Preparation of Organofunctional Bis(stannyl)methanes. Intramolecular Coordination in the Halo Derivatives

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Received November 23, 1982

The preparation of a series of 3,3-bis(trimethylstannyl)-, 3,3-bis(halodimethylstannyl)-, and 3,3-bis(dihalomethylstannyl)propyl derivatives having carboxyl, hydroxy, acetoxy, and sulfoxy as functional groups is described. Intramolecular coordination in the bromostannyl acetates and sulfoxides was examined. 3,3-Bis(bromodimethylstannyl)propyl acetate showed no evidence of coordination in the solid state or in acetonitrile as shown by IR study; the bis(dibromomethylstannyl) analogue showed coordination of the acetate carbonyl to tin in the solid state but not in acetonitrile. Each of the corresponding sulfoxides showed coordination between oxygen and tin in the soid state and in solution. The coordination is probably by way of bridging between the geminal tin atoms rather than coordination to a single tin; it was shown that the complexes are stable on the ^{1}H, ^{13}C, and ^{119}Sn time scales at normal operating probe temperatures.

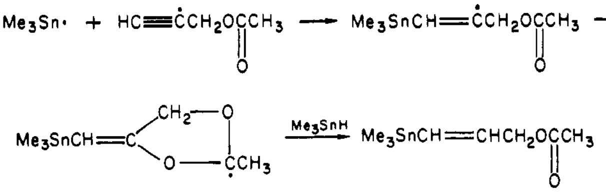
Organostannanes bearing organic functions (organofunctional organostannanes) are of interest because they can provide information concerning structure–reactivity relationships, are useful as intermediates in the synthesis of more complex structures, and may have commercial value. A major contribution toward the preparation of compounds of this type came from the work of van der Kerk and Noltes[1] who showed that hydrostannation of carbon–carbon multiple bonds could be conducted in the presence of various functional groups. These functional groups can be used in the synthesis of more complex organostannanes. They can also be used in the study of intramolecular donor–acceptor interactions if the tin atom bears sufficiently electronegative groups to impart Lewis acidity and the organic function has Lewis base character. Early work on this aspect has been reviewed by Omae.[2] A number of more recent studies have also been made, particularly with ester and ketone carbonyls as donor groups.[3-14] As part of a broad study of di- and polyorganostannanes we have extended earlier studies on organofunctional halostannanes[3] to those bearing the structural unit Sn_2C–C–C and report here on their synthesis and on some of their properties.

A logical starting point for the preparation of the 3,3-bis(stannyl)propane derivatives would involve the bishydrostannation of propargyl alcohol (eq 1). The mono-

$$2R_3SnH + HC{\equiv}CCH_2OH \rightarrow (R_3Sn)_2CHCh_2CH_2OH \qquad (1)$$

hydrostannation with triethylstannane was previously conducted by Leusink, Budding, and Marsman,[15] but the product obtained in 70% yield contained 25% of the 2,1 adduct, along with the desired 1,2 adduct. We found that the bishydrostannation with trimethylstannane led to a mixture that could not be resolved with reasonable effort.

However, use of propargyl acetate instead of the alcohol in the photoinduced bishydrostannation gave a high yield of product from which 3,3-bis(trimethylstannyl)propargyl acetate (6) could be readily obtained in 70% yield. Thus, the acetoxy group has a powerful directive effect on the regioselectivity of the hydrostannation. This may be attributable to a stabilizing effect on the vinylic radical which results from initial attack on the terminal carbon of the triple bond by the organostannyl radical as shown in eq 2. Hydrogen transfer from Me_3Sn–H to vinylic carbon,



(2)

accompanied by cleavage of the C–O bond, would lead to the 3-(trimethylstannyl)allyl acetate. In the subsequent hydrostannation of this product the same kind of argument could be applied for the stabilization of the intermediate radical leading to 3,3-bis(trimethylstannyl)propyl acetate (6) in the high yield observed.

3,3-Bis(chlorodimethylstannyl)propyl acetate (5) was also prepared by hydrostannation with chlorodimethylstannane using photoinitiation. The yield of product was only 40% so 6 was used for further transformation to the halostannanes and other derivatives. These are shown in Scheme I.

Treatment of 6 with 2 molar equiv of bromine in carbon tetrachloride provided bis(bromodimethylstannyl)propyl acetate (7) in 98% yield. Further treatment with two additional molar equivalents of bromine provided 70% of 3,3-bis(dibromomethylstannyl)propyl acetate (8). These brominolyses could also be conducted in methanol, but the product proved to be the alcohol rather than the acetate unless it was worked up as soon as the reaction with bromine was complete. Clearly a transesterification with methanol occurs; this is a fast process undoubtedly due to Lewis acid catalysis, probably intramolecular, by the bromostannyl functions.

Oxidation of 1 with chromic acid occurred selectively at the hydroxyl-bearing carbon leading to an 80% yield of the carboxylic acid 3. Conversion of 1 to the tosylate, followed by treatment with sodium thioethoxide, led to 3,3-bis(trimethylstannyl)propyl ethyl sulfide (9). Oxidation

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[1] Noltes, J. S.; van der Kerk, G. J. M. "Functionally Substituted Organo-tin Compounds", Tin Research Institute: Greenford, England, 1958.

[2] Omae, I. *Rev. Silicon, Germanium, Tin Lead Compds* 1972, *1*, 60.

[3] Kuivila, G. H.; Dixon, J. E.; Maxfield, P. E.; Scarpa, N. M.; Topka, T. M.; Tsai, K.-H.; Wursthorn, K. R. *J. Organomet. Chem.*, 1975, *86*, 89.

[4] Abbas, S. Z.; Poller, R. C. *J. Chem. Soc., Dalton* Trans. 1974, 1769.

[5] Burley, J. W.; Hutton, R. E.; Oakes, V. *J. Chem. Soc., Chem. Commun.* 1976, 803.

[6] Hutton, R. E.; Burley, J. W.; Oakes, V. *J. Organomet. Chem.* 1978, *156*, 369.

[7] Weichmann, H.; Tszchach, A. *Z. Anorg. Allg. Chem.* 1979, *458*, 291.

[8] Hobbs, L. A.; Smith, P. J. *J. Oganomet. Chem.* 1981, *206*, 59.

[9] Maughan, D.; Wardell, J. L. *J. Organomet. Chem.* 1981, *212*, 59.

[10] Das Kumar, V. G.; Weng, N. H. *Inorg. Chim. Acta* 1981, *49*, 149.

[11] Haigh, R. M.; Davies, A. G.; Tse, M.-W. *J. Organomet. Chem.* 1979, *174*, 163.

[12] Gielen, M. *J. Organomet. Chem.* 1981, *214*, 191.

[13] Burley, J. W.; Hutton, R. E. *J. Organomet. Chem.* 1981, *216*, 165.

[14] Podesta, J. C.; Chopa, A. B. *J. Organomet. Chem.* 1982, *229*, 223.

[15] Leusink, A. J.; Budding, H. A.; Marsman, J. W. *J. Organomet. Chem.* 1967, *9*, 285.

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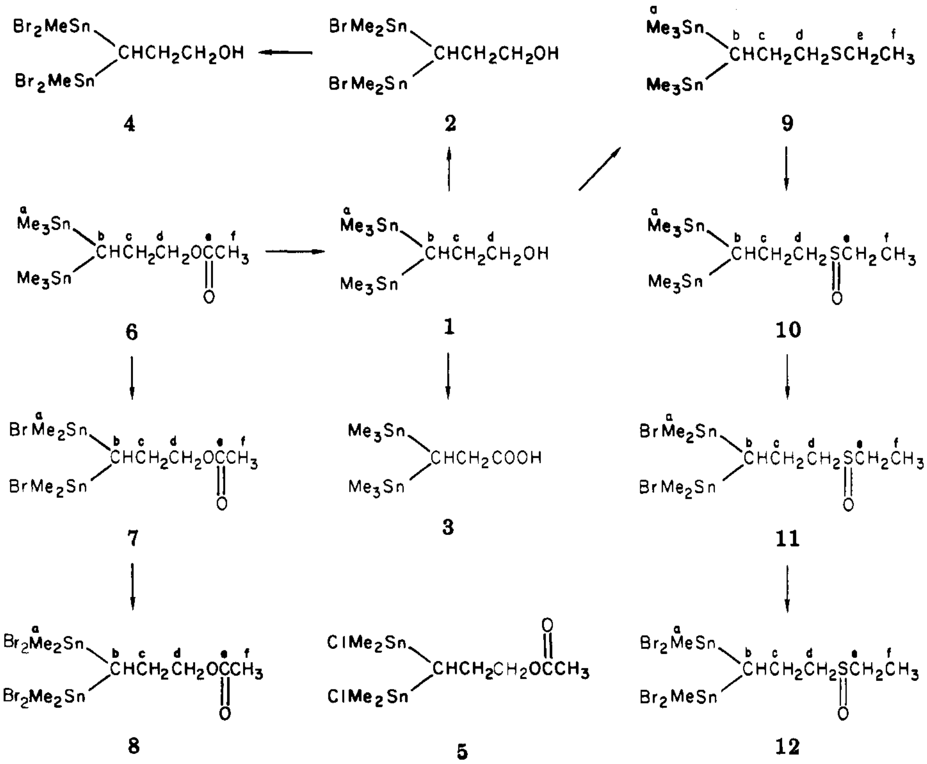
Scheme I



of **9** with hydrogen peroxide yielded the sulfoxide **10**. Treatment of **10** with 2 mol of bromine in carbon tetrachloride provided 98% of 3,3-bis(bromodimethylstannyl)propyl ethyl sulfoxide (**11**). Further treatment of **11** with two additional moles of bromine yielded 70% of 3,3-bis(dibromomethylstannyl)propyl ethyl sulfoxide (**12**).

Similarly, treatment of alcohol **1** with 2 molar equiv of bromine yielded 91% of 3,3-bis(bromodimethylstannyl)propanol (**2**); and bromination, in a very slow reaction, with two additional moles of bromine gave 73% of 3,3-bis(dibromomethylstannyl)propanol (**4**).

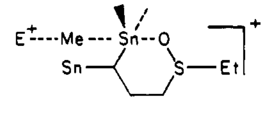
In the bromine cleavages above the reaction occurs only at the methyl–tin bond. This contrasts with the earlier reports that cleavage with bromine and other electrophiles of bis(trimethylstannyl)methane (**13**) occurs at both the tin–methyl and the tin–methylene bonds.[16,17] We have reexamined the cleavage of **13** and of 2,2-bis(trimethylstannyl)propane (**14**) with bromine and have verified these observations. Treatment of **13** with 1 molar/equiv of bromine in CCl_4 yielded product with signals in the ^{1}H NMR spectrum for Me_3SnBr (δ 0.73 ($^2J(^{119}Sn–H)$ = 57.5 Hz), for CH_3Br (δ 2.52), for Me_3SnCH_2Br (δ 0.20 (^2J: 52.0 Hz), 2.4 (^2J = 17 Hz)), for unreacted **13**, and for $Me_3SnCH_2Me_2SnBr$. Integrations of the ^{1}H NMR signals indicated 50% cleavage by each of the two modes. Treatment of **14** under the same conditions yielded signals for CH_3Br and for Me_3SnBr as indicated above, with 66% reaction by Sn–Me cleavage and 33% Sn–methine cleavage. Thus the more hindered substrate **14** provides slightly more Sn–CH_3 cleavage but this is less than that observed for compounds **6** and **10**. A rationale is to be sought elsewhere.

The facility with which the acetate **6**, the sulfoxide **10**, and the alcohol **1** undergo cleavage is a clear indication of intramolecular nucleophilic catalysis of the electrophilic reactions as has been observed before in similar structures. However, this alone cannot account for the regioselectivity, but it can be rationalized if one considers the nature of the transition state for such a catalytic reaction. A schematic representation is shown below in which E^+ represents the electrophile reacting with the sulfoxide at an Sn–Me bond.

Table I. Infrared Spectra of Selected Esters and Sulfoxides

compd	$\nu_{C=O}$
6	1745 (neat), 1736
7	1740 (KBr), 1736[a]
8	1708 (KBr), 1738[a]
	ν_{SO}
10	1054 (neat), 1056[a]
11	952 (KBr), 966[a]
12	953 (KBr), 964[a]

[a] 10% in CH_3CN.



The transition state is assumed to be pseudo trigonal-pyramidal with preferential attack by E^+ occurring at an axial methyl group with the catalyzing sulfoxide oxygen in the other axial position. In this way the two most electronegative groups are in the most stable positions. Such an orientation is not possible for the methine carbon bonded to the two tin atoms because the Sn–C–O angle in a six-membered ring must be considerably less than the preferred 180° for a diaxial arrangement.

As previous studies have shown, intramolecular coordination may occur between electrophilic tin and donor atoms within the same molecule if they are suitably disposed.[2-6,10,13,14] Those esters that have been found to undergo intramolecular coordination with halotin grops have structures such that the rings formed were either five-membered or six-membered. Intramolecular coordination

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(16) Karol, T. J.; Hutchinson, J. P.; Hyde, J. R., Kuivila, H. G.; Zubieta, J. A. *Organometallics* **1983**, *2*, 106.

(17) Kaesz, H. D. *J. Am. Chem. Soc.* **1961**, *83*, 1514.

Table II. ^{13}C NMR Chemical Shifts and ^{13}C-^{119}Sn Coupling Constants of Organofunctional Bis(stannyl)methanes[a]

	carbon[b]						
compd	a	a′	b	c	d	e	f
6[c]	−9.71		2.22	29.5	67.3	170.3	20.61
	^{1}(317.4)		^{1}(288.1)	^{2}(20.8)	^{3}(48.9)		
7[c]	1.47		21.6	28.9	67.9	170.9	21.0
	^{1}(389.4)		^{1}(322.3)	^{2}(23.2)	^{3}(51.3)		
8[d]	15.1		44.0	29.8	65.9	204.6	21.0
	^{1}(547.1)		^{1}(476.5)	^{2}(35.3)	^{3}(66.2)		
9[c]	−8.60		6.94	31.4	36.3	25.9	14.92
	^{1}(312.5)		^{1}(289.3)	^{2}(20.8)	^{3}(52.5)		
10[c]	−8.95		5.72	24.0	55.7	54.2	6.30
	^{1}(319.8)		^{1}(278.3)	^{2}(21.8)	^{3}(43.9)		
11[c]	4.71	5.34	28.7	25.6	50.4	44.8	6.47
	^{1}(471.2)	^{1}(439.6)	^{1}(400.4)	^{2}(20.8)	^{3}(54.9)		
			$^{1'}$(382.1)		$^{3'}$(34.2)		
12[e]	19.82	20.47	62.1	27.0	45.9	44.5	6.88
	^{1}(703.0)	^{1}(714.8)	^{1}(644.2)	*f*	*f*		
			$^{1'}$(638.3)				
12[g]	19.71	20.52	61.73	26.62	45.87	44.47	6.66
	^{1}(693.4)	^{1}(688.5)	$^{1'}$(644.2)[h]	^{2}(31.7)[h]	^{3}(73.2)[h]		

[a] Chemical shifts in ppm from Me_4Si; coupling constants (Hz) in parentheses with superscript to denote number of intervening bonds. [b] Carbon atoms identified on structures in scheme. [c] In CH_2Cl_2 with internal $CDCl_3$ lock. [d] In $CDCl_3$. [e] In $(CD)_3CO$. [f] Coupling not isolated due to overlap with CD_3 signals. [g] In CD_3CN. [h] Sn–C satellites broadened, but unresolved.

between a halotin center and an ester carbonyl leading to a seven-membered ring has not been reported. This would be a requirement in compounds **7** and **8**. The results of IR studies are shown in Table I. It can be seen that the bis(monobromodimethyl)stannyl derivative **7** shows no evidence for such coordination in the solid state or in acetonitrile, the carbonyl stretching frequencies being close that of the tetraalkylated tin derivative **6**. On the other hand, the bis(dibromomethyl)stannyl derivative does show a shift of the frequency from 1745 to 1708 cm^{-1} in KBr, but this coordination is not evident in acetonitrile. Therefore, any enthalpy decrease resulting from coordination is insufficient to overcome the necessary entropy loss on cyclization in solution.

Sulfoxides have not been included in previous studies. Our observations which are shown in Table I show that the S–O frequency of liquid **10** at 1054 cm^{-1} is shifted to 952 and 953 cm^{-1} (KBr) in **11** and **12**, respectively. In acetonitrile the shifts are again to lower frequencies (966 and 964 cm^{-1}) as compared to 1056 cm^{-1} for **10**. Thus the coordination present in the solid state persists in solution, despite the moderately strong coordinating solvent.

The NMR spectra provide further information concerning structures of compounds **6**–**12**. In the proton spectra **6**, **9**, and **10** show normal chemical shifts (ca. 0.1 ppm) and coupling constants (ca. 51 Hz) for the methyl protons. Replacement of methyl by bromine moves the chemical shifts downfield and increases the coupling constants as expected for the acetates **7** and **8**. However, the pattern in **11** and **12** is quite different. In **11** two methyltin proton signals are observed at 0.89 and 0.93 ppm with similar coupling constants (66 and 60 Hz, respectively). In **12** the methyl proton signals appear at 1.50 and 1.54 ppm with coupling constants of 92 Hz in each case. These observations reveal that the two tin atoms are in different environments. Confirmation of this is found in the ^{13}C spectra as shown in Table II. Compound **11** shows methyl carbons on tin at 4.71 and 5.34 ppm with coupling constants to tin of 471 and 440 Hz. The methine carbon C^b shows coupling to two different tin atoms, but these are not resolved in the two-bond coupling to C^c. Relatively large differences observed in the three-bond couplings of 54.9 and 34.2 Hz to C^d are indicative of different dihedral angles about the C^b–C^c bond between C^d and the two tins. In the bis(dibromomethyl) analogue the observations are similar, but a little less definitive. Two methyl carbons are indicated on tin with similar chemical shifts: 19.82 and 20.27 ppm in acetone-d_6 and 19.71 and 20.52 ppm in deuterioacetonitrile. In acetone-d_6 C^b at 62.1 ppm showed couplings at 655 and 638 Hz, but the ^{119}Sn satellites for C^c and C^d were in the same region as the ^{13}C–^{2}H septet region; they could not be assigned unambiguously. In acetonitrile, the differences between the couplings to the two kinds of tin were too small to be resolved for C^b, C^c, and C^d. One novel feature of the parameters of the two kinds of methyl carbons in **11** and **12** are the similarities in the chemical shifts and coupling constants to C^a and $C^{a'}$ in each case.

Futher confirmation of the nonidentity of the two tins in **11** and **12** was obtained from the ^{119}Sn magnetic resonance spectra in acetonitrile solution. Compound **11** showed two lines, broadened by the quadrupolar bromine atoms, at 8.22 and 20.05 ppm, relative to tetramethyltin. Compound **12** also showed two lines, still broader, at −8.02 and 2.01 ppm.[18] Coupling constants could not be observed due to the width of the lines. The differences of about 12 and 10 ppm in chemical shifts between the two tins in **11** and **12**, respectively, makes more obvious the differences between them, which appears to be small as measured by the ^{1}H and ^{13}C chemical shifts and coupling constants.

Several structures may be conidered to account for the inequivalence of the three kinds of nuclei. In one of these, coordination of the sulfoxide oxygen occurs to only one of the tin atoms as in **13a** or **13b**. In this case, the differences would be due to the presence of tetracoordinate and pentacoordinate tins; however, one would expect differences in the NMR parameters than are observed. Also the methyl groups on the pentacoordinate tin in **11** would provide two sets of methyl signals, and those on the tetracoordinate tin would be anisochronous and might also provide two additional sets of signals. If **13a** and **13b** are involved in a rapid exchange the observed two sets of methyl signals would be expected. Another structure to be considered is the oxygen-bridged species **14**. But, in this case the two tins are in different environments, their

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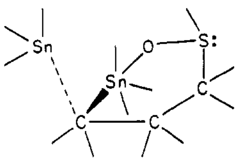
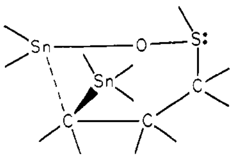
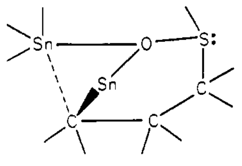
[18] We thank Dr. H. Schwartz of Rensselaer Polytechnic Institute for obtaining the ^{119}Sn spectra.



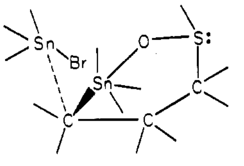
13a



13b



14



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methyl groups do not exchange, and the result would be two pairs of methyl signals. Yet another structure (**15**) has the oxygen coordinated to one tin and one of the bromines on that tin bridging to the other tin. The analysis here is similar to that for **13**: the fixed structure would require twice as many methyl signals as one in which the tin atoms are rapidly exchanging roles. In our earlier work on intermolecular coordination between dimethyl sulfoxide and bis(halostannyl)methanes we have found bridged structures in the solid state and rapid exchange in solution.[16] Although entropy effects would help stabilize cyclic structures in the intramolecular coordination, the rapidly exchanging systems appear more attractive at this juncture.

The molecular weights of **11** and **12** in toluene at 40 °C indicate that they are substantially monomeric as assumed above. The experimental value with an error of ±10% obtained by vapor pressure osmometry for **11** was 12% and that for **12** was 22%, higher than that of the monomer.

Experimental Section

General Data. Proton nuclear resonance spectra were obtained at 60 MHz by using a Varian A-60A or EM360A instrument. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane followed in parentheses by the multiplicity, number of protons, coupling constant, and assignment. Proton-tin-119 coupling constants are reported as $^nJ(^{119}\mathrm{Sn{-}H})$ with the superscript donoting the number of bonds intervening between nuclei. Carbon-13 NMR spectra were obtained by using a Bruker WH-90 spectrometer with a B-NC-12 data system. Spectra were recorded in chloroform-*d* as internal lock and as solvent except where noted; Chemical shifts are given in parts per million from internal tetramethylsilane. Gas chromatographic analyses were performed on an F & M Hewlett-Packard Model 5750 or an F & M 720 instrument using a thermal conductivity detector. All analyses were performed on a 6 ft or 17 ft × 0.25 in. copper column packed with 15% SE-30 on Chromosorb W, 60–80 mesh. Melting points and boiling points are uncorrected. Carbon–hydrogen analyses were done by Instranal of Rensselaer, New York.

3,3-Bis(trimethylstannyl)propyl Acetate (6). Into a 100-mL side-arm test tube fitted with a septum and a balloon on the side arm was transferred trimethylstannane (46.2 g, 280 mmol) by syringe after the tube was flushed with nitrogen. To this was added propargyl acetate (13.3 g, 136 mmol). The reaction vessel was then placed in Rayonet Photochemical Reactor with 300-nm lamps. The mixture was cooled periodically during the first 15 min of irradiation, it was then irradiated for 12 h; 5 mL of carbon tetrachloride was added, and a white crystalline material amounting to 11% of the total initial weight of reactants was filtered off. The filtrate was extracted with carbon tetrachloride (100 mL) and water (700 mL).

The organic layer was washed with water (500 mL) and rotary evaporated at ambient temperature and then with heating to 100 °C for 30 min. A low-boiling component distilled at 52 °C (0.02 torr). The product distilled at 89 °C (0.02 torr) (40.6 g, 70%): ^{1}H NMR ($\mathrm{Cl_3CD}$) δ 0.09 (s, 18, $^2J(^{119}\mathrm{Sn{-}C{-}H})$ = 52.0 Hz, $\mathrm{SnMe_3}$), 0.61 (t, 1, J = 7.5 Hz, $\mathrm{CCH(Sn)_2}$), 1.79–2.32 (m, 2, $\mathrm{CCH_2C}$), 4.0 (t, 2, J = 7.0 Hz, $\mathrm{CH_2O}$), 2.01 (s, 3, $\mathrm{CH_3COO}$); IR (neat, cm^{-1}) 1745 (C=O), 530 (SnC).

Anal. Calcd for $\mathrm{C_{11}H_{26}Sn_2O_2}$: C, 30.89; H, 6.14. Found: C, 30.99; H, 6.06.

3,3-Bis(trimethylstannyl)propanol (1). 3,3-Bis(trimethylstannyl)propyl acetate (5.19 g, 12.1 mmol) was placed in a 50-mL round-bottom flask. Water (2 mL), 0.5 mL of 50% sodium hydroxide solution, and a pellet of KOH were added. Enough ethanol was added to obtain a homogeneous solution which was heated at reflux overnight. The product was extracted with pentane (100 mL) and water (500 mL). The organic layer was then washed with water (500 mL), dried over $\mathrm{MgSO_4}$, and filtered and the solvent removed to yield the product as an oil in 95% yield: ^{1}H NMR ($\mathrm{CCl_4}$) δ 0.08 (s, 18, $^2J(^{119}\mathrm{Sn{-}C{-}H})$ = 50.5 Hz, $\mathrm{SnMe_3}$), 0.58 (t, 1, J = 7 Hz, $\mathrm{CH(Sn)_2}$), 1.84–2.19 (m, 2, $\mathrm{CCH_2C}$), 3.48 (t, 2, J = 7 Hz, $\mathrm{CH_2O}$); IR (neat, cm^{-1}) 3350 (b, OH), 520 (SnC).

Anal. Calcd for $\mathrm{C_9H_{24}Sn_2O}$: C, 28.02; H, 6.28. Found: C, 27.90; H, 6.26.

3,3-Bis(bromodimethylstannyl)propanol (2). 3,3-Bis(trimethylstannyl)propanol (4.63 g, 10.8 mmol) was dissolved in 25 mL of $\mathrm{CCl_4}$ and placed in a 500-mL round-bottom flask equipped with a magnetic stirrer. The flask was cooled to 0 °C and the addition of 44.5 mL of a 0.473 M solution of bromine (21.1 mmol) in $\mathrm{CCl_4}$ conducted so as to keep the color of the solution light yellow and the temperature at 0 °C. The solution containing small amount of white solid was allowed to stand 2 h at 0 °C, then warmed to room temperature, concentrated, and warmed until a saturated solution was obtained at 40 °C. The solution was then slowly chilled to −22 °C and filtered. The process was repeated upon the filtrate to afford the purified product (5.1 g, 91%): mp 119.5–120.0 °C; ^{1}H NMR ($\mathrm{Cl_3CD}$) δ 0.87 (s, 6, $^2J(^{119}\mathrm{Sn{-}C{-}H})$ = 63.5, $\mathrm{SnMe_2Br}$), 1.54–2.50 [m, 3, $\mathrm{C}\mathit{CH_2CH}\mathrm{(Sn)_2}$], 3.81 (t, 2, J = 5.5 Hz, $\mathrm{CH_2O}$); IR (neat, cm^{-1}) 3400 (OH), 545 (SnC).

Anal. Calcd for $\mathrm{C_7H_{18}Sn_2Br_2O}$: C, 16.31; H, 3.53. Found: C, 16.40; H, 3.46.

3,3-Bis(trimethylstannyl)propionic Acid (3). 3,3-Bis(trimethylstannyl)propanol (0.234 g, 0.60 mmol) was dissolved in 20 mL of THF. To a solution of $\mathrm{CrO_3}$ (21.3 g, 0.213 mol) in 125 mL of water was slowly added 16 mL of concentrated $\mathrm{H_2SO_4}$ with stirring, causing a green precipitate to separate and then become a second lower layer. The acid was added until the top layer remained a cherry red for several min, and it was separated, diluted with saturated NaCl solution (50 mL), and extracted with ether (25 mL). Removal of the solvent left the product (0.195 g, 80%) as a viscous oil. ^{1}H NMR analysis indicated that no alcohol was present: ^{1}H NMR ($\mathrm{CCl_4}$) δ 0.08 (s, 18, $^2J(^{119}\mathrm{Sn{-}C{-}H})$ = 52.5 Hz, SnMe), 0.70 (t, 1, J = 7 Hz, $\mathrm{CCH(Sn)_2}$), 2.80 (d, 2, J = 7 Hz, $\mathrm{CCH_2COOH}$); IR (neat, cm^{-1}) 1710 (C=O), 530 (SnC).

Anal. Calcd for $\mathrm{C_9H_{22}Sn_2O_2}$: C, 27.04; H, 5.56. Found: C, 27.40; H, 5.77.

Preparation of 3,3-Bis(dibromomethylstannyl)propanol (4). Into a 200-mL round-bottom flask, was placed 3,3-bis(dimethylbromostannyl)propanol (4.36 g, 8.5 mmol) along with 200 mL of CCl 4, 1 mL o methylene chloride, and 1 mL of methanol. To this solution was added bromine in $\mathrm{CCl_4}$ (29.3 mL of 0.58 M, 16.9 mmol). The reaction was allowed to stand in the dark for 4 days when the ^{1}H NMR spectrum still showed the tin–methyl peak of the starting compound bromine (1.2 mmol) was added. The light yellow solution which resulted on standing was reduced to half the original volume by rotary evaporation, extracted with 125 mL of water, and washed with 125 mL of water. The water layers were combined and used to dissolve the sodium bromide with heating. Colorless crystals (1.21 g, mp 168–169 °C, soluble in acetone) formed upon cooling. The solution was then extracted with methylene chloride (2 × 100 mL) which was dried over $\mathrm{MgSO_4}$ (1 g), filtered, and rotary evaporated to afford a white powder (2.77 g). The crystals and the powder were combined (3.98 g, 6.2 mmol, 75% yield). ^{1}H NMR analysis showed only one tin–methyl peak: ^{1}H NMR (DMK-d_6) δ 1.56 (s, 6, $^2J(^{119}\mathrm{Sn{-}C{-}H})$ = 89 Hz, $\mathrm{SnMeBr_2}$), 2.40–3.00 [m, 3, $\mathrm{C}\mathit{CH_2CH}\mathrm{(Sn)_2}$], 4.01 (t, 2, J = 5.0 Hz, $\mathrm{CH_2O}$).

Anal. Calcd for $\mathrm{C_5H_{11}Sn_2Br_4O}$: C, 9.31; H, 1.88. Found: C, 9.52; H, 1.68.

3,3-Bis(trimethylstannyl)propyl Tosylate. To 225 mL of pyridine distilled from $\mathrm{CaH_2}$ was added 27.0 g (142 mmol) of *p*-toluenesulfonyl chloride which had been recrystallized from benzene. The solution was cooled in an ice-water bath and 45.7 g (118 mmol) of 3,3-bis-(trimethylstannyl) propanol in 150 mL of pyridine added during 0.5 h with stirring, which was continued for 10 h at 4 °C. The mixture was poured into 1 L of ice water, extracted with 150 mL of petroleum ether, which was separated and washed successively with 500-mL portions of water, 0.1 M H_2SO_4, and saturated sodium bicarbonate, and then dried over $MgSO_4$. Removal of the solvent left 56.2 g (88%), of the tosylate which was used without further treatment: ^1H NMR ($CDCl_3$) δ 0.05 (s, 18, $^2J(^{119}Sn-C-H)$ = 51.0 Hz, $SnMe_3$), 0.53 (t, 1, $^2J(^{119}Sn-C-H)$ = 7.5 Hz, Sn_2CH), 2.07 (m, 2, Sn_2CHCH_2), 2.36 (s, 3, $ArCH_3$), 3.87, (t, 2, $^2J(Sn-C-H)$ = 7.0 Hz, CH_2O), 7.17 (d, 2, J = 8.0 Hz, ArH), 7.90 (d, 2, J = 8.0 Hz, ArH).

3,3-Bis(chlorodimethylstannyl)propyl Acetate (5). Chlorodimethylstannane was prepared in a 50-mL flask fitted with a side arm and stopcock from dimethylstannane [prepared from 12.67 g (57.7 mmol) of dichlorodimethylstannane] and 10.8 g (49.4 mmol) of dimethyldichlorostannane. Propargyl acetate (4.7 g, 48.3 mmol) was added by syringe to the dimethylchlorostannane under a blanket of nitrogen. The reaction flask was then stoppered, and a balloon was fitted to the side arm. The reaction was irradiated in a Rayonet photochemical reactor with 300-nm lamps for 12 h. A gray precipitate (10.73 g) was filtered off. The filtrate was shaken with CCl_4 (50 mL), filtered, and rotary evaporated to yield the crude product (9.82 g, 40%). A portion of the crude product was recrystallized from petroleum ether for elemental analysis.

Anal. Calcd for $C_9H_{20}Sn_2O_2Cl_2$: C, 23.07; H, 4.30. Found: C, 23.75; H, 4.38.

3,3-Bis(bromodimethylstannyl)propyl Acetate (7). Bromine (37.80 g, 0.237 mmol) was diluted to 0.5 L in CCl_4 to make a solution of 0.473 M in bromine. Into a 500-mL round-bottom flask equipped with a magnetic stirrer were placed 3,3-bis(trimethylstannyl)propyl acetate (9.36 g, 21.9 mmol) and 25 mL of CCl_4 and chilled to 0 °C. A solution of 0.473 M Br in CCl_4 was added so as to keep the reaction mixture a light yellow. This was continued until 92.6 mL (43.8 mmol of bromine) was added. The solution was then allowed to stand at 0 °C for 3 h and overnight at room temperature. The solution was concentrated, yielding a cloudy liquid that solidified on standing to afford a product (21.0 g, 21.5 mmol) with 1% trimethylbromostannane as impurity (98% yield). A portion of the product was further purified by recrystallization from petroleum ether: mp 53–54 °C; ^1H NMR (CCl_4) δ 0.68 (s, 12, $^2J(^{119}Sn-C-H)$ = 60.5 Hz, $SnMe_2Br$), 1.47 (t, 1, J = 8 Hz, $CCH(Sn)_2$), 1.79 (s, 3, CH_3COO), 2.25 (m, 2, CCH_2C), 4.33 (t, 2, J = 6 Hz, CH_2O); IR (neat, cm^{-1}) 1740, 1690 (C=O), 540 (SnC).

Anal. Calcd for $C_9H_{20}Sn_2O_2Br_2$: C, 19.39; H, 3.62. Found: C, 19.72; H, 3.71.

3,3-Bis(dibromomethylstannyl)propyl Acetate (8). 3,3-Bis(bromodimethylstannyl)propyl acetate (1.30 g, 2.72 mmol) was placed in a 100-mL two-neck, round-bottom flask equipped with a stirrer and 10-mL buret. Minimal CCl_4 was added with slight warming to dissolve the crystals. The solution was stirred as a solution of bromine (6.9 mL, 1.58 M) was added. The flask was sealed and stored in the dark for 1 month. The reaction vessel was cooled to −22 °C, and the crystals were filtered (1.3 g, 70% yield) mp 139–140 °C; ^1H NMR (Cl_3CD) δ 1.68 (s, 6, $^2J(^{119}Sn-C-H)$ = 74.2 Hz, $SnMeBr_2$), 2.18 (s, 3, CH_3COO), 2.70 (m, 3, CH_2CH-$(Sn)_2$, 4.33 (t, 2, J = 5 Hz, CH_2O); IR (neat) 1708 cm^{-1} (C=O).

Anal. Calcd for $C_7H_{14}Sn_2O_2Br_4$: C, 12.23; H, 2.06. Found: C, 12.03; H, 1.89.

3,3-Bis(trimethylstannyl)propyl Ethyl Sulfide (9). Into a 100-mL flask equipped with a magnetic stirrer was placed 1.16 g (18.6 mmol) of ethanethiol in 10 mL of ethanol and 0.8 g (18.7 mmol) of NaOH in 5 mL of water, and the mixture was stirred for 15 min. 3,3-Bis(trimethylstannyl)propyl tosylate (10.1 g, 18.6 mmol) in 15 mL of ethanol was added dropwise. The mixture was refluxed overnight and worked up by addition of 100 mL of petroleum ether and extraction with water (3 × 200 mL). The organic layer was dried and concentrated and the product distilled: bp 60 °C (0.01 torr); 7.9 g (99%); ^1H NMR ($CDCl_3$) δ 0.11 (s, 18, $^2J(^{119}Sn-C-H)$ = 51 Hz, $Sn(CH_3)_3$).

Anal. Calcd for $C_{11}H_{28}SSn_2$: C, 30.75; H, 6.57. Found: C, 31.00, H, 6.71.

3,3-Bis(trimethylstannyl)propyl Ethyl Sulfoxide (10). A 200-mL flask was charged with 5.0 g (11.6 mmol) of 3,3-bis(trimethylstannyl)propyl ethyl sulfide, 60 mL of ethanol, 7 mL of 30% hydrogen peroxide, and 3 mL of concentrated H_2SO_4 and the mixture stirred for 5 h. The reaction mixture was worked up with 50 mL of petroleum ether and 3 × 200 mL of water. The organic layer was dried over $MgSO_4$, filtered, and concentrated and the product distilled: bp 60 °C (0.01 torr); 4.5 g (87%); ^1H NMR ($CDCl_3$) δ 0.13 (s, 18, $^2J(^{119}Sn-C-H)$ = 50.5 Hz, $Sn(CH_3)_3$); IR (neat) 2973, 2909 (CH), 1052 cm^{-1} (SO).

Anal. Calcd. for $C_{11}H_{28}OSSn_2$: C, 29.64; H, 6.33. Found: C, 29.81; H, 6.41.

Reaction of 1:1 Bis(trimethylstannyl)methane with Bromine. In a 50-mL one-neck round-bottomed flask, equipped with magnetic stirrer, 2.08 g (6.1 mmol) of 1:1 bis(trimethylstannyl)methane[16] dissolved in 4 mL of CCl_4 was treated with 6.1 mmol (6.0 mL, 1.014 M solution in CCl_4) of bromine at 0 °C under nitrogen. The bromime reacted as it was added. The reaction mixture was analyzed by GLC and NMR. NMR analysis showed that reaction had occurred to the extent of 50% by tin–methyl cleavage and 50% by tin–methylene cleavage. Following are the assignments: δ 2.42 (s, 3 H, CH_3Br), 0.79 (s, 9 H, $^2J(^{119}Sn-C-H)$ = 58.0 Hz, $(CH_3)_3SnBr$), 0.20 (s, 9 H, $^2J(^{119}Sn-C-H)$ = 52.0 Hz, $(CH_3)_3SnCH_2Br$) [lit.[19] 0.20 (s, 9 H, $^2J(^{119}Sn-C-H)$ = 55.0 Hz], 2.4 (s, 2, $^2J(^{119}Sn-C-H)$ = 17 Hz, $(CH_3)_3$ Sn CH_2Br) [lit.[19] 2.55 (s, 2 H, $^2J(^{119}Sn-C-H)$ = 17.0 H, $(CH_3)_2$ $SnCH_2Br$)], 0.17 (s, 18 H, $^2J(^{119}Sn-C-H)$ = 52.5 Hz, $(CH_3)_3SnCH_2Sn(CH_3)_3$), −0.23 (s, 2 H, $^2J(^{119}Sn-C-H)$ = 63.0 Hz, $(CH_3)_3$ $SnCH_2Sn(CH_3)_3$), 0.06 (s, 9 H, $^2J(^{119}Sn-C-H)$ = 51.0 Hz, $(CH_3)_3SnCH_2Sn(CH_3)_2Br$), 0.65 (s, 3 H, $^2J(^{119}Sn-C-H)$ = 54.0 Hz, $(CH_3)_3SnCH_2Sn(CH_3)_2Br$), 0.68 (s, 12 H, $^2J(^{119}Sn-C-H)$ = 54.0 H, $Br(CH_3)_2SnCH_2Sn(CH_3)_2Br$), 0.98 (s, 2 H, $Br(CH_3)_2SnCH_2Sn(CH_3)_2Br$).

Reaction of 2:2 Bis(trimethylstannyl)propane with Bromine. In a 50-mL one-neck round-bottomed flask, equipped with magnetic stirrer, 2.0 g (5.4 mmol) of 2:2 bis(trimethylstannyl)-propane[16] dissolved in 4 mL of CCl_4 was treated with 5.4 mmol (5.3 mL, 1.014 M solution in CCl_4) of bromine at 0 °C under nitrogen. The bromine reacted as it was added. The reaction mixture was analyzed by GLC and NMR. NMR analysis showed that reaction had occurred to the extent of 66% of tin–methyl cleavage and 33% by tin–methine cleavage. Following are the assignments: δ 2.52 (s, 3 H, CH_3Br), 0.73 (s, 9 H, $^2J(^{119}Sn-C-H)$ = 57.5 Hz, $(CH_3)_3SnBr$)[Lit.[20] ($CDCl_3$) 0.74 (s, 9 H, $^2J(^{119}Sn-C-H)$ = 58.6 Hz, $(CH_3)_3SnBr$], 0.11 (s, 9 H, $^2J(^{119}Sn-C-H)$ = 49.5 Hz, $(CH_3)_3SnC(CH_3)_2Br$), 1.48 (s, 6 H, $^2J(^{119}Sn-C-H)$ = 86.0 Hz, $(CH_3)_3Sn$ $C(CH_3)_2$ Br), 0.03 (s, 18 H, $^2J(^{119}Sn-C-H)$ = 49.0 Hz, $(CH_3)_3SnC(CH_3)_2Sn(CH_3)_3$, 1.38 (s, 6 H, $^2J(^{119}Sn-C-H)$ = 74.0 Hz, $(CH_3)_3SnC(CH_3)_2Sn(CH_3)_3$, 0.7 (s, 12 H, $^2J(^{119}Sn-C-H)$ = 56.0 Hz, $Br(CH_3)_2SnC(CH_3)_2Sn(CH_3)_2Br$), 1.81 (s, 6 H, $^2J(^{119}Sn-C-H)$ = 104.0 Hz, $Br(CH_3)_2SnC(CH_3)_2Sn(CH_3)_2Br$), 0.17 (s, $^2J(^{119}Sn-C-H)$ = 53.0 Hz, unassigned); 0.58 (s, unassigned).

3,3-Bis(bromodimethylstannyl)propyl Ethyl Sulfoxide (11). Into a 50-mL flask equipped with a magnetic stirrer were placed 2.0 g (4.48 mmol) of 3,3-bis(trimethylstannyl)propyl ethyl sulfoxide and 10 mL of dry methanol and the reaction flask was cooled to 0 °C under nitrogen. To this was added dropwise 9.8 mmol bromine in 8.0 mL of carbon tetrachloride. Heat was evolved, and the bromine color disappeared upon addition. The flask was warmed to room temperature, and the solvent was removed on the rotary evaporator. The product was crystallized from carbon tetrachloride to yield 2.0 g (77.5%) of product: mp 94–96 °C; ^1H NMR ($CDCl_3$) δ 0.89 (s, 12, $^2J(^{119}Sn-C-H)$ = 66.0 Hz, $SnMe_2$), 0.93 (s, 12, $^2J(^{119}Sn-C-H)$ = 67.0 Hz, $SnMe_2$); IR (KBr, cm^{-1}) ν_{SO} 952.3).

Anal. Calcd for $C_9H_{22}Br_2OSSn_2$: C, 18.78; H, 3.85; mol. wt., 576. Found: C, 18.69; H, 3.91; mol. wt. 647 (osometric in toluene at 40 °C).[21]

3,3-Bis(dibromomethylstannyl)propyl Ethyl Sulfoxide (12). To a 50-mL flask, equipped with a magnetic stirrer containing 2.0 g (4.48 mmol) of 3,3-bis(trimethylstannyl)propyl ethyl sulfoxide dissolved in 10 mL of dry methanol at 0 °C was added dropwise 17.9 mmol of bromine in 16 mL of CCl_4. After the

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(19) Seyferth, D.; Andrews, S. B. *J.* Organomet. *Chem.* **1971**, *30*, 151.

(20) Kelen, G. P. van der, *Nature* (*London*) **1962**, *193*, 1069.

(21) Obtained through the courtesy of Dr. J. G. Carnahan.

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addition was complete, the flask was slowly warmed to room temperature and allowed to stand until the bromine color was gone (12 days). The solvent was removed by rotary evaporation and the residue heated at 60 °C and 0.01 torr to yield crude product which was recrystallized from methylene chloride: light yellow crystals (2.3 g., 95%): mp 166–168 °C; ^{1}H NMR ($(CD_3)_2CO$) δ 1.50 (s, 6, $^2J(^{119}Sn–C–H)$ = 92.0 Hz, SnMe), 1.54 (s, 6, $^2J(^{119}Sn–C–H)$ = 92.0 Hz, Sn–Me); IR (KBr, cm^{-1}. ν_{SO} 950.0.

Anal. Calcd for $C_7H_{16}Br_4OSSn_2$: C, 11.92; H, 2.28; mol wt, 705. Found: C, 12.10; H, 2.32; mol wt, 858 (osmometric in toluene at 40 °C).[21]

Acknowledgment. This research was supported by the National Science Foundation (Grant CHE-8105021). Acknowledgment is also made to the donors of the Petroleum Fund, administered by the American Chemical Society, for support of this work.

Registry No. 1, 85293-94-3; 2, 85293-95-4; 3, 85293-96-5; 4, 85293-97-6; 5, 85293-98-7; 6, 85293-99-8; 7, 85294-00-4; 8, 85294-01-5; 9, 85294-02-6; 10, 85294-03-7; 11, 85294-04-8; 12, 85294-05-9; 13, 16812-43-4; 14, 83135-43-7; trimethylstannane, 1631-73-8; propargyl acetate, 627-09-8; 3,3-bis(trimethylstannyl)propyl tosylate, 85294-06-0; chlorodimethylstannane, 16561-41-4.

Some Aspects of the Chemistry of Binuclear Bridging Iron Complexes[1a]

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Received September 1, 1982

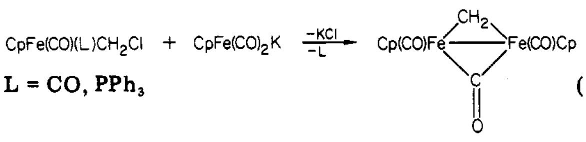
The formation of hydrocarbons from binuclear iron complexes $Cp(CO)Fe(\mu\text{-}CH_2)Fe(CO)Cp$, $Cp(CO)_2Fe(CH_2)_nFe(CO)_2Cp$ (n = 3, 4), and $Cp(CO)_2Fe(C{=}O)(CH_2)_n(C{=}O)Fe(CO)_2Cp$ (n = 2–4) (Cp = $\eta^5\text{-}C_5H_5$) under photolytic and thermolytic conditions was investigated. The studies indicate that bimetallacyclic species $Cp(CO)Fe(\mu\text{-}CO)(CH_2)_nFe(CO)Cp$ (n = 3, 4) might be involved in the reaction sequence which leads to the formation of cyclopropane (n = 3) and olefins (n = 2, 3, 4).

Introduction

To a large extent, the importance of organometallic chemistry is based upon the unique chemical properties of alkyl, alkylidene, or alkylidyne groups when attached to a transition metal, and this area continues to receive much attention.[3] An extension of this field that has been less well developed is where two transition-metal centers are involved. Several interesting aspects appear to exist in this class of compounds, particularly the interactions between the metal centers and the effects of this interaction on the chemical properties of the attached hydrocarbon moieties. Other aspects include the possible relationship of this system to the alkyl groups bonded to metal surfaces which make up most heterogeneous systems.[4] We now wish to report some results from these laboratories pertaining to this class of compounds.[5]

Results and Discussion

Recently, we[6] and others[7] have described the synthesis of the novel organometallic compound $Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}CH_2)Fe(CO)Cp$ (1, Cp = $\eta^5\text{-}C_5H_5$) in which a CH_2 group bridges two iron atoms linked by a single bond. We have found that 1 can also be prepared by the reaction of $CpFe(CO)(L)CH_2Cl$ (L = CO, PPh_3) and $CpFe(CO)_2K$ in tetrahydrofuran (THF) (eq 1). Depending on ligand L, the yield of 1 ranges from 10% (L = CO) to 30% (L = PPh_3). Other products identified in this reaction (L = CO) are methane (2%), ethylene (7%), $CpFe(CO)_2CH_3$ (15%), and $[CpFe(CO)_2]_2$ (65%). As noted by other workers,[7b] separation of 1 from $[CpFe(CO)_2]_2$ was difficult but was accomplished by treating the crude product mixture with excess 1,2-bis(diphenylphosphino)ethane (diphos) prior to separation. This procedure selectively converted $[CpFe(CO)_2]_2$ into its diphos derivative while leaving 1 intact. Complex 1 and the diphos derivative of $[CpFe(CO)_2]_2$ can be easily separated by chromatography.



(1)

1 cis/trans

One mechanism which could explain most of the side products in the synthesis of 1 involves an electron transfer from the $CpFe(CO)_2^-$ to the (chloromethyl)iron complex, followed by loss of chloride ion from the radical anion, to give rise to $CpFe(CO)_2CH_2\cdot$(2) and $CpFe(CO)_2\cdot$(3). Recombination of 3 would yield the observed $[CpFe(CO)_2]_2$. There are at least three different modes of reaction for species 2. It can abstract a hydrogen from solvent to form $CpFe(CO)_2CH_3$ or react with radical 3 to give the bridging methylene complex 1. A third pathway is to couple with

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(1) (a) Taken in part from the Ph.D. dissertation of S. C. Kao, The University of Texas at Austin, 1981. (b) NATO Postdoctoral Fellow, 1981–1982.

(2) Deceased December 10, 1981.

(3) (a) Schrock, R. R.; Parshall, G. W. *Chem. Rev.* **1976**, *76*, 243. (b) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev.* **1976**, *76*, 219. (c) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 1119.

(4) Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6191; **1981**, *103*, 1287.

(5) Analogous results of a portion of this work have been reported recently: Cooke, M.; Forrow, N. J.; Knox, S. A. R. *J. Organomet. Chem.* **1981**, *222*, C21.

(6) Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911.

(7) (a) Jorswagen, R.; Alt, R.; Speth, D.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1049. (b) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134.