A sample (2 mL), withdrawn and carefully concentrated, contained Cp_2TiBr_2 and the appropriate sulfide ($PhCH_2SR$) and disulfide ($PhCH_2SSR$) as determined by its NMR spectrum (C_6D_6) and GC–mass spectrum. The remainder of the reaction solution was concentrated to about 30 mL and cooled (−40 °C) overnight to give dark red crystals of Cp_2TiBr_2, which were collected on a frit.

Reaction of $Cp_2Ti(SR)(SSR)$ with PPh_3. Two NMR samples (C_6D_6), A and B, were prepared containing **3a**, **3b** and **3d**, generated in situ. A slight excess of 1 equiv of PPh_3 was added to sample A. Over a period of several days, the NMR signals due to the starting materials decreased in intensity concomitant with the increase in intensity of peaks due to $Cp_2Ti(SR)_2$ and Ph_3PS until none of the starting complex could be detected (R = 4-C_6H_5Me, 1 day; R = $CHMe_2$, 12 days; R = CH_2Ph, 3 days). After the same period for the control samples B, the ratio $Cp_2Ti(SR)(SSR)$:$Cp_2Ti(SR)_2$ was 2:1 and 5:3 for R = $p\text{-}C_6H_5CH_3$ and CH_2Ph, respectively, while no $Cp_2Ti(SCH(CH_3)_2(SSCH(CH_3)_2)$ was detected.

When the reaction was conducted on the gram scale in toluene, $Cp_2Ti(SCH_2Ph)(SSCH_2Ph)$ was desulfurized by PPh_3 over 3 days to give $Cp_2Ti(SCH_2Ph)_2$ and $SPPh_3$, which were separated by column chromatography and identified by comparison of their ^1H NMR and mass spectra to those of authentic samples.

Bis(η-cyclopentadienyl)(phthalimido)((4-methylphenyl)disulfanido)titanium(IV), $Cp_2Ti(phth)(SS\text{-}4\text{-}C_6H_4Me)$ (4a). As for **3a**, *N*-(4-methylphenyl)bis(thiophthalimide) (1.48 g, 4.92 mmol) was added to a solution of **1** (1.15 g, 4.92 mmol) in toluene (40 mL) and the reaction mixture was stirred for 28 h. A purple powder (yield 0.79 g, 34%; mp 146–149 °C) was collected by filtration, washed (hexanes, 2 × 5 mL) and vacuum-dried. Anal. Calcd for $C_{25}H_{21}NO_2S_2Ti$: C, 62.63; H, 4.41; S, 13.37. Found: C, 62.02; H, 4.29; S, 13.27. ^1H NMR ($CDCl_3$): δ 7.64–7.51 (m, 4 H, phth), 7.43, 7.16 (ABq, 4 H, J(H–H) = 7.8 Hz, C_6*H_4*Me), 6.40 (s, 10 H, Cp), 2.36 (s, 3 H, CH_3), IR (toluene): γ(CO) 1651 cm^{-1}.

$Cp_2Ti(phth)(SSCHMe_2)$ (4b). Yield: 0.88 g, 43%. Mp: 128–130 °C. Anal. Calcd for $C_{21}H_{21}NO_2S_2Ti$: C, 58.46; H, 4.91; S, 14.86. Found: C, 60.94; H, 4.92; S, 12.60. ^1H NMR ($CDCl_3$): δ 7.61–7.48 (m, 4 H, phth), 6.32 (s, 10 H, Cp), 3.31 (septet, 1 H, J(H–H) = 6.8 Hz, C*H*Me_2), 1.43 (d, 6 H, CH_3), IR (toluene) = ν(CO) 1663 cm^{-1}.

$Cp_2Ti(phth)(SSCMe_3)$ (4c). Yield: 1.76 g, 61%. Mp: 163–165 °C. Anal. Calcd for $C_{22}H_{23}NO_2S_2Ti$: C, 59.32; H, 5.20; S, 14.39. Found: C, 59.26; H, 5.27; S, 14.48. ^1H NMR ($CDCl_3$): δ 7.64–7.49 (m, 4 H, phth), 6.35 (s, 10 H, Cp), 1.49 (s, 9 H, CH_3). IR (toluene): ν(CO) 1664 cm^{-1}.

$Cp_2Ti(phth)(SSCH_2Ph)$ (4d). Yield: 0.8 g, 37%. Mp: 138–140 °C. Anal. Calcd for $C_{25}H_{21}NO_2S_2Ti$: C, 62.63; H, 4.41; S, 13.37. Found: C, 62.50; H, 4.49; S, 13.38. ^1H NMR ($CDCl_3$): δ 7.61–7.47 (m, 4 H, phth), 7.40–7.29 (m, 5 H, C_6H_5), 6.20 (s, 10 H, Cp), 4.20 (s, 2 H, CH_2). IR (toluene): ν(CO) 1665 cm^{-1}.

Bis(η-cyclopentadienyl)(ethoxy)(4-methylphenyldisulfanido)titanium-(IV), $Cp_2Ti(OEt)(SS\text{-}4\text{-}C_6H_3Me)$ (5a). Addition of **4a** to EtOH (35 mL) followed by stirring for 45 min gave a dark brown-orange solution, which was taken to dryness in vacuo. Flash chromatography on deactivated alumina (4 × 6 cm) and eluting with CH_2Cl_2 gave a brown band, which was collected. Stripping the band to dryness gave a brown powder (yield 0.85 g, 35%; mp 104–106 °C). Anal. Calcd for $C_{19}H_{22}OS_2Ti$: C, 60.31; H, 5.86; S, 16.94. Found: C, 60.17; H, 5.85; S, 17.05. ^1H NMR (C_6D_6): δ 7.72, 7.00 (ABq, 4 H, J(H–H) = 8.0 Hz, C_6H_4), 5.80 (s, 10 H, Cp), 4.11 (q, 2 H, J(H–H) = 6.8 Hz, CH_2), 2.10 (s, 3 H, C_6H_4*CH_3*), 0.98 (t, 3 H, CH_2*CH_3*).

$Cp_2Ti(OMe)(SS\text{-}4\text{-}C_6H_4Me)$. Using MeOH gave orange microcrystals (yield 0.59 g, 30%; mp 87–89 °C). Anal. Calcd for $C_{18}H_{20}OS_2Ti$: C, 59.33; H, 5.53; S, 17.60. Found: C, 59.44; H, 5.42; S, 17.67. ^1H NMR (C_6D_6): δ 7.67, 6.98 (ABq, 4 H, J(H–H) = 8.2 Hz, C_6H_4), 5.78 (s, 10 H, Cp), 3.88 (s, 3 H, OCH_3), 2.08 (s, 3 H, C_6H_4*CH_3*).

$Cp_2Ti(OEt)(SSCHMe_2)$ (5b). Yield: 0.5 g, 33%. Mp: 61–63 °C. Anal. Calcd for $C_{15}H_{22}OS_2Ti$: C, 54.54; H, 6.71; S, 19.41. Found: C,

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(39) The presence of the $SCMe_3$ and $SSCMe_3$ substituents renders the protons in the 2,5- and 3,4-positions of the MeCp rings diastereotopic, resulting in a total of four different peaks in the NMR spectrum.

54.36; H, 6.80; S, 19.19. ^{1}H NMR (C_6D_6): δ 5.83 (s, 10 H, Cp), 4.14 (q, 2 H, *J*(H–H) = 6.9 Hz, CH_2), 3.01 (septet, 1 H, *J*(H–H) = 6.8 Hz, CH), 1.43 (d, 6 H, Me), 1.02 (t, 3 H, CH_2CH_3).

$Cp_2Ti(OEt)(SSCMe_3)$ (5c). Yield: 1.24 g, 58%, as an oil. Anal. Calcd for $C_{16}H_{24}OS_2Ti$: C, 55.80; H, 7.02; S, 18.62. Found: C, 55.63; H, 7.11; S, 18.72. ^{1}H NMR (C_6D_6): δ 5.88 (s, 10 H, Cp), 4.16 (q, 2 H, *J*(H–H) = 6.8 Hz, CH_2), 1.50 (s, 9 H, Me), 1.06 (t, 3 H, CH_2CH_3).

$Cp_2Ti(OEt)(SSCH_2Ph)$ (5d). Yield: 0.44 g, 28%. Mp: 84–86 °C. Anal. Calcd for $C_{19}H_{22}OS_2Ti$: C, 60.31; H, 5.86; S, 16.94. Found: C, 60.15; H, 5.80; S, 17.10. ^{1}H NMR (C_6D_6): δ 7.38–6.69 (m, 5 H, C_6H_5), 5.77 (s, 10 H, Cp), 4.13 (q, 2 H, *J*(H–H) = 6.9 Hz, CH_2CH_3), 3.95 (s, 2 H, CH_2Ph), 1.00 (t, 3 H, CH_3).

Bis(η-cyclopentadienyl)(chloro)((triphenylmethyl)disulfanido)titanium(IV), $Cp_2Ti(Cl)(SSCPh_3)$ (6). The compound Ph_3CSSCl (1.64 g, 4.79 mmol) was added to a solution of **1** (1.12 g, 4.79 mmol) in toluene (30 mL) at −78 °C. The temperature of the stirred reaction mixture was allowed to rise slowly to 22 °C over a period of 2.5 h. A deep purple powder was obtained after filtration and washing (hexanes, 2 × 10 mL). Addition of the washings to the mother liquors, with cooling to −16 °C, gave a second crop of powder. Flash chromatography on deactivated alumina (1 × 6 cm), eluting with CH_2Cl_2, gave a purple band. The eluate was stripped to dryness and then recrystallized from CH_2Cl_2 layered with hexanes to give a deep purple powder (yield 1.48 g, 54%; mp 155–157 °C dec). Anal. Calcd for $C_{29}H_{25}S_2ClTi\cdot{}^1/_2CH_2Cl_2$: C, 62.88; H, 4.65; S, 11.38. Found: C, 63.14; H, 4.65; S, 11.71. ^{1}H NMR (C_6D_6): δ 7.72–6.98 (m, 15 H, C_6H_5), 5.72 (s, 10 H, Cp).

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^{13}C and ^{31}P CP/MAS NMR Studies of the Polytopal Ligand Rearrangement Process of Tungsten Tris(trimethylphosphine) Hexahydride in the Solid State

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$W(PMe_3)_3H_6$ (**1**), an archetypal nine-coordinate transition-metal complex, has been studied in the crystalline state by variable-temperature ^{13}C and ^{31}P CP/MAS NMR spectroscopy. The NMR spectra are consistent with a tricapped-trigonal-prismatic geometry for the complex, with two phosphine ligands in eclipsed prismatic sites and the third capping the prismatic face opposite the other two. The two prismatic phosphines are shown to be on inequivalent sites. At temperatures above 340 K, exchange broadening shows the occurrence of ligand functionality interchange between the different phosphine environments. Analysis of these line shapes and magnetization-transfer data, in the slow limit of exchange, for both ^{13}C and ^{31}P nuclei shows activation parameters of $E_a = 148.8 \pm 15$ kJ mol^{-1} and $A = 6.6 \times 10^{23}$ s^{-1} for the ligand-functionality-interchange process. The most likely mechanism involves a "double-rearrangement" mechanism with polyhedral edge stretches through a monocapped-square-antiprismatic geometry to a tricapped-trigonal-prismatic intermediate in which all phosphines occupy capping positions. This allows complete scrambling of the ligand functionality, in a manner such that the spatial movement of the phosphine ligands within the crystalline frame need only be relatively small. An additional dynamic process, involving a "tripod" reorientation of the PMe_3 rotors, has been detected by dipolar broadening of the ^{13}C NMR spectra. This process is rapid at room temperature but slows to a rate of ca. 10^5 Hz at the lowest temperature studied, 169 K. The reorientation appears to be slightly more facile in the prismatic environments than in the capping position.

Introduction

For complexes with nine identical ligands, the idealized tricapped-trigonal-prismatic (TTP) geometry (point group D_{3h}) is found from experimental studies to be conclusively favored over the alternative monocapped-square-antiprismatic (MSA) arrangement (point group C_{4v}).[1] In accord with this, calculations based on the interligand repulsion potentials, $E = \sum r_{ij}^{-n}$ (n = 1, 2, ..., 6, i ≠ j), show the TTP polytope to be of lower energy for all forms of the potential, and the MSA geometry lies above with no evidence of a minimum.[1] Transition-metal complexes with nine-coordinate geometries about the metal atom are, however, always fluxional in solution; a facile path for interchange of ligands in the TTP structure has been suggested to be via the MSA arrangement, and $D_{3h} \rightleftharpoons C_{4v} \rightleftharpoons D_{3h}$ rearrangement is generally invoked to explain the ligand-scrambling processes. The energy barrier to such interchange would be low, since only slight distortion of the TTP ligand polyhedron, namely stretching of a single polyhedral edge, is required to attain the MSA geometry,[1] as shown in Figure 1. Indeed, the polytopal rearrangements that equilibrate the ligand environments have in general been observed to be in the fast-exchange limit, even at the lowest temperatures attainable in solution NMR studies, suggesting very low barriers to ligand site interchange; line shape data have not been obtained from solution NMR studies, from which to attempt to ascertain possible permutational mechanisms for the ligand scrambling. Available structural data, which favor rigid TTP geometries,[1] suggest that in solids the barriers to polytopal rearrangement are considerably higher than those pertaining in solution, or those calculated by considering merely the *intra*molecular repulsion potential. Solid-state NMR spectroscopy might, therefore, allow exploration of these reorientational processes at lower rates and thus provide mechanistic information.

A particularly interesting case of nine-coordinate geometry is provided by the group of compounds $W(P)_3H_6$, where (P) represents a phosphine ligand. Low-temperature single-crystal X-ray and neutron diffraction studies of the complex $W(PPh(^iPr)_2)_3H_6$[2,3] show a geometry clearly distinct from the idealized TTP (D_{3h}) structure with the three phosphorus atoms occupying the capping sites originally predicted for such compounds.[4,5] The structure is, however, much closer to TTP than to MSA, with two phosphorus atoms in eclipsed prismatic sites and the third residing in the capping position of the prismatic face opposite the other two phosphorus atoms[2,3] (see Figure 2). The phosphorus atoms in the prismatic environments show bond lengths to tungsten that are approximately 0.1 Å longer than the W–P bond length for

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