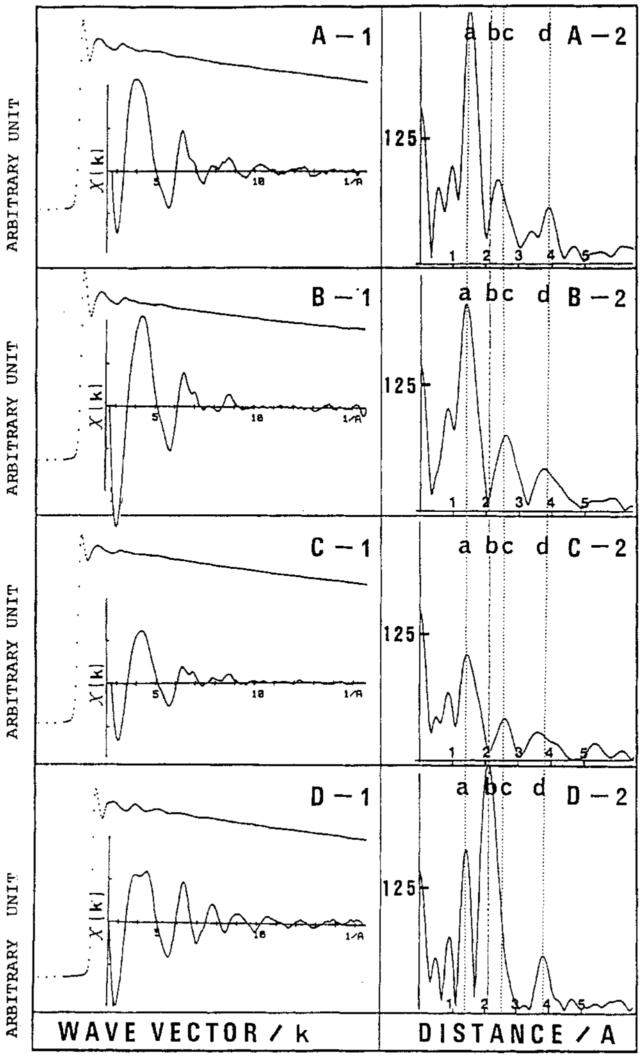

**Figure 1.** EXAFS spectra and the associated Fourier transforms of $Ph_4Ge$ (A), $Ph_3GeH$ (B), $Ph_2GeH_2$ (C), and $Ph_3Ge–GePh_3$ (D).

The effect of the number of phenyl rings and that of the Ge–Ge bond on the EXAFS spectra were studied for four reference materials: $Ph_4Ge$, $Ph_3GeH$, $Ph_2GeH_2$, and $Ph_3Ge–GePh_3$. EXAFS spectra and the associated Fourier transforms of the reference materials are shown in Figure 1A–D. Extracted oscillations used to Fourier transform were taken over the same wave vector range of $2.8 < k < 11$ Å$^{-1}$. Therefore, the comparison of the coordination number of each Fourier transform can be done precisely. The peaks a, c, and d in Figure 1 correspond to the interatomic distances of Ge and the first, second, and third nearest carbon of the aryl ring, respectively. Indeed, a calculation including the phase factor shows that the peaks are at representive interatomic distances of 1.94–1.97 Å, which agree well with the known Ge–C bond distance.[7] The heights of the peaks on the line change with the increasing number of aryl rings and serve as a ring number marker. The peak b is observed only for $Ph_3Ge–GePh_3$. It is certain that this peak at around 2.2 Å corresponds to the Ge–Ge bond,[7-9] since after the correction for the phase factor, the interatomic distance is determined to be 2.43 Å, which coincides with the reported value of 2.44 Å for a similar molecule. This peak is the strongest one in Figure 1D, since the Ge atom has much stronger back-scattering amplitude than carbon. Therefore, if Ge═Ge bond exists in the product, the corresponding peak should appear prominently at around 2.2 Å, in addition to those corresponding to Ge—C bonds. The number of aryl rings should be determined from the intensities of Ge–C peaks.

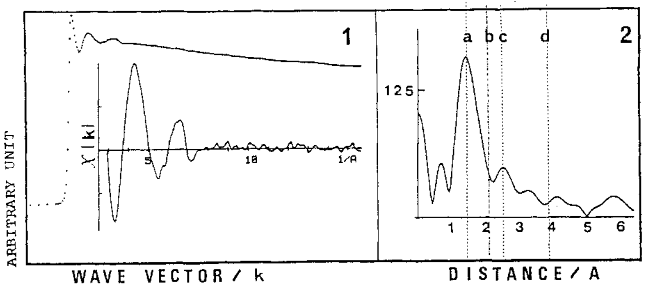

**Figure 2.** EXAFS spectrum and the associated Fourier transform of 1.

Extracted oscillation and the associated Fourier transform of the EXAFS of the product is shown in Figure 2. From a comparison of extracted oscillation, the product is similar to that of $Ph_2GeH_2$; on the Fourier transform, the bond length and the intensity of the first and the second nearest peaks agree with those of $Ph_2GeH_2$. In addition, no peak is observed around 2.2 Å, where the Ge–Ge bond is expected if it exists at all. Therefore, EXAFS results clearly show that the local structure around Ge atoms in the product has only two aryl groups and does not have Ge═Ge bond. Therefore, the structure of the product is concluded to be a carbene structure.

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## Synthesis and Structure of [$(NMe_2)_3TiFe(CO)_2(Cp)$]: A Stable Iron–Titanium Bond

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*Summary:* [$Ti(NMe_2)_4$] reacts with [$FeH(CO)_2(Cp)$] to form [$(NMe_2)_3TiFe(CO)_2(Cp)$] (**1**), by the elimination of 1 equiv of $HNMe_2$. This compound was spectroscopically characterized, and its structure was determined by single-crystal X-ray diffraction ($R$ = 4.0%, $R_w$ = 4.4%). There is a direct, unsupported bond between iron and titanium in **1**, with bond lengths of 2.567 (1) and 2.569 (1) Å in two independent molecules. The relative orientation of the ligands on iron and titanium suggests that there may be a $\pi$-component of the metal–metal bond. Amide methyl groups distal to iron show unusually obtuse Ti–N–C angles of about 130°. Analogous complexes with alkoxide ligands on titanium are more labile than **1**.

The nature of "strong metal-support interactions" (SMSI) in catalysts which consist of low-valent, late transition metals deposited on early-transition-metal oxide supports is not fully understood.[1] We are interested in preparing compounds that contain an early transition metal surrounded by "hard" $\pi$-donor ligands such as alkoxide, amido, or oxo bonded to a late transition metal surrounded by "soft" $\pi$-acceptor ligands such as CO or unsaturated hydrocarbons as possible models for catalysts that display SMSI. Binuclear elimination reactions, in which molecules such as $H_2$, alkanes, alcohols, or amines are eliminated, are effective methods for preparing heteronuclear metal–metal bonds.[2] For example, Caulton and co-workers have used alcohol, amine, and dihydrogen elimination, as well as more conventional halide displacement and condensation reactions, to form hydride-bridged Cu–Os,[3] Rh–Zn,[4] Re–Zr, Os–Zr,[5] Re–Al,[6] Ir–Cu, and Ir–Ag[7] compounds. Warner and Norton have prepared numerous heterobinuclear compounds by binuclear alkane (or aldehyde) elimination.[8] Casey and co-workers have prepared compounds with Ru–Zr and Fe–Zr bonds by reacting $K[M(CO)_2(Cp)]$ (M = Fe or Ru) with $[ZrXY(Cp)_2]$ (X = halide, Y = $OCMe_3$, Me, etc.), but the iron compounds are generally quite labile and have not been structurally characterized.[9] Several compounds with phosphides and other strong bridging ligands between group 4 and late transition metals have also been reported.[10] We recently reported the synthesis of $[(NMe_2)_3TiRu(CO)_2(Cp)]$, which contains a unbridged titanium–ruthenium bond, by the reaction of $[Ti(NMe_4)]$ with $[RuH(CO)_2(Cp)]$.[11] We report here the synthesis of $[(NMe_2)_3TiFe(CO)_2(Cp)]$, which contains the first structurally characterized iron–titanium bond.

$[Fe_2(CO)_4(Cp)_2]$ (0.6125 g, 1.73 mmol) was converted to $[FeH(CO)_2(Cp)]$ by the method of Baird et al.[12] This bright yellow solution of $[FeH(CO)_2(Cp)]$ was added to a solution of 0.674 g (3.0 mmol) of $[Ti(NMe_2)_4]$[13] dissolved in ca. 15 mL of pentane. After being left standing at −40 °C for ca. 15 h, the solution was evaporated to dryness in vacuo. The residue was extracted with 15 mL of pentane, and the extract was reduced in volume and chilled to −40 °C. Yellow crystals of $[(NMe_2)_3TiFe(CO)_2(Cp)]$ (1) formed in 44.5% yield. Spectroscopic properties of 1[14] were similar to those of $[(NMe_2)_3TiRu(CO)_2(Cp)]$,[11] and the absence of an infrared absorption at ca. 1600 $cm^{-1}$ suggested the absence of an "isocarbonyl" between iron and titanium in 1.[15]

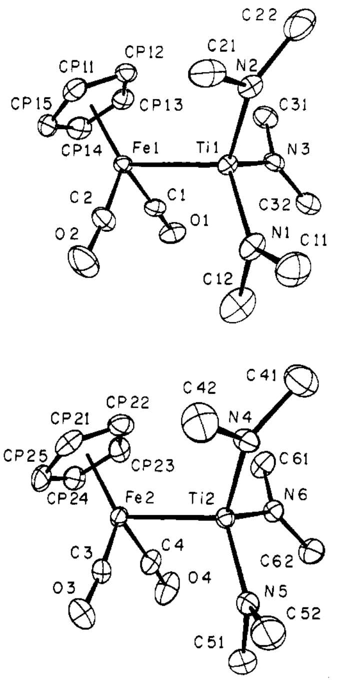

**Figure 1.** ORTEP[17] plot of the structure of 1 showing 50% probability ellipsoids. Selected bond distances (Å): molecule 1, Fe1–Ti1 = 2.567 (1), Fe1–C1 = 1.710 (6), Fe1–C2 = 1.756 (6), Fe1–Cp10 = 1.741 (6), Ti1–N1 = 1.889 (4), Ti1–N2 = 1.880 (4), Ti1–N3 = 1.888 (4), C1–O1 = 1.177 (6), C2–O2 = 1.147 (6); molecule 2, Fe2–Ti2 = 2.569 (1), Fe2–C4 = 1.743 (6), Fe2–C3 = 1.715 (6), Fe2–Cp20 = 1.731 (6), Ti2–N5 = 1.876 (4), Ti2–N4 = 1.884 (4), Ti2–N6 = 1.888 (4), C4–O4 = 1.149 (6), C3–O3 = 1.172 (6). Selected bond angles (deg): molecule 1, Ti1–Fe1–C1 = 80.5 (2), Ti1–Fe1–C2 = 82.3 (2), Ti1–Fe1–Cp10 = 122.7 (2), Fe1–Ti1–N1 = 112.5 (1), Fe1–Ti1–N2 = 111.9 (1), Fe1–Ti1–N3 = 109.8 (1), Ti1–N1–C11 = 128.7 (4), Ti1–N1–C12 = 120.4 (4), Ti1–N2–C21 = 114.2 (3), Ti1–N2–C22 = 133.3 (4), Ti1–N3–C31 = 117.8 (3), Ti1–N3–C32 = 129.8 (4), Fe1–C1–O1 = 176.8 (5), Fe1–C2–O2 = 174.5 (5); molecule 2, Ti2–Fe2–C3 = 81.0 (2), Ti2–Fe2–C4 = 81.4 (2), Ti2–Fe2–Cp20 = 128.2 (2), Fe2–Ti2–N5 = 110.7 (1), Fe2–Ti2–N4 = 111.4 (1), Fe2–Ti2–N6 = 110.9 (1), Ti2–N5–C51 = 121.2 (3), Ti2–N5–C52 = 129.1 (4), Ti2–N4–C41 = 130.3 (4), Ti2–N4–C42 = 118.2 (4), Ti2–N6–C61 = 117.5 (3), Ti2–N6–C62 = 130.8 (4), Fe2–C3–O3 = 174.8 (5), Fe2–C4–O4 = 176.8 (5). Selected torsion angles (deg): Cp10–Fe1–Ti1–N3 = −87.8, Cp20–Fe2–Ti2–N6 = −84.5. Cp10 and Cp20 are the centroids of the cyclopentadienyl rings Cp11–Cp15 and Cp21–Cp25, respectively.

The structure of 1 was determined by X-ray crystallography.[16] ORTEP[17] plots and selected bond distances and

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angles are presented in Figure 1. The most striking structural feature of 1 is the unsupported bond between Ti and Fe (average bond length 2.568 (1) Å for two independent molecules). The only previous structure with an unbridged bond between Ti and a first-row late transition metal is $[(Cp)Ti\{Co(CO)_4\}\{OCCo_3(CO)_9\}_2]$, with a Ti–Co distance of 2.614 Å.[18] The iron–titanium distance in iron–titanium alloy is 2.577 Å,[19] almost identical with that of 1. Coordination about Ti, formally an 8-electron center (or 14 electrons including $\pi$-donation from the amides), is roughly tetrahedral. The Ti–N bonds are rather short, averaging 1.884 Å, and the $Ti-NMe_2$ groups are planar, as is typical for compounds in which nitrogen to metal $\pi$-donation is important.[20] The dimethylamido groups are rotated about the Ti–N bonds such that one methyl group is proximal to iron and the other is distal. The proximal methyl carbons (C12, C22, C32, C42, C51, C61; $\bar{d}$(C–Fe) = 4.050 (8) Å) have Ti–N–C angles averaging 118°, 12° more acute than the same angle for the distal methyl carbons (C11, C21, C31, C41, C52, C62; $\bar{d}$(C–Fe) = 4.837 (8) Å). There is no apparent steric crowding at these carbons (the closest approach of any other atom is about 3.6 Å). Obtuse distal methyl–nitrogen–metal angles have been observed in other metal dialkylamides.[21] The effect is more pronounced in metal amides with a metal–metal bond[22] than in those without,[23] although in $[U(NPh_2)_4]$ pairs of U–N–C differ by up to 47°.[24] The titanium atoms do not interact with the carbonyl ligands. Ti–C distances in 1 average 2.89 Å, and Ti–O distances average 3.92 Å. Shriver's $\Omega$ parameter[15] averages 2.21 for the four carbonyls, a clear indication of their nonbridging character. The geometry of the $[Fe(CO)_2(Cp)]$ group is similar to that found in numerous iron–group 14 compounds such as $[Fe(SnCl_3)(CO)_2(Cp)]$.[25] The relative orientation of the ligands on the two metals is roughly gauche. In 1, as in $[(NMe_2)_3TiRu(CO)_2(Cp)]$, one of the Ti–N vectors lies nearly perpendicular to the $[M(CO)_2(Cp)]$ symmetry plane (see Figure 1 caption). We believe that this may be due to late-metal to early-metal donation from the "perpendicular" HOMO of $\pi$-symmetry on the $[M(CO)_2(Cp)]$ fragment[26] to an empty orbital of $\pi$-symmetry on titanium.

Compound 1 is quite labile, decomposing to $[Fe_2(CO)_4(Cp)_2]$ and intractable titanium products at room temperature, quickly in solution and more slowly in the solid state. Related iron–titanium alkoxides $[(OCHMe_2)_3TiFe(CO)_2(Cp)]$ and $[(NMe_2)(2,6\text{-}Me_2C_6H_4O)_2TiFe(CO)_2(Cp)]$ are formed from $[FeH(CO)_2(Cp)]$ and the appropriate titanium alkoxyamide. Iron–zirconium complexes can be prepared in a similar manner. In general, these iron compounds are strikingly less stable than their ruthenium congeners. Like $[(NMe_2)_3TiRu(CO)_2(Cp)]$,[11] compound 1 reacts with *tert*-butyl alcohol to give $[FeH(CO)_2(Cp)]$, which in turn decays to $[Fe_2(CO)_4(Cp)_2]$, and with $[MoH(CO)_3(Cp)]$ to give $[(NMe_2)_2Ti\{(\mu\text{-}CO)Mo(CO)_2(Cp)\}_2]$ and $[FeH(CO)_2(Cp)]$. Tertiary amines and ethers do not cleave the metal–metal bond of 1.

Thus, amine elimination is an effective means for preparing even very labile metal–metal bonded complexes under mild conditions. The key to the outcome of an amine elimination may be the acidity of the metal hydride component. Weakly acidic metal hydrides such as $[FeH(dppe)(Cp)]$ (estimated $pK_a > 30$) do not react at all with group 4 amides. $[FeH(CO)_2(Cp)]$ ($pK_a = 19.4$) and $[RuH(CO)_2(Cp)]$ (20.2)[27a] give metal–metal bonded products, whereas $[MoH(CO)_3(Cp)]$ (13.9)[27b,c] gives isocarbonyl-bridged products.[28] Molecular orbital calculations by Bursten[26a] on $[Cr(CO)_3(Cp)]^-$ and $[Fe(CO)_2(Cp)]^-$ show that the metal 3d based HOMO on $[Cr(CO)_3(Cp)]^-$ is a bonding orbital with about 35% population at the carbonyl oxygen, whereas the metal 3d based HOMO on $[Fe(CO)_2(Cp)]^-$ is nonbonding with essentially no population at the carbonyl, suggesting that the bonding mode is largely orbital-controlled. Darensbourg's extensive work on ion-pairing effects in organometallic systems supports this view.[29] Additional studies of group group 4–8 complexes will be reported in due course.

**Acknowledgment.** We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, Occidental Research Corp., the Institute for Mining and Minerals Research (subgrant from the U.S. Bureau of Mines), and Ashland Oil Corp. for financial support.

**Supplementary Material Available:** Listings of crystal structure data, positional and thermal parameters, bond distances

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(16) Crystal data for 1: A single-crystal, obtained by recrystallization from isooctane at −40°, was sealed in a nitrogen-filled 0.5-mm glass capillary. Data were collected at ambient temperature on an Enraf-Nonius CAD 4 diffractometer using Mo K$\alpha$ radiation: space group $P2_1/n$, $Z$ = 8 (2 independent molecules), $a$ = 15.148 (7) Å, $b$ = 15.369 (4) Å, $c$ = 16.381 Å, $\beta$ = 113.52°, $V$ = 3496.90 Å$^3$, $\rho_{calcd}$ = 1.357 g/cm$^3$, $\mu$ = 12.85 cm$^{-1}$. A total of 6401 refections with $0° < \theta < 25°$ were collected, and of these 3513 with $(F_o)^2 > 3\sigma(F_o)^2$ were used. The metal atoms were located by using MULTAN 77, and the remaining atoms (including several hydrogen atoms) were located by using DIRDIF.[30] The remaining hydrogen atoms were placed in idealized positions with $d$(C–H) = 1.0 Å, and their positions were adjusted after each cycle of refinement. All non-hydrogen atoms were refined by using anisotropic thermal parameters, and hydrogen atoms were held fixed with $B$ = 6.0 Å$^3$. Full-matrix least-squares refinement converged at $R$ = 4.0% and $R_w$ = 4.4%.

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and angles, torsion angles, and least-squares planes (11 pages); a listing of experimental and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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# Isolation and Characterization of the First σ-Organomanganese(III) Complex. Crystal and Molecular Structure of (2,4,6-Trimethylphenyl)dibromobis(trimethylphosphine)manganese(III)

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*Summary:* Alkylation of $MnBr_2$ with the mesityl (2,4,6-trimethylphenyl) reagent $Mg(C_6H_2Me_3)_2(THF)_2$ in the presence of trimethylphosphine followed by reaction with 1 equiv of oxygen yields dark red crystals of $Mn(C_6H_2Me_3)Br_2(PMe_3)_2$, which is the first isolated example of a σ-organomanganese(III) complex. This high-spin ($\mu$ = 4.8 $\mu_B$) complex adopts a distorted trigonal-bipyramidal structure of approximate $C_{2v}$ symmetry with the phosphine ligands occupying the axial sites. The metal-ligand distances are consistent with a trivalent oxidation state, while the orientation of the mesityl ring in the equatorial plane and the interligand angles can be rationalized on steric grounds.

The chemistry of manganese in its trivalent oxidation state is of interest due to the role of $Mn^{III}$ in biological redox reactions[1–12] and as inorganic oxidants;[13–15] the recently demonstrated ability of high-valent manganese porphyrin complexes to oxidize alkanes has stimulated substantial efforts to determine the mechanistic details of manganese-mediated organic oxidation processes.[16–21] Despite these studies, in no case has a manganese(III) compound been prepared that contains a metal–carbon σ-bond. We now report the synthesis and characterization of an organomanganese(III) complex derived from a divalent starting material and molecular oxygen.

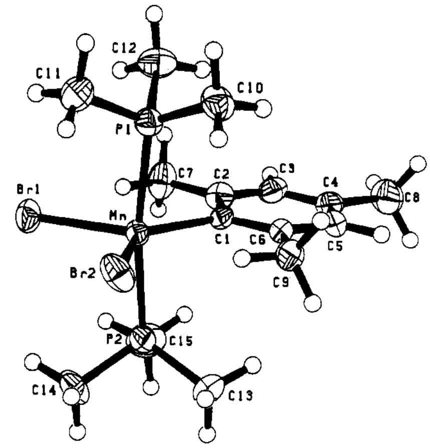

**Figure 1.** Molecular structure of $Mn(C_6H_2Me_3)Br_2(PMe_3)_2$. Important bond distances (Å) and angles (deg): Mn–C1 = 2.089 (8), Mn–P1 = 2.424 (3), Mn–P2 = 2.427 (3), Mn–Br1 = 2.505 (1), Mn–Br2 = 2.490 (2), C1–Mn–Br1 = 128.6 (2), C1–Mn–Br2 = 129.8 (2), C1–Mn–P1 = 86.0 (2), C1–Mn–P2 = 85.9(2), P1–Mn–P2 = 171.6 (1), Br1–Mn–Br2 = 101.68 (6).

Interaction of $MnBr_2$ in diethyl ether with trimethylphosphine[22–26] and $^1/_2$ equiv of the mesityl (2,4,6-trimethylphenyl) reagent $Mg(C_6H_2Me_3)_2(THF)_2$[27] generates pale yellow solutions of a monomesityl intermediate that is assigned a monomeric, 13-electron manganese(II) structure of stoichiometry $Mn(C_6H_2Me_3)Br(PMe_3)_2$ or $[Mn(C_6H_2Me_3)Br_2(PMe_3)]^-$, on the basis of previous studies of the reactions of manganese dihalides with alkylmagnesium reagents and phosphines.[28–31] Although the monomesityl intermediate has not yet been obtained as a pure material, addition of an additional $^1/_2$ equiv of dimesitylmagnesium generates $Mn(C_6H_2Me_3)_2(PMe_3)_2$,[32] which may be isolated as air-sensitive, pale yellow prisms by crystallization from diethyl ether. This 13-electron complex possesses an EPR spectrum essentially identical with those of other rhombically distorted $S = {}^5/_2$ complexes such as $Mn(CH_2CMe_2Ph)_2(PMe_3)_2$[28] and $Mn(t\text{-}Bu)_2(dmpe)$,[29] where dmpe is 1,2-bis(dimethylphosphino)ethane. Interestingly, these manganese(II) dialkyl species have been reported to give brightly colored solutions upon reaction with oxygen, but no organometallic products could be isolated;[28,31] identical behavior is observed upon oxidation of $Mn(C_6H_2Me_3)_2(PMe_3)_2$.

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[32] Yield: 61%. Anal. Calcd: C, 64.7; H. 9.05. Found: C, 63.2; H, 8.86. The carbon analyses are low evidently due to the air-sensitive nature of the complex and the volatility of the phosphine ligand.

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