excellent indication that the absolute structure assignment was correct.

Registry No. $EtGe(SePh)_3$, 118112-64-4; $LiEt_3BH$, 22560-16-3; Ph_2Se_2, 1666-13-3; $GeCl_4$, 10038-98-9; $Ge(SePh)_4$, 118141-54-1.

Supplementary Material Available: Tables of general temperature expressions for $Ge(SePh)_4$ and $EtGe(SePh)_3$ (2 pages); listings of structure factors for $Ge(SePh)_4$ and $EtGe(SePh)_3$ (42 pages). Ordering information is given on any current masthead page.

Reactions of (1–3-η-Vinylcarbene)tricarbonyliron Complexes with Carbon Monoxide or Tertiary Phosphines. "Insertion" of Carbon Monoxide into a Carbon–Metal Double Bond and Reactivities of the Formed Tricarbonyl(η^3:η^1-allylacyl)irons

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A (η^3-vinylcarbene)iron complex, tricarbonyl(1–3-η-1-methoxy-2-(methoxycarbonyl)prop-2-en-1-ylidene)iron (**3a**), reacts with carbon monoxide (1 atm) or tertiary phosphines (L) at 30–35 °C to give $Fe(\eta^3:\eta^1\text{-allylacyl})(CO)_2L$ (**6**, L = CO; **7**, L = PPh_3; **8**, L = PPh_2Me; **9**, L = $PPhMe_2$) in good to excellent yields; the insertion of a carbon monoxide into the carbene–iron bond readily occurs. Complex **7** crystallizes in space group $P2_1/c$ with $a = 13.926$ (2) Å, $b = 10.227$ (2) Å, $c = 35.835$ (7) Å, $\beta = 101.81$ (2)°, and $Z = 8$. Pertinent bond distances are C(2)–Fe = 1.899 (7) Å, C(2)–C(3) = 1.484 (11) Å, C(3)–C(4) = 1.403 (10) Å, and C(4)–C(5) = 1.416 (11) Å. These data show that for the description of **7**, (η^3:η^1-allylacyl)tricarbonyliron, is preferable to (η^4-vinylketene)tricarbonyliron. Complex **3a** reacts with 2 mol equiv of $PPhMe_2$ to give a ferracyclopent-2-en-5-one derivative, **12**, in 19% yield. $Fe(\eta^3:\eta^1\text{-allylacyl})(CO)_2L$ (**8**, L = PPh_2Me; **9**, L = $PPhMe_2$) further reacts with carbon monoxide, PPh_2Me, or $PPhMe_2$ to give a ferracyclopent-2-en-5-one derivatives (**10**, L = L′ = PPh_2Me; **11**, L = $PPhMe_2$ L′ = CO; **12**, L = L′ = $PPhMe_2$). Complex **11** crystallizes in space group $P2_1/n$ with $a = 13.393$ (4) Å, $b = 16.906$ (3) Å, $c = 8.774$ (2) Å, $\beta = 93.10$ (2)°, and $Z = 4$. Tricarbonyl(1–3-η-1-methoxy-2,3-bis(methoxycarbonyl)prop-2-en-1-ylidene)iron (**3b**) reacts with carbon monoxide to give tricarbonyl(3–6-η-4-(methoxycarbonyl)-5,6-dimethoxy-2-pyrone)iron (**13**). Complex **13** belongs to the orthorhombic space group *Pbca* with $a = 13.104$ (1) Å, $b = 19.646$ (2) Å, $c = 11.346$ (2) Å, and $Z = 8$. Complex **3b** reacts with PPh_3 at 50 °C to afford the phosphine-substituted η^3-vinylcarbene complex **19**. Complex **3b** reacts with PPh_2Me or $PPhMe_2$ to give the corresponding $Fe(\eta^3:\eta^1\text{-allylacyl})(CO)_2L$ (**14** and **15**) which further react with carbon monoxide or $PPhMe_2$ to give ferracyclopent-3-en-2-ones (**16**, **17**, and **18**).

Introduction

The chemistry of transition-metal vinylcarbene or allylidene complexes have recently attracted considerable attention.[1-25] Two kinds of vinylcarbene complexes are known; one is a η^1-vinylcarbene or 1-metalla-1,3-butadiene complex, **1**,[17,18,24] and the other is a η^3-vinylcarbene or

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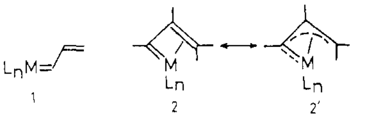
η^3-allylidene complex, 2.[2,4-13] The examples of both com-



1 2 2′

plexes were isolated and were well characterized.[2,11,13] These complexes are often postulated to be key intermediates in the reactions of carbene complexes with acetylenes involving the Dötz reaction[19] and polymerization of acetylenes.[25] These processes sometimes involve further "insertion" of carbon monoxide into the carbon–metal double bond of the vinylcarbene complexes resulting in the formation of coordinated vinylketenes.[19,24,26,27]

On the other hand, insertion of carbon monoxide into a transition-metal–carbon single bond (or a migration of an alkyl group on a coordinated carbon monoxide) is one of the most important and fundamental reaction forming carbon–carbon bonds in catalytic or noncatalytic organic syntheses by transition metals.[28,29] The reaction has been well studied, and it seems that the mechanism is established experimentally[29] and theoretically.[30] However, "insertion" of carbon monoxide into a carbon–metal double bond has not ben well understood. Although the importance of this reaction has been pointed out in several reactions[19] including the carbon–carbon bond formation reaction in the hydrogenation of carbon monoxide,[31,32] there have been only a few examples that directly show the "insertion" of carbon monoxide into a carbon–metal double bond.[2,6,13,33-35] This paper deals with the full details of the first example of "insertion" of carbon monoxide into a carbon–metal double bond of (η^3-vinylcarbene)iron complexes **3a** and **3b**.[6,36] Complexes **3a** and **3b** are the first examples of a (1–3-η-vinylcarbene)metal complex,

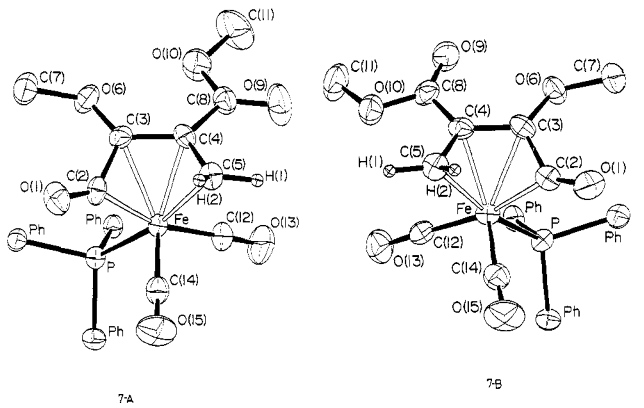
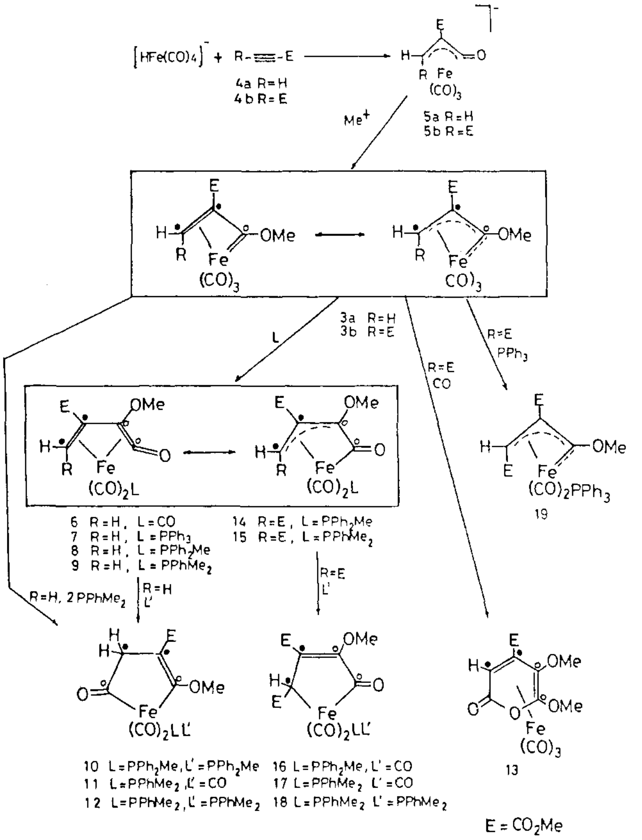


Figure 1. The molecular structure of complex **7**. The structures **7-A** and **7-B** are different in the orientation of the methoxycarbonyl groups.

Scheme I



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(36) After the first report by us (ref 6), analogous carbonylation of a complicated (η^3-vinylcarbene)iron complex was briefly reported (ref 13).

Table I. Summary of Crystallographic Data

	7	11	13
formula	$C_{27}H_{23}FeO_6P$	$C_{18}H_{19}FeO_7P$	$C_{12}H_{10}FeO_9$
mol wt	530.30	434.17	354.05
cryst system	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/n$	*Pbca*
cell parameter			
a, Å	13.926 (2)	13.393 (4)	13.104 (1)
b, Å	10.227 (2)	16.906 (3)	19.646 (2)
c, Å	35.835 (7)	8.774 (2)	11.346 (2)
α, deg	90	90	90
β, deg	101.81 (2)	93.10 (2)	90
γ, deg	90	90	90
cell vol., Å^3	4995 (1)	1983.7 (8)	2920.7 (6)
Z	8	4	8
cryst dimens, mm	0.3 × 0.3 × 0.25	0.36 × 0.27 × 0.21	0.43 × 0.17 × 0.11
cryst color	orange yellow	orange yellow	yellow
d_{calcd}, g cm^{-3}	1.4104	1.4538	1.6104
μ, cm^{-1}	7.27	8.99	11.06
radiatn	Mo Kα	Mo Kα	Mo Kα
2θ range	0–50	0–50	0–50
no. of reflctn used in $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$	5508	2699	1741
R^a	0.0656	0.0412	0.0534
R_w^b	0.0659	0.0427	0.0358

$^a R = \sum \lvert\lvert F_o\rvert - \lvert F\rvert\rvert/\sum\lvert F_o\rvert$. $^b R_w = [\sum w\lvert\lvert F_o\rvert - \lvert F\rvert\rvert^2/\sum w(F_o)^2]^{1/2}$.

Table II. Positional Parameters and Their Estimated Standard Deviations for 7-A

atom	*x*	*y*	*z*
Fe	0.1925 (1)	0.4215 (1)	0.4650 (1)
P	0.3011 (1)	0.2611 (2)	0.4856 (1)
O(1)	0.0182 (4)	0.2554 (5)	0.4685 (2)
C(2)	0.0785 (5)	0.3147 (7)	0.4554 (2)
C(3)	0.0980 (5)	0.3287 (7)	0.4164 (2)
C(4)	0.1182 (5)	0.4590 (7)	0.4084 (2)
C(5)	0.0906 (5)	0.5506 (7)	0.4339 (2)
O(6)	0.1138 (4)	0.2270 (5)	0.3941 (1)
C(7)	0.0592 (6)	0.1090 (8)	0.3976 (3)
C(8)	0.1682 (5)	0.5060 (7)	0.3783 (2)
O(9)	0.1833 (5)	0.6206 (6)	0.3742 (2)
O(10)	0.1939 (5)	0.4141 (6)	0.3566 (2)
C(11)	0.2420 (8)	0.4581 (11)	0.3269 (3)
C(12)	0.2952 (5)	0.5273 (7)	0.4599 (2)
O(13)	0.3598 (4)	0.5912 (6)	0.4571 (2)
C(14)	0.1680 (5)	0.4685 (7)	0.5096 (2)
O(15)	0.1464 (5)	0.4974 (7)	0.5372 (2)
C(16)	0.3959 (5)	0.2429 (6)	0.4572 (2)
C(17)	0.3668 (5)	0.2482 (8)	0.4180 (2)
C(18)	0.4348 (6)	0.2391 (8)	0.3947 (2)
C(19)	0.5322 (6)	0.2254 (8)	0.4107 (2)
C(20)	0.5622 (5)	0.2215 (9)	0.4493 (3)
C(21)	0.4942 (5)	0.2286 (8)	0.4734 (2)
C(22)	0.3711 (5)	0.2749 (7)	0.5344 (2)
C(23)	0.4030 (6)	0.1653 (8)	0.5559 (2)
C(24)	0.4559 (6)	0.1711 (9)	0.5925 (2)
C(25)	0.4769 (6)	0.2921 (10)	0.6094 (2)
C(26)	0.4472 (6)	0.4037 (9)	0.5887 (2)
C(27)	0.3938 (5)	0.3961 (7)	0.5516 (2)
C(28)	0.2476 (5)	0.0982 (6)	0.4852 (2)
C(29)	0.1761 (5)	0.0797 (7)	0.5069 (2)
C(30)	0.1306 (5)	−0.0400 (8)	0.5072 (2)
C(31)	0.1540 (6)	−0.1404 (8)	0.4854 (2)
C(32)	0.2243 (6)	−0.1241 (7)	0.4644 (2)
C(33)	0.2733 (6)	−0.0044 (7)	0.4650 (2)

which was prepared by the methylation of the corresponding (1–3-η-acryloyltricarbonyl)ferrate **5a** and **5b** derived by the addition of $[HFe(CO)_4]^-$ to acetylenes **4a** and **4b** (Scheme I.)[11,12] Complexes **3a** and **3b** have an adjacent carbene and an olefinic group coordinated to an iron atom, whose distorted structure has been exhibited by an X-ray diffraction study.[11] Complex **3b** has a very short carbene–iron bond (1.819 Å), and the delocalization of π-electrons over the vinylcarbene ligand as represented in **2′** was suggested. The (η^3-vinylcarbene)metal complex is regarded to be a carbene complex "anchored" on the metal by the adjacent olefinic group or a chelated carbene complex. The "insertion" of carbon monoxide into the carbene–metal bond in these complexes occurs under very mild reaction conditions to give (η^3:η^1-allylacyl)iron complexes **6–9**, **14**, and **15**; further reactivities of which with tertiary phosphines and carbon monoxide will also be described. The preliminary results appear in communications.[6-8]

Results

The reactions performed in this work are summarized in Scheme I.

Reactions of the (η^3-Vinylcarbene)iron Complex 3a with Carbon Monoxide or Tertiary Phosphines. Tricarbonyl(1-3-η-1-methoxy-2-(methoxycarbonyl)prop-2-en-1-ylidene)iron (**3a**) readily reacted with carbon monoxide (1 atm) or with an equimolar amount of tertiary phosphines (L) in dichloromethane at room temperature to give Fe(1-4-η-vinylketene)$(CO)_2$L or Fe(η^3:η^1-allylacyl)$(CO)_2$L (see below) in good to excellent yields (**6**, L = CO, yield 38%; **7**, L = PPh_3, 94%; **8**, L = PPh_2Me, 68%; **9**, L = $PPhMe_2$, 71%). The reaction of **3a** with pressurized carbon monoxide (80 atm) gave **6** in 49% yield. The reaction of **3a** with 2 mol equiv of $PPhMe_2$ afforded a ferracyclopentenone complex, **12**, in 19% yield. Thus the reactions of **6–9** with carbon monoxide or tertiary phosphines were also performed (see below). Complexes **6–9** are diamagnetic yellow crystals and stable in air for several hours.

X-ray Molecular Structure of 7. The structure of **7** was determined by an X-ray analysis. The result was shown in Figure 1, while Tables I, II, and V summarize the results obtained. Two independent molecules, A and B in Figure 1, which are very similar to each other except for the orientation of the methoxycarbonyl groups are found in a unit cell. The complex appears to contain a stabilized vinylketene skeleton; a carbonyl group is "inserted" between the carbene–iron bond of **3a**. The introduced triphenyphosphine is cis to the acyl group and trans to the methylene group. The findings described in the discussion (vide infra) showed that the description (η^3-allyl + η^1-acyl)Fe^{II} is preferable to (1–4-η-vinylketene)Fe^0 for complex **7**.

IR and ^{1}H and ^{13}C NMR Spectra. The IR spectrum of **7** in KBr disk showed three strong ν(CO) absorptions

Table III. Positional Parameters and Their Estimated Standard Deviation for 11

atom	*x*	*y*	*z*
Fe	0.2150 (1)	0.0564 (1)	0.1215 (1)
P	0.3518 (1)	0.0861 (1)	0.2750 (1)
C(1)	0.1889 (2)	0.1728 (2)	0.1041 (3)
C(2)	0.2290 (2)	0.2123 (2)	−0.0110 (3)
C(3)	0.2909 (3)	0.1631 (2)	−0.1116 (4)
C(4)	0.3037 (2)	0.0801 (2)	−0.0498 (4)
C(5)	0.0394 (3)	0.2411 (4)	0.1633 (6)
C(6)	0.2271 (3)	0.2987 (2)	−0.0337 (4)
C(7)	0.2913 (4)	0.4024 (3)	−0.1805 (6)
C(8)	0.1342 (3)	0.0458 (2)	0.2826 (4)
C(9)	0.1196 (3)	0.0468 (2)	−0.0258 (4)
C(10)	0.2478 (3)	−0.0472 (2)	0.1133 (4)
C(11)	0.4393 (3)	0.0044 (2)	0.2969 (5)
C(12)	0.3248 (3)	0.1085 (3)	0.4707 (4)
C(13)	0.4275 (2)	0.1693 (2)	0.2197 (4)
C(14)	0.3957 (3)	0.2460 (2)	0.2483 (4)
C(15)	0.4508 (3)	0.3099 (2)	0.2012 (5)
C(16)	0.5362 (3)	0.2980 (3)	0.1281 (5)
C(17)	0.5690 (3)	0.2242 (3)	0.1006 (5)
C(18)	0.5152 (3)	0.1587 (2)	0.1438 (4)
O(1)	0.1320 (2)	0.2076 (2)	0.2106 (3)
O(2)	0.1877 (3)	0.3478 (2)	0.0421 (3)
O(3)	0.2819 (2)	0.3192 (1)	−0.1510 (3)
O(4)	0.3612 (2)	0.0342 (1)	−0.1050 (3)
O(5)	0.0829 (2)	0.0392 (2)	0.3807 (3)
O(6)	0.0611 (2)	0.0421 (2)	−0.1243 (3)
O(7)	0.2663 (3)	−0.1125 (2)	0.0992 (3)

at 2010, 1970, and 1960 cm^{-1} while in a $CHCl_3$ solution two absorptions at 2020 and 1968 cm^{-1} were observed. The three absorptions in the KBr disk were confirmed to be a solid effect by the X-ray analysis; it is due to the two independent molecules having different orientation of the methoxycarbonyl group in the crystal. Medium absorptions at 1705 and 1713 cm^{-1} (KBr disk) were assigned to ν(C=O) of an η^1-acyl carbonyl and ν(C=O) of an ester group, respectively. The ^{1}H NMR spectrum of **7** showed signals of η^3-allyl protons at δ 1.23 (t, $J_{H(1)-H(2)} = J_{H(1)-P} = 2.2$ Hz, H_{syn}) and 2.43 [dd, $J_{H(1)-H(2)} = 2.2$ Hz, $J_{H(2)-P} = 1.0$ Hz, H_{anti}) in addition to those of methoxy groups and phenyl groups of triphenylphosphine. The ^{13}C NMR spectrum of **7** exhibited four resonances of the allylacyl skeleton at δ 24.4 (t, $J_{C-H} = 164$ Hz, C^5), 85.5 (s, C^4), 103.5 (s, C^3), and 241.7 (d, $J_{C-P} = 7.3$ Hz, C^2). The spectral data of **6**, **8**, and **9** shown in the Experimental Section are fully consistent with the structure.

Reactions of η^3:η^1-Allylacyl Complexes 8 and 9 with Carbon Monoxide or Tertiary Phosphines. Since **3a** reacted with 2 mol of $PPhMe_2$ to give a ferracyclopentenone complex, **12**, reactions of (η^3:η^1-allylacyl)(tricarbonyl)iron **8** and **9** with carbon monoxide or tertiary phosphines were performed. Treatment of **9** (L = $PPhMe_2$) with 1 mol equiv of $PPhMe_2$ or carbon monoxide (1 atm) at room temperature for several hours gave yellow crystals of the 1:1 adducts, 5-methoxy-4-(methoxycarbonyl)ferracyclopent-4-en-2-one derivatives, **12** and **11**, in 45 and 65% yields, respectively.[37] The reaction of **8** with PPh_2Me also gave **10** in 13% yield. The molecular structure was determined by X-ray analysis (see below). The reactions of **6** and **7** with carbon monoxide (80 atm) or PPh_3 were performed, however, only the starting materials were recovered.

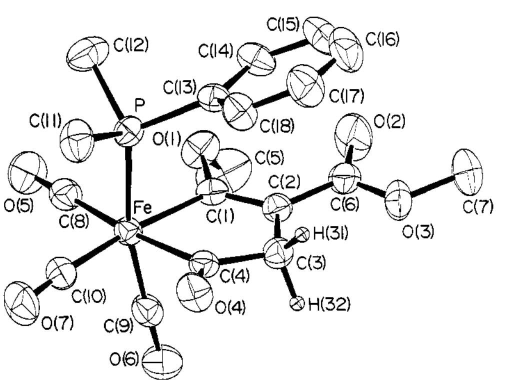


Figure 2. The molecular structure of complex **11**.

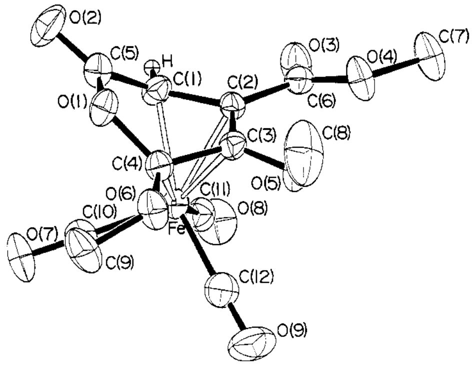
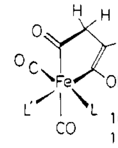


Figure 3. The molecular structure of complex **13**.

X-ray Molecular Structure of 11. The molecular geometry and atom numbering system are shown in Figure 2, while Table I, III, and VI summarize the results obtained. These results showed that the geometry of the coordination is pseudooctahedral [P–Fe–C(9) = 167.9 (1)°]. Both C(1) and C(4) are in the cis positions about the dimethylphenylphosphine. The phenyl group is oriented toward the ferracyclopentenoene ring, which is not planar but envelope-like; C(4)=O(4) deviates from the plane Fe–C(1)–C(2)–C(3). The geometry of **10** and **12** was deduced to be as shown (L and L′ are cis) on the basis of the X-ray analysis of **11** and the following spectral observations: (1) ^{1}H and ^{13}C NMR spectra of **10** and **12** exhibited nonequivalence of the methyl groups of the methylphenylphosphines and the methylene protons showing the absence of a plane of symmetry in the complexes; (2) the ^{13}C NMR signals for the Fe-(C=O) groups in **10** and **12** were triplets (J_{C-P}(L) = J_{C-P}(L′) = 23.2 and 21.5 Hz, respectively).



10 L = L′ = PPh_2Me
12 L = L′ = $PPhMe_2$

When the structure of **10**–**12** is compared with that of **6**–**9**, a decarbonylation of the acyl group in **8** and **9** and the carbonylation of the terminal methylene group in **8** and **9** occur; to our knowledge this is the first example of decarbonylation–carbonylation rearrangement of the allylacyl or vinylketene ligand.[7]

IR and ^{1}H and ^{13}C NMR Spectra of 10–12. The IR spectrum of **11** showed an absorption of ν(C=O) of ester at 1708 cm^{-1} and ν(C=O) of an acyl group at 1650 cm^{-1} as well as ν(C=C) at 1553 cm^{-1}. The ^{1}H NMR spectrum of **11** showed an AB quartet at δ 3.32 (1 H) and 2.78 (1 H) ($|J_{AB}| = 21.0$ Hz) due to nonequivalent sp^3 methylene protons, in addition to signals for OMe, CO_2Me, and $PPhMe_2$. The ^{13}C NMR spectrum of **11** showed four signals characteristic of a ferracyclopentenone ring; the signal

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[37] The formation of analogous ferracyclopentenone complex was observed in the acylation of (η^3-acryloyl)tricarbonylferrate: Mitsudo, T.; Watanabe, H.; Watanabe, Y.; Takegami, Y. *J. Chem. Soc., Chem. Commun.* 1979, 265–266.

Table IV. Positional Parameters and Their Estimated Standard Deviations for 13

atom	x	y	z
Fe	0.1671 (1)	0.0796 (1)	0.1617 (1)
O(1)	0.0404 (2)	0.1703 (1)	0.0227 (3)
O(2)	−0.0166 (3)	0.0976 (2)	−0.1109 (3)
O(3)	0.3468 (2)	0.0256 (2)	−0.0671 (3)
O(4)	0.4071 (2)	0.1296 (2)	−0.0351 (3)
O(5)	0.2969 (2)	0.2067 (1)	0.1212 (3)
O(6)	0.0935 (2)	0.2276 (1)	0.1867 (3)
O(7)	−0.0364 (2)	0.0428 (2)	0.2466 (4)
O(8)	0.2616 (3)	−0.0568 (2)	0.1741 (3)
O(9)	0.2618 (3)	0.1202 (2)	0.3839 (3)
C(1)	0.1413 (3)	0.0726 (2)	−0.0160 (4)
C(2)	0.2352 (3)	0.1095 (2)	0.0093 (4)
C(3)	0.2197 (3)	0.1684 (2)	0.0776 (4)
C(4)	0.1161 (3)	0.1760 (2)	0.1130 (4)
C(5)	0.0489 (3)	0.1116 (2)	−0.0415 (4)
C(6)	0.3354 (3)	0.0830 (2)	−0.0354 (4)
C(7)	0.5082 (4)	0.1082 (3)	−0.0744 (5)
C(8)	0.2866 (5)	0.2781 (3)	0.0996 (6)
C(9)	−0.0008 (4)	0.2225 (3)	0.2526 (5)
C(10)	0.0427 (4)	0.0563 (2)	0.2145 (4)
C(11)	0.2256 (3)	−0.0046 (2)	0.1691 (4)
C(12)	0.2243 (4)	0.1041 (2)	0.2983 (4)

Table V. Selected Bond Lengths and Angles in Complex 7-A

Bond Lengths (Å)			
Fe–C(2)	1.899 (7)	C(3)–C(4)	1.403 (10)
Fe–C(3)	2.174 (7)	C(3)–O(6)	1.356 (9)
Fe–C(4)	2.113 (6)	C(4)–C(5)	1.416 (11)
Fe–C(5)	2.086 (7)	C(4)–C(8)	1.480 (11)
Fe–C(12)	1.832 (8)	O(6)–C(7)	1.444 (10)
Fe–C(14)	1.768 (8)	C(8)–O(9)	1.204 (10)
Fe–P	2.251 (2)	C(12)–O(13)	1.132 (10)
C(2)–C(3)	1.484 (11)	C(14)–O(15)	1.133 (10)
C(2)–O(1)	1.207 (9)		
Bond Angles (deg)			
Fe–C(2)–C(3)	78.9 (4)	C(2)–Fe–C(12)	164.2 (3)
Fe–C(2)–O(1)	147.3 (6)	C(2)–Fe–C(14)	90.6 (3)
O(1)–C(2)–C(3)	133.7 (6)	C(3)–Fe–C(4)	38.2 (3)
C(2)–C(3)–C(4)	111.4 (6)	C(3)–Fe–C(5)	67.3 (3)
C(2)–C(3)–O(6)	124.2 (6)	C(3)–Fe–C(12)	122.4 (3)
C(4)–C(3)–O(6)	123.2 (7)	C(3)–Fe–C(14)	130.2 (3)
Fe–C(3)–C(2)	59.0 (3)	C(3)–Fe–P	101.6 (2)
Fe–C(3)–C(4)	68.6 (4)	C(4)–Fe–C(5)	39.4 (3)
Fe–C(3)–O(6)	131.4 (5)	C(4)–Fe–C(12)	92.1 (3)
C(3)–C(4)–C(5)	113.9 (7)	C(4)–Fe–C(14)	132.1 (3)
C(3)–C(4)–C(8)	126.9 (7)	C(4)–Fe–P	127.7 (2)
C(5)–C(4)–C(8)	119.2 (6)	C(5)–Fe–C(12)	91.9 (3)
Fe–C(4)–C(3)	73.3 (4)	C(5)–Fe–C(14)	94.2 (3)
Fe–C(4)–C(5)	69.3 (4)	C(5)–Fe–P	167.1 (2)
Fe–C(4)–C(8)	123.2 (5)	C(12)–Fe–C(14)	103.2 (4)
Fe–C(5)–C(4)	71.4 (4)	C(12)–Fe–P	88.7 (2)
C(2)–Fe–C(3)	42.1 (3)	C(14)–Fe–P	98.2 (2)
C(2)–Fe–C(4)	72.8 (3)	O(13)–C(12)–Fe	178.8 (6)
C(2)–Fe–C(5)	79.4 (3)	O(15)–C(14)–Fe	175.8 (7)
C(2)–Fe–P	96.9 (2)		

of the methylene group at δ 61.5 (dt, J_{CH} = 128.7 Hz, J_{CP} = 2.8 Hz), two olefinic carbons at δ 120.8 (d, J_{CP} = 3.8 Hz) and 209.5 (d, J_{C-P} = 32.5 Hz), and an acyliron group at δ 265.7 (d, J_{C-P} = 20.9 Hz). Spectral data of **10** and **12** were entirely analogous to those for **11**.

Reaction of η^3-Vinylcarbene Complex 3b with Carbon Monoxide. The reaction of tricarbonyl(1–3-η-*trans*-1-methoxy-2,3-bis(methoxycarbonyl)prop-2-en-1-ylidene)iron (**3b**) with carbon monoxide at 80 atm in dichloromethane at 25 °C for 12 h afforded yellow crystals of tricarbonyl(η^4-5,6-dimethoxy-4-(methoxycarbonyl)-2-pyrone)iron (**13**) in 79% yield.[8,38]

Table VI. Selected Bond Lengths and Angles in Complex 11

Bond Lengths (Å)			
Fe–P	2.271 (1)	C(2)–C(6)	1.475 (5)
Fe–C(1)	2.003 (3)	C(3)–C(4)	1.510 (5)
Fe–C(4)	2.006 (3)	C(4)–O(4)	1.213 (4)
Fe–C(8)	1.835 (4)	C(5)–O(1)	1.405 (5)
Fe–C(9)	1.775 (3)	C(6)–O(2)	1.202 (5)
Fe–C(10)	1.808 (4)	C(8)–O(5)	1.136 (5)
C(1)–C(2)	1.347 (4)	C(9)–O(6)	1.137 (4)
C(1)–O(1)	1.370 (4)	C(10)–O(7)	1.140 (5)
C(2)–C(3)	1.496 (5)		
Bond Angles (deg)			
P–Fe–C(1)	87.7 (1)	Fe–P–C(12)	114.3 (1)
P–Fe–C(4)	84.8 (1)	Fe–P–C(13)	117.2 (1)
P–Fe–C(8)	93.2 (1)	Fe–C(1)–C(2)	118.0 (2)
P–Fe–C(9)	168.0 (1)	Fe–C(1)–O(1)	118.1 (2)
P–Fe–C(10)	92.8 (1)	C(2)–C(1)–O(1)	123.9 (3)
C(1)–Fe–C(4)	81.6 (1)	C(1)–C(2)–C(3)	115.0 (3)
C(1)–Fe–C(8)	92.7 (1)	C(1)–C(2)–C(6)	126.0 (3)
C(1)–Fe–C(9)	85.3 (1)	C(3)–C(2)–C(6)	118.6 (3)
C(1)–Fe–C(10)	172.1 (2)	C(2)–C(3)–C(4)	111.2 (3)
C(4)–Fe–C(8)	174.0 (2)	Fe–C(4)–C(3)	113.2 (2)
C(4)–Fe–C(9)	84.5 (1)	Fe–C(4)–O(4)	125.9 (3)
C(4)–Fe–C(10)	90.5 (2)	C(3)–C(4)–O(4)	120.9 (3)
C(8)–Fe–C(9)	96.9 (2)	Fe–C(8)–O(5)	178.9 (3)
C(8)–Fe–C(10)	95.2 (2)	Fe–C(9)–O(6)	177.1 (3)
C(9)–Fe–C(10)	92.9 (2)	Fe–C(10)–O(7)	175.9 (3)
Fe–P–C(11)	113.0 (1)	C(1)–O(1)–C(5)	119.0 (3)

Table VII. Selected Bond Lengths and Angles in Complex 13

Bond Lengths (Å)			
Fe–C(1)	2.049 (4)	O(5)–C(3)	1.354 (5)
Fe–C(2)	2.033 (4)	O(5)–C(8)	1.431 (6)
Fe–C(3)	2.104 (4)	O(6)–C(4)	1.347 (5)
Fe–C(4)	2.083 (4)	O(6)–C(9)	1.447 (6)
Fe–C(10)	1.796 (5)	O(7)–C(10)	1.131 (6)
Fe–C(11)	1.824 (4)	O(8)–C(11)	1.132 (5)
Fe–C(12)	1.788 (5)	O(9)–C(12)	1.133 (6)
O(1)–C(4)	1.430 (5)	C(1)–C(2)	1.457 (6)
O(1)–C(5)	1.368 (5)	C(1)–C(5)	1.461 (6)
O(2)–C(5)	1.197 (6)	C(2)–C(3)	1.408 (6)
O(3)–C(6)	1.193 (5)	C(2)–C(6)	1.500 (6)
O(3)–C(7)	1.313 (5)	C(3)–C(4)	1.423 (6)
O(4)–C(7)	1.460 (6)		
Bond Angles (deg)			
C(1)–Fe–C(2)	41.8 (2)	Fe–C(3)–O(5)	122.7 (3)
C(2)–Fe–C(3)	39.7 (2)	Fe–C(3)–C(2)	67.4 (2)
C(3)–Fe–C(4)	39.7 (2)	Fe–C(3)–C(4)	69.3 (2)
C(10)–Fe–C(11)	97.8 (2)	O(5)–C(3)–C(2)	123.3 (4)
C(10)–Fe–C(12)	99.2 (2)	O(5)–C(3)–C(4)	123.4 (4)
C(11)–Fe–C(12)	91.6 (2)	C(2)–C(3)–C(4)	112.3 (4)
C(4)–O(1)–C(5)	113.1 (3)	Fe–C(4)–O(1)	109.9 (3)
C(3)–O(5)–C(8)	114.4 (4)	Fe–C(4)–O(6)	126.2 (3)
C(4)–O(6)–C(9)	117.1 (3)	Fe–C(4)–C(3)	70.9 (2)
Fe–C(1)–C(2)	68.5 (2)	O(1)–C(4)–O(6)	110.6 (3)
Fe–C(1)–C(5)	107.3 (3)	O(1)–C(4)–C(3)	116.8 (4)
C(2)–C(1)C(5)	118.6 (4)	O(6)–C(4)–C(3)	117.6 (4)
Fe–C(2)–C(1)	69.7 (2)	O(1)–C(5)–O(2)	119.0 (4)
Fe–C(2)–C(3)	72.9 (3)	O(1)–C(5)–C(1)	113.8 (4)
Fe–C(2)–C(6)	124.8 (3)	O(2)–C(5)–C(1)	127.2 (4)
C(1)–C(2)–C(3)	113.3 (4)	O(3)–C(6)–C(2)	122.7 (4)
C(1)–C(2)–C(6)	120.0 (4)	O(4)–C(6)–C(2)	112.6 (4)
C(3)–C(2)–C(6)	126.7 (4)	Fe–C(10)–O(7)	178.6 (4)
		Fe–C(11)–O(8)	179.7 (4)
		Fe–C(12)–O(9)	178.9 (4)

X-ray Molecular Structure of (η^4-2-Pyrone)iron Complex 13. The molecular geometry and atom-numbering system of **13** are shown in Figure 3, while Tables I, IV, and VII summarize the results obtained. These results indicate that **13** is tricarbonyl(η^4-5,6-dimethoxy-

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[38] Complex **13** isomerizes to tricarbonyl(η^4-5,6-dimethoxy-3-(methoxycarbonyl)-2-pyrone)iron at 58 °C in 1,2-dichloroethane; see ref 8.

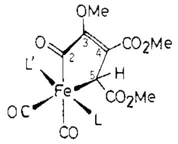
[39] (a) Mills, O. S.; Robinson, G. *Acta Crystallogr.* **1963**, *16*, 758. (b) Cotton, G. A.; Day, V. W.; Frenz, B. A.; Hard-Castle, K. I.; Troup, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 4522–4528.

4-(methoxycarbonyl)-2-pyrone)iron. Although several η^4-2-pyrone complexes are known, no molecular structure has been reported. Complex **13** is the first example of 2-pyrone complex with a fully determined molecular structure. The characteristics of the molecular structure is that the pyrone ring coordinated to the iron atom is a "boat" form and the bond lengths between the iron atom and the terminal carbons of the butadiene moiety [Fe–C(1) and Fe–C(4) = 2.05–2.08 Å] are shorter than those found in the derivatives of (butadiene)Fe(CO)$_3$ (2.09–2.14 Å)[39] which may ascribed to the effect of the 2-pyrone ring rather than to the substituents on the ring.[8]

IR and ^{1}H and ^{13}C NMR Spectra of 13. The IR spectrum of **13** showed ν(C=O) of the lactone at 1760 cm^{-1} as well as the absorptions of terminal ν(C≡O) at 2070, 2010, 1995, and 1975 cm^{-1} and ester ν(C=O) at 1730 cm^{-1}. The ^{1}H NMR spectrum of **13** exhibited the resonance of an olefinic proton at δ 2.92 in addition to the signals of three methoxy groups. The ^{13}C NMR spectrum of **13** showed four signals characteristic of a butadiene moiety coordinated to the iron atom at δ 38.4 (d, J(CH) = 192 Hz), 78.2 (s), 119.5 (s), and 127.7 (s), in addition to those for a lactone and an ester carbonyl carbon at δ 166.3 and 168.6. The spectral data were fully consistent with the results of the X-ray analysis.

Reaction of the η^3-Vinylcarbene Complex 3b with Tertiary Phosphines. Complex **3b** reacted with 1 mol equiv of triphenylphosphine in 1,2-dichloroethane at 50 °C to give orange yellow crystals of **19** in 89% yield. The molecular weight, elemental analysis, and the spectral data (see below) showed that **19** is a η^3-vinylcarbene complex derived by the substitution of one of the carbonyl groups by triphenylphosphine. The characteristic IR absorption which was tentatively assigned to ν_{asym}(C=–C=–C) of a η^3-vinylcarbene group was found at 1525 cm^{-1} in addition to those of terminal carbonyl group at 2005 and 1945 cm^{-1}. These absorptions are shifted to lower wavenumbers compared with those of **3b** by the coordination of the triphenylphosphine to the iron atom. The ^{1}H NMR spectrum of **19** showed the olefinic proton coordinated to the iron atom at 3.73 (d, J_{PH} = 10.7 Hz) ppm and the phenyl protons of the triphenylphosphine introduced at 7.36–7.42 ppm. The ^{13}C NMR spectrum of **19** exhibited the signal of the carbene carbon at 272.6 (d, J_{CP} = 31.2 Hz) ppm and the signals of the coordinated olefinic carbons [δ 39.5 (dd, J_{CH} = 160 Hz, J_{PC} = 5.9 Hz) and 54.0 (s)]. These observations demonstrate **19** to be dicarbonyl(triphenylphosphine)[1–3-η-*trans*-1-methoxy-2,3-bis(methoxycarbonyl)prop-2-en-1-ylidene]iron, which is the first example of a η^3-vinylcarbene complex having a tertiary phosphine ligand. The reactions of **3b** with diphenylmethylphosphine or phenyldimethylphosphine under the same reaction conditions (at 50 °C) gave no isolable products. However, under milder reaction conditions, i.e. in dichloromethane at 25 °C, the corresponding (η^3:η^1-allylacyl)dicarbonyl(phosphine)iron complexes **14** and **15** were obtained in 76 and 92% yields, respectively, as yellow microcrystals. Both microcrystals contained ca. 10% of unseparable isomers whose structure could not be assigned. The reaction of **3b** with triphenylphosphine in CH$_2$Cl$_2$ at 25 °C gave a 1:1 mixture of two complexes in 63% yield, both could not be isolated in pure form by column chromatography on silica gel. The one corresponded to (η^3:η^1-allylacyl)(CO)$_2$(PPh$_3$)Fe, and the other could not be assigned. When the mixture was heated at 50 °C in 1,2-dichloroethane, **19** was obtained in 85% yield.

Reaction of 14 and 15 with Carbon Monoxide or PPhMe$_2$. Complex **15** further reacted with 1 mol equiv of L′, carbon monoxide (80 atm), or PPhMe$_2$ at room temperature to give yellow crystals of **17** (L = PPhMe$_2$, L′ = CO) and **18** (L = L′ = PPhMe$_2$), in 51 and 76% yields, respectively. The reaction of **14** with carbon monoxide (65 atm) also gave **16** (L = PPh$_2$Me, L′ = CO) in 50% yield. On the basis of the following spectral data, which are quite different from those of **10–12**, **16–18** were deduced to be ferracyclo-3-en-2-one derivatives. The IR spectrum of **17** showed a band of an ester (ν(C=O)) at 1705 cm^{-1} and that of an acyl (ν(C=O)) at 1625 cm^{-1} as well as ν(C=C) at 1610 cm^{-1}. The ^{1}H NMR spectrum showed a signal for methine proton at δ 2.95 (d, J_{PH} = 10.0 Hz) in addition to three signals for methoxy groups. The ^{13}C NMR spectrum exhibited a signal for an acyl carbon at δ 255.8 (d, J_{CP} = 24.5 Hz) showing the presence of an acyl–iron group. The spectrum also showed a signal for sp^3 methine carbon at δ 33.7 (dd, J_{CP} = 11.7, J_{CH} = 138.7 Hz); the large values of J_{PH} and J_{CP} showed that the –CHCO$_2$Me group is attached to the iron atom directly. The signals for uncoordinated olefinic carbons were observed at 139.7 (s) and 180.5 (s) ppm. On the basis of these spectral data, **17** was deduced to be 1,1,1-tricarbonyl-1-(dimethylphenylphosphine)-3-methoxy-4,5-bis(methoxycarbonyl)ferracyclopent-3-en-2-one. Spectral data for **16** and **18** unequivocally showed that these complexes are the analogues of **17**. The coupling constants of $J_{\text{P(C2)}}$ and $J_{\text{P(C5)}}$ [$J_{\text{PC(2)}}$ = 23.4 (**16**), 25.4 (**17**), 27.3 (**18**) (triplet) Hz and $J_{\text{PC(5)}}$ = 13.7 (**16**), 13.7 (**17**), 12.6 (**18**) (triplet) Hz] strongly suggest that the structure of **16–18** are as follows.



16 L = PPh$_2$Me L′ = CO
17 L = PPhMe$_2$ L′ = CO
18 L = L′ = PPhMe$_2$

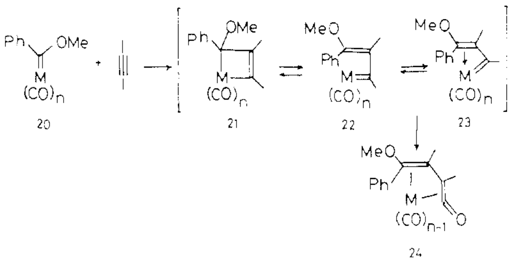
Discussion

Reaction of 3a with Carbon Monoxide. The carbonylation of the carbene carbon in **3a** readily occurred under mild reaction conditions (under an atmospheric pressure of carbon monoxide at 30 °C). Cutler reported that a cationic iron methylene complex readily reacts with carbon monoxide,[33a] however, in general, carbonylation of carbene carbons of neutral complexes requires rather severe reaction conditions. The carbonylation of a manganese diphenylcarbene complex[34a] and (phenylalkoxycarbene)pentacarbonylchromium[34c] requires 650 and 150 atm of carbon monoxide, respectively, and no (ketene)iron complexes have been so far isolated by carbonylation of a Fischer-type iron carbene complex. The successful carbonylation of **3** with atmospheric pressure of carbon monoxide may be partly due to the highly distorted structure of **3**[11] and the stability of the (η^3:η^1-allylacyl)metal complex.

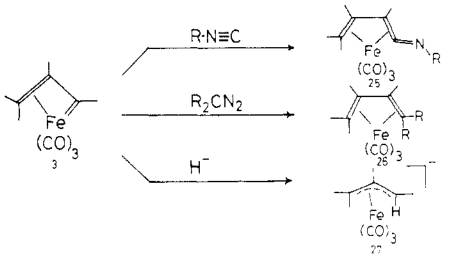
In the reaction of the (phenylalkoxycarbene)carbonylmetal complex **20** with acetylene, it has been postulated that a metallacyclobut-2-ene complex, **21**, is formed and **21** isomerizes to **22** (η^1) or the η^3-vinylcarbene complex **23**, the carbonylation of which would give a η^3:η^1-allylacyl or a vinylketene complex, **24**[19b] (Scheme II); in several cases vinylketene complexes have been isolated.[19b,f] The present result suggests that the carbonylation of a η^3-vinylcarbene complex may occur in the Dötz reaction.

There are two possible routes for the formation of **6** in the reaction of **3a** with carbon monoxide: the first route is that the carbon monoxide directly couples with the

Scheme II



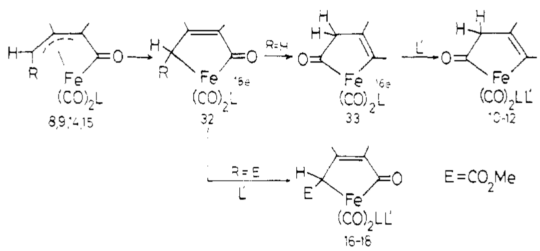
Scheme III

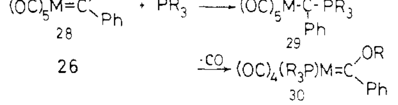


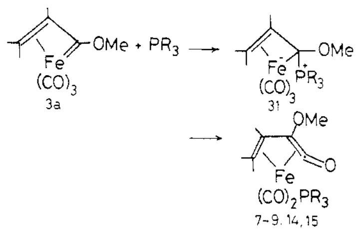
carbene carbon on the iron atom and the second one is that the coordination of carbon monoxide to the iron atom induces the insertion of one of the ligated carbon monoxides into the iron–carbene bond of **3a**. Cutler reported that the atmospheric carbon monoxide inserts into a carbene–iron bond of a cationic methylene complex giving a cationic ketene complex.[33a] To distinguish these two mechanisms the reaction of **3a** with ^{13}CO was performed, the results of which were followed by the ^{13}C NMR method; however unfortunately, rapid scrambling of both the carbonyl groups occurred; 1 molar equiv of ^{13}CO was introduced and the intensities of the signals of the acyl carbon and the terminal carbonyl carbons in **6** were 1:3. This result could not reveal the mechanism of the insertion. Taking into account that nucleophilic reagents such as isonitriles,[9] diazomethane,[10] and a hydride[40] directly attack the carbene carbon of the (η^3-vinylcarbene)iron complexes **3** to give (η^4-vinylketene imine)tricarbonyliron,[25] (η^4-buta-1,3-diene)tricarbonyliron,[26] and (η^3-allyl)tricarbonylferrate,[27] respectively (Scheme III), there is a possibility that the direct insertion or the coupling of carbon monoxide would take place.[41]

The reaction path of the formation of **7–9** by the reaction of **3a** with tertiary phosphine is tentatively considered as follows. Taking into account the reaction of carbene complex, **28**, with a tertiary phosphine to give a ylide complex, **29**, and a phosphine–carbene complex, **30**, reported by Fischer et al. (eq 2),[42] a tertiary phosphine would attack the carbene carbon of **3a**[43] to give the ylide complex **31**. Then the tertiary phosphine migrates to the iron atom inducing the insertion of the coupling of a carbon monoxide molecule with the carbene carbon to give **7–9**. Attempts to detect **31** by ^{13}C NMR were unsuccessful.

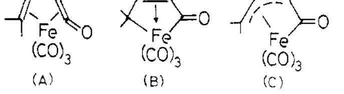
Scheme IV







Molecular Structure of (η^3:η^1-Allylacyl)tricarbonyliron Complex. (η^3:η^1-Allylacyl)iron or (η^4-vinylketene)iron complexes have been prepared by other method: the reaction of cyclopropenes[26,27] or allyl compounds with $Fe_2(CO)_9$.[44] The molecular structure of these complexes were determined by X-ray analyses. The representative bond lengths and angles of the reported (η^4-vinylketene)iron complexes are summarized in Table VIII. When these bond lengths are compared, in general, as Templeton pointed out,[27a] no simple bonding description adequately describes the vinylketene–metal linkage. The contribution of the following structures may be valid. The following findings for complex **7** showed that the triphenylphosphine ligand and/or the methoxy and methoxycarbonyl groups on the vinylketene skeleton may emphasize the contribution of the structure C. (1) The bond lengths C(3)–C(4) and C(4)–C(5) (1.403 (10) Å and 1.416 (11) Å) are in the range of those found in known (η^3-allyl)Fe complexes.[45] (2) The C(2)–C(3) bond (1.484 (11)



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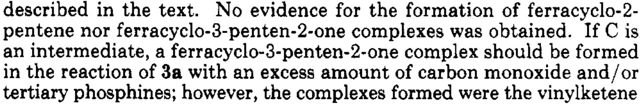
[40] Mitsudo, T.; Watanabe, H.; Watanabe, Y., unpublished work.

[41] One of the reviewers, to whom we are grateful, pointed out a possibility that the carbonylation of the vinylcarbene complex would proceed via the insertion of CO into an Fe–carbon single bond of a 16-electron ferracyclobutene complex (A), the isomer of the η^3-vinylcarbene complex, via a ferracyclo-3-penten-2-one complex (C). He also claimed that this mechanism would explain the scrambling of ^{13}CO.



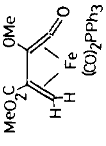
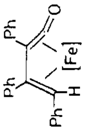
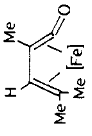
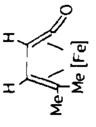
Although this mechanism cannot be ruled out completely, the reasons cited in the text and the following observations lead us to the mechanism described in the text. No evidence for the formation of ferracyclo-2-pentene nor ferracyclo-3-penten-2-one complexes was obtained. If C is an intermediate, a ferracyclo-3-penten-2-one complex should be formed in the reaction of **3a** with an excess amount of carbon monoxide and/or tertiary phosphines; however, the complexes formed were the vinylketene complexes (**6–9**), from which ferracyclo-4-penten-2-ones (**10–12**) were derived by further reaction with carbon monoxide and tertiary phosphines. The scrambling of ^{13}CO in the vinylketene complex may be explained by the ^{13}CO exchange in C or **32** (Scheme IV) derived from the vinylketene complex via complex B. Further studies should be devoted to conclude the mechanisms of these reactions.

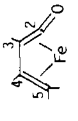
[42] Fischer, H.; Fischer, E. O.; Kressl, F. R. *J. Organomet. Chem.* **1974**, *64*, C41–C44.

[43] Preliminary MO calculation of the vinylcarbene complex **3b** exhibited that the LUMO is localized on the carbene carbon showing that the nucleophiles would attack the carbene carbon: Yamabe, T.; Hori, K.; Mitsudo, T.; Watanabe, Y., unpublished work. For the MO calculation on Fischer type carbene complexes, see: Block, T. F.; Fenske, R. F.; Casey, P. *J. Am. Chem. Soc.* **1976**, *98*, 441–443. Nakatsuji, H.; Ushio, J.; Han, S.; Yonezawa, T. *J. Am. Chem. Soc.* **1983**, *105*, 426–434.

[44] Hill, A. E.; Hoffmann, H. M. R. *J. Chem. Soc., Chem. Commun.* **1972**, 574–575.

Table VIII. Selective Bond Distances (Å) and Bond Angles (deg) in (η^4-Vinylketene)iron Complexes[a]

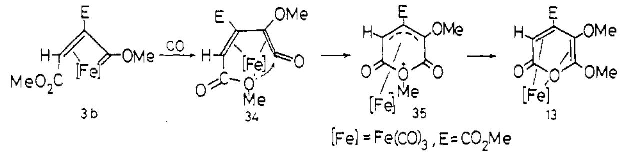
complex	Fe–C(2)	Fe–C(3)	Fe–C(4)	Fe–C(5)	C(2)–C(3)	C(3)–C(4)	C(4)–C(5)	C(2)=O	C(3)–C(4)–C(5)	Fe–C(2)–C(3)	C(3)–C(2)–O	ref
	1.899 (7)	2.174 (7)	2.113 (6)	2.086 (7)	1.484 (11)	1.403 (10)	1.416 (10)	1.207 (9)	113.9 (7)	78.9 (4)	133.7 (6)	this work
	1.917 (2)	2.135 (4)	2.129 (4)	2.168 (2)	1.469 (5)	1.415 (5)	1.433 (3)	1.191 (3)	114.4 (3)	76.9 (3)	137.4 (4)	26d
	1.918 (3)	2.107 (3)	2.092 (3)	2.201 (3)	1.439 (5)	1.397 (4)	1.414 (4)				137	26b
	1.929 (6)	2.109 (6)	2.090 (5)	2.235 (5)	1.422 (9)	1.407 (8)	1.416 (8)	1.188 (8)	121.6 (5)		136.5 (6)	26a

[a] 

Å) is longer than typical coordinated carbon–carbon double bonds, and its length is typical of C(sp^2)–C(sp^2) single bond.[46] (3) The C(2)–Fe bond length (1.899 (7) Å) is much shorter than normal acyl–Fe bond length (1.96–1.97 Å),[47] and it is comparable to that found in $[(PPh_3)_2N]^+[(\eta^3\text{-acryloyl})Fe(CO)_3]^-$ (1.897 Å).[48]

Reaction of 3a with 2 Molar Equiv of Phosphines and Reactions of 8 and 9 with Carbon Monoxide or Tertiary Phosphines. The vinylcarbene complex **3a** reacted with 2 mol equiv of $PPhMe_2$ to give ferracyclopentenone complex **12**. The reaction of **3a** with carbon monoxide (80 atm) or with an excess of PPh_3 did not give the corresponding ferracylopentenone complexes. The η^3:η^1-allylacyl complexes **8** and **9** reacted with additional PPh_2Me, $PPhMe_2$, or carbon monoxide to give **10**, **12**, or **11**. When the ligand of the η^3:η^1-allylacyl complex was CO or PPh_3, complex **6** or **7** did not react with CO or PR_3 and the starting complex was recovered. Only when L was an electron-donating ligand, a ferracylopentenone complex was obtained. In this reaction, the η^3:η^1-allylacyl or the vinylketene ligand is rearranged by the decarbonylation–carbonylation reaction. One of the plausible mechanisms would be explained as follows (Scheme IV). (1) The allylacyl complex **8** or **9** isomerizes to a 16-electron intermediate, **32**, by the dissociation of the olefinic group in **8**. When R in **32** is a hydrogen, **32** rearranges to **33** by the decarbonylation–carbonylation reaction to give the product **10**. When R is CO_2Me, the Fe–CH(CO_2Me) bond is more stable because of the electron-withdrawing methoxycarbonyl group and because rearrangement does not occur to give complex **18**.

Mechanism of the Formation of the Pyrone Complex 13 by the Carbonylation of 3b. A possible mechanism of the formation of the pyrone complex **13** from **3b** is as follows.



First, the carbonylation of the carbene carbon gives a η^3:η^1-allylacyl complex, **34**, in which the methoxycarbonyl group at the anti position can be very close to the ketene group. Although there is no evidence, nucleophilic attack of the methoxy group to the carbonyl of the ketene may give an oxonium π-allyl complex, **35**, which gives **13**. This mechanism has also been reasonably proposed in the reaction of 2-alkoxyfuran with $Fe_2(CO)_9$ or $Ru_3(CO)_{12}$ to give a (η^4-2-pyrone)iron or -ruthenium complex.[5]

Recently, it was found that the reaction of tetracarbonyl(ethoxyphenylcarbene)iron (**36**) with acetylene gives tricarbonyl(η^4-2-pyrone)iron complexes **13′**.[19g] Although the proposed mechanism is different from the present one in detail, the principle of the reaction is the cyclization of the *anti*-(ethoxycarbonyl)(vinylketene)iron complex **37**.

Reaction of 3b with Triphenylphosphine. The η^3-vinylcarbene complex **3b** reacts with tertiary phosphines at 25 °C to give a mixture of two kinds of 1:1 adducts: the η^3:η^1-allylacyl complex and an unassigned product. When

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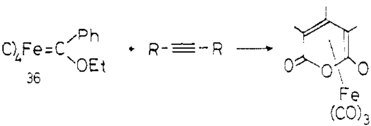
(45) Cotton, F. A.; Frenz, B. A.; Troup, J. M. *J. Organomet. Chem.* **1973**, *61*, 337–346.

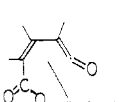
(46) E.g., Mills, O. S.; Robinson, G. *Proc. Chem. Soc.* **1960**, 421–422.

(47) E.g., Churchill, M. R.; Chang, W. Y. *Inorg. Chem.* **1975**, *14*, 1680–1685.

(48) Nakatsu, K.; Inai, Y.; Mitsudo, T.; Watanabe, Y.; Nakanishi, H.; Takegami, Y. *J. Organomet. Chem.* **1978**, *159*, 111–122.



36 13'



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a solution of the mixture of the triphenylphosphine complexes was heated to 50 °C, no η^4-pyrone complex was formed but dicarbonyl(η^3-vinylcarbene)(triphenylphosphine)iron (**19**) was formed in high yield. The present result shows that the carbonyl group of the η^3:η^1-allylacyl ligand is decarbonylated to the η^3-vinylcarbene ligand. This decarbonylation reaction of an η^3:η^1-allylacyl complex was also reasonably proposed in the isomerization of the (η^4-2-pyrone)Fe(CO)$_3$ complex **13**.[8] In case of PMe$_2$Ph or PMePh$_2$, the corresponding (η^3-vinylcarbene)phosphine complex was not isolated.

It would be worthwhile to examine the origin of the carbons in the skeletons of the complexes is Scheme I. The symbols (○) and (●) show that the carbon atom is derived from carbon monoxide and from acetylene, respectively. In complexes **7–9**, **14**, and **15**, one of the acetylenic carbons is doubly carbonylated. In complexes **13** and **16–18**, the doubly carbonylated structure is kept, and in **10–12**, both acetylenic carbons are carbonylated by the decarbonylation–carbonylation rearrangement. The origin of the difference would be the substituent effects of the substrates on the (η^3:η^1-allylacyl)iron complexes as described above.

Experimental Section

All manipulations were performed under a dry argon atmosphere with standard Schlenk techniques. Methylene dichloride and 1,2-dichloroethane were distilled from CaCl$_2$; diethyl ether was distilled from LiAlH$_4$; petroleum ether (bp 35–40 °C) was distilled from sodium. Complexes **3a** and **3b**,[12b] methyldiphenylphosphine,[49] and dimethylphenylphosphine[49] were prepared by literature methods. Other reagents were used as obtained from commercial sources. Melting points were determined under an argon atmosphere on a Yanagimoto micro melting point apparatus. Infrared spectra were recorded on a Hitachi EPI G2 spectrometer and calibrated with a polystyrene standard. ^{1}H NMR spectra were recorded on a Varian HA-100 or a JEOL FX-100 spectrometer. Carbon-13 NMR spectra (25.05 MHz) were obtained on a JEOL FX-100 FT-NMR spectrometer. Molecular weight were measured by a cryoscopic method in benzene.

Reaction of 3a with Carbon Monoxide. With Atmospheric Pressure of Carbon Monoxide. A solution of **3a** (1.61 g, 6 mmol) in CH$_2$Cl$_2$ (10 cm^3) was stirred under an atmosphere of carbon monoxide (1 atm) at 30 °C for 4 h. After removal of the solvent in vacuo, the residual solid was extracted with three 10 cm^3 portions of diethyl ether. The extract was concentrated to 5 cm^3, and the addition of petroleum ether (30 cm^3) afforded a brown oil. The supernatant liquid was concentrated to ca. 5 cm^3 and was gradually cooled on dry ice to afford yellow crystals, which were collected and washed with five 2 cm^3 portions of cold petroleum ether gave **6** (0.67 g, 38%).

With Pressurized Carbon Monoxide. A solution of **3a** (4.29 g, 16 mmol) in CH$_2$Cl$_2$ (20 cm^3) was placed into an autoclave, and then it was charged with 80 atm of carbon monoxide. The mixture was stirred at 25 °C for 4 h. The workup described above gave 2.3 g of **6** (7.7 mmol, yield 49%).

6: mp 75–76 °C; IR (KBr) ν(C≡O) 2075 (vs), 2020 (vs), 1990 (b, vs), 1960 (s), ν(CO) 1728 (br, vs) cm^{-1}; IR (CHCl$_3$) 1740 (vs), 1720 (sh, m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.95 (s, 3 H, CO$_2$Me), 3.84 (s, 3 H, OMe), 2.92 (d, J = 2.9 Hz, 1 H, H$_{syn}$), 0.87 (d, J = 2.9 Hz, 1 H, H$_{anti}$; ^{13}C NMR (CD$_2$Cl$_2$) δ 233.5 (s, FeC═O), 206.6 (s, C≡O), 166.1 (s, C═O), 102.6 (s, C—OMe), 91.72 (s), 58.0 (q, J = 147.9 Hz), 52.9 (q, $^1J_{CH}$ = 147.9 Hz, CO$_2$Me), 29.0 (dd, $^1J_{CH}$ = 167.2 Hz, $^1J_{CH}$ = 162.9 Hz); mol wt 299 (calcd 296.0). Anal. Calcd for C$_{10}$H$_8$O$_7$Fe: C, 40.58; H, 2.72. Found: C, 40.60; H, 2.57.

Reaction of 3a with Triphenylphosphine. To a solution of **3a** (1.53 g, 5.7 mmol) in diethyl ether (10 cm^3) was added triphenylphosphine (1.5 g, 5.7 mmol) in diethyl ether (10 cm^3), and the solution was stirred at 30 °C for 1 h. Concentration of the solution gave yellow crystals which were collected and washed with petroleum ether to give **7** (2.9 g, 5.4 mmol, yield 94%).

7: mp 113–114 °C; IR (KBr) ν(C≡O) 2010 (vs), 1970 (vs), 1960 (vs), ν(C═O ester) 1720 (s), ν(C═O acyl) 1707 (m) cm^{-1}; IR (CHCl$_3$) ν(C≡O) 2020 (vs), 1968 (vs), ν(C═O) 1713 (br, vs), 1705 (m, sh) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 7.8–7.2 (m, 15 H, Ph), 3.77 (s, 3 H, CO$_2$Me), 3.07 (s, 3 H, OMe), 2.43 (dd, $^3J_{PH}$ = 1.0 Hz, $^2J_{HH}$ = 2.2 Hz), 0.23 (t, $^3J_{PH}$ = $^2J_{HH}$ = 2.2 Hz); ^{13}C NMR (CDCl$_3$) δ 241.7 (d, $^2J_{PC}$ = 7.3 Hz, FeC═O), 213.0 (d, $^2J_{PC}$ = 12.2 Hz, FeCO), 210.0 (d, $^2J_{PC}$ = 17.1 Hz), 167.4 (s, CO$_2$Me), 134.7–128.0 (m, Ph), 103.6 (s, COMe), 85.5 (s, CCO$_2$Me), 56.6 (q, $^1J_{CH}$ = 146.5 Hz, OMe), 52.0 (q, $^1J_{CH}$ = 146.5 Hz, CO$_2$Me), 24.4 (t, $^1J_{CH}$ = 163.6 Hz, CH$_2$); mol wt 484 (calcd 530.3). Anal. Calcd for C$_{27}$H$_{23}$O$_6$FeP: C, 61.16; H, 4.37. Found: C, 61.14, H, 4.44.

Reaction of 3a with Diphenylmethylphosphine. To a solution of **3a** (0.59 g, 2.2 mmol) in methylene dichloride (10 cm^3) was added PPh$_2$Me (0.44 g, 2.2 mmol) at 0 °C, and the mixture was stirred at 25 °C for 1 h. Evaporation of the solvent gave a red-brown liquid of **8** (0.70 g, 1.5 mmol, 68%).

8: IR (neat) ν(C≡O) 2020 (vs), 1950 (br, vs), ν(CO acyl) 1720 (sh, s), ν(CO ester) 1710 (br, vs) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 7.7–7.2 (m, 10 H, Ph), 3.75 (s, 3 H, CO$_2$Me), 3.40 (s, 3 H, OMe), 2.50 (t, $^3J_{PH}$ = $^2J_{HH}$ = 2.4 Hz, H$_{anti}$), 2.21 (d, $^2J_{PH}$ = 8.4 Hz, 3 H, PMe), 0.20 (dd, $^3J_{PH}$ = 5.6 Hz, $^2J_{HH}$ = 2.4 Hz, H$_{syn}$); ^{13}C NMR (CDCl$_3$) δ 242.7 (d, J_{CP} = 11.7 Hz, FeCO), 211.7 (d, $^2J_{CP}$ = 9.7 Hz, FeCO), 210.1 (d, $^2J_{CP}$ = 13.7 Hz, FeCO), 167.7 (s, CO$_2$Me), 137.8–128.3 (m, Ph), 101.7 (s, COMe), 88.6 (s, CCO$_2$Me), 56.9 (q, $^1J_{CH}$ = 146.5 Hz, OMe), 52.2 (q, $^1J_{CH}$ = 146.5 Hz, CO$_2$Me), 26.8 (t, $^1J_{CH}$ = 162.1 Hz, CH$_2$), 16.3 (dq, $^2J_{CP}$ = 31.7 Hz, $^1J_{CH}$ = 130.8 Hz, PMe). Anal. Calcd for C$_{22}$H$_{21}$O$_6$PFe: C, 56.43; H, 4.52. Found: C, 56.24; H, 4.87.

Reaction of 3a with Dimethylphenylphosphine. To a solution of **3a** (1.58 g, 5.9 mmol) in methylene dichloride (10 cm^3) was added PPhMe$_2$ (0.82 g, 5.9 mmol) at 0 °C, and the mixture was stirred for 1 h. Evaporation of the solvent gave a red-brown liquid of **9** (1.70 g, 4.2 mmol, yield 71%).

9: IR (neat) ν(C≡O) 2010 (vs), 1950 (br, vs), ν(C═O) 1710 (vs), ν(FeC═O) 1720 (m, sh) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.7–7.2 (m, 5 H, Ph), 3.77 (s, 3 H, CO$_2$Me), 3.55 (s, 3 H, OMe), 2.40 (dd, $^2J_{HH}$ = 2.0 Hz, $^3J_{PH}$ = 1.0 Hz, 1 H, H$_{syn}$), 1.85 (d, $^2J_{HP}$ = 6.0 Hz, 3 H, PMe), 1.70 (d, $^2J_{HP}$ = 6.0 Hz, 3 H, PMe), 0.17 (dd, $^3J_{HP}$ = 10.0 Hz, $^2J_{HH}$ = 2.0 Hz, H$_{anti}$); ^{13}C NMR (CD$_2$Cl$_2$) δ 243.0 (d, $^2J_{PC}$ = 17.1 Hz, FeC═O), 211.5 (d, $^2J_{PC}$ = 14.6 Hz, FeCO), 210.0 (d, $^2J_{PC}$ = 7.3 Hz), 167.7 (s, CO$_2$Me), 139.9–128.5 (m, Ph), 100.7 (s, COMe), 89.6 (s, CCO$_2$Me), 57.1 (q, $^1J_{CH}$ = 146.5 Hz, OMe), 52.1 (q, $^1J_{CH}$ = 146.5 Hz, CO$_2$Me), 27.3 (t, $^2J_{CH}$ = 162.4 Hz, CH$_2$), 17.0 (dt, $^1J_{CH}$ = 129.4 Hz, $^1J_{PC}$ = 31.7 Hz, PMe). Anal. Calcd for C$_{17}$H$_{19}$O$_6$PFe: C, 50.27; H, 4.72. Found: C, 50.20; H, 4.50.

Reaction of 8 with Methyldiphenylphosphine. To a solution of **8** (1.35 g, 2.9 mmol) in methylene dichloride (10 cm^3) was added 0.61 g (3.0 mmol) of PPh$_2$Me, and the mixture was stirred at 30 °C for 12 h. After evaporation of the solvent, the residue was chromatographed on silica gel (Merck). Elution by benzene–ether (1:1) and evaporation of the solvent gave yellow microcrystals of **10** (0.25 g, 0.38 mmol, yield 13%).

10: mp 49–53 °C; IR (KBr) ν(C≡O) 2000 (vs), 1945 (br, vs), ν(C═O) 1670 (m), ν(C═O) 1610 (s), ν(C═C) 1515 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.7–7.2 (m, 20 H, Ph), 3.70 (s, 3 H, CO$_2$Me), 3.48 (s, 3 H, OMe), 2.01 (d, $^2J_{PH}$ = 2.5 Hz, 3 H, PMe), 2.00 (s, br, 2 H, CH$_2$), 1.97 (d, $^2J_{PH}$ = 4.5 Hz, 3 H, PMe); ^{13}C NMR (CDCl$_3$) 284.0 (tt, $^2J_{PC}$ = 21.5 Hz, $^2J_{CH}$ = 5.9 Hz, FeC═O), 219.4 (t, $^2J_{PC}$ = 30.3 Hz, FeCOMe), 212.0 (t, $^2J_{PC}$ = 19.6 Hz, FeC═O), 211.3 (t, $^2J_{PC}$ = 15.7 Hz, FeC═O), 163.5 (s, CO$_2$Me) 137.7–127.5 (m, Ph), 110.4 (s, CCO$_2$Me), 63.4 (q, $^1J_{CH}$ = 144.5 Hz, COMe), 62.3 (t, $^2J_{CH}$ = 128.9 Hz, CH$_2$), 50.1 (q, $^1J_{CH}$ = 144.5 Hz, CO$_2$Me), 17.0

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(49) Mathur, M. A.; Myers, W. H.; Sisler, H. H.; Ryschkewitsch, G. E. *Inorg. Synth.* **1973**, *15*, 128–133.

(tq, $^3J_{PC}$ = 16.1 Hz, $^1J_{CH}$ = 130.9 Hz, PMe); mol wt 695 (calcd 688.4). Anal. Calcd for $C_{35}H_{34}O_6P_2Fe$: C, 62.89; H, 5.13. Found: C, 62.78; H, 5.15.

Reaction of 9 with Carbon Monoxide. A methylene dichloride solution (10 cm^3) of **9** (2.4 g, 5.9 mmol) was stirred under an atmosphere of carbon monoxide at 30 °C for 12 h. After evaporation of the solvent, the residue was dissolved in 4 cm^3 of diethyl ether and then 10 cm^3 of petroleum ether was added. The formed yellow microcrystals were filtered and washed with a small amount of diethyl ether–petroleum ether (1:5) (**11**, 1.7 g, 3.8 mmol, 65%).

11: mp 82–83 °C; IR (KBr, cm^{-1}) ν(C≡O) 2050 (vs), 2000 (vs), 1988 (vs), ν(C=O ester) 1708 (s), ν(FeC=O) 1650 (s), ν(C=C) 1553 (m); ^{1}H NMR ($CDCl_3$) δ 7.6–7.3 (m, 5 H, Ph), 3.90 (s, 3 H, CO_2Me), 3.63 (s, 3 H, OMe), 3.19 (dd, $^4J_{PH}$ = 2.0 Hz, $^2J_{HH}$ = 21.0 Hz, 1 H), 2.69 (dd, $^4J_{PH}$ = 0.7 Hz, $^2J_{HH}$ = 21.0 Hz, 1 H), 1.82 (d, $^2J_{HP}$ = 5.0 Hz, 3 H, PMe), 1.72 (d, $^2J_{HP}$ = 5.0 Hz, 3 H, PMe); ^{13}C NMR δ 265.7 (d, $^2J_{PC}$ = 20.9 Hz, FeC=O), 209.5 (d, $^2J_{PC}$ = 32.5 Hz, FeCOMe), 207.3 (d, $^2J_{PC}$ = 32.4 Hz, FeCO), 205.3 (d, $^2J_{PC}$ = 17.6 Hz, FeCO), 204.8 (d, $^2J_{PC}$ = 15.4 Hz, FeCO), 161.6 (d, $^4J_{PC}$ = 3.8 Hz, CO_2Me), 137.5–128.1 (m, Ph), 120.8 (d, $^3J_{PC}$ = 3.8 Hz, CCO_2Me), 61.5 (dt, $^3J_{PC}$ = 2.8 Hz, $^2J_{HC}$ = 128.7 Hz, CH_2), 60.8 (dq, $^4J_{PC}$ = 2.2 Hz, J_{HC} = 144.0 Hz, OMe), 50.6 (q, J_{CH} = 146.2 Hz, CO_2Me), 16.7 (d, J_{PC} = 9.9 Hz, PMe), 14.5 (d, J_{PC} = 11.5 Hz, PMe); mol wt 390 (calcd 434.2). Anal. Calcd for $C_{18}H_{19}O_7PFe$: C, 49.79; H, 4.41. Found: C, 49.68; H, 4.38.

Reaction of 3a with 2 Mol Equiv of Dimethylphenylphosphine. To a solution of **3a** (0.53 g, 2.0 mmol) in methylene dichloride (5 cm^3) was added 0.61 g of $PPhMe_2$ (4.4 mmol), and the mixture was stirred at 35 °C for 4 h. After the removal of the solvent, the residue was extracted with four 10 cm^3 portion of diethyl ether. After the solution was concentrated to ca. 10 cm^3, 10 cm^3 of petroleum ether was added and the mixture cooled on dry ice to give yellow crystals of **12** (0.21 g, 0.39 mmol, 19%).

12: mp 102–103 °C; IR (KBr) ν(C≡O) 2000 (vs), 1945 (br, vs), ν(C=O) 1690, ν(C=O) 1630, ν(C=C) 1535 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.5–7.1 (m, 10 H, Ph), 4.00 (s, 3 H, CO_2Me), 3.64 (s, 3 H, OMe), 3.31 (dd, $^2J_{HH}$ = 21.0 Hz, $^4J_{PH}$ = 2.0 Hz, 1 H), 2.78 (dd, 2 J_{HH} = 21.0 Hz, $^4J_{PH}$ = 1.0 Hz, 1 H), 1.50 (d, $^2J_{PH}$ = 7.3 Hz, 3 H, PMe), 1.45 (d, $^2J_{PH}$ = 9.0 Hz, 3 H, PMe), 1.43 (d, J_{PH} = 9.0, 3 H, PMe) 1.34 (d, J_{PH} = 7.5 Hz, 3 H, PMe); ^{13}C NMR (CD_2Cl_2) δ 274.1 (t, $^2J_{PC}$ = 24.4 Hz, FeCO), 215.6 (dd, $^2J_{PC}$ = 34.2 Hz, $^2J_{PC}$ = 12.0 Hz, FeCOMe), 211.8 (dd, $^2J_{PC}$ = 31.8 and 14.6 Hz, FeCO), 211.4 (t, J_{PC} = 19.1 Hz, FeCO), 162.4 (s, CO_2Me), 141.8–128.7 (m, Ph), 112.9 (s, CCO_2Me), 62.5 (q, $^1J_{CH}$ = 146.5 Hz, OMe), 61.9 (t, $^1J_{CH}$ = 129.4 Hz, CH_2), 50.5 (q, $^2J_{CH}$ = 146.5, CO_2Me), 18.5–14.5 (m, PMe); mol wt 521 (calcd 544.3). Anal. Calcd for $C_{25}H_{30}O_6P_2Fe$: C, 55.16; H, 5.55. Found: C, 54.85, H, 5.42.

Reaction of 9 with Dimethylphenylphosphine. To a solution of **9** (1.87 g, 4.6 mmol) in methylene dichloride (5 cm^3) was added 0.65 g (4.7 mmol) of $PPhMe_2$, and the mixture was stirred at 35 °C for 2 h. After evaporation of the solvent, the residue was extracted with two 10 cm^3 portions of diethyl ether and filtered. The solution was concentrated to 5 cm^3, and 5 cm^3 of petroleum ether was added and then the mixture cooled on dry ice. The formed yellow microcrystals were collected and washed with a small amounts of a 1:1 mixture of diethyl ether–petroleum ether (**12**, 1.1 g, 2.1 mmol, yield 45%); mp 102–103 °C.

Reaction of 3b with Carbon Monoxide. A solution of **3b** (0.55 g, 1.69 mmol) in CH_2Cl_2 (15 cm^3) was placed in a 100 cm^3 autoclave under an argon atmosphere. After argon was purged with carbon monoxide, the autoclave was charged with 80 atm of carbon monoxide and the solution was stirred at 25 °C for 12 h. After the solvent was distilled off in vacuo, the residual oil was dissolved in a mixture of *n*-hexane–diethyl ether (4:1, 10 cm^3). Concentration of the solution gave yellow crystals which were collected and recrystallized from petroleum ether–acetone (5:1) to give 0.49 g of **13** (yield, 79%).

13: mp 67–68 °C; IR (KBr) ν(C≡O) 2070 (vs), 2010 (vs), 1995 (vs), 1975 (vs), ν(C=O pyrone) 1760 (vs), ν(C=O ester) 1730 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 3.98 (s, 3 H, OMe), 3.94 (s, 3 H, OMe), 3.84 (s, 3 H, OMe), 2.98 (s, 1 H, =CH); ^{13}C NMR ($CDCl_3$) δ 206.5 (s, br, FeCO), 168.6 (s, C=O), 166.3 (s, C=O), 127.7 (s, OCOMe), 119.5 (s, =COMe), 60.6 (q, $^1J_{CH}$ = 147.9 Hz, OMe), 59.3 (q, $^1J_{CH}$ = 147.9 Hz, OMe), 53.4 (q, $^1J_{CH}$ = 147.9 Hz, CO_2Me), 38.4 (d, $^1J_{CH}$ = 171.9 Hz, =CH); mol wt 330 (calcd 354.1). Anal. Calcd for $C_{12}H_{10}O_9Fe$: C, 40.70; H, 2.85. Found: C, 40.41; H, 2.67.

Reaction of 3b with Methyldiphenylphosphine. To a solution of **3b** (1.4 g, 4.4 mmol) in methylene dichloride (10 cm^{-3}) was added PPh_2Me (0.88 g, 4.4 mmol), and the mixture was stirred at 25 °C for 1 h. After evaporation of the solvent the residue was extracted with two 10 cm^3 portions of diethyl ether. The solution was concentrated to about 5 cm^3, then 25 cm^3 of petroleum ether was added, and the mixture cooled on dry ice. The yellow microcrystals that formed were collected and washed with a small amount of petroleum ether (**14**, 1.8 g, 3.2 mmol, yield 76%).

14: mp 97–100 °C; IR (KBr) ν(C≡O) 2020 (vs), 1975 (vs) ν(C=O ester and acyl) 1740 (m), 1710 (s), 1700 (sh, m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.8–7.2 (m, 10 H, Ph), 3.95 (s, 3 H, CO_2Me), 3.80 (s, 3 H, CO_2Me), 3.46 (s, 3 H, OMe), 2.15 (d, $^1J_{PH}$ = 10.0 Hz, PMe), 1.23 (d, $^3J_{PH}$ = 8.0 Hz, 1 H, CH); in addition a small signal at δ 3.50 (s) was observed; ^{13}C NMR ($CDCl_3$) δ 239.5 (d, $^2J_{PC}$ = 25.4 Hz, FeCO), 214.9–204.5 (m, FeCO), 174.0 (s, CO_2Me), 132.0–128.4 (m, Ph), 99.6 (s, br, COMe), 86.8 (s, br, CCO_2Me), 57.0 (q, $^1J_{CH}$ = 146.5 Hz, OMe), 53.0 (q, $^1J_{CH}$ = 148.5 Hz, CO_2Me), 51.6 (q, $^1J_{CH}$ = 146.5 Hz, CO_2Me), 34.1 (d, br, $^1J_{CH}$ = 175.8 Hz, CH), 15.4 (qd, $^1J_{PC}$ = 33.1 Hz, PMe); mol wt 542 (calcd 526.3). Anal. Calcd for $C_{24}H_{23}O_8PFe$: C, 54.78; H, 4.40. Found: C, 54.75; H, 4.40.

Reaction of 3b with Dimethylphenylphosphine. To a solution of **3b** (1.6 g, 5.1 mmol) in methylene dichloride (20 cm^3) was added $PPhMe_2$ (0.72 g, 5.2 mmol), and the solution was stirred at 25 °C for 1 h. After evaporation of the solvent, the residue was dissolved with 10 cm^3 of diethyl ether. The concentration of the solution to half the volume gave yellow microcrystals which were collected and washed with a small amount of diethyl ether (**15**, 2.2 g, 4.7 mmol, yield 92%).

15: mp 105–109 °C dec; IR (KBr) ν(C≡O) 2025 (vs), 1960 (b, vs) ν(C=O ester and acyl) 1740 (m), 1725 (s), 1705 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.5–7.3 (m, 5 H, Ph), 3.93 (s, 6 H, CO_2Me), 3.62 (s, 3 H, OMe), 1.93 (d, $^1J_{PH}$ = 9.5 Hz, 3 H, PMe), 1.72 (d, $^1J_{PH}$ = 9.5 Hz, 3 H, PMe), 1.25 (d, $^3J_{PH}$ = 6.0 Hz); in addition small signals at δ 3.83 (s), 3.72 (s), and 3.45 (s) were observed; ^{13}C NMR ($CDCl_3$) δ 241.4 (br, FeC=O), 210.9–204.7 (br, m, FeC≡O), 173.9 (s, CO_2Me), 165.2 (s, CO_2Me), 137.6–128.5 (m, Ph), 100.3 (s, COMe), 97.1 (s, CCO_2Me), 57.1 (q, $^1J_{CH}$ = 146.5 Hz, OMe), 53.0 (q, $^1J_{CH}$ = 146.5, CO_2Me), 51.5 (q, $^1J_{CH}$ = 146.5 Hz, CO_2Me), 30.8 (d, $^1J_{HC}$ = 167.9 Hz, CH), 16.2 (qd, J_{PC} = 9.3 Hz, PMe), 14.8 (qd, J_{PC} = 23.5 Hz, PMe); mol wt 428 (calcd 464.2). Anal. Calcd for $C_{19}H_{21}O_8PFe$: C, 49.16; H, 4.56. Found: C, 48.64; H, 4.34.

Reaction of 14 with Carbon Monoxide. A solution of **14** and its isomer (1.3 g, 2.4 mmol) in methylene dichloride (10 cm^3) was placed into an 100 cm^3 autoclave, which was charged with 65 atm of carbon monoxide, and the mixture was stirred at 25 °C for 6 h. After removal of the solvent in vacuo, the residue was extracted with two 10 cm^3 portions of diethyl ether and filtered. The solution was concentrated to 5 cm^3, and 20 cm^3 of petroleum ether was added. The formed brown oil was dryed in vacuo to give yellow microcrystals of **16** (0.71 g, 1.2 mmol, yield 50%).

16: IR (KBr) ν(C≡O) 2070 (vs), 2000 (vs, br), ν(C=O acyl) 1710, ν(C=O ester) 1700 (s), 1635 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.9–7.2 (m, 10 H, Ph), 3.63 (s, 6 H, CO_2Me), 3.60 (s, 3 H, OMe), 3.13 (d, $^3J_{PH}$ = 10.4 Hz, 1 H, CH), 2.00 (d, $^1J_{PH}$ = 8.8 Hz, 3 H, PMe); ^{13}C NMR ($CDCl_3$) δ 255.7 (d, $^2J_{PC}$ = 23.4 Hz, FeC=O), 205.4 (d, P_{PC} = 27.3 Hz, FeC=O), 204.9 (d, ^2J = 21.5 Hz, FeCO), 203.3 (d, $^2J_{PC}$ = 23.4, FeCO), 180.3 (s, COMe), 166.1 (s, CO_2Me), 165.1 (s, CO_2Me), 139.1 (s, CCO_2Me), 133.2–128.4 (m, Ph), 60.2 (q, $^1J_{CH}$ = 146.5 Hz, OMe), 51.6 (q, $^1J_{CH}$ = 146.5 Hz, CO_2Me), 51.0 (q, J_{CH} = 146.5 Hz, CO_2Me), 33.5 (dd, J_{PC} = 13.7 Hz, $^1J_{CH}$ = 138.7 Hz, CH), 13.9 (dq, $^1J_{PC}$ = 33.2 Hz, $^1J_{CH}$ = 132.8 Hz, PMe); mol wt 570 (calcd 554.3). Anal. Calcd for $C_{25}H_{23}O_9PFe$: C, 54.17; H, 4.18. Found: C, 54.30; H, 4.42.

Reaction of 15 with Carbon Monoxide. A solution of **15** and its isomer (2.0 g, 4.2 mmol) in methylene dichloride (10 cm^3) was placed into an 100 cm^3 autoclave, which was then charged with 80 atm of carbon monoxide. The mixture was stirred at 40 °C for 6 h. After evaporation of the solvent, the residue was extracted with 10 cm^3 of diethyl ether and filtered. Addition of 20 cm^3 of petroleum ether gave a brown solid which was chromatographed on silica gel (eluent diethyl ether). Concentration of the eluent gave yellow crystals which was collected on a glass filter and washed with a small amount of diethyl ether–petroleum ether (1:5) to give 1.1 g (2.1 mmol) of **17** (yield 51%).

17: mp 78–79 °C; IR (KBr) ν(C≡O) 2060 (vs), 2000 (vs), 1995 (s, sh) ν(C=O) 1705 (s), ν(CO acyl) 1630 (s), ν(C=C) 1620 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.5–7.3 (m, 5 H, Ph), 3.75 (s, 3 H, CO$_2$Me), 3.70 (s, 3 H, CO$_2$Me), 3.40 (s, 3 H, OMe), 2.95 (d, $^3J_{PH}$ = 10.0 Hz, 1 H, CH), 1.77 (d, $^1J_{PH}$ = 9.5 Hz, 3 H, PMe), 1.71 (d, $^1J_{PH}$ = 9.5 Hz, 3 H, PMe); ^{13}C NMR (CDCl$_3$) δ 255.8 (d, $^2J_{PC}$ = 25.4 Hz, FeC=O), 205.8 (d, $^2J_{PC}$ = 23.5 Hz, FeCO), 205.0 (d, $^2J_{PC}$ = 13.7 Hz, FeCO), 204.8 (d, $^2J_{PC}$ = 9.8 Hz, FeCO), 180.5 (s, COMe), 166.6 (s, CO$_2$Me), 165.6 (s, CO$_2$Me), 139.6–128.9 (m, Ph), 139.7 (s, CCO$_2$Me), 60.3 (q, $^1J_{CH}$ = 146.5 Hz, OMe), 51.7 (q, $^1J_{CH}$ = 146.5, CO$_2$Me), 50.9 (q, $^1J_{CH}$ = 146.5 Hz, CO$_2$Me), 33.7 (dd, $^2J_{PC}$ = 11.7 Hz, $^1J_{CH}$ = 138.7 Hz, CH), 14.4 (tq, $^1J_{PC}$ = 32.0 Hz, $^1J_{CH}$ = 130.5 Hz); mol wt 497 (calcd 492.2). Anal. Calcd for $C_{20}H_{21}O_9PFe$: C, 48.80; H, 4.30. Found: C, 48.96; H, 4.26.

Reaction of 15 with Dimethylphenylphosphine. To a solution of **15** and its isomer (1.3 g, 2.7 mmol) in methylene dichloride (10 cm^3) was added PPhMe$_2$ (0.38 g, 2.7 mmol), and the mixture was stirred at 35 °C for 6 h. After the solvent was removed off in vacuo, the residue was extracted with four 10 cm^3 portions of diethyl ether and filtered. After concentration of the solution to ca. 10 cm^3, 20 cm^3 of petroleum ether was added and the mixture cooled on dry ice to give pale yellow crystals of **18** (1.3 g, 2.0 mmol, 74%).

18: mp 112–113 °C dec; IR (KBr) ν(C≡O) 2000 (vs), 1950 (vs) ν(C=O ester) 1728 (m), 1710 (m, sh), ν(C=O acyl) 1685 (s) ν(C=C) 1590 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.6–7.1 (m, 10 H, Ph), 3.70 (s, 3 H, CO$_2$Me), 3.65 (s, 3 H, CO$_2$Me), 3.30 (s, 3 H, OMe), 2.85 (dd, $^3J_{PH}$ = 8.0 Hz, $^3J_{PH}$ = 4.4 Hz, 1 H, CH), 1.67 (d, $^2J_{PH}$ = 9.0 Hz, 6 H, PMe), 1.56 (d, $^2J_{PH}$ = 9.5 Hz, 3 H, PMe), 1.33 (d, $^2J_{PH}$ = 9.5 Hz, 3 H, PMe); ^{13}C NMR (CDCl$_3$) δ 270.7 (t, $^2J_{PC}$ = 27.3 Hz, FeC=O), 210.5 (t, $^2J_{PC}$ = 23.4 Hz, FeC=O), 209.9 (dd, $^2J_{PC}$ = 11.7 and 25.4 Hz, FeCO), 182.3 (s, COMe), 168.1 (s, CO$_2$Me), 163.7 (s, CO$_2$Me), 139.8–127.9 (m, Ph), 137.8 (s, CCO$_2$Me), 59.6 (q, $^1J_{CH}$ = 144.5 Hz, OMe), 51.5 (q, $^1J_{CH}$ = 146.5 Hz, CO$_2$Me), 49.8 (q, $^1J_{CH}$ = 146.5 Hz, CO$_2$Me), 31.8 (td, $^3J_{PC}$ = 12.6 Hz, $^1J_{CH}$ = 132.8 Hz), 16.7, 15.6, 14.6 and 13.6 (qd, $^1J_{PC}$ = 27.3 Hz, $^1J_{CH}$ = 130.9 Hz, 4 PMe); mol wt 622 (calcd 602.3). Anal. Calcd for $C_{27}H_{32}O_8P_2Fe$: C, 53.83; H, 5.36. Found: C, 53.75; H, 5.15.

Reaction of 3b with Triphenylphosphine. (1) At 50 °C in 1,2-Dichloroethane. To the solution of **3b** (0.65 g, 2.0 mmol) in 1,2-dichloroethane (5 cm^3) was added triphenylphosphine (0.51 g, 2.0 mmol) in 1,2-dichloroethane (5 cm^3), and the solution was stirred at 50 °C for 5 h. After removal of the solvent in vacuo the residual oil was crystallized by the addition of diethyl ether (0.6 cm^3). Yellow crystals formed were washed two times with a small amount of hexane–diethyl ether (7:1) to give **19** (1.72 g, 89%).

19: mp 155 °C dec; IR (KBr) ν(C≡O) 2005 (vs), 1945 (vs), ν(C=O ester 1717 (s), 1695 (s), ν(C=C=C$_{asym}$) 1525 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.4 (m, 15 H, Ph), 4.57 (s, 3 H, OMe), 3.62 (s, 3 H, CO$_2$Me), 3.31 (s, 3 H, CO$_2$Me), 3.73 (d, $^3J_{PH}$ = 10.7 Hz, 1 H, CH); ^{13}C NMR (CDCl$_3$) δ 272.6 (d, $^2J_{PC}$ = 31.2 Hz, Fe=COMe), 215.4 (d, $^2J_{PC}$ = 7.7 Hz, FeCO), 213.7 (d, $^2J_{PC}$ = 19.5 Hz, FeCO), 177.9 (s, CO$_2$Me), 165.7 (s, CO$_2$Me), 134.1–128.0 (m, Ph), 67.4 (q, $^1J_{CH}$ = 147.8 Hz, OMe), 54.6 (s, CCOMe), 52.1 (q, $^1J_{CH}$ = 146.5 Hz, CO$_2$Me), 51.9 (q, $^1J_{CH}$ = 146.5 Hz, CO$_2$Me), 39.5 (dd, J_{CH} = 160.2 Hz, $^2J_{PC}$ = 5.9 Hz, CH). Anal. Calcd for $C_{28}H_{25}O_7PFe$: C, 60.02; H, 4.50. Found: C, 59.61; H, 4.49.

(2) At 25 °C in Dichloromethane. To a solution of **3b** (0.98 g, 3.0 mmol) in CH$_2$Cl$_2$ (5 cm^3) was added 1.6 g (6.0 mmol) of triphenylphosphine, and the mixture was stirred at 25 °C for 1.5 h. After evaporation of the solvent the residue was recrystallyzed from diethyl ether–CH$_2$Cl$_2$–petroleum ether at −70 °C. Yellow microcrystals of a mixture of two isomers of 1:1 adducts were obtained (1.11 g, 1.89 mmol, 63%): mp 117–120 °C dec; IR (KBr) ν(C≡O) 2040 (s), 1965 (s, br), ν(C=O) 1750 (m), 1710 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.7–7.3 (m, 15 H, Ph), 3.93, 3.70, 3.67, 3.48, 3.26, 2.93 (singlets with equal intensities, total 9 H), 1.20 (d, J_{PH} = 2.0 Hz); ^{13}C NMR (CDCl$_3$) δ 239.1 (s, acyl), 215.0 (s), 214.5 (s), 213.8 (s), 177.7 (s), 174.3 (s), 167.0 (s), 165.2 (s), 134–127 (m, Ph), 67.4 (q), 53.1 (q), 53.6 (q), 52.4 (q), 51.9 (q), 51.6 (q), 40.0 (d); mol wt 576 (calcd 602.3). Anal. Calcd for $C_{29}H_{25}O_8PFe$: C, 59.20; H, 4.28. Found: C, 58.73; H, 4.29.

Reaction of 3a with ^{13}C-Enriched Carbon Monoxide. A methylene dichloride solution (3 cm^3) of **3a** (0.40 g, 1.5 mmol) in a 20 cm^3 flask was cooled in liquid nitrogen, and the flask was evacuated and ^{13}CO was introduced. The mixture was stirred at 25 °C for 12 h. The workup for **6** described above gave ^{13}C-enriched **6′** (0.089 g, 0.30 mmol, 20%).

X-ray Crystal Structure Determination of 7, 11, and 13. Specimens used for X-ray diffraction studies were sealed in thin-walled glass capillaries under an argon atmosphere. The crystal systems and space group were obtained from preliminary oscillation and Weisenberg photographs about the *c* axis (for **7**, the *b* axis) with Cu Kα radiation. Accurate cell parameters were determined by a least-squares treatment of the 2θ angles of several reflections measured on a Rigaku computer-controlled four-circle automatic diffractometer with Mo Kα radiation (λ = 0.710 69 Å). The crystal data obtained were summarized in Table I.

Solution and Refinement of the Structures. The structures were solved by the heavy-atom method. The structures were refined by the diagonal least-squares calculations with isotropic thermal factor for all the atoms. The hydrogen atoms were located from a difference Fourier map. The structure was then refined by the block-diagonal least squares with anisotropic thermal factors for the non-hydrogen atoms. In the refinement the function minimized was $\sum w(\Delta F)^2$, where the weight $1/w$ was $\sigma^2(|F_o|) + p|F_o|^2$ for the block-diagonal least-squares. The constant p was chosen to give approximately equal distribution of the mean $w(\Delta F)^2$ for several subgroups of increasing $|F_o|$ and was 0.000 06, 0.0005, and 0.0005 in the final cycles of the refinement, respectively. In the final cycle of least-squares refinement no individual parameter except in the hydrogen atoms shifted by more than one-half of its estimated standard deviation. In the final difference map there were not any significant peaks. Atomic scattering factors were taken from ref 50, including corrections for the effects of anomalous dispersion. All computations were performed on a FACOM 230/38 computer and a MELCOM 70/30 computer at Kwansei Gakuin University.

Results are shown in Figures 1–3 and Tables I–VII. In the figures, thermal ellipsoids enclose at 40% probability except those for hydrogens, which are drown by a sphere of an arbitrary radius. The hydrogen atoms of the methyl group and phenyl groups of the phosphines are not shown for clarity.

Registry No. **3a**, 61111-92-0; **3b**, 60941-31-3; **6**, 67507-17-9; **6′**, 118275-20-0; **7**, 67588-74-3; **8**, 72251-34-4; **9**, 72256-40-7; **10**, 118275-21-1; **11**, 72251-36-6; **12**, 72251-35-5; **13**, 78491-98-2; **14**, 118275-22-2; **15**, 118275-23-3; **16**, 118297-33-9; **17**, 118275-24-4; 18, 118275-25-5; **19**, 118275-26-6; Fe(η^4-(MeO$_2$CCH=C(CO$_2$Me)C(OMe)=C=O)(CO)$_2$(PPh$_3$), 118275-19-7.

Supplementary Material Available: Tables of fractional coordinates and temperature factors, bond distances, bond angles, symmetry operations, and least-squares planes for complexes **7**, **11**, and **13** (32 pages). Ordering information is given on any current masthead page.

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(50) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birminham, England, 1974; Vol. IV, values for iron are taken from p 78 and those for hydrogen, carbon, and oxygen taken from pp 72–73. Anomalous dispersion correction for Fe, C, and O are taken from p 149.