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Synthesis and Mössbauer Effect Study of Several Novel Bridged Derivatives of $Me_2Si[(\eta^5\text{-}C_5H_4)_2Fe_2(CO)_4]$ and the Crystal Structure of $Me_2Si[(\eta^5\text{-}C_5H_4)_2(CO)Fe(\mu\text{-}CO)_2Fe(Ph_2PCH_2PPh_2)]$

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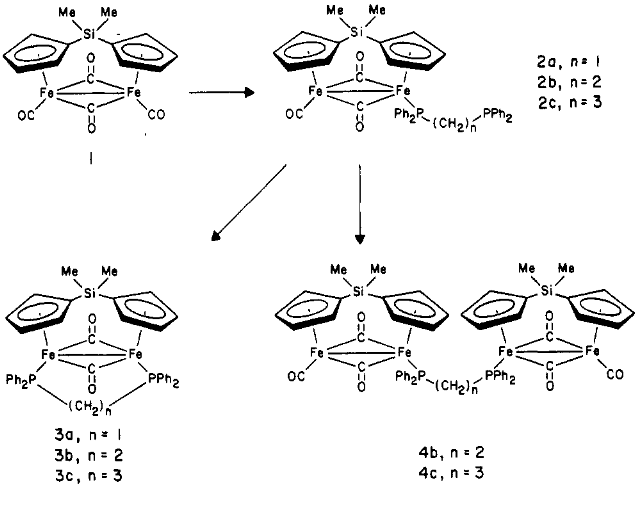
Irradiation of a benzene solution containing $Me_2Si[(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2$ (1) and either $Ph_2PCH_2PPh_2$ or $Ph_2PCH_2CH_2PPh_2$ has led to the isolation of the monosubstituted complexes $Me_2Si[(\eta^5\text{-}C_5H_4)_2(CO)Fe(\mu\text{-}CO)_2Fe(Ph_2P(CH_2)_nPPh_2)]$, where n is one, **2a**, or two, **2b**. The key feature in these syntheses is the use of a 450-W medium-pressure Hg lamp which has lost a considerable amount of its intensity through at least 2000 h of use. The crystal and molecular structure of **2a** has been determined by single-crystal X-ray diffraction. Complex **2a** crystallizes in the space group $P2_1/c$ with a = 12.389 (4) Å, b = 21.525 (7) Å, c = 13.507 (3) Å, and β = 91.81 (2)° with Z = 4. The structure is refined to R_1 = 0.057 and R_2 = 0.063 for 3270 independent reflections having $I > 3\sigma(I)$. The Mössbauer effect spectra of 1 and 2 as well as of the complexes with intramolecular bidentate bis(phosphine) ligands, 3, and intermolecular bridging bis(phosphine) ligands, 4, have been measured. The resulting spectra indicate only one iron site in 1, 3, and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (5) whereas two iron sites are observed in 2 and 4. The Me_2Si bridge in 1 has little effect on the symmetry at the iron site as indicated by the similarity of its Mössbauer quadrupole splitting with that of 5. In addition, the average isomer shift increases upon phosphine substitution as a result of more extensive phosphine to iron π-bonding. The variation in the isomer shift in view of the almost constant iron–iron bond distance in these dimers provides further experimental support for the lack of direct iron–iron bonding in these compounds.

Introduction

The synthesis of a large number of metal–metal bonded bridged binuclear transition-metal complexes have been described in recent years.[1] The interest in binuclear systems is in part due to the increasing evidence that certain transition-metal-mediated processes depend on catalysts or intermediates containing more than one metal.[2] Often the placement of a noninteractive bridge in the binuclear systems produces a unique metal environment[5] which leads to interesting catalytic behavior. The chemistry of one such compound, $Me_2Si[(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2$ (1), was initially examined by Wegner et al.,[3] and more recently two of us have prepared several derivatives of 1 and explored their chemical reactivity.[4] In this paper we wish to report details of the synthesis and characterization of the new bridged metal–metal bonded complexes $Me_2Si[(\eta^5\text{-}C_5H_4)_2(CO)Fe(\mu\text{-}CO)_2Fe(Ph_2P(CH_2)_nPPh_2)]$, where n is one, **2a**, or two, **2b**. Further we report herein the crystal and molecular structure of **2a**.

Some of our recent work on the Mössbauer spectral properties of binuclear,[5,6] trinuclear,[7] and tetranuclear[8] organoiron clusters has indicated the importance of such studies in understanding the detailed electronic properties of such clusters. As a result we have undertaken a detailed Mössbauer effect study of compounds 1 and 2 as well as of $Me_2Si[(\eta^5\text{-}C_5H_4)_2Fe_2(\mu\text{-}CO)_2(Ph_2P(CH_2)_nPPh_2)]$ (**3a**, **3b**, and **3c**), where n equals 1, 2, and 3, respectively, and $Ph_2P(CH_2)_nPPh_2$ acts as a bidentate ligand bridging the iron atoms[4a,9] in the dimer, and $\{Me_2Si[(\eta^5\text{-}C_5H_4)_2Fe_2(CO)_3]\}_2Ph_2P(CH_2)_nPPh_2$ (**4b** and **4c**), where n equals 2 and

Scheme I



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3, respectively, and the phosphine ligand bridges *two* of the iron dimer units.[4a] The results of these studies are also reported herein,

Experimental Section

All manipulations of complexes and solvents were carried out by using standard Schlenk techniques under an atmosphere of purified argon or nitrogen. Solvents were degassed and purified by distillation under nitrogen from standard drying agents.[9] Spectroscopic measurements utilized the following instrumentation: proton NMR, a Bruker WM 250 FT (at 250 MHz); carbon-13 NMR, a Bruker WM 250 FT (at 62.9 MHz); phosphorus-31 NMR, a Bruker WM 250 FT (at 101.3 MHz); IR, a Perkin-Elmer 983. NMR chemcial shifts are reported in δ versus Me_4Si by assigning the $CDCl_3$ resonance in carbon-13 spectra at 77.00 ppm. Phosphorus-31 chemical shifts are relative to external 85% H_3PO_4 with the downfield chemical shifts reported as positive. Carbon-13 spectra are run with proton decoupling, and resonances may be assumed to be singlets unless a multiplicity is specified.

The compounds 1,[4c] 3,[4a] and 4[4a] have been prepared by literature methods. Bis(diphenylphosphino)methane and 1,2-bis(diphenylphosphino)ethane were obtained from Strem Chemical Co. and used as received. The alumina (Woelm N32-63) for the medium-pressure chromatography was purchased from Universal Scientific and deactivated to grade III. Medium-pressure chromatography utilized a column 15 × 500 mm. NMR solvents were routinely degassed by three consecutive freeze-pump-thaw cycles and stored under nitrogen. Irradiations were carried out in Pyrex flasks that were placed along side a quartz finger containing a medium-pressure Hg lamp (2000 h of logged use) and a Pyrex filter.

Preparation of $Me_2Si[(\eta^5\text{-}C_5H_4)_2(CO)Fe(\mu\text{-}CO)_2Fe(Ph_2PCH_2PPh_2)]$ (2a). A benzene (50 mL) solution containing 1 (0.50 g, 1.2 mmol) and bis(diphenylphosphino)methane (1.90 g, 4.8mmol) was irradiated for 6 h. The solution was filtered through Celite and the solvent removed under vacuum. The residue was dissolved in CH_3CN (25 mL) and held at −25 °C for 4 h. The crystalline product was collected and washed twice with 25 mL of CH_3CN. Medium-pressure chromatography (alumina III, benzene) of this precipitate gave two bands. The inital blue-green band was collected and the solvent removed to yield **2a** (0.55 g, 60%). The second green band was identified as **3a**. For the new compound **2a**: IR (in CH_2Cl_2) γ(CO) 1952 and 1728 cm^{-1}; proton NMR (δ, $CDCl_3$) 7.74–6.89 (m, 20, C_6H_5), 5.30 (dd, 2, J = 2.0 Hz, C_5H_4), 5.00 (dd, 2, J = 2.0 Hz, C_5H_4), 4.77 (s, 2, C_5H_4), 4.40 (m, 2, C_5H_4), 1.99 (s, 3, CH_3CN), 1.90 (dd, 2, J = 2.1, 5.3 Hz, CH_2), 0.40 (s, 6, $SiCH_3$); carbon-13 NMR (δ, $CDCl_3$) 283.30 (C═O), 217.73 (C═O), 132.92–127.82 (C_6H_5), 96.26, 94.45, 90.50, 90.14, 86.40, 82.89 (C_5H_4), 27.43 (dd, J = 19.8, 16.7 Hz, CH_2), −3.19 ($SiCH_3$); phosphorus-31 NMR (δ, $CDCl_3$) 66.37 (d, J = 27 Hz), −24.21 (d, J = 27 Hz). Anal. Calcd for $C_{40}H_{36}Fe_2O_3P_2Si{\cdot}CH_3CN$: C, 62.47, H, 4.87. Found: C, 62.16, H, 4.75.

Preparation of $Me_2Si[(\eta^5\text{-}C_5H_4)_2(CO)Fe(\mu\text{-}CO)_2Fe(Ph_2PCH_2CH_2PPh_2)]$ (2b). A benzene solution (50 mL) containing 1 (0.50 g, 1.2 mmol) and 1,2-bis(diphenylphosphino)ethane (1.90 g, 4.8mmol) was irradiated for 6 h. The solution was treated and chromatographed as described above. Green and blue-green bands, consisting of **3b** and **2b** (0.61 g, 65%), are eluted in that order. Complex **2b** is readily recrystallized by dissolving the oil obtained from the chromatography in CH_3CN (25 mL) and maintaining the solution at −25 °C for 24 h. For the new compound **2b**: IR (in CH_2Cl_2) ν(CO) 1954 and 1732 cm^{-1}; proton NMR (δ, $CDCl_3$) 7.52, 7.04 (m, 20, C_6H_5), 5.29 (dd, 2, C_5H_4), 4.32 (m, 2, C_5H_4), 1.99 (s, 3, CH_3CN), 1.53 (m, 2, C_2H_4), 1.30 (m, 2, C_2H_4), 0.38 (s, 6, $SiCH_3$); carbon-13 NMR (δ, $CDCl_3$) 282.98 (d, J = 15 Hz, C═O), 216.64 (C═O), 137.98–128.07 (C_6H_5), 96.37, 95.00, 90.00, 86.32, 82.90 (C_5H_4), 24.91 (t, J = 20 Hz, C_2H_4), 22.95 (dd, J = 7, 9 Hz, C_2H_4), −3.23 ($SiCH_3$); phosphorus-31 NMR 67.74 (d, J = 32 Hz), 12.38 (d, J = 32 Hz). Anal. Calcd. for $C_{41}H_{38}Fe_2O_3P_2Si{\cdot}CH_3CN$: C, 62.87, H, 5.03, N, 1.79. Found: C, 62.85, H, 5.03, N, 1.75.

Table I. Summary of Crystallographic Data for Crystalline 2a

space group	$P2_1/c$ (no. 14)
a, b, c, Å	12.389 (4), 21.525 (7), 13.507 (3)
β, deg	91.81 (2)
V, $Å^3$	3600.2 (18)
d_{calcd}, g/cm^3	1.41
fw, Z	766.45, 4
cryst size, mm	0.15 × 0.30 × 0.40
μ(Mo $K\bar{\alpha}$), cm^{-1}	9.6
diffractometer	Syntex $P2_1$
monochromator	graphite crystal
scan method	θ–2θ
scan speed, deg/min	3.0–29.3 (variable)
bkgd time	half the scan time
2θ limits, deg	4.0–50.0
no. of unique data	6849
no. of data with $\|F_o^2\| > 3\sigma\|F_o^2\|$	3270
R_1	0.057
R_2	0.063
no. of variables	433
goodness of fit	1.9

Crystal Structure of 2a. Dark green, shiny air-stable single crystals of **2a** are obtained from a saturated acetone solution at −25 °C. A crystal of **5a** was mounted on a glass fiber in air by using epoxy cement and inspected by rotation photography on the Syntex P2 diffractometer with Mo $K\alpha$ (λ = 0.71073 Å) radiation and a graphite monochromator. The ω-scan peak profiles of several reflections show an average half-width of 0.20°. The standard Syntex $P2_1$ centering (25 random reflections), indexing, and data collection programs were utilized. A summary of data collection and refinement parameters is presented in Table I, and complete details of the structure determination can be found in Table II of the supplementary material. Standard Lorentz and polarization corrections were applied to the data. With the modest size of the crystal and the low μ(Mo $K\alpha$) of 9.6 cm^{-1} no absorption correction was deemed necessary. During data collection three standard reflections were measured every 297 reflections. The standard intensities remained constant within experimental error throughout the entire time required for data collection.

The structure was initially solved by direct methods using the 1978 version of the MULTAN program.[11] The remaining non-hydrogen atoms were located by standard difference Fourier techniques. The entire structure, 48 non-hydrogen atoms, was refined by utilizing isotropic thermal parameters to convergence with R_w = 0.087. The structure was then refined by employing anisotropic thermal parameters dividing the molecule into three molecular fragments and refining each fragment in random order to convergence. No effort was made to locate the hydrogen atoms in the structure. The largest peak found in the final difference Fourier map was 0.58 $e/Å^3$. The final agreement factors were 0.057 and 0.063 for R_1 and R_2, respectively, for 3270 reflections[12] having

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(12) A reviewer has correctly pointed out that a redundancy of data is present in the structure determination, that being F_{hk0} and $F_{\bar{h}k0}$ observed were not averaged.

Table III. Final Atomic Positions for Non-Hydrogen Atoms in Crystalline 2a[a]

atom type[b]	x	y	z
Fe_a	0.52377 (9)	0.38759 (6)	0.69474 (8)
Fe_b	0.34037 (8)	0.38329 (6)	0.60686 (8)
P(1)	0.2153 (2)	0.41325 (10)	0.7095 (2)
P(2)	0.1573 (2)	0.45483 (10)	0.9239 (2)
C(1)	0.4302 (7)	0.4513 (4)	0.6377 (6)
O(1)	0.4370 (5)	0.5064 (3)	0.6276 (4)
C(2)	0.4022 (6)	0.3302 (4)	0.7055 (6)
O(2)	0.3848 (5)	0.2846 (3)	0.7501 (4)
C(3)	0.5095 (6)	0.4165 (4)	0.8130 (6)
O(3)	0.5128 (5)	0.4355 (3)	0.8939 (5)
C_b	0.2652 (6)	0.4352 (3)	0.8340 (5)
Si	0.5366 (2)	0.3046 (1)	0.4738 (2)
C_{m1}	0.6024 (7)	0.3252 (5)	0.3530 (6)
C_{m2}	0.5278 (9)	0.2192 (4)	0.4952 (9)
C_{pa1}	0.6110 (6)	0.3422 (4)	0.5796 (6)
C_{pa2}	0.6413 (6)	0.4076 (4)	0.5849 (7)
C_{pa3}	0.6851 (6)	0.4206 (5)	0.6812 (7)
C_{pa4}	0.6835 (6)	0.3624 (5)	0.7357 (7)
C_{pa5}	0.6388 (6)	0.3141 (4)	0.6743 (6)
C_{pb1}	0.3975 (6)	0.3379 (4)	0.4773 (5)
C_{pb2}	0.3033 (8)	0.3050 (5)	0.5108 (6)
C_{pb3}	0.2166 (7)	0.3491 (6)	0.5094 (6)
C_{pb4}	0.2552 (8)	0.4073 (5)	0.4724 (6)
C_{pb5}	0.3667 (7)	0.4006 (4)	0.4521 (5)
C(4)	0.1142 (6)	0.3517 (4)	0.7351 (6)
C(5)	0.1376 (7)	0.3092 (4)	0.8125 (6)
C(6)	0.0638 (8)	0.2609 (4)	0.8295 (8)
C(7)	−0.0316 (8)	0.2558 (5)	0.7700 (9)
C(8)	−0.0533 (7)	0.2983 (5)	0.6906 (8)
C(9)	0.0190 (7)	0.3484 (4)	0.6739 (6)
C(10)	0.1302 (6)	0.4800 (4)	0.6747 (6)
C(11)	0.0283 (7)	0.4893 (4)	0.7145 (6)
C(12)	−0.0277 (8)	0.5447 (5)	0.6969 (8)
C(13)	0.0156 (10)	0.5891 (5)	0.6349 (10)
C(14)	0.1194 (9)	0.5811 (5)	0.5935 (8)
C(15)	0.1759 (7)	0.5261 (4)	0.6130 (6)
C(16)	0.2199 (7)	0.4220 (4)	1.0372 (6)
C(17)	0.1665 (8)	0.3693 (4)	1.0742 (7)
C(18)	0.213 (1)	0.3392 (5)	1.1594 (8)
C(19)	0.309 (1)	0.3618 (5)	1.2038 (8)
C(20)	0.3611 (9)	0.4145 (5)	1.1646 (8)
C(21)	0.3153 (8)	0.4442 (4)	1.0796 (7)
C(22)	0.1760 (6)	0.5392 (4)	0.9452 (6)
C(23)	0.1306 (7)	0.5619 (5)	1.0307 (7)
C(24)	0.1287 (8)	0.6262 (5)	1.0486 (8)
C(25)	0.1723 (9)	0.6671 (5)	0.9793 (9)
C(26)	0.2139 (10)	0.6440 (5)	0.8917 (8)
C(27)	0.2190 (8)	0.5784 (5)	0.8737 (7)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit(s). [b] Atoms are labeled in agreement with Figure 1.

an intensity greater than $3\sigma(I)$.

Final atomic positional parameters are listed in Table III. A complete listing of anisotropic thermal parameters (Table IV), bond lengths and angles (Table V), and structure factors (Table VI) are available as supplementary material.

Mössbauer effect spectra were obtained at room temperature and 78 K on a conventional Ranger Scientific constant acceleration spectrometer which utilized a room-temperature rhodium matrix cobalt-57 source. The spectra were fit to Lorentzian line shapes by using standard least-squares computer minimization techniques.[10] The error analysis was carried out by using standard error propagation techniques. All of the spectra consist of either a single or two partially resolved quadrupole doublets. In our fitting procedure each component of a quadrupole doublet was constrained to have equal line widths. In the spectra of compounds with two different iron sites, the two quadrupole doublets were constrained to have equal areas.

Results and Discussion

Both $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (**5**) and $Me_2Si[(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2$ (**1**) are known to readily substitute a single phosphine or phosphite ligand, L, for carbon monoxide to give complexes of the type $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3L$[13] and $Me_2Si[(\eta^5\text{-}C_5H_4)Fe_2(CO)_3L]$,[14] respectively. The replacement, of the two terminal carbon monoxide ligands in $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (**5**) and **1**, by the bidentate bis(phosphine) ligands, $Ph_2P(CH_2)_nPPh_2$, where n is equal to 1, 2, and 3 has been established[4a,15] and in the latter case gives **3a**, **3b**, and **3c**. In preparing complexes like **3**, we find that, as the irradiation source, a medium-pressure Hg lamp, drops in intensity due to extended use, compounds of type **2** prevail. For example, by employing a Hg lamp, with ca. 2000 h of use, and a Pyrex filter in the photolysis of a benzene solution containing 1 equiv of **1** and 4 equiv of $Ph_2PCH_2PPh_2$ gives **2a** as the major product in 60% yield. The product **2a** is contaminated with **3a** which is removed by using medium-pressure chromatography (alumina III, benzene). Complex **2a** is obtained as an air-stable, highly crystalline green solid. The phosphorus-31 NMR spectrum of **2a** displays resonances at 66.37 (d, J = 27 Hz) and 24.21 (d, J = 27 Hz). The two phosphorus-31 lines are consistent with a structure having one coordinated and one uncoordinated phosphorus atom. It is worth noting that in the reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ with bis(phosphine)s there has been a report[15] of unstable intermediates analogous to **2**, however, the intermediates could not be isolated. In contrast, complexes **2a** and **2b** are extremely stable to chromatography and are air-stable in the crystalline state.

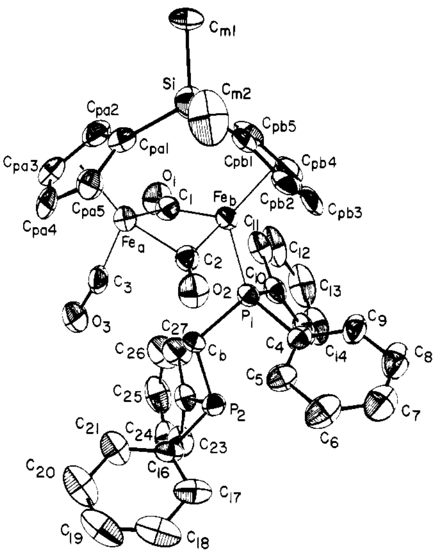

Figure 1. A perspective drawing of **2a** with the appropriate atom labels.

Complex **2b** was prepared in a fashion similar to **2a**. Final purification of **2b** was also fulfilled by a combination of medium-pressure chromatography (alumina III, benzene) and recrystallization from CH_3CN at −25 °C which affords **2b** in 65% yield. Spectroscopic and analytical data are consistent with a monosubstituted species, such as **2b**, and the cocrystallization of one molecule of CH_3CN per molecule of **2b**.

To examine any possible structural changes induced by the bis(phosphine) ligand a complete structural characterization was undertaken. The resulting structure is illustrated in Figure 1 which shows an ORTEP perspective

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Table VII. Selected Geometric Parameters for Crystalline 2a[a]

atom type[b]	length, Å	atom type[b]	bond angle, deg
Fe_a–Fe_b	2.532 (2)	Fe_b–Fe_a–C(3)	109.3 (4)
Fe_b–P(1)	2.208 (3)	Fe_a–Fe_b–P(1)	109.4 (2)
Fe_a–C(3)	1.729 (8)	C(1)–Fe_a–C(2)	91.4 (4)
Fe_b–C(1)	1.939 (9)	C(1)–Fe_b–C(2)	95.2 (4)
Fe_a–C(2)	1.958 (8)		
Fe_b–C(2)	1.898 (8)		
Fe_a–C_{pa1}	2.155 (8)	Fe_a–C(1)–Fe_b	83.1 (4)
Fe_a–C_{pa2}	2.154 (9)	Fe_a–C(2)–Fe_b	82.1 (4)
Fe_a–C_{pa3}	2.135 (8)	Fe_a–C(1)–O(1)	134.6 (6)
Fe_a–C_{pa4}	2.109 (8)	Fe_a–C(2)–O(2)	135.0 (6)
Fe_a–C_{pa5}	2.152 (8)	Fe_b–C(1)–O(1)	142.2 (6)
		Fe_b–C(2)–O(2)	141.9 (6)
Fe_b–C_{pb1}	2.145 (7)	Fe_a–C(3)–O(3)	172.1 (6)
Fe_b–C_{pb2}	2.167 (10)		
Fe_b–C_{pb3}	2.121 (9)	C_{m1}–Si–C_{m2}	113.1 (5)
Fe_b–C_{pb4}	2.135 (9)	C_{pa1}–Si–C_{pb1}	104.4 (4)
Fe_b–C_{pb5}	2.158 (7)	C_{m1}–Si–C_{pa1}	110.0 (4)
		C_{m1}–Si–C_{pb1}	110.7 (4)
P(1)–C_b	1.834 (7)	C_{m2}–Si–C_{pa1}	109.9 (5)
P(1)–C(4)	1.863 (9)	C_{m2}–Si–C_{pb1}	108.4 (5)
P(1)–C(10)	1.835 (9)		
P(2)–C_b	1.882 (8)	C_b–P(1)–C(4)	102.8 (4)
		C_b–P(1)–C(10)	102.0 (4)
Si–C_{pa1}	1.862 (8)	C_b–P(1)–Fe_b	115.4 (4)
Si–C_{pb1}	1.868 (8)	Fe_b–P(1)–C(4)	113.5 (3)
Si–C_{m1}	1.900 (9)	Fe_b–P(1)–C(10)	118.5 (4)
Si–C_{m2}	1.864 (9)	P(1)–C_b–P(2)	115.1 (5)
C(1)–O(1)	1.198 (11)		
C(2)–O(2)	1.175 (11)		
C(3)–O(3)	1.166 (11)		

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit(s). [b] Atoms are labeled in agreement with Figure 1.

drawing along with the atom labeling scheme employed.

Selected molecular parameters for **2a** are compiled in Table VII. The overall coordination geometry about the iron atoms **2a** does not show any significant geometric deviations from that of **1**. Of course Fe_b is bonded to a phosphorus in **2a** whereas in **1** both iron centers have terminal carbonyl ligands. However, the torsional angles for the two terminal ligands (L–Fe–Fe–L) in both **1** and **2a** are ca. 0.0°. The methylene group in the bis(phosphine) ligand is found positioned directly below the Fe–carbonyl plane. The proton NMR spectrum of **2a** shows the methylene resonance (δ 1.90) of the $Ph_2PCH_2PPh_2$ ligand to be upfield from the uncoordinated ligand (δ 2.17). The shielding of the methylene protons is most likely a result of a ring current in the Fe–(μ-CO) plane.[15]

The Mössbauer effect spectra of **1**–**5** have been measured at room temperature and at 78 K. The resulting spectral parameters are presented in Table VIII and the spectra of **2a** and **3a** are illustrated in Figures 2 and 3. The spectral parameters for **1** and **5** are virtually identical and indicate that the Me_2Si group, which ties the cyclopentadienyl groups together via a noninteracting bridge, has little effect on the symmetry of bonding at the iron site. The similarity of the bonding is reflected in the values of the iron–iron bond distances in **1** and **5** (see Table IX and further discussion below). The similarity in the quadrupole interaction in the two compounds is not surprising in view of the similar values obtained[16,17] for the cis and trans isomers of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$.

Table VIII. Mössbauer Effect Spectral Parameters[a]

	296 K												78 K											
	site A					site B							site A					site B						
compd	δ	$\Delta\delta$	ΔE_Q	Γ	% A	δ	$\Delta\delta$	ΔE_Q	Γ	% A	δ_{av}	χ^2	δ	$\Delta\delta$	ΔE_Q	Γ	% A	δ	$\Delta\delta$	ΔE_Q	Γ	% A	δ_{av}	χ^2
1	0.132 (1)	0.000	1.84 (1)	0.24	100						0.132	1.51	0.215 (1)	0.000	1.86 (1)	0.27	100						0.215	2.30
2a	0.152 (5)	0.020	1.92 (1)	0.22	50[b]	0.242 (5)	0.110	1.84 (1)	0.22	50[b]	0.197	0.65	0.222 (4)	0.007	1.90 (1)	0.26	50[b]	0.330 (4)	0.115	1.88 (1)	0.26	50[b]	0.276	1.85
2b	0.168	0.036	1.94	0.23	50[b]	0.218	0.086	1.86	0.23	50[b]	0.193	0.70	0.239	0.024	1.89	0.27	50[b]	0.324	0.109	1.90	0.27	50[b]	0.282	1.08
3a						0.209 (5)	0.077	1.73 (1)	0.25	100	0.209	1.06						0.297 (5)	0.082	1.78 (1)	0.28	100	0.297	1.77
3b						0.225 (1)	0.093	1.86 (1)	0.27	100	0.225	0.98						0.310 (1)	0.095	1.86 (1)	0.29	100	0.310	0.76
3c						0.254 (1)	0.122	1.89 (1)	0.24	100	0.254	0.64						0.334 (1)	0.119	1.90 (1)	0.28	100	0.334	0.95
4b	0.174	0.042	1.93	0.24	50[b]	0.244	0.112	1.83	0.24	50[b]	0.209	0.80	0.229	0.014	1.95	0.25	50[b]	0.329	0.114	1.87	0.25	50[b]	0.279	1.19
4c	0.153	0.021	1.91	0.23	50[b]	0.238	0.106	1.91	0.23	50[b]	0.196	0.65	0.206	−0.009	1.91	0.28	50[b]	0.321	0.106	1.88	0.28	50[b]	0.264	1.64
5	0.141 (6)	0.009	1.87 (1)	0.23	100						0.141	1.07	0.222 (6)	0.007	1.89 (1)	0.28	100						0.222	0.95

[a] All data in mm/s relative to room temperature natural abundance α-iron foil. [b] Constrained to the value given.

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(16) (a) Bryan, R. F.; Greene, P. T.; Newlands, M. J.; Field, D. S. *J. Chem. Soc. A* **1970**, 3068. (b) Bryan, R. F.; Greene, P. T. *J. Chem. Soc. A* **1970**, 3064.

(17) Long, G. J., unpublished results.

Table IX. Selected Bond Distances (Å)

compd	Fe–Fe	Fe–(η^5-C_5)	Fe–(μ-CO)	Fe–t(CO)	Fe–P	ref
1	2.520 (1)	1.740	1.920 (2)	1.726 (3)		3
2a	2.532 (2)	1.738	1.939 (9) 1.928 (8)	1.729 (8)	2.208 (3)	this work
3a	2.497 (1)	1.795	1.916 (4) 1.896 (4)		2.185 (1)	4f
3c	2.521 (3)	1.734	1.908 (8) 1.902 (9)		2.200 (3) 2.183 (3)	4f
5	2.531 (2)	1.742 (5)	1.918 (7) 1.917 (7)	1.730 (7) 1.760 (8)		15a
6	2.534 (2)	1.754 (6)	1.910 (5)	1.748 (6)		15b

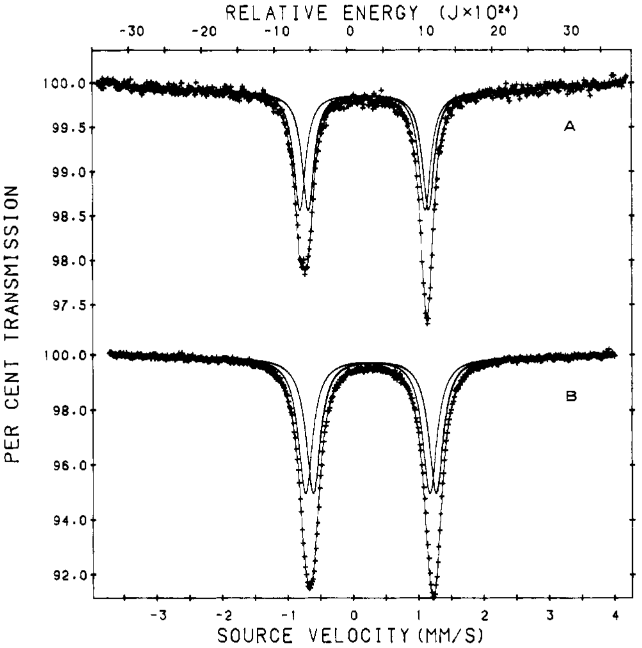

Figure 2. The Mössbauer effect spectrum of **2a** obtained at 296 K, A, and 78 K, B.

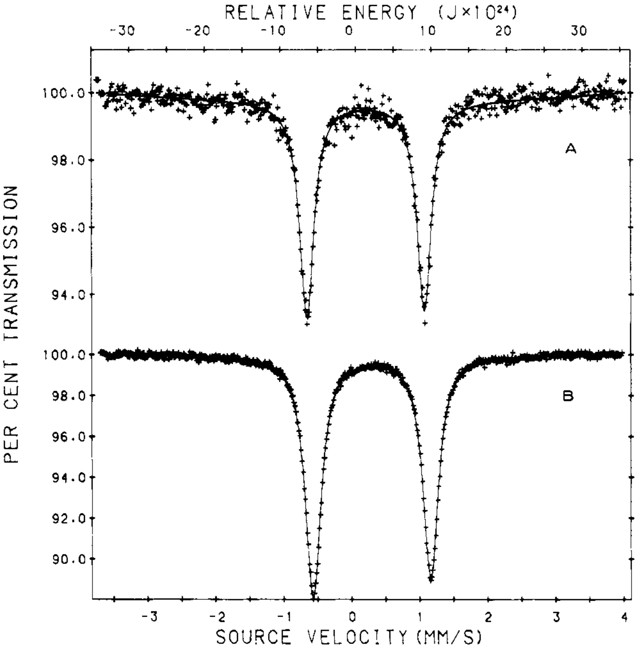

Figure 3. The Mössbauer effect spectrum of **3a** obtained at 296 K, A, and 78 K, B.

The Mössbauer spectra may be divided into two groups, those expected and found to contain only one iron site, **1**, **3**, and **5**, and those with two different sites, **2** and **4**. It was found that the first group could be fit with a single quadrupole doublet whereas the second group required two quadrupole doublets in order to obtain reasonable fits. The χ^2 values were much higher if only one doublet was used. When two doublets are used, it is necessary to make an assignment of individual lines to each doublet (see below). The assignment problem may be avoided by using the average isomer shift values which are, of course, independent of spectral assignment if the spectral fits are good, which is the case in this study as indicated by the low χ^2 values and the fits illustrated in Figures 2 and 3. The average isomer shift values, δ_{av}, given in Table VIII, clearly indicate that the isomer shift increases upon substitution of a terminal carbonyl group with a phosphine derivative. This increase in isomer shift corresponds to a decrease in the s-electron density at the iron nucleus when the iron is bonded to the phosphine ligand as compared to the carbonyl ligand. This results because of the more extensive ligand to metal π-bonding of the phosphine producing increased d-electron shielding and a reduced effective nuclear charge for the iron 4s electrons.

It is interesting to note that the isomer shifts[18,19] in *cis*- and *trans*-$[(\eta^5\text{-}C_5H_5)Fe(CO)PMe_2]_2$ and *cis*- and *trans*-$[(\eta^5\text{-}C_5H_5)Fe(CO)PPh_2]_2$ decrease relative to that of **5**. Apparently, the PPh_2 and PMe_2 ligands act as better ligand to metal σ-donors and π-acceptors than do the phosphine ligands used in this study. This bonding would of course lead to both decreased d-electron shielding and increased s-electron density at the iron nucleus and the resultant lower isomer shift.

Further information can be obtained by studying the isomer shift in each quadrupole doublet. These isomer shifts do depend upon the assignment as discussed above. In our assignment we have chosen the "left and right" rather than the "nested" assignment of the components of the quadrupole components. This assignment is based on a comparison of the resulting spectral parameters for compounds **2** and **4** with those of **1** and **3** which only contain one type of iron site each. In this analysis, we have divided the iron coordination into two types or sites. In site type A the iron is bonded to a terminal carbonyl group as in **1**, whereas in site type B the iron is bonded to a phosphine ligand as in **3**. Molecules **2** and **4** contain both type A and B sites, and our assignments have maintained a consistent isomer shift for each site as shown in Table VIII. This is perhaps best understood in terms of a "reference" compound as has proven very useful in some of our earlier studies of iron carbonyl clusters.[7,8] In this case we have chosen **1** as the reference compound and calculated a change in isomer shift, $\Delta\delta$, for each of the sites in **2**, **3**, and **4** relative to that in **1**. In this way it can be seen in Table VIII that site A shows a typical $\Delta\delta$ of ca. 0.02 mm/s, a value only a few times the standard error associated with these values. In contrast, site B shows a $\Delta\delta$ of ca. 0.10 mm/s, a significant shift as expected in view

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(18) Gibb, T. C.; Greatrex, R.; Greenwood, N. N.; Thompson, D. T. *J. Chem. Soc. A* **1967**, 1663.

(19) Herber, R. H.; Hayter, R. G. *J.* Am. *Chem. Soc.* **1964**, *86*, 301.

of the values obtained for **3** where only B sites are present. The alternate assignment leads to isomer shift values showing no obvious relationship to those found in **1**, **4**, and **5**.

If the above assignments are accepted, it is then possible to reach some interesting additional conclusions about the bonding in these materials. Table IX contains a summary of the bond distances found in several of the compounds under study. The most striking feature of this table is the lack of variation in these distances in spite of distinct changes in the ligands. This is particularly true of the iron–iron bond distance which varies only 1.4% over the compounds studied. If **3a** is excluded (see below), the variation is less than 0.5%. This seems surprising in view of the changes in the iron Mössbauer effect isomer shift with changing ligand. We believe that this lack of variation in the iron–iron bond distance is further evidence for the lack of direct iron–iron bonding in these compounds. If there were such a bond, it seems reasonable that its bonding order and hence bond length should reflect the s-electron density variation at the iron. The lack of any such variation implies that the distance is really determined by the steric constraints imposed by the ideal bonding of the two bridging carbonyl groups. Recent ab initio molecular orbital studies[20] have revealed that the iron–iron interaction in *trans*-$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (**6**) was either nonbonding or partially antibonding. The iron atom–iron atom spin coupling is apparently accomplished through a multicentric molecular orbital derived from the iron d orbitals and the π-antibonding orbitals of the bridging carbonyl ligands. The absence of iron–iron bonding in *trans*-$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (**6**) was also revealed by both X-ray and neutron diffraction results.[21,22] The X–N derived electron density deformation maps indicate virtually no increase in electron density between the iron atoms. The different isomer shift values found for the A and B sites in **2a**, **2b**, **4b**, and **4c** provides further experimental support for the lack of direct iron–iron bonding in these compounds. We have observed a similar isomer shift difference in a related η^3-allyl organoiron complex.[5] It is interesting to note that **3a**, with the shortest diphosphine ligand, $Ph_2PCH_2PPh_2$, also has the shortest iron–iron distance. In this case the short bridging phosphine ligand apparently is responsible for shortening the iron–iron bond.

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Registry No. **1**, 42830-83-1; **2a**, 99797-91-8; **2b**, 99797-92-9; **3a**, 78373-20-3; **3b**, 78357-02-5; **3c**, 87174-20-7; **4b**, 78357-01-4; **4c**, 87156-99-8; **5**, 12154-95-9; Fe, 7439-89-6.

Supplementary Material Available: Tables of anisotropic thermal parameters and bond lengths and angles, a crystallographic report, and a listing of structure factors (23 pages). Ordering information is given on any current masthead page.

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Studies of Deuterium Exchange in Alkenes Added to Iron–Ethylene-d_4 Matrices

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When iron atoms are cocondensed with C_2D_4 at 77 K and alkenes are added to the resulting matrix, a selective exchange of deuterium into the alkene is observed. Both propene and 1-butene preferentially exchange the H at C_2 while the predominant reaction of (*E*)- or (*Z*)-2-butene is exchange of the H at C_2 with *E*–*Z* isomerization. Cyclopentene exchanges all hydrogens at equal rates and is postulated to undergo exchange of allylic hydrogen followed by a more rapid allylic rearrangement. Norbornadiene does not undergo exchange. These results have been rationalized by an associative mechanism involving addition of an Fe–D to the double bond followed by rotation about either a C–C or an Fe–C bond and cis elimination of Fe–H. The reactivity of the Fe–C_2D_4 matrix is different from that of either Fe–C_2D_2 or Fe–D_2 matrices.

Hydrogenation catalyzed by mono- and polynuclear metal complexes and finely divided metals is perhaps the most common reaction in organometallic chemistry. Many studies of these hydrogenations have sought to elucidate the mechanism of the first step of the reaction by investigating the reversible exchange of deuterium into alkenes.[1]

In a recent investigation of the reactivity of the complex formed when iron atoms are cocondensed with ethylene at 77 K, we have reported that condensation of Fe with a mixture of C_2H_4 and C_2D_4 results in statistical scrambling of the label in the ethylene recovered upon warming.[2] In order to rationalize this rapid exchange of vinylic hydrogens, we proposed that an initial iron–ethylene complex, **1**, undergoes insertion into a C–H bond to generate vinyl hydride **2** which can insert another ethylene into the Fe–H bond to give **3** as shown in eq 1. If this reaction is rapid and reversible, substitution of C_2D_4 for one C_2H_4 will lead

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