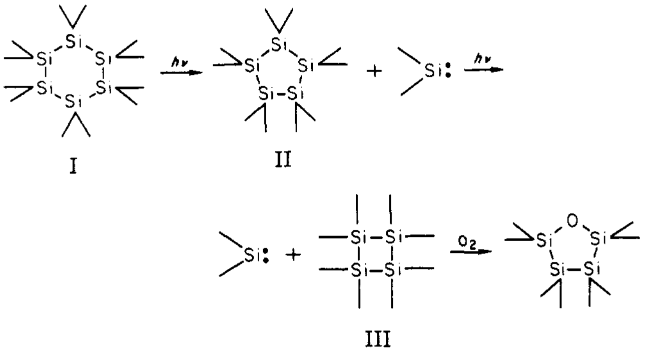
Table I. Products Derived from Photolysis of 1,4,5,6-Tetraphenyl-2,3-benzo-7,7-dimethyl-7-silanorbornadiene, IV, in Benzene Solutions of Various Substrates at 25 °C

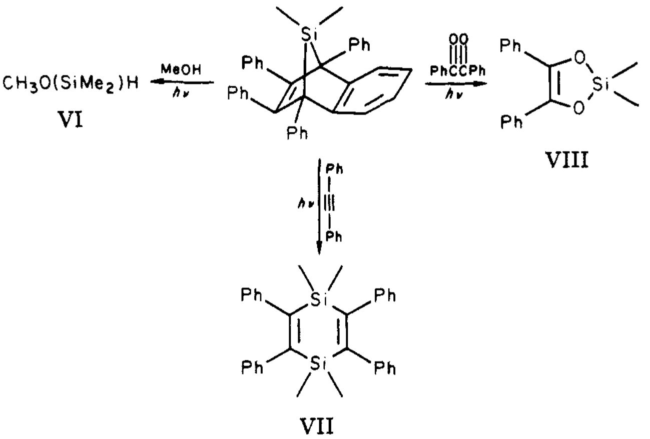
substrate (M)	[IV], M	product	conversn of IV,[a] %	product yield,[a] %
methanol (0.5)	0.20	VI	66	>90
diphenylacetylene (0.05)	0.02	VII	25	~5[b]
benzil (0.03)	0.02	VIII	57	85

[a] By GC analysis and NMR analysis. The samples were all photolyzed under the same conditions. [b] A wide variety of other products were also formed each in low yield and included *cis*- and *trans*-1,2-diphenylethylene.

Scheme I



Scheme II



methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (1.5 g, 3.6 mmol)[14] was added to magnesium (0.2 g, 8.3 mmol, activated by iodine) in dry tetrahydrofuran (30 mL) under argon. To this mixture was added 2-bromofluorobenzene (1.5 g, 8.6 mmol) dropwise with stirring at 0–5 °C. The mixture was warmed to room temperature after which the stirring was continued for 2 h, and it was finally heated at 40 °C for 30 min. The tetrahydrofuran was evaporated and was replaced by methylene chloride (20 mL). Unreacted magnesium was filtered off, and ethanol (20 mL) was added to the filtrate. Cooling caused IV (1.48 g, 83% yield) to crystallize as a while solid. Further recrystallization from ethanol did not change the melting point (232–233 °C) [lit.[14] 232.5–233.5 °C): δ ($CDCl_3$) 0.08 (s, 3 H, SiMe), 0.59 (s, 3 H, SiMe), 7.3–8.7 (m, 24 H, 5Ph). The product was found to be insensitive toward oxygen and moisture.

While thermolysis of IV at 300 °C has been used as a thermal source of dimethylsilylene,[14] its photochemistry does not appear to have been investigated. We used standard scavengers to trap dimethylsilylene and found that photolysis (λ = 250 nm) of a mixture of IV (10^{-2} M) with methanol[9] (0.5 M), diphenylacetylene[14] (0.05 M), or benzil[5] (0.03 M) at 37 °C gave the corresponding adducts VI, VII, and VIII, respectively, as shown in Scheme II. Further details are given in Table I. Compounds V, VI, VII, and VIII were identified by their ^{1}H NMR and from parent ions in their GC/mass spectra or by comparison with authentic samples.

Photolysis of IV in an isopentane glass at −196 °C gave rise to the uv-visible absorption spectrum of V, indicating that decomposition had occurred but it did not give rise to a band at 450 nm that has previously been associated with dimethylsilylene.[6] Laser flash photolysis of IV in cyclopentane solvent at room temperature gave a transient spectrum similar to that obtained by photolyzing the naphthalene V alone under the same conditions.[17] The transient, which had absorption maxima at 470 and 350 nm, had a lifetime of 2.5 μs and was quenched by oxygen. We therefore assign it to triplet V. The quantum yield for its formation was independent of the flow rate used to sweep products formed from sample cell and was directly proportional to the laser power. We therefore conclude that triplet V is formed directly from photoexcited IV within 20–30 ns of the start of laser pulse (eq 2). Moreover, since dimethylsilylene was presumably formed in its singlet ground state,[7] spin conservation dictates that the photoexcited state of IV that leads to these products must itself be a triplet.

$$IV \xrightarrow{h\nu} IV^T \rightarrow \rightarrow V^T + Me_2Si: \qquad (2)$$

In conclusion 1,4,5,6-tetraphenyl-2,3-benzo-7,7-dimethyl-7-silanorbornadiene can be easily synthesized in high yield as stable, white crystalline solid that is an excellent photochemical source of dimethylsilylene at room temperature.

Acknowledgment. We thank Dr. J. C. Scaiano for the use of the laser flash photolysis equipment and Dr. J. Lusztyk for help in its operation. Thanks are also due to Drs. W. P. Neumann and W. P. Weber for helpful discussions.

Registry No. IV, 18816-24-5; V, 751-38-2; VI, 18033-75-5; VII, 751-37-1; VIII, 55629-19-1; dimethylsilylene, 6376-86-9; 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene, 7641-40-9; 2-bromofluorobenzene, 1072-85-1.

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(17) In fact, the ratio of optical densities for the 350- and 470-nm bands was 3.1 for the photolysis of IV vs. 2.1 for V. This implies the presence of a second transient in the photolysis of IV which absorbs at 350 nm and has a lifetime of ~2.5 μs. It is possible that this additional absorption is due to dimethylsilylene.

Synthesis of an η^2-CH(SMe) Carbene Ligand by Protonation of the Carbyne in $[HB(pz)_3](CO)_2W(\equiv CSMe)$. A Possible Model Step in CO Hydrogenation

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Summary: Protonation of $[HB(pz)_3](CO)_2W(\equiv CSMe)$ with strong acids gives $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ in

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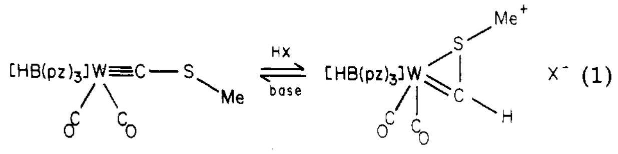
which the carbene ligand is bonded to the metal through both the C and S atoms, as shown by an X-ray diffraction study. A similar protonation of the hydroxycarbyne M≡COH to give M[η^2-CH(OH)] is proposed as a possible step in the catalytic hydrogenation of CO.

Terminal carbyne ligands in transition-metal complexes are frequently observed to undergo attack at the carbyne carbon by a variety of nucleophiles.[1] In contrast, electrophilic attack is far less common; in fact, there are only two examples of H^+ addition to the carbyne carbon. Schrock and co-workers[2] described the protonation of W(≡CH)$(PMe_3)_4$Cl with CF_3SO_3H to give W(=CH_2)$(PMe_3)_4Cl^+$, which was believed to contain "a grossly distorted alkylidene ligand". Roper and co-workers[3] reported the reaction of Os(≡CR)(Cl)(CO)$(PPh_3)_2$, where R = *p*-tolyl, with HCl that resulted in the formation of Os(=CHR)$(Cl)_2$(CO)$(PPh_3)_2$. In this communication, we describe the protonation of the carbyne carbon in the hydrotris(pyrazolylborate)mercaptocarbyne complex $[HB(pz)_3](CO)_2W(\equiv CSMe)$, **1**. This reaction leads to the C- and S-coordinated mercaptocarbene complex $[HB(pz)_3](CO)_2W[\eta^2\text{-CH(SMe)}]^+$, **2**, whose structure has been established by an X-ray diffraction investigation.

The addition of equimolar CF_3SO_3H to a CH_2Cl_2 solution of **1**[4] at 0 °C produces an immediate color change from orange to the violet color of product **2**, according to eq 1.



1 **2**

X = CF_3SO_3, BF_4, CF_3CO_2; base = NaH, K_2CO_3, Et_3N

After the solvent is removed under vacuum, the resulting violet solid is washed several times with hexane. Violet crystals of **2** are obtained from CH_2Cl_2/Et_2O at −20 °C in essentially quantitative yield. The compound is characterized by elemental analysis, solution conductivity, and IR, ^1H and ^{13}C NMR, and fast atom bombardment mass spectra.[5] Reaction 1 also occurs with $HBF_4 \cdot Et_2O$ and CF_3CO_2H but not with acetic acid.

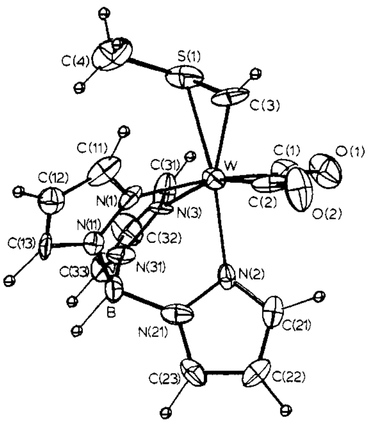
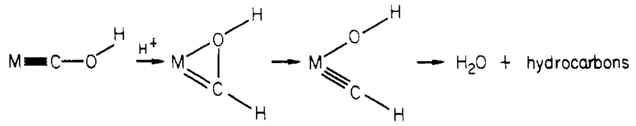


Figure 1. ORTEP plot of $\{[HB(pz)_3](CO)_2W[\eta^2\text{-CH(SMe)}]\}CF_3SO_3$, **2**. Selected bond distances (Å) and angles (deg) are W–S(1) = 2.481 (6), average W–N = 2.20, average W–CO = 2.06, W–C(3) = 1.93 (2), S(1)–C(3) = 1.72 (2), S(1)–C(4) = 1.85 (2), S(1)–W–C(3) = 43.8 (6), average N–W–N = 82.4, C(1)–W–C(2) = 89.3 (8), W–S(1)–C(3) = 51.0 (7), W–S(1)–C(4) = 110.5 (7), W–C(3)–S(1) = 85.3 (8), C(3)–S(1)–C(4) = 105.9 (10).

Scheme I



An X-ray structure determination[6] of a deep violet single crystal of **2** reveals the η^2-carbene ligand bonded to the tungsten through both the C and S atoms as shown in Figure 1. The W–C(3) bond distance (1.93 (2) Å) is between the W–C(sp^2) single bond distance (2.32 (2) Å) in $Cp(CO)_3W\text{-}Ph$[7] and the W≡C triple bond distances (1.82 (2), 1.81 (2), and 1.81 (1) Å) in $Cp(CO)_2W\equiv C$(*p*-tolyl),[8] $Cp(CO)_2W\equiv CSiPh_3$,[9] and $Cp(CO)(Ph_3P)W\equiv CSPh$,[10] respectively; however, the W–C(3) distance is closer to the W=C distances in the carbene complexes $Cp(CO)_2W\!=\!C(CF_3)C(CF_3)COSMe)$, 1.962 (8) Å, and $Cp_2W\!=\!CHPh$, 2.05 (2) Å.[11] This suggests that the W=C(3) bond is best represented as a carbene-like interaction. The W–S(1) distance (2.481 (6) Å) is very similar to that (2.440 (2) Å) in $Cp(CO)_2W[C(CO_2Me)\!=\!C(CO_2Me)C(O)SMe]$.[12] The C(3)–S(1) distance (1.72 (2) Å), although considerably shorter than C(4)–S(1), 1.85 (2) Å, appears to be shorter than an S–C(sp^2) distance as in $C(S\text{-}Ph)_4$, 1.776 Å average;[13] however, the magnitude of the standard deviation

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(1) For example, see the following: (a) Fischer, E. O.; Clough, R. L.; Besl, G.; Kreissl, F. R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 543. (b) Fischer, E. O.; Stückler, P.; Kreissl, F. R. *J. Organomet. Chem.* **1977**, *129*, 197. (c) Fischer, E. O.; Meineke, E. W.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 1140. (d) Fischer, E. O.; Ruhs, A.; Kreissl, F. R. *Ibid.* **1977**, *110*, 805. (e) Fischer, E. O.; Frank, A. *Ibid.* **1978**, *111*, 3740. (f) Fischer, E. O.; Schambeck, W.; Kreissl, F. R. *J. Organomet. Chem.* **1979**, *169*, C27. (g) Fischer, E. O.; Schambeck, W. *Ibid.* **1980**, *201*, 311. (h) Kostic, N. M.; Fenske, R. F. *J. Am. Chem. Soc.* **1981**, *103*, 4677. (i) Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 489.

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(4) Complex 1 was prepared from $HB(pz)_3W(CO)_2(CS)^-$ and MeI as reported previously: Greaves, W. W.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 2983.

(5) $\{[HB(pz)_3]W(CO)_2[\eta^2\text{-CH(SMe)}]\}CF_3SO_3$, **2**: IR($CH_2Cl_2$) ν(CO) 2067 (m), 1996 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) 12.93 (s, CH), 7.93, 7.87 (m, H3 and H5 of pz), 6.49 (t, J = 2.44 Hz, due to overlapping d of d, H4 of pz), 2.39 (SMe); ^{13}C NMR (CD_2Cl_2) 227.75 (WC), 212.32 (CO), 212.76 (CO), 146.89, 146.02, 145.59 (C3 of pz), 138.57, 138.22, 138.05 (C5 of pz), 108.75, 108.14 (C4 of pz), 28.23, 27.02 (SMe); conductivity (CH_2Cl_2) Λ = 33.93 Ω^{-1} cm^2 mol^{-1} at 10^{-3} M (1:1 electrolyte); MS (FAB), parent cation at *m/e* 513. Anal. Calcd for $C_{14}H_{14}BN_6O_5S_2WF_3$: C, 25.40; H, 2.13; N, 12.69. Found: C, 25.31; H, 2.47; N, 12.71.

(6) Crystallographic data for **2**: mol wt 662.08; monoclinic, space group $P2_1/c$; a = 9.841 (4) Å, b = 11.374 (3) Å, c = 21.305 (9) Å, β = 109.15 (4)°, V = 2170.5 Å^3, ρ_{calcd} = 2.026 g/cm^3 for Z = 4 at −40 °C, μ = 58.9 cm^{-1} (Mo Kα). Diffraction data were collected at −40 °C using a Syntex $P2_1$ automated diffractometer (Mo Kα radiation, ω scan) and corrected for absorption (3931 measured reflections with $2\theta \leq 50°$; 2111 observed reflections with $I \geq 1.5\sigma_I$ were used for structural solution and refinement). The structure was solved by analysis of a sharpened Patterson map followed by successive electron density maps to locate the lighter atoms and then refined by a combination of block and full matrix refinement techniques; all non-hydrogen atoms anisotropic; hydrogen atoms at calculated positions. The anion exhibited disorder in the oxygen and fluorine atom positions. R = 0.072 and R_w = 0.050 ($w = \sigma_F^{-2}$).

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does not permit a definite conclusion. While no other η^2-CH(SMe) complexes have been reported, the C–S distances in several η^2-CH_2SMe complexes are known; the examples closest to the present system are $Cp(CO)_2Mo(\eta^2\text{-}CH_2SMe)$[14] and $[Me_2Ga(N_2C_3H_3)[OCH_2CH_2NMe_2)]Mo(CO)_2(\eta^2\text{-}CH_2SMe)$[15] that have C–S distances of 1.78 (1) and 1.744 (3) Å, respectively. The dihedral angle between the C(3)–S(1)–C(4) and W–C(3)–S(1) planes is 103.8°.

The addition of bases, NaH in THF and K_2CO_3 or Et_3N in CH_2Cl_2, to **2** results in the regeneration of carbyne complex **1** (eq 1) in 10% yield. This deprotonation of **2** represents a new route to carbyne complexes. Other products of this reaction have not been identified.

Recently, Nicholas[16] argued for the likely involvement of hydroxycarbyne species M≡COH as intermediates in catalytic hydrogenation reactions of CO. Using this species, he rationalizes the formation of alcohols and methyl formate in these processes. The studies reported in this communication suggest a mechanism (Scheme I) whereby the hydroxycarbyne intermediate may also account for the formation of hydrocarbons. Proton transfer to the carbyne C, as in eq 1, would give an η^2-CH(OH) group that could undergo C–OH bond cleavage to (HO)-M≡CH. This latter species would be expected to react with hydrogen to give H_2O and CH_4, as well as higher hydrocarbons through carbene (CH_2) and methyl (CH_3) intermediates by mechanisms suggested previously.[17-19] Thus, M≡COH, M[η^2-CH(OH)], and (HO)M≡CH intermediates are reasonable alternatives to those commonly proposed[17-19] for catalytic reactions of CO and H_2.

Acknowledgment. This material is based upon work supported by the National Science Foundation under Grant CHE-8100419 (R.J.A.). X-ray diffraction studies were supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Materials Sciences Division, under Contract W-7405-ENG-82.

Supplementary Material Available: Tables of positional and thermal parameters, all bond distances and angles, and structure factors (8 pages). Ordering information is given on any current masthead page.

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Synthesis and X-ray Structure of the $[Fe_4S_4(CO)_{12}]^{2-}$ Ion: An Example of Intermolecular Disulfide Formation by the $(\mu\text{-}S)_2Fe_2(CO)_6$ Unit

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Summary: Reaction of $(\mu\text{-}S)_2Fe_2(CO)_6$ with 1 equiv of $LiEt_3BH$ in tetrahydrofuran produces the green complex anion $[Fe_4S_4(CO)_{12}]^{2-}$ (**1**). The crystal structure of the Ph_4As^+ salt of **1** shows that the anion contains two $[(\mu\text{-}S)_2Fe_2(CO)_6]^-$ units linked by an S–S bond.

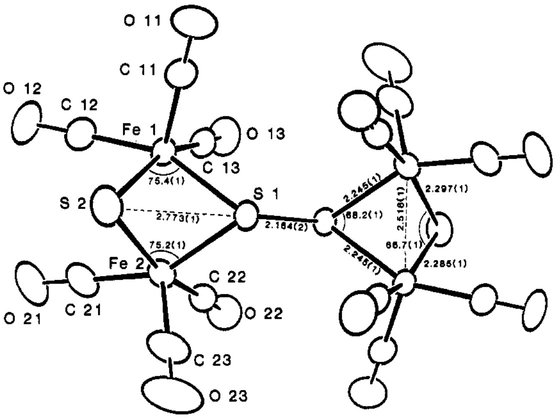

Figure 1. Structure of the $[Fe_4S_4(CO)_{12}]^{2-}$ ion, showing the atomic labeling scheme and selected distances and angles.

The chemistry of transition-metal carbonyl complexes containing heteroatoms is of substantial current interest.[2] One particularly well-characterized system is the complex (μ-dithio)bis(tricarbonyliron), originally reported by Brendel[3] and by Hieber and Gruber.[4] Seyferth et al.[5] have demonstrated that the S–S bond of the parent compound exhibits reactions typical of organic disulfides, the most notable being reduction to produce a dianion that undergoes reactions comparable to those of an organic dithiolate, e.g., alkylation,[5-7] protonation,[7,8] metalation,[5,7-10] and addition to olefins.[11] Oxidative addition of the S–S bond to low-valent metals has also been reported,[2b,12-14] providing a route to heterometallic clusters. We report herein the synthesis and structure of a new tetranuclear cluster, the $[Fe_4S_4(CO)_{12}]^{2-}$ ion, which demonstrates the ability of the $(\mu\text{-}S)_2Fe_2(CO)_6$ unit to form *intermolecular* disulfide bonds in addition to the known *intramolecular* disulfide of the parent compound.

Slow addition of $LiEt_3BH$ (1 equiv) in THF to a solution of $(\mu\text{-}S)_2Fe_2(CO)_6$ in THF at −78 °C produces a deep green solution; addition of $Ph_4As^+Cl^-$ (1 equiv) in a minimum volume of acetonitrile and slow warming to −20 °C results in the separation of deep green needles of the Ph_4As^+ salt of **1** in 75% yield.[15] The compound is stable to air in the solid state for brief periods but decomposes slowly in so-

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[1] Alfred P. Sloan Foundation Fellow, 1981–1984.

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(15) IR spectrum (CH_3CN): ν_{CO} 1955 (vs), 1997 (vs), 2012 (s) cm^{-1}. Electronic spectrum (DMF): λ (ε) 608 nm (690 M^{-1} cm^{-1}), 440 (3980), 310 (sh).