157. Intramolecular Dynamics of Five-coordinate Iron Carbonyl Complexes with Olefinic Ligands as Studied by Variable-Pressure ^{1}H-NMR Spectroscopy

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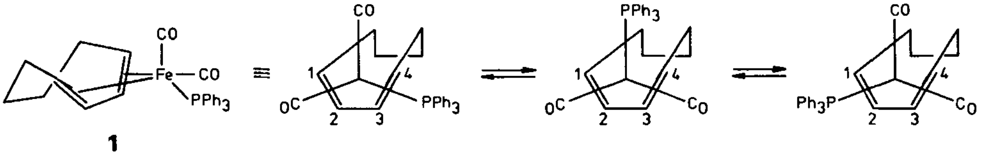
Variable-pressure ^{1}H-NMR spectroscopy has been used to study the fluxionality of some five-coordinated Fe complexes in solution. For $[Fe(CO)_2(1,3\text{-cyclooctadiene})(PPh_3)]$, the CO site exchange is known (by analogy with $[Fe(CO)_3(1,3\text{-cyclooctadiene})]$) to be a non-dissociative process, and an activation volume of *ca.* 0 cm^3 · mol^{-1} was indeed obtained. However, for $[Fe(CO_2)\{2,3\text{-}\eta:O\text{-}\sigma\text{-}(7,7\text{-dimethoxybicyclo}[2.2.1]\text{hept-2-ene})\}(PPh_3)]$, the activation volume of +5 cm^3 mol^{-1} suggests that an unprecedented dissociation process is responsible for the CO site exchange. The molecular structure of $[Fe(CO)_2(1,3\text{-cyclooctadiene})(PPh_3)]$ was ascertained by single-crystal X-ray diffractometry. The crystals are triclinic, space group $P\bar{1}$, $a = 9.606(3)$, $b = 16.795(2)$, $c = 7.743(8)$ Å, $\alpha = 97.83(4)$, $\beta = 109.63(4)$, $\gamma = 83.37(2)°$. The structure determination has shown that the complex possesses a tetragonal pyramidal coordination, with the endocyclic C=C bond and PPh$_3$ occupying basal sites.

Introduction. – Stereochemical fluxionality is a common characteristic of many five-coordinate organometallic [1–3] and coordination compounds of the transition metals. The dynamic behaviour of $[Fe(CO)_5]$ and its derivatives have been explored in detail [4][5]. All the results concerning derivatives with monodentate olefins indicate that CO site exchange takes place through a concerted non-dissociative process [6–9]. That this also applies to analogous complexes with bidentate ligands is commonly assumed [10]. The present report aims to show through a counter-example that the CO site exchange in five-coordinate iron carbonyl complexes may also take place *via* a dissociative process involving the bidentate ligand.

Variable-Pressure ^{1}H-NMR Study. – The best parameter to distinguish between dissociative and non-dissociative kinetic processes in metal complexes is the activation volume. Variable-pressure (VP) NMR is well suited to determine this parameter, as demonstrated by numerous kinetic studies of intermolecular exchanges on solvato complexes [11]. We have, therefore, chosen the variable-pressure ^{1}H-NMR technique to investigate the fluxionality of some Fe complexes with olefinic ligands and to determine the activation volume of CO site exchange. To our knowledge, this technique has not previously been used to study the dynamic processes of organometallic compounds.

The tetragonal pyramidal $[Fe(CO)_3(1,3\text{-cyclooctadiene})]$ is known to be fluxional in solution with a CO site exchange due to the rotation of the $M(CO)_3$ fragment around its local C_3 axis [12]. Hence, the fluxional process should have an activation volume of

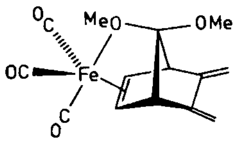
Scheme 1



0 cm^3·mol^{-1}, but cannot be measured by this method, since the olefinic protons are pair-wise magnetically identical. We have, therefore, prepared [Fe(CO)$_2$(1,3-cyclooctadiene)PPh$_3$] (**1**) by UV irradiation of [Fe(CO$_4$)PPh$_3$] in the presence of excess 1,5- (or 1,3)-cyclooctadiene. We have ascertained that this complex is effectively tetragonal pyramidal by X-ray analysis (see below).

The ^{1}H-NMR spectra of **1** in (D$_8$) toluene at 183 K show four signals for the olefinic H's at 5.25, 4.24, 3.59, and 2.73 ppm. Upon heating, these protons exchange pair-wise to give two signals at 4.74 and 3.16 ppm by 243 K. Similary, its ^{13}C-NMR spectrum shows four signals for the olefinic C-atoms at 198 K, which coalesce pair-wise upon heating. All signals were subsequently considered as singlets, and line-shape analysis (see *Experimental*) of the variable-temperature ^{1}H-NMR spectra at atmospheric pressure gave $\Delta H^{\neq} = 59 \pm 7$ kJ·mol^{-1} and $\Delta S^{\neq} = +99 \pm 30$ J·K^{-1}·mol^{-1}. The slow-exchange domain is reached at 200 K, the rate constant k_0 (at P = 0) was calculated to be 280 ± 3 s^{-1} at 200.5 K. This temperature was used when recording the ^{1}H-NMR spectra of **1** at variable pressure. Qualitatively, the various spectra appeared identical, and the rate constants were evaluated by line-shape analysis (see *Experimental*). An activation volume $\Delta V^{\neq}$ of +05. ± 0.2 cm^3·mol^{-1} was obtained from the equation $\ln k = \ln k_0 - \Delta V^{\neq} P/RT$. The value is sufficiently close to zero to be consistent with the expected nondissociative nature of the site exchange of the olefinic protons in **1** (*Scheme 1*). Hence, this result appears to validate the application of VP-NMR to the study of fluxionality in organometallic compounds.

The basicity and cone angle of the phosphine ligand do not seem to have any marked effect upon the rate of the fluxional process. Indeed, the coalescence temperatures of the ^{1}H and the ^{13}C olefinic signals of **1** and of [Fe(CO)$_2$(1,3-cyclooctadiene){P(cyclohexyl)$_3$}] are nearly the same. We have prepared the analogous complexes [Fe(CO)$_2$(norbornadiene)L] (L = PPh$_3$, P(cyclohexyl)$_3$) by irradiating a solution of [Fe(CO)$_3$(norbornadiene)] and L in THF at –30°. Unfortunately, their ^{1}H- and ^{13}C-NMR spectra indicate that the CO site exchange process is still too rapid at 173 K to be studied by VP-NMR.



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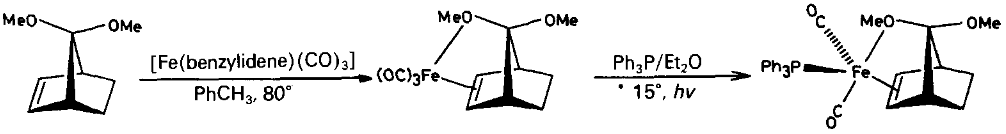
The complex tricarbonyl[2,3-η:O-σ-(7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene)]iron (**2**) has a trigonal bipyramidal structure with one MeO O-atom occupying an axial site and with the endocyclic C=C bond on a equatorial site [13].

This complex is fluxional, but since the two olefinic protons are magnetically equivalent, and the CO site exchange is still rapid at 173 K, a VP-NMR study could not be carried out. The related iron complex **4** containing one PPh$_3$ ligand and the simpler

Scheme 2



3 **4**

7,7-dimethoxynorbornene ligand was, therefore, synthetised *(Scheme 2)*. Its structure is assumed to derive from that of the complex mentioned above.

The ^{13}C-NMR spectrum of **4** indicates that the PPh$_3$ is in an equatorial position: the CO signal appears as a *singlet* at 218.8 ppm and a *doublet* at 219.2 ppm (J(C,P) = 27 Hz). Likewise, the two olefinic C-atoms appear as a *doublet* at 51.0 ppm (J(C,P) = 11 Hz) and a *singlet* at 49.4 ppm. Raising the temperature leads to a pair-wise coalescence of the CO signals, of those of C(2) and C(3), and of C(1) and C(4). The couplings with the P-atom are still observed in the fast-exchange domain. The rate constants for the site-exchange process at atmospheric pressure were obtained from the variable-temperature ^{13}C-NMR spectra, as well as the following activation parameters: $\Delta H^{\neq} = 32 \pm 2$ kJ·mol^{-1} and $\Delta S^{\neq} = -71 \pm 9$ J·K^{-1}mol^{-1}. Line-shape analysis of the CO signals and of the C(1) and C(4) signals of the bidentate ligand gave identical rate constants within experimental error (*e.g.* $k = 147 \pm 83$ and 112 ± 47 s^{-1} at 240 K), indicating that the same fluxional process is being observed in both cases.

The ^{1}H-NMR spectrum of **4** in CD$_2$Cl$_2$ at 243 K exhibits in the slow-exchange domain two signals at 3.24 and 2.94 ppm corresponding to H–C(1) and H–C(4). A temperature

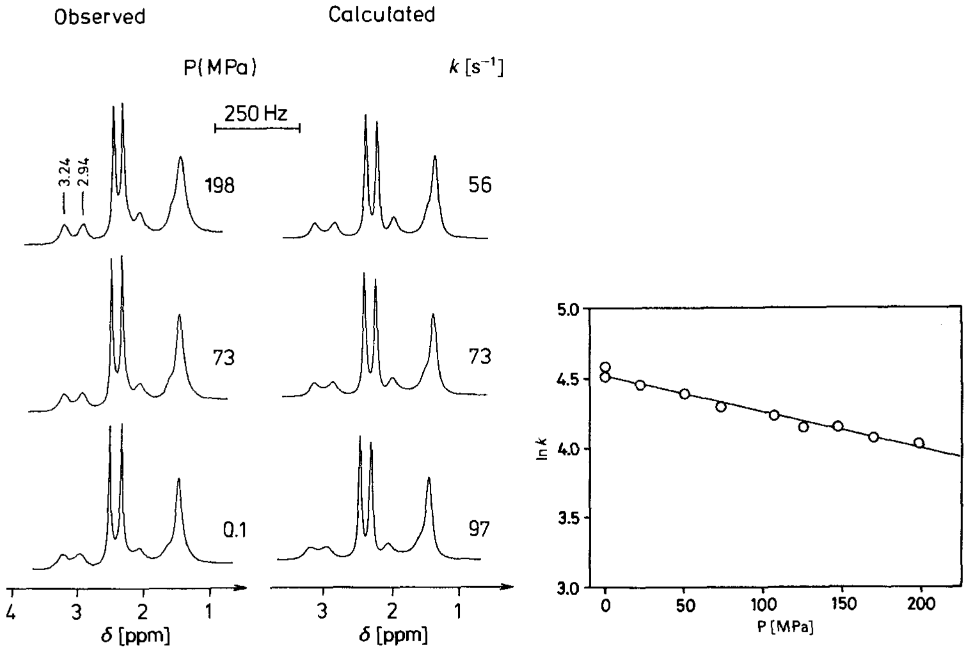
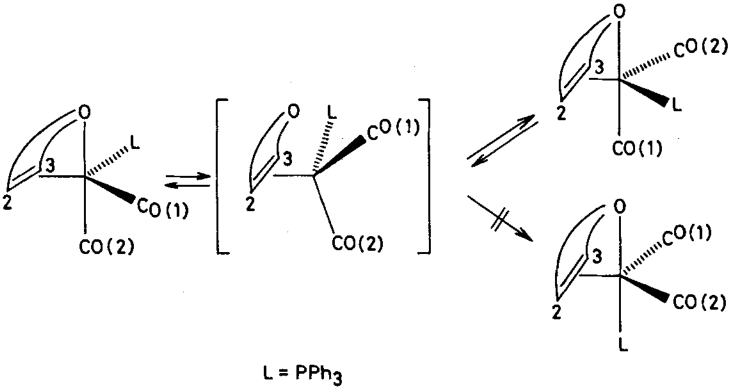


Fig. 1. *Variable-pressure ^{1}H-NMR spectra of* **4** *in CD$_2$Cl$_2$ at 240.2 K*

Scheme 3



of 240.2 K was chosen for the VP ^{1}H-NMR measurements, and a series of spectra were recorded between 0.1 and 198 MPa. The site-exchange process was observed to slow down as the pressure increased (*Fig. 1*), and a $\Delta V^{\neq}$ value of +5.3 ± 0.3 $cm^3 \cdot mol^{-1}$ was obtained from the equation $\ln k = \ln k_0 - \Delta V^{\neq} P/RT$ with $k_0 = 92 \pm 2\ s^{-1}$ at 240.2 K.

A positive $\Delta V^{\neq}$ indicates that the intramolecular CO site exchange is induced by a dissociative process. Since the coupling between the P-atom and C(2,3) is preserved in the fast-exchange domain, dissociation of the olefin-metal linkage is excluded. Therefore, it must be the Fe—O bond which ruptures in the transition state. A rotation of the fragment $Fe(CO)_2PPh_3$ around the axis passing through the metal and the midpoint of the C=C bond brings about the observed CO site exchange (*Scheme 3*).

This model is in agreement with the observed exchange between C(2) and C(3). Coordination of the O-atom *via* the P—Fe—CO(1) face of the four-coordinate transition state brings the molecule back to its initial configuration, whereas coordination *via* the P—Fe—CO(2) face brings about the observed exchange. The approach of the MeO group towards the CO(1)—Fe—CO(2) face apparently does not take place. This would lead to a non-observed isomer of **4** with the PPh_3 group in axial position.

The above result provides a counter-example to the generally accepted view that intramolecular CO exchange in five-coordinate carbonyliron complexes with bidentate ligands occurs through a non-dissociative process.

Crystal Structure of 1. – The molecular structure of **1** together with the atomic labelling is shown in *Fig. 2*. Relevant bond distances and angles are listed in *Table 1*; fractional atomic coordinates in *Table 2*. The ligand distribution around the Fe-centre describes a tetragonal pyramid (*Fig. 3*). The basal sites are occupied by the P-atom of the PPh_3 group, one CO-group (C(2)); and the midpoints of the C=C bonds of the cyclic ligand. The coordination geometry of **1** recalls that of [$Fe(CO)_3$(1,5-cyclooctadiene)] [14]. The organic ligand adopts a slightly twisted boat configuration with the sp^3-C-atom 'bending away' from the other ligands. C—C bond lengths within the ligand indicate that the two double bonds are substantially weakened (1.43(1), 1.42(1) Å) by the π interaction with the Fe-atom, and that there is an extensive electronic delocalisation over the four C-atoms bound to the metal centre, bond angles conform the sp^2-hybridized atoms. The remaining part of the ligand shows C—C bonds and C—C—C angles falling within the

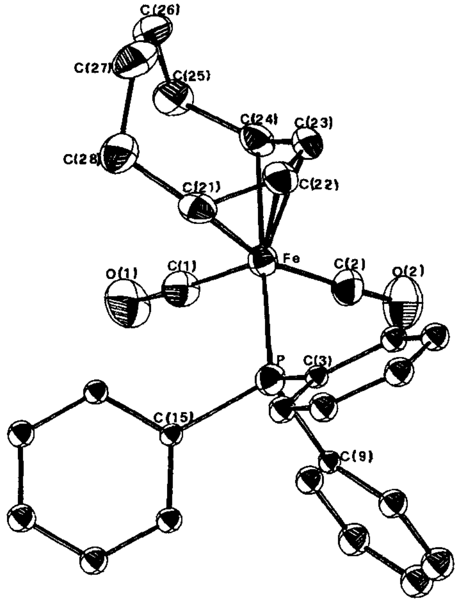


Fig. 2. *Molecular structure of* **1**

Table 1. *Relevant Bond Lengths* [Å] *and Angles* [°] *for* **1**

Fe–P	2.222(2)	P–C(15)	1.847(5)
Fe–C(1)	1.766(7)	C(21)–C(22)	1.43(1)
Fe–C(2)	1.766(7)	C(22)–C(23)	1.41(1)
C(1)–O(1)	1.147(8)	C(23)–C(24)	1.42(1)
C(2)–O(2)	1.151(9)	C(24)–C(25)	1.52(1)
Fe–C(21)	2.137(7)	C(25)–C(26)	1.53(1)
Fe–C(22)	2.056(8)	C(26)–C(27)	1.52(1)
Fe–C(23)	2.056(7)	C(27)–C(28)	1.54(1)
Fe–C(24)	2.113(7)	C(21)–C(28)	1.54(1)
P–C(3)	1.834(6)	average C–C (Ph groups)	1.39(1)
P–C(9)	1.839(7)		
Fe–C(1)–O(1)	177.2(7)	C(21)–Fe–C(2)	157.0(3)
Fe–C(2)–O(2)	177.6(6)	C(22)–Fe–C(2)	117.9(3)
C(1)–Fe–P	97.3(2)	C(23)–Fe–C(2)	92.0(3)
C(2)–Fe–P	91.5(2)	C(24)–Fe–C(2)	92.5(3)
C(1)–Fe–C(2)	100.6(3)	C(28)–C(21)–C(22)	124.7(6)
C(21)–Fe–P	89.1(2)	C(21)–C(22)–C(23)	119.8(6)
C(22)–Fe–P	100.2(2)	C(22)–C(23)–C(24)	122.4(5)
C(23)–Fe–P	134.3(2)	C(23)–C(24)–C(25)	129.1(7)
C(24)–Fe–P	172.9(2)	C(24)–C(25)–C(26)	115.4(6)
C(21)–Fe–C(1)	102.1(3)	C(25)–C(26)–C(27)	115.9(7)
C(22)–Fe–C(1)	136.9(3)	C(26)–C(27)–C(28)	115.0(7)
C(23)–Fe–C(1)	126.6(3)	C(27)–C(28)–C(21)	115.1(5)
C(24)–Fe–C(1)	87.8(3)		

range expected for sp^3-C-atoms belonging to an eight-membered ring. The H-atoms bound to the sp^2-C-atoms were directly located from the *Fourier* maps (see *Experimental*); they were found slightly bent towards the metal centre (average elevation from the C(21)–C(22)–C(23)–C(24) plane 0.27 and 1.57 Å for the H- and Fe-atoms, respec-

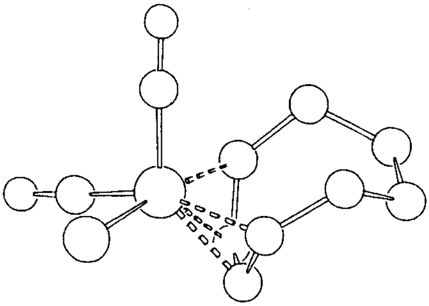


Fig. 3. *Ligand distribution in* **1**

Table 2. *Fractional Atomic Coordinates and Thermal Parameters* [Å^2] *for* **1**

Atom	x	y	z	U_{iso} or U_{eq}
Fe	0.13180(10)	0.34532(6)	0.83327(14)	0.0271(6)
P	0.1731(2)	0.2260(1)	0.9421(2)	0.028(1)
C(1)	0.1778(7)	0.4050(4)	1.0479(9)	0.036(4)
O(1)	0.2078(6)	0.4464(3)	1.1837(7)	0.061(4)
C(2)	−0.0614(7)	0.3434(4)	0.7820(9)	0.038(4)
O(2)	−0.1877(5)	0.3450(3)	0.7491(8)	0.068(4)
C(21)	0.3398(7)	0.3257(4)	0.7845(9)	0.035(4)
C(22)	0.2163(7)	0.3191(4)	0.6191(8)	0.036(4)
C(23)	0.1051(7)	0.3827(4)	0.5813(9)	0.034(4)
C(24)	0.1069(7)	0.4528(4)	0.7066(9)	0.035(4)
C(25)	0.2227(8)	0.5141(4)	0.7825(9)	0.041(4)
C(26)	0.3276(8)	0.5150(4)	0.6723(10)	0.053(5)
C(27)	0.4377(8)	0.4419(5)	0.6779(11)	0.060(5)
C(28)	0.4560(7)	0.3882(4)	0.8312(10)	0.047(5)
C(3)	0.2106(6)	0.1381(4)	0.7913(8)	0.032(1)
C(4)	0.3295(7)	0.0814(4)	0.8421(10)	0.044(2)
C(5)	0.3458(8)	0.0151(4)	0.7196(10)	0.050(2)
C(6)	0.2435(8)	0.0053(4)	0.5463(10)	0.051(2)
C(7)	0.1262(7)	0.0614(4)	0.4893(10)	0.046(2)
C(8)	0.1084(7)	0.1280(4)	0.6107(9)	0.041(2)
C(9)	0.0210(6)	0.1939(3)	1.0044(8)	0.030(1)
C(10)	−0.0360(7)	0.2485(4)	1.1217(9)	0.047(2)
C(11)	−0.1565(8)	0.2303(5)	1.1686(11)	0.060(2)
C(12)	−0.2186(9)	0.1587(5)	1.1026(11)	0.062(2)
C(13)	−0.1631(8)	0.1036(5)	0.9865(11)	0.062(2)
C(14)	−0.0425(7)	0.1218(4)	0.9376(10)	0.049(2)
C(15)	0.3265(6)	0.2165(3)	1.1611(8)	0.030(1)
C(16)	0.4371(7)	0.2704(4)	1.2199(9)	0.035(2)
C(17)	0.5504(7)	0.2660(4)	1.3899(9)	0.042(2)
C(18)	0.5520(8)	0.2077(4)	1.5000(10)	0.047(2)
C(19)	0.4432(7)	0.1548(4)	1.4444(10)	0.045(2)
C(20)	0.3321(7)	0.1580(4)	1.2770(9)	0.037(2)

tively). The Fe–C interactions can be grouped in two distinct sets of 'short' (mean 2.056(7) Å) and 'long' (mean 2.130(7) Å). This difference can probably be ascribed to steric factors, since a similar effect is not observed in the structure of [Fe(CO)$_3$(1,5-cyclooctadiene)]. A detailed comparison of the Fe–diene bonding in **1** and [Fe(CO)$_3$(1,5-

cyclooctadiene)] reveals shorter average Fe–C distances (2.093(7) *vs.* 2.174(3) Å) and longer average $C(sp^2)$–$C(sp^2)$ distances (1.42(1) *vs.* 1.37(5) Å). These differences suggest more efficient back-donation in **1** with the substitution of one CO group for a PPh_3 ligand.

Experimental. – See [15] for general comments and for the preparation of **2**. Variable-temperature spectra were recorded on a *Bruker WH-360* spectrometer (^{1}H-NMR at 360 MHz and ^{13}C-NMR at 90.55 MHz). Variable-pressure measurements were made on a *Bruker CXP-200* spectrometer using a special probe designed in our laboratories [16]. Rate constants were calculated by line-shape analysis involving simulation of experimental spectra with EXCHNG program [17]. Activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were determined by linear regression of *Eyring* equation $\ln(k/t) = \ln(kB/h) + \Delta H^{\neq}/RT - \Delta S^{\neq}/R$. The relation between the rate constant k and the pressure P was given by $\ln k = \ln k_0 - \Delta V^{\neq} P/RT + \Delta\beta^{\neq} P^2/2RT\Delta V^{\neq}$, where $\Delta V^{\neq}$ represents the activation volume, $\Delta\beta^{\neq}$ the compressibility coefficient, and k_0 the rate constant at $P = 0$. When $\Delta\beta^{\neq}$ is close to zero, with regard to experimental errors, the equation can be simplified to $\ln k = \ln k_0 - \Delta V^{\neq}\, p/RT$.

Variable-Pressure Data for **1** ((D_8)toluene, 200.5 K; k in s^{-1}; P in MPa): 273.5 (0.1); 285.4 (0.1); 275.3 (60); 272.8 (76); 281.4 (102); 272.5 (126); 270.9 (150); 261.5 (176); 263.1 (204).

Variable Pressure Data for **4** (CD_2Cl_2, 240.2 K; k in s^{-1}; P in MPA): 97.1 (0.1); 91.0 (0.1); 85.6 (22.0); 80.3 (50.0); 73.0 (73.0); 68.6 (106); 62.8 (125); 63.4 (147); 58.4 (169); 56.0 (198).

Crystal Structure Determination. Crystal data and details of measurements are reported in *Table 3*[1]. Diffraction intensities were collected at r.t. on an *Enraf-Nonius CAD-4* diffractometer equipped with Mo-*Kα* radiation. The structure was solved by direct-methods and refined by full-matrix least squares. For all calculations, the SHELX76 program was used [18]. H-Atoms of the Ph groups were added in calculated positions and refined 'riding' on their corresponding C-atoms; a similar procedure was adopted for the methylenic H-atoms of the C_8H_{10} ligand. The four H-atoms bound to the unsaturated part of the ligand were directly located from the final difference *Fourier* maps and their distance kept constant (1.01 ± 0.01 Å) during the refinement cycles. All atoms, but the H-atoms, were allowed to vibrate anisotropically. Two isotropic thermal parameters were refined for H(Ph) and $H(C_8H_{10})$-atoms (0.09 and 0.06 $Å^2$, respectively). Residual peaks, not higher than $0.4\ e \cdot Å^{-3}$, were found in the final difference map in the proximity of the P- and Fe-atoms.

Synthesis of Complexes. – *Dicarbonyl[2,3-η:5,6-η-(1,3-cyclooctadiene)](triphenylphosphine)iron* (**1**). A soln. of $[Fe(CO)_4PPh_3]$ [19] (1.72 g, 4.0 mmol) and 1,5-cyclooctadiene (1.08 g, 10 mmol) in THF (10 ml) was irradiated 20 h at −10° *(Philips HPK 125)* in a 100-ml vacuum sealed tube. The tube was opened carefully.The solvent was removed under vacuum, and the residue was chromatographed on degassed silica gel using petroleum ether/AcOEt 4:1. The product was recrystallised at −25° from hexane/CH_2Cl_2 and dried under vacuum. Yield: 1.42 mg (2.9 mmol, 74%). Yellow crystals. M.p. 129–130°. IR (hexane): 1975, 1925 (CO). ^{1}H-NMR ((D_8)toluene, 183 K): 7.7–7.1 (*m*, 15 H, Ph); 5.25, 4.24 (2 br. *s*, H–C(2), H–C(3)); 3.59, 2.73 (2 br. *s*, H–C(1), H–C(4)); 2.48, 2.32, 1.64, 1.55 (4*m*, 2 H–C(5), 2 H–C(6), 2 H–C(7), 2 H–C(8)). ^{13}C-NMR (CD_2Cl_2, 183 K); 221.6, 214.0 (2s, CO); 134.0 (*d*, ^1J(C,P) = 38, Ph); 132.0, 131.7, 128.6 (3*d*, *J* = 149, 131, 142, Ph); 94.1, 88.6, 61.9, 55.1 (4*d*, *J* = 178, 166, 154, 154, C(2), C(3), C(1), C(4)); 27.2, 23.8, (*d*, *J* = 126, 129, C(3), C(4), C(7), C(8)); MS: 454 (2, M^+ – CO), 426 (14, M^+ – 2 CO), 318 (100, $(Ph_3P)Fe^+$), 262 (22, Ph_3P^+). Anal. calc. for $C_{28}H_{27}FeO_2P$ (482.34): C 69.72, H 5.64; found: C 69.12, H 5.57.

Dicarbonyl[2,3-η:5,6-η-(1,3-cyclooctadiene)][tri(cyclohexyl)phosphine]iron. Prepared as for **1** starting with $[Fe(CO)_4P(C_6H_{11})_3]$ [19]. Yellow crystals. M.p. 145°. IR (hexane): 1960, 1900 (CO). ^{1}H-NMR ((D_8)toluene, 198 K): 5.51, 5.29, 3.46, 2.84 (4 br. *s*, H–C(1), H–C(2), H–C(3), H–C(4)); 2.46, 1.94, 1.85, 1.65, 1.46, 1.33 (6*m*, 2 H–C(5), 2 H–C(6), 2 H–C(7), 2 H–C(8), $(C_6H_{11})_3P$). MS: 500 (5, M^+–CO), 444 (69, M^+ – 2 CO), 364 (100, $Ph_3PFe(CO)^+$), 280 (64, Ph_3P^+). Anal. calc. for $C_{28}H_{45}FeO_2P$ (500.49): C 67.23, H 9.00; found: C 67.26, H 9.09.

Dicarbonyl[2,3-η:5,6-η-(bicyclo[2.2.1]hepta-2,5-diene)](triphenylphosphine)iron. A soln. of PPh_3 (524 mg, 2 mmol) in THF (5 ml) was added to a frozen soln. of $[Fe(CO)_3$(bicyclo[2.2.1]hepta-2,5-diene)] (464 mg, 2 mmol) [20] in a 25-ml *Pyrex* tube. The system was sealed under vacuum and irradiated for 15 h at −30° *(Philips HPK 125)*. The soln. was cooled to −25°, and on crystallisation the tube was opened carefully. The solvent was removed under vacuum and the residue was chromatographed on degassed silica gel using petroleum ether/CH_2Cl_2 7:3. The product was recrystallised at −25° from hexane/CH_2Cl_2 and dried under vacuum. Yield: 766 mg (1.64 mmol, 82%). Yellow crystals. M.p. 155–156°. IR (hexane): 1965, 1905 (CO). ^{1}H-NMR ($CD_2Cl_2/CHClF_2$ 1:1, 183 K): 7.43 (*m*,

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[1] Complete lists of atom parameters and lists of structure factors may be obtained from *D.B.* upon request.

Table 3. *Crystal Data of* **1**

Formula	$C_{28}H_{27}FeO_2P$	Radiation	Mo–$K\alpha$ (λ = 0.71069)
Molecular wt.	482.1	$F(000)$	504
Dimensions [mm]	0.10 × 0.12 × 0.10	Scan type	$\omega/2\vartheta$
Crystal system	triclinic	Scan width [°]	0.70
Space group	$P\bar{1}$	Pre-scan speed [°min^{-1}]	5
a [Å]	9.606(3)	2ϑ limits[°]	2.5 – 25
b [Å]	16.795(2)	Data collected	$\pm h$, $\pm k$, $+l$
c [Å]	7.743(8)	Unique total data	2627
α [°]	97.83(4)	Data in refinement [$F_o > 4\sigma(F_o)$]	1655
β [°]	109.63(4)	No. of variables	213
γ [°]	83.37(2)	Solution method	Direct methods and *Fourier*
V [Å^3]	1162.3	Refinement method	Least squares
Z	2	R	0.042
$D_{calc.}$[gcm^{-3}]	1.38	$R_w = \Sigma[(F_o - F_c)w^{1/2}]/\Sigma(F_o w^{1/2})$	0.041
μ[cm^{-1}]	6.84	$w = k/[\sigma^2(F) + \lvert g \rvert F^2]$	k = 0.9391, g = 0.0008

15 H, Ph); 3.22 (*s*, 2 H); 2.36 (*s*, 4 H); 0.97 (*s*, 2 H). *Singlet* at 2.36 was found to broad from *ca.* 163 K. ^{13}C-NMR ($CDCl_3$, 283 K): 222.6 (*d*, ^2J(C,P) = 22, CO); 135.3 (*d*, ^1J(C,P) = 41, Ph); 133.6, 129.6, 128.0 (3 *d*, *J* = 161, 153, 154, Ph); 57.6 (*t*, *J* = 132, C(7)); 42.8 (*d*, *J*(C,H) = 149, C(1), C(4)); 35.6 (*d*, *J* = 179, C(2), C(3), C(5), C(6)). MS: 466 (5, M^+), 438 (10, M^+ – CO), 410 (100, M^+ – 2 CO), 262 (73, Ph_3P^+). Anal. calc. for $C_{27}H_{23}FeO_2P$ (466.30): C 69.55, H 4.97; found: C 69.58, H 4.99.

Dicarbonyl[2,3-η:5,6-η-(bicyclo[2.2.1]hepta-2,5-diene)][tri(cyclohexyl)phosphine]iron. Prepared as further complex starting with tricyclohexylphosphine. Yellow crystals. M.p. 154°. IR (hexane): 1945, 1890 (CO). ^{1}H-NMR ((D_8)toluene, 183 K): 3.43 (br. *s*, 2 H, H–C(1), H–C(4)); 2.93 (br. *s*, H–C(2), H–C(3), H–C(5), H–C(6)); 2.25, 1.96, 1.8–1.7, 1.4–1.3 (*m*, $(C_6H_{11})_3P$); 0.59 (*s*, 2 H–C(7)). ^{13}C-NMR (CD_2Cl_2, 183 K): 224.6 (*d*, ^2J(C,P) = 22, CO); 56.6 (*t*, *J* = 132, C(7)); 42.5 (*d*, *J* = 150, C(1), C(4)); 34.7 (*dd*, ^1J(C,H) = 121, *J*(C,P) 17, CH-P); 29.0, 27.1, 25.7 (3*t*, *J* = 127, 122, 121, $(C_6H_{11})_3P$); 24.4 (*d*, *J* = 178, C(2), C(3), C(5), C(6)). MS: 484 (5, M^+), 456 (6, M^+ – CO), 428 (100, M^+ – 2 CO), 280 (25, $(C_6H_{11})_3P^+$).

*Tricarbonyl[(1*R,2S,3R,4S*)-2,3-η:*O*-σ-(7,7-dimethoxybicyclo[2.2.1]hept-2-ene)]iron* (**3**). A soln. of 7,7-dimethoxybicyclo[2.2.1]hept-2-ene (0.92 g, 6 mmol) [21] [$Fe(CO)_3$(benzylidene)] (3.42 g, 12 mmol) in toluene (250 ml) was heated for 24 h under N_2 at 80° in a sealed system. The solvent was removed under vacuum and the residue was chromatographed on degassed silica gel using petroleum ether/AcOEt 9:1. Evaporation *in vacuo* afforded **3** as a red oil. Yield: 1 g (3.4 mmol, 57%). IR (hexane): 2045, 1955, 1945 (CO). ^{1}H-NMR ($CDCl_3$): 3.55 (*s*, H–C(1), H–C(4)); 3.05, 3.02 (2*s*, 2 CH_3O); 2.14 (*s*, H–C(2), H–C(3)); 1.71, 1.65 (2*d*, 2 H–C(5), 2 H–C(6)), (^2J(H_n–C(5), H_x–C(5)) = 9.9. ^{13}C-NMR ($CDCl_3$): 214.9 (*s*, CO); 116.4 (*s*, C(7)); 61.4, 51.4 (2*q*, *J* = 146, 143, CH_3O); 53.7 (*d*, *J* = 170, C(2), C(3)); 41.7 (*d*, *J* = 146, C(1), C(4)); 26.6 (*t*, *J* = 135, C(5), C(6)). MS: 294 (12, M^+), 266 (48, M^+ – CO), 238 (91, M^+ – 2 CO), 210 (100, M^+ – 3CO), 154 (12, L^+).

*Dicarbonyl[(1*RS,2SR,3RS,4SR*)-2,3-η:*O*-σ-(7,7-dimethoxybicyclo[2.2.1]hept-2-ene)](triphenylphosphine)iron* (**4**). A soln. of **3** (529 mg, 1.8 mmol) and PPh_3 (577 mg, 2.2 mmol) in Et_2O (6 ml) was placed in a 20 ml *Pyrex* tube. The tube was vacuum sealed and was irradiated for 15 h at –15° *(Philips HPK 125)*. The soln. was then cooled to –25° on crystallisation. The tube was opened carefully. The crystals were collected under Ar washed with degassed hexane, and dried under vacuum. Yield: 770 mg (1.5 mmol, 81%). Red crystals. M.p. 166° (dec.). IR (hexane): 1965, 1900 (CO). ^{1}H-NMR (CD_2Cl_2, 203 K): 7.54, 7.36 (*m*, 15 H, Ph); 3.24, 2.94 (2*s*, H–C(1), H–C(4)); 2.49, 2.28 (2*s*, 2 CH_3O); 2.08, 1.61 (2*s*, H–C(2), H–C(3)); 1.51, 1.43 (2 br. *s*, 2 H–C(5), 2 H–C(6)). ^{13}C-NMR (CD_2Cl_2, 203 K): 219.2 (*d*, ^2J(C,P) = 27, CO); 218.8 (*s*, CO); 135.9 (*d*, ^1J(C,P) = 30, Ph); 132.5, 128.5, 127.3 (3*d*, *J* = 160, 162, 161, Ph); 114.8 (*s*, C(7)); 59.1, 50.1 (2*q*, *J* = 146, 143, CH_3O); 51.0 (*dd*, *J*(C,H) = 161, *J*(C,P) = 11, C(2)); 49.4 (*d*, *J* = 161, C(3)); 42.7, 38.8 (2*d*, *J* = 145, C(1), C(4)); 26.0 (*t*, *J* = 134, C(5), C(6)). MS: 528 (1, M^+), 500 (6, M^+ – CO), 472 (35, M^+ – 2 CO), 262 (100, Ph_3P^+). Anal. calc. for $C_{29}H_{29}FeO_4P$ (528.37): C 65.92, H 5.53; found: C 64.94, H 5.41.

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