Ph_4As^+ salt of the $[(\mu\text{-S})(\mu\text{-S}_2\text{-}t\text{-Bu})Fe_2(CO)_6]^-$ ion (3). The compound is air-stable for brief periods in the solid state and is stable in solution in aprotic solvents room temperature for prolonged periods in the absence of oxygen.

The crystal structure of the Ph_4As^+ salt of 3 shows that the anion contains a $(\mu\text{-S})_2Fe_2(CO)_6$ unit linked via a disulfide bond to a t-BuS unit in a pseudoequatorial fashion[21] (e-linked[9]). Selected distances and angles are given in Figure 1. The $(\mu\text{-S})_2Fe(CO)_6$ unit has a conformation similar to that in $(\mu\text{-S}_2)Fe_2(CO)_6$,[22] $(\mu\text{-EtS})_2Fe_2(CO)_6$,[23] $(\mu\text{-RS})(\mu\text{-RHgS})Fe_2(CO)_6$,[9] $[Fe_4S_4(CO)_{12}]^{2-}$,[15] and $(\mu\text{-PhS})Fe_2(CO)_6(\mu\text{-S}_2)Fe_2(CO)_6(\mu\text{-SPh})$,[16] with a dihedral angle of 88.91° between the FeS_2 planes. Although a number of examples of both η^1-[24] and η^2-coordinated[25] persulfide units are now known, there appear to be only two crystallographically characterized examples of bridging persulfides analogous to that in 3, namely, $\{[(C_5H_5)Cr(NO)]_2(\mu\text{-S-}t\text{-Bu})(\mu\text{-S}_2\text{-}t\text{-Bu})\}$[26] (4) and $[Mo_2(NTol)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSEt)]$[27] (5). The S–S bonds in 4 and 5, at 2.076 (4) and 2.068 (2) Å, respectively, are only marginally shorter than that in 3, and the M–S–M angles at the bridging persulfide are ca. 10° (4) and 2° (5) larger than that in 3. As found for 2, the iron bonds to the disulfide sulfur (S2) in 3 are actually 0.03–0.04 Å shorter than those to the bridging sulfide (S1). The disulfide bond (S2-S3) in 3 is ca. 0.05 Å shorter than in 2, approaching a normal S–S single bond value[27] (as seen in 4[26]). This is not, however, accompanied by a compensating increase in the "nonbonded" S1···S2 distance, which is actually 0.04 Å less in 3 than in 2 and is thus well within the range reported for S···S bonding interactions.[28] The long S2–S3 and short S1···S2 distances in 3 are consistent with a delocalized bonding description involving all three sulfur atoms, as originally suggested for 2[15] and supported by recent theoretical calculations.[29]

Compound 3 must arise by nucleophilic attack of RS^- on the bridging S_2^{2-} unit of 1 (Scheme I, reaction 1), in a reaction analogous to that proposed[4] for the reaction of hydride and alkyllithium reagents with 1 to produce $[(\mu\text{-S})(\mu\text{-SH})Fe_2(CO)_6]^-$ and $[(\mu\text{-S})(\mu\text{-SR})Fe_2(CO)_6]^-$, respectively. We postulate that 3 is not stable for most thiolates and spontaneously dimerizes to form 2, presumably via intermediate 4, with elimination of RSSR as shown in Scheme I, reaction 2. The fact that the reaction stops at 3 for R = t-Bu must be due to steric hindrance of nucleophilic attack by a second molecule of 3; electronic factors should most favor formation of 2 with t-BuS$^-$, since it is the strongest reductant of the thiolates examined. Compound 3 is stable both in solution as well as in the solid state, differing from 2 in the former respect; thus it may prove to be an even more convenient precursor to the $[(\mu\text{-S})_2Fe_2(CO)_6]^{2-}$ dianion than 2 and a useful reagent for cluster syntheses.

Acknowledgment. This research was supported by grants from the U.S. Department of Agriculture Competitive Research Grants Office (82-CRCR-1-1123 and 86-CRCR-1-2033).

Supplementary Material Available: Tables of atomic coordinates, interatomic distances and angles, and thermal parameters (5 pages); a listing of calculated and observed structure factors (17 pages). Ordering information is given on any current masthead page.

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A Double Intramolecular Ring Metalation: Formation, Spectroscopic Characterization, and Molecular Structure of $(C_5Me_3(CH_2)_2)Ta(H)_2(PMe_3)_2$

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Summary: Treatment of $(C_5Me_5)TaCl_4$ with sodium amalgam in THF solution containing PMe_3 gives rise to the compound $(C_5Me_3(CH_2)_2)Ta(H)_2(PMe_3)_2$ (**1**), in which two ring methyl C–H bonds have been cleaved. NMR and X-ray crystallographic studies show that the abstracted hydrogens remain bound to the metal and the resulting ring methylene groups are located on adjacent ring-carbon atoms, being best described as sp^2, olefin-type CH_2 groups. Migration of the metal-bound hydrogens back to the $C_5Me_3(CH_2)_2$ ligand is shown by the reaction of **1** with CO affording $(C_5Me_5)Ta(CO)_2(PMe_3)_2$.

The importance of the pentamethylcyclopentadienyl ligand (η^5-C_5Me_5 or Cp*) in contemporary organometallic chemistry coupled with recent interest in C–H activation[2] and the reactivity of metal–hydrocarbyl fragments[3] has led

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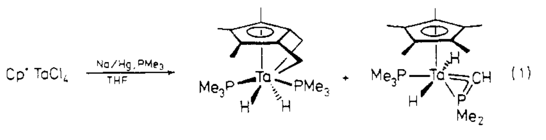
to reports of several examples of ring-metalated species, which arise via intramolecular insertion of a ring-attached metal atom into the C–H bond of a ring methyl substituent.[4]

Several examples of hydrogen abstraction from one methyl group to give η^6-1,2,3,4-tetramethylfulvene (or η^5,η^1-$C_5Me_4CH_2$) complexes have been reported. These include Cp*(η^6-$C_5Me_4CH_2$)TiMe which results from the thermal decomposition of $Cp^*_2TiMe_2$,[5] Cp*(η^6-$C_5Me_4CH_2$)WH which forms during photolysis of $Cp^*_2WH_2$,[6] Cp*(η^6-$C_5Me_4CH_2$)TiH, observed in solutions of Cp^*_2 Ti,[7] and Cp*(η^5,η^1-$C_5Me_4CH_2$)$HfCH_2C_6H_5$ formed as an intermediate in the thermal decomposition of $Cp^*_2Hf(CH_2C_6H_5)_2$.[3c] However, the abstraction of a hydrogen from a second methyl substituent to give a double ring-metalated product has been observed on only rare occasions.[6,8] In these cases, the abstracted hydrogens do not remain bound to the metal and the resultant ring system has not been structurally characterized.

Here, we wish to report that the reductive activation of the tantalum atom in Cp^*TaCl_4 by sodium amalgam in the presence of trimethylphosphine leads to the double ring-metalated compound $(C_5Me_3(CH_2)_2)Ta(H)_2(PMe_3)_2$ (1) in which the abstracted hydrogens are retained within the coordination sphere of the metal. Thus, Cp^*TaCl_4 (1.1 mmol), PMe_3 (5.7 mmol), and Na/Hg (4.4 mmol of 0.5% amalgam) were combined in 25 mL of THF. After the mixture was stirred under argon for 22 h at room temperature, the solvent was removed in vacuo and the residue extracted with several portions of petroleum ether. This solution was concentrated and slowly cooled to −78 °C to obtain the air- and moisture-sensitive product 1 in 65% yield. Although seldom required, further purification is possible by sublimation (75 °C; 5×10^{-3} Torr). 1 has been characterized[9] by elemental analysis, IR and NMR spectroscopies, mass spectrometry, and a single-crystal X-ray structure determination. Close analysis of a ^1H NMR spectrum on the dried, crude petroleum ether extract showed that 1 and a second species are formed in the ratio 5:1 and constitute >90% of the petroleum ether soluble Cp*-containing products (eq 1). The minor component is readily identified as the phosphine-metalated species $Cp^*Ta(PMe_3)(H)_2(\eta^2$-$CHPMe_2)$ (2) which has been described previously.[10]



1 2 (<20%)

The ^1H NMR of 1 in C_6D_6 shows two singlets assigned to the ring methyl groups at δ 1.97 (6 H, $C_5\mathit{Me}_2Me(CH_2)_2$) and 1.86 ppm (3 H, $C_5Me_2\mathit{Me}(CH_2)_2$). The diastereotopic hydrogens of the equivalent methylene groups exhibit complex multiplets at δ 1.30 (2 H, H_a) and 2.66 ppm (2 H, H_b) whose assignments were facilitated by difference NOE experiments.[11] The metal-bound hydrides occupy equivalent solution environments and are located at δ 2.64 ppm (2 H, dd, $^2J_{PH} = 55.9, 25.7$ Hz). Finally, two doublets at δ 1.14 and 1.32 ppm (both 9 H, $^2J_{PH} = 7.0$ Hz) are present for the inequivalent phosphine ligands. Thus, the ^1H NMR data are consistent with a ring system of the form $C_5Me_3(CH_2)_2$, with two equivalent methylene groups. However, it does not distinguish between methylene groups on adjacent (vicinal) or nonadjacent ring-carbon atoms. This feature of the molecule has been established by a single-crystal X-ray study: the methylene groups are on adjacent ring-carbon atoms.

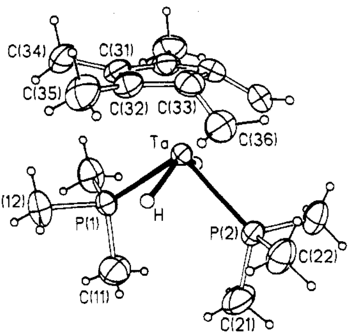
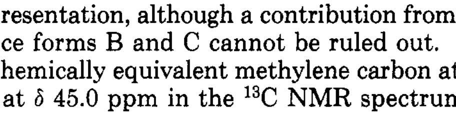


Figure 1. Molecular structure with thermal ellipsoids at 40% probability level (spheres of arbitrary radius for H atoms). Selected distances (Å): Ta–P(1), 2.567 (1); Ta–P(2), 2.568 (1); Ta–H, 1.74 (4); Ta–C(31), 2.569 (5); Ta–C(32), 2.409 (4); Ta–C(33), 2.172 (3), Ta–C(36);, 2.394 (4); C(31)–C(32), 1.407 (5); C(32)–C(33), 1.445 (5); C(33)–C(33′), 1.460 (8); C(31)–C(34), 1.502 (8); C(32)–C(35), 1.503 (6); C(33)–C(36), 1.429 (6). C(33′) is related to C(33) by the mirror plane.

A number of structures may be proposed to account for the ring π-bonding and the ring-to-metal interactions. Structure A may be described as a fused η^4-butadiene/η^3-allyl system, B and C are equivalent resonance forms of an η^7-heptatrienyl anion, and D is a normal cyclopentadienyl ring with two additional sp^3-type methylene bridges to the metal atom. Of these possible structures, NMR and the X-ray data indicate that structure A is the best representation, although a contribution from the two resonance forms B and C cannot be ruled out.



The chemically equivalent methylene carbon atoms are located at δ 45.0 ppm in the ^{13}C NMR spectrum with a one-bond C–H coupling constant of 151.1 Hz.[12] This value is more consistent with the sp^2-hybridized carbon atoms of A, B, or C (typically 150–160 Hz[13]). Furthermore, broad-band ^{31}P decoupling of the methylenic hydrogens reveals a geminal $^2J_{HH}$ coupling constant of 2.7 Hz,[14] in

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(11) Difference NOE (360 MHz, C_6D_6): irradiation of the signal at δ 1.97 ppm ($C_5\mathit{Me}_2Me(CH_2)_2$) leads to considerable enhancement (3.4%) of the signal at δ 2.66 ppm and has no detectable effect on the signal at δ 1.30 ppm. Thus, the multiplet at δ 2.66 ppm is assigned to the exo-enantiotopic hydrogens, H_b.

(12) Quite similar $^1J_{CH}$ coupling constants have been reported for $Cp^*(C_5Me_4CH_2)TiMe$ (150 Hz), $Cp^*(C_5Me_4CH_2)WH$ (151.3 Hz), Cp^*-$(C_5Me_3(CH_2)_2)W$ (152 Hz), and $Cp^*(C_5Me_3(CH_2)_2)Ti$ (160 Hz).

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(14) Geminal HH coupling constants of 1.8 and 4.4 Hz have been reported for $Cp^*(C_5Me_3(CH_2)_2)W$ and $Cp^*(C_5Me_3(CH_2)_2)Ti$, respectively. See ref 5 and 7.

close agreement with values expected for geminal hydrogen atoms attached to sp^2-hybridized carbon (typically 0–3 Hz; cf. 12–15 Hz for geminal hydrogens attached to sp^3-hybridized carbon[15]). Finally, an olefinic C–H stretching band at 3055 cm^{-1} is seen in the infrared spectrum (Nujol mull).[16]

The crystal structure of $(C_5Me_3(CH_2)_2)Ta(H)_2(PMe_3)_2$ has been determined in the orthorhombic space group *Pnma*.[17] The molecule is located on the mirror plane that contains the two phosphorus atoms and the tantalum atom and bisects the five-membered ring between the methylene groups (Figure 1). Important distances are shown in the figure caption. The tantalum atom is clearly displaced away from C(31) toward the C(33)–C(33′) edge (0.44 Å from the ring centroid as determined by a normal from the ring plane through the metal atom), presumably due to the additional bonding interactions between the metal atom and the methylene carbon atoms C(36) and C(36′). The Ta–C(36) distance is more than 1 Å shorter than the metal–methyl distance found in $(\eta^5\text{-}C_5Me_5)Ta$ compounds.[19] The methylene carbon atoms, which are closer to the metal atom partially by virtue of the 0.44 Å ring displacement, are also bent below the plane of the ring by 33.4°. Similar bending of a methylene group toward a metal atom has been observed in the molecular structures of related fulvene complexes.[20–24] The inter ring-carbon distance C(31)–C(32) is short at 1.407 (5) Å, while C(33)–C(33′) is relatively elongated at 1.460 (8) Å. Finally, the C(ring)–C(methylene) distances are 1.429 (6) Å, values consistent with coordinated double bonds. Thus, the description of the $C_5Me_3(CH_2)_2$ ligand as an η^4-butadiene/η^3-allyl system would seem most appropriate.

A potentially useful feature of 1 is the retention of the abstracted ring hydrogens within the metal coordination sphere, thus offering an opportunity to exploit reversible metal-to-ring hydrogen migrations for the generation of coordinatively unsaturated, electron-rich metal fragments of tantalum. For example, the migration of both metal hydride hydrogens to the $C_5Me_3(CH_2)_2$ ligand is demonstrated by the reaction of an inert solvent solution of 1 with carbon monoxide resulting in the formation of $Cp^*Ta(PMe_3)_2(CO)_2$ (70% by ^1H NMR), which has been characterized by comparison with data from an authentic sample.[25] Reactivity studies are presently being extended to other substrate molecules, in addition to assessing the mechanism of formation and interrelationship of the tautomers 1 and 2.

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Supplementary Material Available: High-field NMR data for compound 1 and tables of positional and anisotropic thermal parameters and bond lengths and angles (7 pages); a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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[16] A band at 3040 cm^{-1} was observed for $Cp^*(C_5Me_4CH_2)TiMe$. See ref 4.

[17] Crystallographic data: $C_{16}H_{33}P_2Ta$, $M_r = 468.3$, orthorhombic, *Pnma*, $a = 11.2309$ (6) Å, $b = 11.9809$ (5) Å, $c = 14.4881$ (7) Å, $V = 1949.5$ (2) $Å^3$, and $Z = 4$, $D_{calcd} = 1.595$ g cm^{-3}. Data were collected on a Siemens AED2 diffractometer in ω/θ scan mode, with Mo Kα radiation ($\lambda = 0.71073$ Å), $2\theta_{max} = 60°$, and on-line profile fitting;[18a] $T = 295$ K. A total of 8915 reflections (three equivalent sets) were corrected for Lorentz and polarization effects, absorption ($\mu = 5.73$ mm^{-1}, crystal size 0.25 × 0.3 × 0.3 mm, transmission 0.11–0.16), and intensity drift (ca. 5%) of three standards, to give 2972 unique reflections, 2635 with $F > 4\sigma_c(F)$ (σ_c from counting statistics only, $R_{int} = 0.019$). The structure was solved by heavy-atom methods and refined by blocked-cascade least squares on F with all non-hydrogen atoms anisotropic. Methyl H atoms were constrained to give C–H = 0.96 Å and H–C–H = 109.5°; CH_2 and tantalum-bound H were freely refined; $U(H) = 1.2U_{eq}(C)$ except for the freely refined isotropic U for the hydrides.[18b] Residuals of $R = 0.0253$, $R_w = 0.0193$, and $S = 0.97$ were obtained, with weighting[18c] $w^{-1} = \sigma_c^2(F) + 9 + 29G + 8G^2 - 23S + 19S^2 - 65GS$, where $G = F_o/F_{max}$ and $S = \sin\theta/\sin\theta_{max}$, for 116 refined parameters.

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The First Salt- and Solvent-Free Monocyclopentadienyl Lanthanide Dialkyl Complex. X-ray Structure Determinations of $La(\eta^5\text{-}C_5Me_5)[CH(SiMe_3)_2]_2$ and of Its Tetrahydrofuran Adduct: Compounds Containing Agostic Si–C Bonds

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Summary: The synthesis and single-crystal X-ray structure determinations of the first salt- and solvent-free monocyclopentadienyl lanthanide alkyl complex $La(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}_2$ and of its THF adduct precursor are reported. These complexes contain unusual agostic Si–C bonds that facilitate stabilization of the unsaturated lanthanum center. We also report a novel and simple chemical method to remove coordinated THF from highly reactive, electrophilic organolanthanide complexes.

Olefin polymerization is of considerable commercial interest. We have previously reported[1] the synthesis, characterization, and molecular structures of some mo-

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[1] Van der Heijden, H.; Pasman, P.; de Boer, E. J. M.; Schaverien, C. J.; Orpen, A. G., submitted for publication in *Organometallics*.