Zirconium(IV) metalloazines from hydrazones: an umpolung of a carbonyl group derivative

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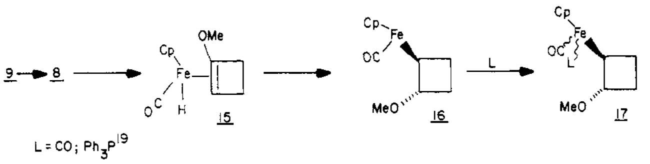
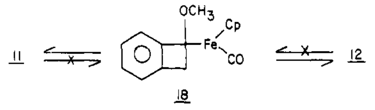
Scheme II



The Fe–C(7a) distance of 1.958 (6) Å is not significantly different from the value of 1.968 (2) Å for a similar bond.[10] Both distances are significantly shorter than the values of 1.991 (8),[12] 2.037 (5),[13] and 2.120[14] reported for Fe–C-(phenyl) bonds in non-carbene-type complexes. The C-(5)–C(6) distance in the phenyl ring appears to be short but may be related to thermal motion in the ring. The dimensions of the Cp ring, the Fe–Cp ring distance, and the Fe–CO group dimensions are not unusual.

Where methoxy stabilizes a carbene complex enough to induce rearrangement in the cyclopropyl σ-complex **3**, we have found that the corresponding thiocresyl cyclopropyl σ-complex is photostable.[15] Assuming that this is due to the poorer electron-donating ability of sulfur as compared with oxygen, we thought it would be interesting to see if the presumed increase in strain relief resulting from expanding benzocyclobutene to a metallocyclopentadiene (as in **10** to **11**) would be enough to offset the loss of substituent stabilization. To this end **13**[5] was prepared in 66% yield as shown in Scheme I. Photolysis[16] in C_6D_6 at 5–10 °C gave a mixture in which the major product (75–80% of reacted material) showed spectroscopic properties[17] that are sufficiently similar to those of **11** (especially the ^{13}C resonance at 340.4 ppm) to lead us to tentatively assign it structure **14**. Unfortunately, all attempts to isolate this new material failed. For instance, although TLC (silica gel, EtOAc/hexane (10/90, v/v)) indicated a clean separation of the major product and flash chromatography on silica gave a sharp green band, evaporation of solvent invariably gave a gumlike, intractable material.[18]

Reaction of **9** with CO or Ph_3P at room temperature readily gives the rearranged σ-complex **17** which we have suggested[3] originates by the mechanism outlined in Scheme II. To test for a similar rearrangement of **12**, a sample was sealed under 6.5 atm of CO (ca. 100 molar equiv), and the solution was monitored at room temperature by ^1H NMR for 6 months. During this time virtually no reaction occurred. That the sluggishness of this reaction was due to slow contraction to **18** (rather than a slow later step) is clear since, if **18** were formed but could react no further, it should preferentially expand back to **11** rather than **12**.



For an estimation of a minimum barrier for contraction of **11** or **12** to **18**, samples were heated in C_6D_6 to 77 °C and monitored by ^1H NMR. In neither case (**11** heated for 18 h and **12** heated for 39 h) was any detectable isomerization observed. Assuming a first-order reaction and an NMR detection level of 5% leads to a minimum $\Delta G^{\ddagger}$ of about 30–31 kcal/mol. The difference between this and that observed for **9** ($\Delta G^{\ddagger} \leq 21.6$ kcal/mol)[19] is presumably primarily due to the difference in strain energies of cyclobutane and benzocyclobutene.

Acknowledgment. This work was partially supported by the National Science Foundation to whom the authors are grateful. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The support from the Royal Norwegian Council for Scientific and Industrial Research (NTNF) to Y.S. is greatly appreciated. High-field NMR spectra were obtained on a Nicolet NT-300 spectrometer, operating at a field of 7 T; therefore, acknowledgment is made to the Instrument Program, Chemistry Division, National Science Foundation, for financial assistance in the purchase of the instrument.

Registry No. **10**, 49624-85-3; **11**, 104090-23-5; **12**, 104090-24-6; **13**, 104090-22-4; **14**, 104090-25-7; Fp^-, 12107-09-4; *p*-Me-PhSH, 106-45-6; 7-bromobicyclo[4.2.0]octa-1,3,5-triene, 21120-91-2.

Supplementary Material Available: Tables of atomic coordinates, bond lengths, and bond angles (3 pages); a listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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[11] Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1.

[12] Carre, F. H. *Cryst. Struct. Commun.* **1982**, *11*, 1009.

[13] Vierling, P.; Riess, J. G.; Grand, A. *J. Am. Chem. Soc.* **1981**, *103*, 2466.

[14] Semion, V. A.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1969**, *10*, 88.

[15] Unpublished results of N. Conti, University of Florida.

[16] Photolysis was carried out under a N_2 atmosphere with a 450-W Hanovia medium-pressure lamp using a $CoSO_4$ filter. The reaction progress was monitored by NMR. The rearranged product is exceedingly sensitive, and it was found that if the temperature were allowed to rise, the $CoSO_4$ filter omitted or photolysis carried out beyond ca. 75% conversion, the reaction mixture became very complex, at least partly due to further reaction of the carbene complex.

[17] (a) 1-Carbonyl-1-(η^5-cyclopentadienyl)-2-*p*-thiocresyl-1-ferraindene (**14**): ^1H NMR (60 MHz, C_6D_6) δ 1.98 (s, 3 H, CH_3), 3.65 (s, 1 H),[17b] 3.75 (s, 1 H),[17b] 4.70 (s, 5 H, Cp), 6.5–7.5 (m, 8 H); ^{13}C NMR (25. MHz, C_6D_6) δ 21.08 (CH_3), 66.02 (CH_2), 89.31 (Cp), 119.91, 121.86, 122.93, 125.86, 130.44, 132.39, 134.82, 137.36, 142.42, 152.47, 160.85 (aromatic carbons), 221.47 (CO), 340.38 (carbene C). (b) As is the case for **11** and **12** these apparent singlets may well be doublets with very low intensity wings. However, as mentioned, this carbene complex could not be isolated in pure form, and it was therefore not possible to positively identify the wings. There is doubt about the major features of the spectrum.

[18] Interestingly, the photolysis showed a major and minor product in about 9/1 ratio (from the Cp resonances) which we suspect correspond to the thiocresyl analogues of **11** and **12**, but this is very tentative since we have no further evidence for the analogue of **12**.

[19] Unpublished results of Y. Stenstrøm.

Zirconium(IV) "Metalloazines" from Hydrazones: An "Umpolung" of a Carbonyl Group Derivative

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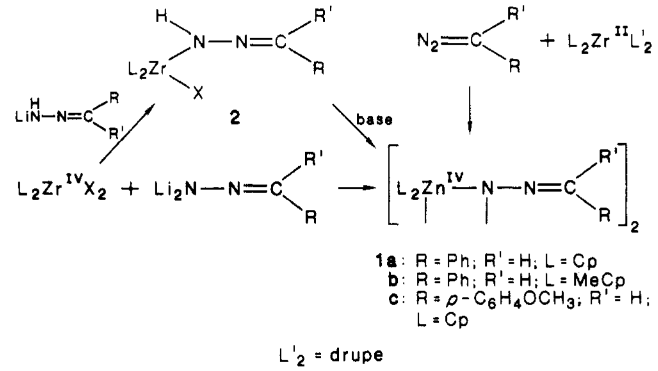
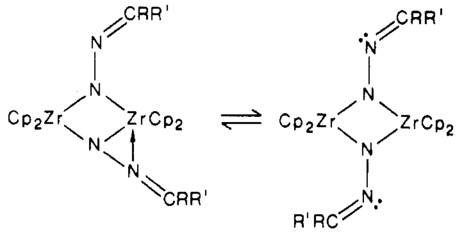
Summary: Zr(IV) "metalloazines" have been prepared from Zr(IV) salts and hydrazone derivatives (or from Zr(II) phosphine complexes and diazoalkanes). They are dimeric; X-ray analysis reveals an unsymmetrically bridged dizirconium center, and NMR analysis shows that the complexes are fluxional. They demonstrate susceptibility to electrophilic attack at carbon and thus represent an "umpolung" of the carbonyl group from which they were derived.

To activate an organic molecule toward an unusual transformation by coordination to a transition-metal center is a continuing theme in organometallic chemistry. Of

Scheme I



Scheme II



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particular note in this context is olefin activation to nucleophilic attack effected by complexation to Pd(II),[1] for example. In the course of our investigations aimed at activation of organic carbonyl group containing materials, we have prepared Zr(IV) "metalloazines" by reaction between $Cp_2Zr^{IV}XY$ species and readily available hydrazone derivatives of aldehydes or ketones. These "metalloazines" show some interesting structural features but display an unprecedented "umpolung" of reactivity[2] of the "carbonyl" group from which they were derived.

Hydrazone derivative "metalloazine" **1a** is easily formed by ligand metathesis between Cp_2ZrCl_2 and $Li_2NNC(H)Ph$ (prepared from the hydrazone and 2 equiv of butyllithium) in THF at −78 °C. However, best yields of **1a** result from a stepwise synthesis in which the intermediate $Cp_2Zr(Cl)NHNC(H)Ph$ (**2a**) is prepared and isolated. In a typical procedure, LiNHNC(H)Ph was obtained by addition of 4.0 mL of a 2.5 M solution of *n*-BuLi (10 mmol) in hexane to 1.2 g (10 mmol) of $H_2NNC(H)Ph$ in 10 mL of dry THF at −78 °C under N_2. The cold solution was transferred to a suspension of 2.92 g (10 mmol) of Cp_2ZrCl_2 in 20 mL of toluene at −78 °C, and then the mixture was allowed to reach room temperature. Lithium chloride was removed by filtration, and the resulting bright yellow solution was concentrated and cooled to give yellow crystals of **2a** (60%).[3,4] Complex **1a** was obtained by stirring 1.02 g (3 mmol) of **2a** and 0.32 g (3 mmol) of LDA in 15 mL of dry toluene for 4 h; LiCl was removed by filtration, and the resulting bright orange solution was concentrated and cooled to give crystals of **1a**[6,7] (78% yield) which was recrystallized from toluene. (A "redox" reaction between $Cp_2Zr^{II}(dmpe)$[8] and $PhCHN_2$ in toluene at −50 °C also produces **1a**, analogous to reactions we have noted for molybdenum derivatives.[9,10])

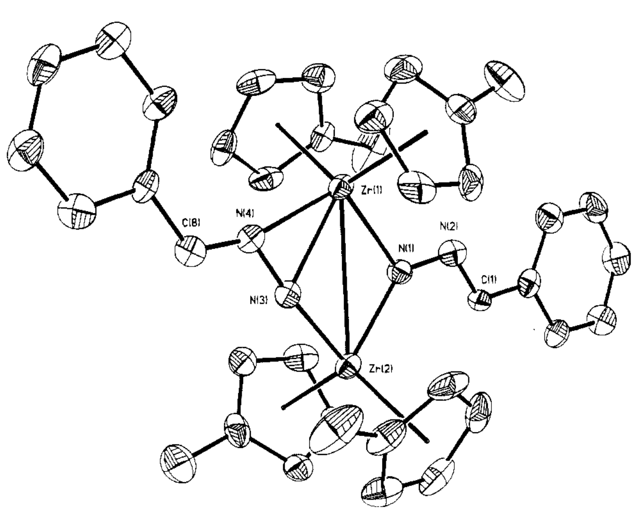
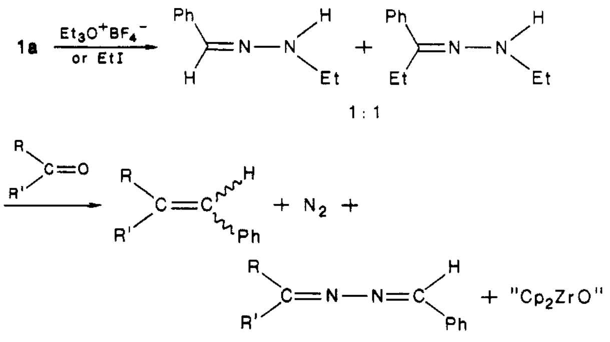


Figure 1. An ORTEP diagram of complex **1b**. Bond distances (Å): Zr(1)-N(1), 2.180 (7); Zr(1)-N(3), 2.213 (7); Zr(1)-N(4), 2.232 (7); Zr(2)-N(1), 2.063 (7); Zr(1)-N(3), 2.004 (7); N(1)-N(2), 1.36 (1); N(2)-C(1), 1.29 (1); N(3)-N(4), 1.32 (1); N(4)-C(8), 1.29 (1). Bond angles (deg): Zr(1)-N(1)-N(2), 120.7 (5); Zr(2)-N(1)-N(2), 139.4 (6); Zr(1)-N(3)-N(4), 73.5 (4); Zr(2)-N(3)-N(4), 174.1 (6).

Scheme III



The mass spectrum of **1a** indicated its dimeric nature,[12] and an X-ray crystallographical analysis of **1b** revealed an unusual, unsymmetrical bridging ligand system.[13] The

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[1] For example, see: Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: New York, 1980.

[2] "Umpolung" is the formal reversal of the polarity of a functional group. See: Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239.

[3] ^1H NMR (250 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.5 Hz, 2 H), 7.47 (s, 1 H), 7.21 (t, *J* = 7.5 Hz, 2 H), 7.10 (t, *J* = 7.5 Hz, 1 H), 6.89 (s, 1 H), 5.95 (s, 10 H). IR (KBr): 3206 (m), 3102 (w), 1547 (w), 1439 (m), 1261 (w), 1096 (sh), 1065 (sh), 1042 (vs), 1015 (s), 806 (vs), 752 (s) cm^{-1}.

[4] The complex $Cp_2Zr(Cl)NHNCPh_2$ has been prepared[5] from $Cp_2Zr(H)Cl$ and Ph_2CN_2; the ^1H NMR and IR spectra of **2** confirm a structural analogy with this complex.

[5] (a) Gambarotta, S.; Basso-Bert, M.; Floriani, C.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1982**, 374–375. (b) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1983**, *22*, 2029–2034.

[6] ^1H NMR ($CDCl_3$): δ 7.75 (d, *J* = 7.8 Hz, 2 H), 7.70 (s, 1 H), 7.46 (t, *J* = 7.7 Hz, 2 H), 7.29 (t, *J* = 7.7 Hz, 1 H), 5.95 (s, 10 H). ^{13}C NMR ($CDCl_3$): δ 137.3, 133.5, 129.0, 126.8, 125.3, 109.5. IR (KBr): 2958 (w), 2916 (w), 1523 (s), 1512 (m), 1258 (m), 1180 (m), 1096 (vs), 1061 (s), 1015 (s), 795 (vs) cm^{-1}.

[7] Other metalloazines (**1**) have been made by this route, including the following: R = Ph, R′ = CH_3; R = H, R′ = $(CH_2)_4CH_3$; R = CH_3, R′ = $(CH_2)_4CH_3$.

[8] Gell, K. I.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1979**, 244–246.

[9] Smegal, J. A.; Meier, I. K.; Schwartz, J. *J. Am. Chem. Soc.* **1986**, *108*, 1322–1323.

[10] The reaction between $CpTi^{III}Cl_2$ and Ph_2CN_2 has been shown to form an analogous Ti(IV) dinuclear complex,[11] for which no chemistry has been described.

[11] Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1982**, *104*, 1015–1017.

[12] Exact mass calcd 676.0870, found 676.0848 ± 0.007.

[13] (a) Figure 1 shows an ORTEP diagram for **1b**, indicating the most significant bond distances and angles,[14] which reveals an interesting structural feature. Although the overall gross dimeric structure of **1b** is not unlike that of symmetrically nitrogen-bridged zirconium alkylimido complexes[15] (however, with a slight increase in Zr(1)-N(1) and Zr(1)-N(3) bond lengths vs. those for Zr(2)), one of the bridging N-N ligands is clearly η^2-bonded to Zr(1); Zr(1)-N(4) is only slightly longer than is Zr(1)-N(3). While both symmetrically bridged and η^2-N,N-bonded units[16] are known individually, **1** is the first case in which both types of structural features are present in the same molecule. (b) ^1H NMR (C_6D_6): δ 7.85 (s, 1 H), 7.76 (s, 2 H), 7.35 (t, *J* = 6.8 Hz, 2 H), 7.20 (m, 1 H) 5.85 (m, 4 H), 5.62 (m, 4 H) 2.16 (s, 6 H).

^{13}C NMR of **1a** (in CD_2Cl_2) at room temperature showed a single sharp resonance at δ 109.5 (Cp, Cp′); upon cooling to −80 °C two broadened resonances at δ 109.7 and 108.2 are observed, and warming the solution back to room temperature causes coalescence of these two peaks. This fluxional process may involve symmetrical intermediate **3** as shown in Scheme II.

Zirconium "metalloazine" complexes are susceptible to *electrophilic* attack at C as well as at Zr–N, demonstrating an "umpolung" of reactivity with regard to the hydrazones from which they are derived. For example, addition of $(Et_3O)^+BF_4^-$ to a solution of **1a** gave both C-alkylated and N-alkylated hydrazones in approximately equal amounts, yet careful hydrolysis of **1a** leads to $H_2NNCHPh$ as the sole organic product (no attack by H_2O at sp^2 C). Furthermore, the addition of organic carbonyl compounds, such as aldehydes or ketones, gives a mixture of condensation products resulting from attack either at carbon or at nitrogen. Reactions with enones lead to the olefin, exclusively, in good yield. In a typical experiment, to 1.20 g (1.77 mmol) of **1a** in 25 mL of dry THF is added butyraldehyde (1.8 mmol) by syringe. The bright orange reaction mixture slowly fades to yellow over the course of 6 h and is then hydrolyzed with 0.5 mL of dilute aqueous KOH solution, dried over K_2CO_3, and concentrated to a viscous oil. The product mixture is separated by column chromatography (Florisil; hexane). Yield: olefin, 30% (*Z:E* = 25:1),[17] and azine, 60%. In similar fashion, **1a** reacted with other representative substrates: cyclohexanecarboxaldehyde [olefin (52%; *Z:E* = 16:1); azine (44%)]; 1-acetylcyclohexene [olefin (60%; *Z:E* = 3:1); azine (0%)]; *trans*-cinnamaldehyde [olefin 70%; *Z:E* = 2.5:1); azine (0%)]; benzaldehyde [olefin (47%; *Z:E* = 4.1:1; azine (42%)]; *p*-cyanobenzaldehyde [olefin (62%; *Z:E* = 4.2:1; azine (26%)]. Also **1b** reacted with cyclohexanecarboxaldehyde [olefin (57%; *Z:E* = 15:1); azine (40%)] and **1c** reacted with *p*-cyanobenzaldehyde [olefin (77%; *Z:E* = 1.5:1; azine (0%)]; cyclohexanecarboxaldehyde [olefin (58%; *Z:E* = 10:1); azine (13%)].

We are now exploring the scope of synthetic utility of these new complexes.

Acknowledgment. We acknowledge support for this work given by the National Science Foundation and the National Institutes of Health.

Supplementary Material Available: Tables of atom coordinates, anisotropic thermal parameters, bond distances, and bond angles (5 pages); a listing of structure factors (18 pages). Ordering information is given on any current masthead page.

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(14) Crystals of **1b** are orthorhombic of space group $P2_12_12_1$ with a = 8.262 (3) Å, b = 19.441 (7) Å, c = 21.922 (9) Å, V = 3521 (2) Å^3, and d_{calcd} = 1.47 g cm^3 for Z = 4 ($C_{38}H_{40}N_4Zr_2\cdot{}^1/_2C_6H_{14}$, fw = 778.4 g). An orange crystal of dimensions 0.16 × 0.20 × 0.24 mm was mounted on a glass fiber. The intensity data were measured on a Nicolet R3m diffractometer equipped with a graphite monochrometer and Mo Kα radiation (λ = 0.71069 Å) utilizing an ω scan technique with variable scan rates. The data were corrected for decay but not absorption μ(Mo Kα) = 6.2 cm^{-1}). A total of 3513 independent reflections were measured for $2\theta < 50°$ of which 2996 unique data were considered to be observed [$F_o > 3.0\ \sigma(F_o)$]. The structure was solved by conventional heavy-atom methods (Patterson and Fourier) and was refined by blocked-cascade least squares. All calculations were carried out by using the SHELXTL program. In the final stages of refinement, anisotropic thermal parameters were used for the non-hydrogen atoms. The phenyl and Cp hydrogen atoms were located on a difference Fourier map and were entered at idealized positions. The methyl hydrogens were not located. The hydrogen atoms were assigned isotropic temperature factors of $B_H = 1.2B_C$. A hexane molecule of solvation, located on a difference Fourier map and refined with isotropic thermal parameters, is disordered around the 2-fold screw axis in the x direction. At convergence, R = 0.056 and R_w = 0.057 for 2996 data and 409 variables.

(15) Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1979**, *18*, 2030–2032.

(16) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 7195–7301.

(17) Olefinic isomers were separated by preparative GC.

Monomeric, Three-Coordinate Tin(II) and Lead(II) Complexes with a MCP_2 Coordination Sphere: $Sn[CH(PPh_2)_2]_2$ and $Pb[CH(PPh_2)_2]_2$

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Summary: $Li[CH(PPh_2)_2]$ reacts with $SnCl_2$ or $PbCl_2$ in tetrahydrofuran to yield the homoleptic complexes $Sn[CH(PPh_2)_2]_2$ or $Pb[CH(PPh_2)_2]_2$. X-ray crystallographic studies reveal similar structures with a monomeric, pyramidal MCP_2 core and two distinctly different bis(diphenylphosphino)methanide ligands.

Bis(diphenylphosphino)methanide, $CH(PPh_2)_2^-$, is a versatile ligand[1] and building block for the construction of more complex structures, particularly new ligands. Here we report the use of this anion to produce novel, low-coordinate and monomeric tin(II) and lead(II) complexes. There has been considerable recent interest in the chemistry of these species, partly because of their relation to divalent carbon and carbenes.[2a]

Treatment of anhydrous tin(II) chloride over a 1-h period with 2 equiv of lithium bis(diphenylphosphino)methanide, $LiCH(PPh_2)_2$ (**1**),[1a] in dry dioxygen-free tetrahydrofuran followed by 1 h of stirring produces a brown solution from which brown needles of $Sn[CH(PPh_2)_2]_2$ (**2**) (mp 145–148 °C dec) are obtained in 72% yield after evaporation of THF, redissolution in ethyl ether, filtration, and cooling to −10 °C.[2b] Similarly, the reaction between anhydrous lead(II) chloride and **1** produces orange ($Pb[CH(PPh_2)_2]_2$ (**3**) (mp 141–146 °C dec) in 55% yield.

Characterization through X-ray crystallography reveals that compounds **2**[3] and **3**[4] have similar structures. Perspective drawings of **3** are shown in Figure 1. Compound

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(1) (a) Issleib, K.; Abicht, H. P. *J. Prakt. Chem.* **1970**, *312*, 456. (b) Issleib, K.; Abicht, H. P.; Winkelmann, H. *Z. Anorg. Allg. Chem.* **1972**, *388*, 89. (c) Camus, A.; Marsich, N.; Nardin, G.; Randaccio, L. *J. Organomet. Chem.* **1973**, *60*, C39. (d) Schmidbauer, H.; Mandl, J. R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 640. (e) Bassett, J.-M.; Mandl, J. R.; Schmidbaur, H. *Chem. Ber.* **1980**, *113*, 1145. (f) Schmidbaur, H.; Mandl, J. R.; Bassett, J.-M.; Blaschke, G.; Zimmer-Gasser, B. *Chem. Ber.* **1981**, *114*, 433. (g) Brown, M. P.; Yavari, A.; Manojlovic-Muir, L.; Muir, K. W; Moulding, R. P.; Seddon, K. R. *J. Organomet. Chem.* **1982**, *236*, C33. (h) Briant, C. E.; Hall, K. P.; Mingos, D. M. P. *J. Organomet. Chem.* **1982**, *260*, C5. (i) Brauer, D. J.; Hietkamp, S.; Stelzer, O. *J. Organomet. Chem.* **1986**, *299*, 137.

(2) (a) Harrison, P. G. *Annu. Rep. Prog. Chem.* **1984**, *81*, 114; **1983**, *80*, 96 and references therein. (b) **Note Added in Proof**: An independent synthesis and NMR study of this tin compound have recently been reported: Karsch, H. H.; Appelt, A.; Müller, G. *Organometallics* **1986**, *5*, 1664.

(3) Brown prisms of **2**·$(C_2H_5)_2O$ were obtained by cooling a saturated tetrahydrofuran/ethyl ether (1/9, v/v) solution of **2** to −10 °C. They crystalize in the monoclinic space group $P2_1/c$ with a = 18.124 (5) Å, b = 14.589 (7) Å, c = 18.291 (8) Å, β = 91.50 (3)°, V = 4835 Å^3, and Z = 4 at 130 K. Refinement yielded R = 0.0637 for 1902 relfections with $I > 3\sigma(I)$ and 272 parameters.

(4) Orange parallelepipeds of **3**·$(C_2H_5)_2O$ were obtained by cooling a saturated tetrahydrofuran/ethyl ether (1/9, v/v) solution of **3** to −10 °C. They crystallize in the monoclinic space group $P2_1/c$ (No. 14) with a = 18.075 (8) Å, b = 14.713 (6) Å, c = 18.099 (8) Å, β = 92.29 (4)°, V = 4810 (4) Å^3, and Z = 4 at 130 K which is isomorphic with **2**·$(C_2H_5)O$. Tests for an orthorhombic C-centered cell show it is not present. Refinement yielded R = 0.0571 for 3899 reflections with $I > 3\sigma$(I) and 272 parameters.

0276-7333/86/2305-2159$01.50/0