

Carbon-Carbon Bond Formation at a Diiron Center. 5. Versatile Action of Phosphines on $\text{Fe}_2(\text{CO})_6(\mu\text{-COEt})(\mu\text{-CR}(\text{C}(\text{R}')\text{H}))$ Complexes ($\text{R} = \text{R}' = \text{Ph}, \text{H}$)

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The reaction of $\text{Fe}_2(\text{CO})_6(\mu\text{-COEt})(\mu\text{-CR}(\text{C}(\text{R}')\text{H}))$ complexes ($\text{R} = \text{R}' = \text{Ph}, \text{H}$) with the phosphines PPh_3 and PMe_2Ph is dependent on both phosphine and R . In the case where $\text{R} = \text{R}' = \text{Ph}$, reaction with PPh_3 leads only to the formation of $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ in boiling hexane. With PMe_2Ph the reaction occurs with CO substitution to give $\text{Fe}_2(\text{CO})_5(\text{PMe}_2\text{Ph})(\mu\text{-C}(\text{Ph})\text{C}(\text{Ph})\text{C}(\text{OEt})\text{H})$ (**3**), in which the organic fragment is $\eta^1:\eta^3$ bound through the carbons to the two iron atoms and $\eta^1(\text{O})$ bound through oxygen of the ethoxy group to an iron atom. In the case where $\text{R} = \text{R}' = \text{H}$, reaction with PMe_2Ph leads to the formation of $\text{Fe}(\text{CO})_{5-n}(\text{PMe}_2\text{Ph})_n$ ($n = 1, 2$) in boiling hexane. With PPh_3 , coupling of the two organic bridges is observed and the reaction occurs without CO loss, leading to $\text{Fe}_2(\text{CO})_6(\text{PPh}_3)(\mu\text{-C}(\text{OEt})\text{CH}(\text{Me})_2)$ (**5**). Protonation of **5** with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ gives $[\text{Fe}_2(\text{CO})_7(\text{PPh}_3)(\mu\text{-C}(\text{OEt})\text{CH}(\text{Me}))][\text{BF}_4]$, the structure of which has been established by an X-ray structure determination: triclinic; space group $P\bar{1}$; $a = 12.305$ (1) Å, $b = 16.069$ (2) Å, $c = 8.210$ (1) Å; $\alpha = 95.61$ (1)°, $\beta = 90.35$ (1)°, $\gamma = 87.10$ (1)°; $Z = 2$. The structure was solved and refined to R and R_w values of 0.031 and 0.032, respectively, with use of 3226 reflections.

Introduction

The study of the reactivity of $\text{Fe}_2(\text{CO})_6(\mu\text{-COEt})(\mu\text{-CR}(\text{C}(\text{R}')\text{H}))$ complexes (**1a**, $\text{R} = \text{R}' = \text{Ph}$; **1b**, $\text{R} = \text{R}' = \text{H}$) toward alkynes has shown that the reactions are dependent on both the nature of the alkynes and the R and R' groups.¹ The results are summarized in Scheme 1. In the case of compound **1a** we have detected **2** as a byproduct in the reactions, which is also observed by leaving the compound **1a** in solution at room temperature. An X-ray structure determination² of **2** showed that it possessed a $\text{Fe}_2(\text{CO})_6$ unit which is bridged by an organic group that results from the coupling of the carbyne and ethoxy bridges. Moreover, one of the double bonds of the R' phenyl group is π bonded to an iron atom and it was presumed that this complexation assisted the coupling reaction.

Expecting that the action of an external ligand such as a phosphine could induce the same type of coupling reactions, we examined the reactivity of triphenylphosphine and dimethylphenylphosphine toward **1a** and, for comparison, with **1b**. In fact, the results obtained show that the behaviors of **1a** and **1b** are quite different. The reactions do not lead to the same mode of coupling. In the case of **1a** the carbon-carbon bond coupling reaction is only observed with PMe_2Ph and occurs with departure of carbon monoxide and formation of a $\text{C}(\text{Ph})\text{C}(\text{Ph})\text{C}(\text{OEt})\text{H}$ fragment in which the ethoxy group is O-bonded to an iron center.

In the case of **1b** the coupling reaction is observed only with the PPh_3 ligand and it occurs without departure of carbon monoxide, leading to the expected $\text{C}(\text{OEt})\text{CH}(\text{Me})_2$ group $\eta^1:\eta^3$ bonded to the two iron centers. The reactivity

of this last product toward a Brønsted acid is also reported.

Results and Discussion

Reaction of $\text{Fe}_2(\text{CO})_6(\mu\text{-COEt})(\mu\text{-C}(\text{Ph})\text{C}(\text{Ph})\text{H})$ (1a**) with PMe_2Ph and PPh_3 .** In boiling hexane the reaction of PPh_3 with **1a** gives an intractable mixture of compounds in which $\text{Fe}_2(\text{CO})_6(\mu\text{-COEtC}(\text{Ph})\text{C}(\text{Ph})\text{H})^2$ and $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ have been detected.

Under the same conditions, PMe_2Ph leads to the formation of **3** as the only detectable product after chromatography in a 21% yield. Mass spectrometry data and chemical analysis are in accordance with the formation of **3** as $\text{Fe}_2(\text{CO})_5(\text{PMe}_2\text{Ph})(\text{COEtC}(\text{Ph})\text{C}(\text{Ph})\text{H})$. Proton NMR data show that except for the phenyl and ethoxy group resonances a single absorption at 5.22 ppm for the CH group is observed. This value is in the range found for the CH resonances in the dinuclear complexes $\text{Fe}_2(\text{CO})_6(\mu\text{-CR}(\text{C}(\text{R}')\text{C}(\text{OEt})\text{H}))$ ($\text{R} = \text{R}' = \text{Ph}$ (**4a**); $\text{R} = \text{Ph}, \text{R}' = \text{Me}$ (**4b**)), for which an X-ray structure determination has shown that the organic fragment is $\eta^1(\text{C}):\eta^3(\text{C})$ bonded and $\eta^1(\text{O})$ bonded through the oxygen atom of the ethoxy group.³ Confirmation of this structure comes from the ^{13}C NMR resonances of **3** and in particular the $\text{CH}(\text{OEt})$ resonance, which is observed at 96.3 ppm as a doublet ($J_{\text{CH}} = 183$ Hz) (95.4 ppm in the case where $\text{R} = \text{R}' = \text{Ph}$ ($J_{\text{CH}} = 186$ Hz)).

From these data it appears that treatment of **1a** with PMe_2Ph induces a quite complex reaction, resulting in not only carbon-carbon bond formation between the diphenylethenyl and ethoxycarbyne bridges but also migration of hydrogen onto the $\text{C}(\text{OEt})$ group.

From the NMR data it is difficult to assess the position of the phosphine ligand, and so the two possible structures shown in Figure 1 have to be considered. However, from the position of the ν_{CO} absorptions structure **3a** seems

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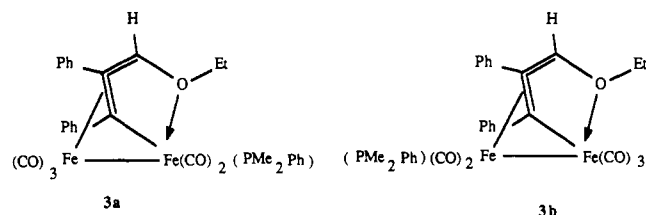


Figure 1. Proposed structures for compound 3.

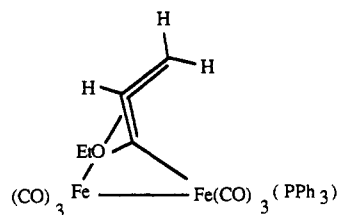
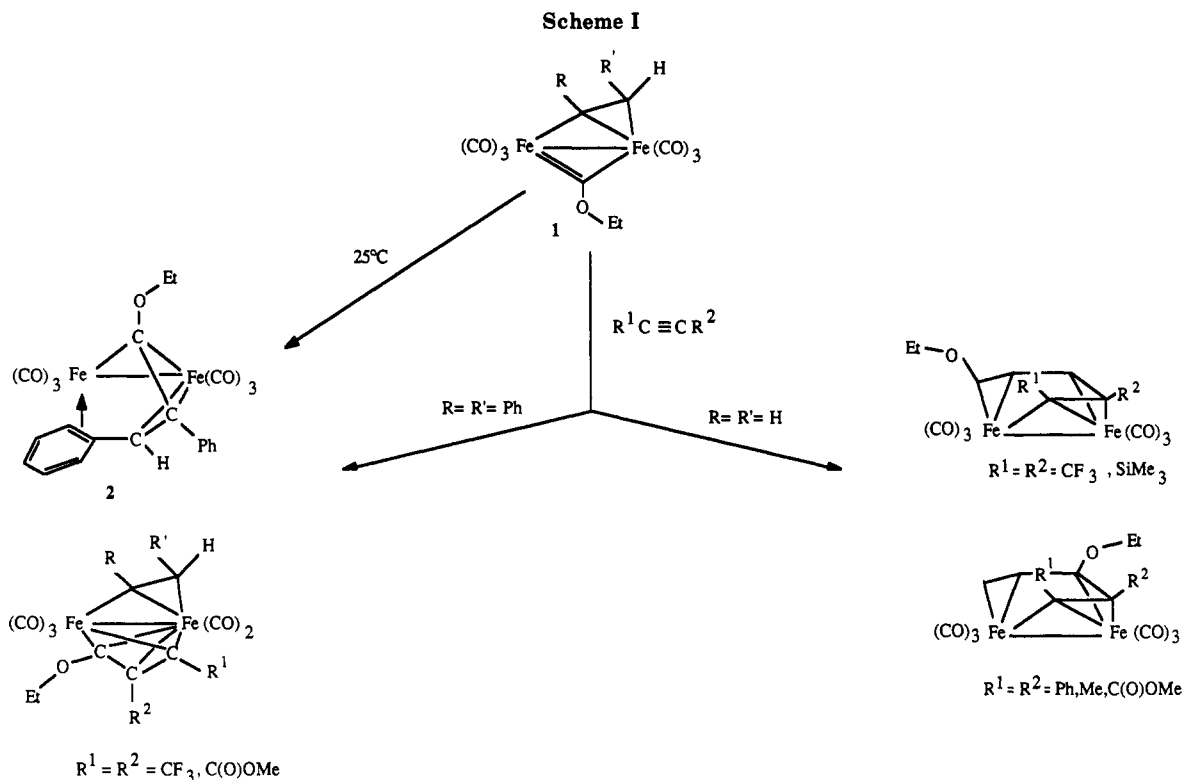


Figure 2. Structure of complex 5.



unlikely, since it implies that one iron center has two good donating ligands. If this were the case, ν_{CO} stretching absorptions at low frequencies would have been expected.

Reaction of Fe₂(CO)₆(μ-COEt)(μ-CHCH₂) (1b) with PMe₂Ph and PPh₃. No reaction occurs between 1b and PMe₂Ph at room temperature. In boiling hexane reaction leads to decomposition of 1a and formation of Fe(CO)₄(PMe₂Ph) and Fe(CO)₃(PMe₂Ph)₂, which were identified by infrared spectroscopy.

In boiling hexane, the reaction of PPh₃ with 1b gives the new complex 5 in 13% yield as the only isolable product. The analysis and mass spectral data are in accordance with the Fe₂(CO)₆(PPh₃)(COEtCHCH₂) formulation. In addition to the phenyl and ethoxy group resonances, the proton NMR spectrum shows a triplet at 4.77 ppm ($J = 8$ Hz) and two doublets of doublets centered at 2.15 and 1.85 ppm ($J_1 = 8$ Hz, $J_2 = 3.4$ Hz). These data are consistent with the presence of a π -bonded CHCH₂ group, as they closely resemble the proton NMR data for the known Fe₂(CO)₆(PPh₃)($\eta^1:\eta^3$ -CHCHCH₂).⁴

¹³C NMR data are also consistent with the Fe₂(CO)₆PPh₃($\eta^1:\eta^3$ -COEtCHCH₂) formulation. Indeed, a resonance at 221 ppm is characteristic for the bridging C(OEt) carbon⁵ and the CH and CH₂ resonances are observed at 70.1 ppm ($J_{CH} = 159$ Hz) and 37.4 ppm ($J_1 = 161$ Hz, $J_2 = 154$ Hz), respectively.

These results show that treatment of 1b with PPh₃ has induced the coupling of the ethoxycarbonyne and the vinyl group to form a $\eta^1:\eta^3$ -bonded vinylcarbene. Furthermore, the reaction has occurred without loss of carbon monoxide. The structure proposed for 5 is shown in Figure 2.

In summary, 1a and 1b show very different behaviors toward the two phosphines PPh₃ and PMe₂Ph, the carbon-carbon coupling reactions occurring only with one phosphine in each case. These results are difficult to rationalize; there must be a delicate balance between electronic and steric effects either from the phosphine ligand or from the ethenyl bridge. Another problem in proposing a mechanism for these reactions comes from the several possibilities for the mode of entry of the phosphine into the coordination sphere of iron atoms: this can occur through the opening of the iron-ethenyl π bond, through carbon monoxide departure, or through nucleophilic attack of the phosphine at the ethenyl carbon-carbon double bond.⁶

It should be noted that there is a certain analogy between the reactions of phosphines and of alkynes with complexes 1: the reaction occurs with CO departure for 1a and without CO departure for 1b, suggesting a specific effect of the 1,2-diphenylethenyl bridge that could be of steric origin. This hypothesis seems to be supported by the fact that the coupling reaction occurs only with the less bulky phosphine PMe₂Ph. (We have also verified that the

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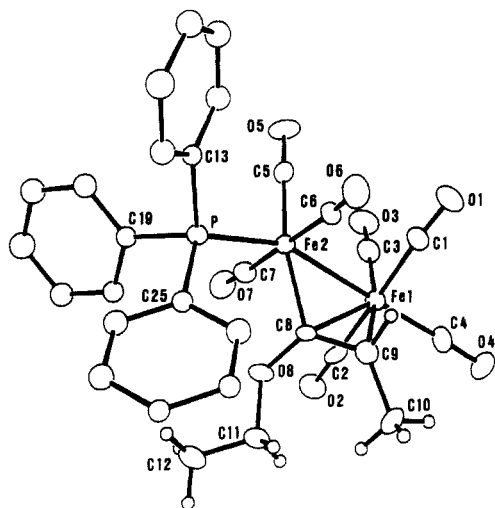


Figure 3. Ortep¹⁷ view of the cationic part of **6** (with ellipsoids at the 25% level of probability) showing the atomic numbering scheme.

reaction of **4** with PMe_2Ph does not lead to **3**, which suggests that the formation of **3** may be the result of a concerted mechanism.)

Reactivity of 5 toward $\text{HBF}_4 \cdot \text{Et}_2\text{O}$. To probe the reactivity of the vinylcarbene ligand in **5**, the reaction with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ has been studied. As could have been expected by analogy with the reactivity of the closely related η^3 -allyl complexes,⁷ the formation of the $\text{C}(\text{OEt})\text{CH}(\text{Me})$ vinyl group was observed. Indeed, **5** reacts smoothly with a slight excess of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in dichloromethane solution to give, after crystallization, the bright red solid **6**. The infrared spectrum in the ν_{CO} stretching region shows only terminal carbonyl groups, and as expected for a cationic complex, the absorptions are shifted to higher frequencies compared to those of **5**. Proton NMR resonance data gave good evidence for the formation of the $\text{C}(\text{OEt})\text{CH}(\text{Me})$ group since a doublet and a quartet were observed in a 3/1 intensity ratio ($J_{\text{H-H}} = 6.2$ Hz). ¹³C NMR data are also consistent with this formulation. A resonance is observed at 238.8 ppm, which is attributed to the $\text{C}(\text{OEt})$ carbon, and a doublet is observed at 57.6 ppm for the CH group ($J_{\text{CH}} = 157$ Hz), which is consistent with a π -bonded vinyl group.

The formulation of **6** was not clear from analytical data. Indeed, the conversion, via protonation, of the vinylcarbene ligand into a vinyl group results in the replacement of a four-electron ligand by a three-electron one. With the positive charge, **6** is two electrons short of a saturated electronic structure if no ligand is added during the reaction. This additional ligand could be a carbonyl group or could be provided by coordination of the oxygen of the ethoxy group. To solve this problem, an X-ray structure determination was performed. The ORTEP view of the cationic part of the molecule is shown in Figure 3, and bond distances and bond angles of interest are given in Table I.

The cation consists of a $\text{Fe}_2(\text{CO})_7(\text{PPh}_3)$ unit linked by the vinyl bridge $\text{C}(\text{OEt})\text{CH}(\text{Me})$. This result shows that the protonation reaction has occurred with the addition of a carbonyl group onto Fe(1) which was certainly provided by partial decomposition of **5**. (It has to be pointed that, unexpectedly, when the protonation is effected under a carbon monoxide atmosphere no significant improvement

Table I. Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for **5**

Fe(1)–Fe(2)	2.6910 (7)	Fe(2)–P	2.2738 (9)
Fe(1)–C(1)	1.833 (4)	Fe(2)–C(5)	1.788 (3)
Fe(1)–C(2)	1.804 (4)	Fe(2)–C(6)	1.808 (3)
Fe(1)–C(3)	1.810 (4)	Fe(2)–C(7)	1.805 (4)
Fe(1)–C(4)	1.819 (4)	Fe(2)–C(8)	1.974 (2)
Fe(1)–C(8)	2.306 (3)	Fe(1)–C(9)	2.209 (3)
C(1)–O(1)	1.139 (4)	C(8)–O(8)	1.346 (4)
C(2)–O(2)	1.140 (5)	C(9)–H(C9)	0.97 (3)
C(3)–O(3)	1.119 (4)	C(9)–C(10)	1.519 (5)
C(4)–O(4)	1.138 (5)	O(8)–C(11)	1.419 (3)
C(5)–O(5)	1.162 (4)	C(11)–C(12)	1.445 (5)
C(6)–O(6)	1.137 (5)	C(8)–C(9)	1.417 (4)
C(7)–O(7)	1.123 (4)		
Fe(1)–C(1)–O(1)	170.4 (3)	Fe(1)–C(2)–O(2)	177.5 (3)
Fe(1)–C(3)–O(3)	178.9 (3)	Fe(1)–C(4)–O(4)	176.5 (3)
Fe(2)–C(5)–O(5)	176.0 (3)	Fe(2)–C(6)–O(6)	172.4 (3)
Fe(2)–C(7)–O(7)	174.9 (3)	Fe(1)–Fe(2)–P	155.94 (3)
Fe(2)–Fe(1)–C(1)	80.3 (1)	Fe(1)–Fe(2)–C(5)	103.5 (1)
Fe(2)–Fe(1)–C(2)	99.7 (1)	Fe(2)–Fe(1)–C(3)	91.3 (1)
Fe(2)–Fe(1)–C(4)	161.5 (1)	Fe(1)–Fe(2)–C(6)	94.0 (1)
Fe(1)–Fe(2)–C(7)	84.6 (1)	Fe(1)–Fe(2)–C(8)	56.77 (8)
C(1)–Fe(1)–C(2)	177.1 (2)	P–Fe(2)–C(5)	100.5 (1)
C(1)–Fe(1)–C(3)	86.0 (2)	P–Fe(2)–C(6)	86.5 (1)
C(1)–Fe(1)–C(4)	90.1 (2)	P–Fe(2)–C(7)	94.9 (1)
C(2)–Fe(1)–C(3)	91.1 (2)	P–Fe(2)–C(8)	99.18 (9)
C(2)–Fe(1)–C(4)	90.7 (2)	C(5)–Fe(2)–C(6)	93.5 (1)
C(3)–Fe(1)–C(4)	103.8 (2)	C(5)–Fe(2)–C(7)	86.4 (1)
C(6)–Fe(2)–C(7)	178.6 (1)	C(5)–Fe(2)–C(8)	159.7 (1)
C(6)–Fe(2)–C(8)	92.8 (1)	C(7)–Fe(2)–C(8)	86.8 (1)
O(8)–C(8)–C(9)	124.5 (2)	C(8)–C(9)–H(C9)	111 (1)
Fe(2)–C(8)–O(8)	113.5 (2)	C(10)–C(9)–H(C9)	122 (1)
Fe(2)–C(8)–C(9)	121.7 (2)	C(8)–C(9)–C(10)	127.0 (3)

of the yield was observed.) Otherwise the structure confirms the formation of the $\text{CH}(\text{Me})$ group resulting from the protonation of the vinyl part of the $\eta^1:\eta^3$ -ethoxyvinylcarbene bridge.

The Fe(1)–Fe(2) distance is quite long, but it is in the range of values found for iron–iron single-bond distances.⁸ Examination of bond distances in the bridging vinyl group shows that while the Fe(2)–C(8) distance is in a normal range for this type of bonding,⁹ the Fe(1)–C(8) and Fe(1)–C(9) distances are long. This is particularly true for the Fe(1)–C(8) bond, and it is certainly due to the effect of the electron-donating OEt group. The same phenomenon has been observed in other iron complexes.^{1,10}

The other bond distances and bond angles in the vinyl group do not deserve special comment and are in the range expected for this ligand with this mode of bonding.

The Fe–CO bond distances are normal, and curiously there are no significant differences between the two iron centers, even though one is bearing a formal positive charge (Fe(1)) and the other is bonded to the phosphine ligand.

In summary, the successive action of PPh_3 and $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ on **1b** has allowed the transformation, on two iron centers, of the ethoxycarbene and the vinyl bridge into an $\eta^1:\eta^3$ -bonded ethoxyvinylcarbene ligand and then into an $\eta^1:\eta^2$ -1-ethoxypropenyl bridge.

Experimental Section

All reactions were performed under an atmosphere of nitrogen by using the standard Schlenk-tube technique. Infrared spectra were recorded with a Perkin-Elmer 225 spectrometer in hexane

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solution. ¹H NMR spectra were obtained on a Bruker WH90 spectrometer and the ¹³C NMR spectra on a Bruker WM250 machine.

Mass spectra were obtained on a Hewlett-Packard 2985 GC/MS spectrometer or on a Varian MAT 311A instrument.

The Fe₂(CO)₆(μ-COEt)(μ-CRCH) complexes were prepared as previously described for R = Ph² and R = H.^{1a}

Reaction of Fe₂(CO)₆(μ-COEt)(μ-CPhPhH) (1a) with PMe₂Ph: Synthesis of 3. A 0.13-g amount of 1a was refluxed with 0.02 mL of PMe₂Ph in hexane solution for 15 min. After evaporation of the solution the mixture was chromatographed on a SiO₂ column with a 4/1 mixture of hexane/benzene as eluant. A red band of the product was collected. Crystallization in a dichloromethane/methanol mixture gave 0.035 g of Fe₂(CO)₆(PMe₂Ph)(μ-CPhPhCH(OEt)) (3) as red crystals (21% yield). Anal. Calcd for C₃₀H₂₇Fe₂O₆P: C, 57.6; H, 4.31. Found: C, 57.11; H, 4.39. IR (ν_{CO}, hexane): 2015 (s), 1970 (s), 1942 (m), 1935 (sh) cm⁻¹. ¹H NMR (CDCl₃): δ 7.3–7.1 (C₆H₅), 5.22 (H), 3.30 (m, OCH₂), 1.37, 1.27 (d, J = 4.7 Hz, PMe₂), 0.77 (t, J = 7.0 Hz, CH₃) ppm. ¹³C NMR (CD₂Cl₂; except phenyl resonances): δ 217.2, 216.4, 215.7, 215.4 (CO), 171.3 (C(Ph)), 96.3 (d, J = 182.6 Hz, CH(OEt)), 93.2 (CPh), 73.1 (t, J = 146.5 Hz, OCH₂), 15.8 (dd, J_{PC} = 29 Hz, J_{CH} = 106 Hz, PCH₃), 14 (q, J = 127.5 Hz, OCH₂CH₃), 13.3 (dd, J_{PC} = 24 Hz, J_{CH} = 104 Hz, PCH₃) ppm.

Reaction of Fe₂(CO)₆(μ-COEt)(μ-CHCH₂) (1b) with PPh₃: Synthesis of 5. A 0.6-g amount of 1b and 0.38 g of PPh₃ were refluxed in hexane for 15 min. After chromatography of the mixture on SiO₂ with a 5/1 hexane/benzene mixture as eluant, an orange band was collected. After recrystallization in hexane 0.14 g of Fe₂(CO)₆(PPh₃)(μ-COEtCHCH₂) was obtained as orange crystals (13% yield). Anal. Calcd for C₂₉H₂₃Fe₂O₇P: C, 55.59; H, 3.67. Found: C, 55.77; H, 4.11. Mass spectrometry: m/z 626 with successive loss of 6 CO. IR (ν_{CO}, hexane): 2064 (m), 2017 (m), 1990 (s), 1969 (m), 1954 (sh) cm⁻¹. ¹H NMR (CDCl₃): δ 7.4 (C₆H₅), 4.77 (t, J = 8 Hz, H), 3.72 (m, OCH₂), 2.15 (dd, J₁ = 8 Hz, J₂ = 3.4 Hz), 1.85 (dd, J₁ = 8 Hz, J₂ = 3.4 Hz), 1.05 (t, J = 7 Hz, CH₃) ppm. ¹³C NMR (CD₂Cl₂; except phenyl resonances): δ 221.2 (C(OEt)), 214.3 (CO), 71.4 (d, J = 159 Hz, CH), 66.5 (t, J = 145 Hz, OCH₂), 37.5 (dd, J₁ = 161 Hz, J₂ = 154 Hz, CH₂), 14.4 (q, J = 126 Hz, OCH₂CH₃) ppm.

Reaction of 5 with HBF₄·Et₂O. A 0.5-g amount of 5 was dissolved in dichloromethane, and a slight excess of HBF₄·Et₂O (0.2 mL) was added. The solution was stirred for 1 h and then evaporated to dryness. Crystallization in methanol gave 0.19 g of [Fe₂(CO)₇PPh₃(μ-COEtCH(Me))][BF₄] (6) as dark red crystals (32% yield). Anal. Calcd for BC₃₀H₂₄Fe₂F₄O₈P: C, 48.51; H, 3.23. Found: C, 48.62; H, 3.12. IR (ν_{CO}, CH₂Cl₂): 2017 (m), 2058 (m), 2035 (s), 1999 (w), 1950 (w, broad) cm⁻¹. ¹H NMR ((CD₃)₂CO): δ 7.83 (C₆H₅), 4.35 (q, J = 7 Hz, OCH₂), 4.12 (q, J = 6 Hz, H), 2.01 (d, J = 6 Hz, CH₃), 1.1 (t, J = 7 Hz, CH₃) ppm. ¹³C NMR (CD₂Cl₂; except phenyl resonances): δ 238.8 (C(OEt)), 209.3, 209, 208.3, 207.1, 204.3, 203.7, 200.5 (CO), 74.5 (t, J = 146 Hz, OCH₂), 57.6 (d, J = 157 Hz, CH(Me)), 22.1 (q, J = 128.8 Hz, CH₃), 14.5 (q, J = 127.8 Hz, OCH₂CH₃).

X-ray Structure Analysis of [Fe₂(CO)₇PPh₃C(OEt)CH(Me)]BF₄. Collection and Reduction of X-ray Data. Crystals belong to the triclinic system, space group P $\bar{1}$. An orange-red parallelepiped of 0.35 × 0.20 × 0.075 mm size was glued on a glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer. Cell constants were obtained from the least-squares fit of the setting angles of 25 reflections in the range 14 < 2θ < 24°. A summary of crystal and intensity collection data is given in Table II. The 5050 recorded reflections (±h, ±k, ±l) were reduced¹¹ in the usual way. Three orientation reflections were checked every 400 reflections. There was no reorientation, the maximum allowed variation being 10%. Three intensity standards, monitored every 2 h, showed only random, statistical fluctuations. Reflections were corrected for empirical absorption¹² (μ = 10.1 cm⁻¹; calculated transmission range 0.85–1.00), with use of a ψ scan of four reflections having χ > 80°.

Table II. Crystal Data and Data Collection Details

Crystal Data			
formula	BC ₃₀ F ₄ Fe ₂ H ₂₄ O ₈ P	α, deg	95.61 (1)
fw	742.0	β, deg	90.35 (1)
cryst syst	triclinic	γ, deg	87.10 (1)
space group	P $\bar{1}$	V, Å ³	1613.5 (6)
a, Å	12.305 (1)	Z	2
b, Å	16.069 (2)	F(000)	752
c, Å	8.210 (1)	D(calcd), g cm ⁻³	1.527
		μ(Mo Kα), cm ⁻¹	10.1
Data Collection			
temp, °C	20		
radiation	Mo Kα (λ = 0.710 73 Å) from graphite monochromator		
θ (min–max), deg	1.5–24		
scan mode	ω–2θ		
scan range, deg	0.70 + 0.35 tan θ		
scan speed, deg min ⁻¹	1.1–5.5		
no. of collected rflns	5050		

Table III. Fractional Atomic Coordinates with Estimated Standard Deviations in Parentheses

atom	x/a	y/b	z/c
Fe(1)	0.47039 (4)	0.23604 (3)	0.46097 (6)
Fe(2)	0.65003 (4)	0.30555 (2)	0.36211 (5)
P	0.81581 (6)	0.30700 (5)	0.2419 (1)
C(1)	0.4080 (3)	0.3091 (2)	0.3255 (5)
O(1)	0.3575 (2)	0.3557 (2)	0.2565 (3)
C(2)	0.5311 (3)	0.1682 (2)	0.6026 (5)
O(2)	0.5676 (2)	0.1271 (2)	0.6966 (3)
C(3)	0.4482 (3)	0.3196 (2)	0.6236 (5)
O(3)	0.4361 (2)	0.3711 (2)	0.7249 (3)
C(4)	0.3455 (3)	0.1801 (2)	0.4574 (5)
O(4)	0.2697 (2)	0.1421 (2)	0.4492 (4)
C(5)	0.6327 (2)	0.4124 (2)	0.4453 (4)
O(5)	0.6180 (2)	0.4803 (1)	0.5067 (3)
C(6)	0.5929 (2)	0.3262 (2)	0.1659 (4)
O(6)	0.5686 (2)	0.3398 (2)	0.0369 (4)
C(7)	0.7037 (3)	0.2847 (2)	0.5600 (4)
O(7)	0.7345 (2)	0.2774 (2)	0.6871 (3)
C(8)	0.6265 (2)	0.1846 (2)	0.3242 (4)
C(9)	0.5314 (3)	0.1542 (2)	0.2457 (4)
H(C9)	0.494 (2)	0.198 (1)	0.188 (3)
C(10)	0.4973 (3)	0.0642 (2)	0.2263 (5)
O(8)	0.7040 (2)	0.1363 (1)	0.3909 (3)
C(11)	0.7241 (3)	0.0492 (2)	0.3486 (4)
C(12)	0.8367 (3)	0.0272 (2)	0.3827 (5)
C(13)	0.8277 (2)	0.3924 (1)	0.1107 (2)
C(14)	0.7748 (2)	0.4703 (1)	0.1523 (2)
C(15)	0.7797 (2)	0.5333 (1)	0.0475 (2)
C(16)	0.8375 (2)	0.5184 (1)	-0.0990 (2)
C(17)	0.8904 (2)	0.4404 (1)	-0.1405 (2)
C(18)	0.8855 (2)	0.3774 (1)	-0.0357 (2)
C(19)	0.9287 (2)	0.3181 (1)	0.3854 (2)
C(20)	0.9946 (2)	0.3864 (1)	0.3889 (2)
C(21)	1.0848 (2)	0.3909 (1)	0.4926 (2)
C(22)	1.1091 (2)	0.3271 (1)	0.5926 (2)
C(23)	1.0432 (2)	0.2588 (1)	0.5890 (2)
C(24)	0.9530 (2)	0.2543 (1)	0.4854 (2)
C(25)	0.8583 (1)	0.2137 (1)	0.1077 (2)
C(26)	0.9679 (1)	0.1881 (1)	0.0895 (2)
C(27)	0.9988 (1)	0.1196 (1)	-0.0212 (2)
C(28)	0.9200 (1)	0.0768 (1)	-0.1137 (2)
C(29)	0.8104 (1)	0.1024 (1)	-0.0955 (2)
C(30)	0.7795 (1)	0.1709 (1)	0.0152 (2)
B	0.2975 (3)	0.1884 (2)	0.9331 (4)
F(1)	0.3974 (2)	0.2206 (1)	0.9316 (2)
F(2)	0.2705 (2)	0.1798 (2)	1.0905 (3)
F(3)	0.2241 (2)	0.2431 (2)	0.8714 (4)
F(4)	0.2971 (3)	0.1146 (2)	0.8459 (5)

Structure Solution and Refinement. After Fe atoms were located from a Patterson map, the full-matrix least-squares refinement and difference Fourier processes were achieved with the SHELX-76 program¹³ with 3226 reflections having F_o² ≥ 3σ(F_o²).

(11) SDP, Structure Determination Package from B. A. Freng and Associates, Inc., College Station, TX 77840, and Enraf-Nonius, Delft, Holland, 1985.

(12) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* 1968, A24, 351.

(13) Sheldrick, G. M. SHELX-76, Program for Crystal Structure Determination; University of Cambridge: Cambridge, England, 1976.

Phenyl rings were refined as isotropic rigid groups ($C-C = 1.395 \text{ \AA}$). All hydrogens, except that bonded to C(9), were introduced into calculations in constrained geometry ($C-H = 0.97 \text{ \AA}$). H(C9) was allowed to vary with a fixed U value of 0.06 \AA^2 . All H isotropic thermal parameters were first refined; then, from the found values, they were kept fixed to 0.07 \AA^2 for methyls, 0.06 \AA^2 for ethyls, and 0.065 \AA^2 for other groups. All other atoms were refined anisotropically. The atomic scattering factors used were those proposed by Cromer and Waber¹⁴ with anomalous dispersion effects¹⁵ and those by Stewart et al.¹⁶ for H atoms.

(14) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.B, pp 99-101.

(15) Cromer, D. T. In ref 14, Table 2.3.1, p 149.

(16) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(17) Johnson, C. K. ORTEP; Report ORNL 3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

The final full-matrix least-squares refinement converged to $R = \sum(|F_o| - |F_c|) / \sum|F_o| = 0.031$ and $R_w = [(\sum|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.032$ with $w = [\sigma^2(F_o) + 0.01F_o^2]^{-1}$. The error in an observation of unit weight was $S = [\sum w(|F_o| - |F_c|)^2 / (n - m)]^{1/2} = 1.13$ with $n = 3226$ observations and $m = 292$ variables. An analysis of variance showed no unusual trends. In the last cycle of refinement the maximum parameter shift/esd was 0.4 (a H parameter). A final difference Fourier map showed a residual electron density of 0.3 e/\AA^3 near F atoms. The final fractional atomic coordinates are listed in Table III.

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Supplementary Material Available: Tables of hydrogen atom coordinates, thermal parameters, and bond lengths and angles (4 pages); a listing of structure factors (16 pages). Ordering information is given on any current masthead page.

Reagents Based on Cyclopentadienyl Derivatives of the Group 14 Elements for the Synthesis of Indium(I) Derivatives. Crystal and Molecular Structure of $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$

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Cyclopentadienyl trimethyl derivatives of the group 14 elements ($\text{C}_5\text{H}_4\text{MMe}_3$, $M = \text{Si, Ge, Sn}$) have been investigated for their effects on indium(I) chemistry. The compounds $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$ and $\text{In}(\text{C}_5\text{H}_4\text{GeMe}_3)$ have been prepared from the corresponding lithium cyclopentadienyl reagent $\text{LiC}_5\text{H}_4\text{MMe}_3$ and InCl . Characterization data have included partial elemental analyses (C, H), physical properties, IR and ^1H NMR spectroscopic data, oxidation reactions with dilute aqueous HCl, and a single-crystal X-ray structural study in the case of $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$. When cyclopentadienyltrimethyltin, $\text{C}_5\text{H}_5\text{SnMe}_3$, was combined with InCl in diethyl ether, $\text{In}(\text{C}_5\text{H}_5)$ and Me_3SnCl were formed in good yields. $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$ crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^2 ; No. 14) with $a = 9.171(5) \text{ \AA}$, $b = 9.910(6) \text{ \AA}$, $c = 11.677(7) \text{ \AA}$, $\beta = 97.30(5)^\circ$, $V = 1052.6(11) \text{ \AA}^3$, and $Z = 4$. Diffraction data (Mo $K\alpha$ radiation, $2\theta = 4.5\text{--}50.0^\circ$) were collected on a Syntex P2₁ automated four-circle diffractometer, and the structure was solved and refined to $R_F = 5.0\%$ and $R_{wF} = 4.0\%$ for all 1851 independent reflections ($R_F = 3.1\%$ and $R_{wF} = 3.5\%$ for those 1336 data with $|F_o| > 6\sigma|F_o|$). The solid-state structure consists of infinite zigzag chains of $[\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)]_\infty$. Each indium atom interacts with two $\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$ ligands with a centroid...In...centroid angle of 131.78° , and each $\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$ ligand is linked to two indium atoms with In...centroid...In angles of 175.94° . There are no short interstrand In...In interactions, the shortest such distance being 5.428 \AA . Thus, $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$ is the first cyclopentadienylindium(I) derivative with no apparent indium-indium interactions.

Introduction

The low-oxidation-state compounds of the group 13 elements provide the focus for an interesting area of research. The cyclopentadienylindium(I) derivatives $\text{In}(\text{C}_5\text{H}_5)^1$ and $\text{In}(\text{C}_5\text{H}_4\text{Me})^1$ exist in the solid state as zigzag chains but with slightly different structures. The packing of the $\text{In}(\text{C}_5\text{H}_5)$ units leads to a structure in which each indium atom is $3.986(1) \text{ \AA}$ away from two other indium atoms. The structure of $\text{In}(\text{C}_5\text{H}_4\text{Me})$ has one indium atom at $3.986(1) \text{ \AA}$ from only one other indium atom. The compound $\text{In}[\text{C}_5(\text{CH}_2\text{Ph})_5]^3$ forms quasi-dimeric units with indium-indium distances of $3.631(2) \text{ \AA}$, the shortest ob-

served to date. It is noteworthy that the pentamethylcyclopentadienyl moiety in $\text{In}(\text{C}_5\text{Me}_5)^4$ leads to apparent hexameric clusters in the solid state with indium-indium distances of $3.963(1)$ and $3.943(1) \text{ \AA}$. These observations suggest that the nature of the cyclopentadienyl moiety influences the number of indium-indium interactions per indium atom. There are no two cyclopentadienylindium(I) derivatives that have identical structures. It is of significance to realize that the interactions between the indium atoms are apparently weak. Only monomeric species have been observed by electron diffraction techniques for the gas phase of $\text{In}(\text{C}_5\text{H}_5)$,¹ $\text{In}(\text{C}_5\text{H}_4\text{Me})$,¹ and $\text{In}(\text{C}_5\text{Me}_5)$.^{4a} The gas-phase structure of $\text{In}[\text{C}_5(\text{CH}_2\text{Ph})_5]$ has not been reported. Thus, in order to learn more about the factors that

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