

the sodium ions could not be well resolved ($\bar{B} \sim 14 \text{ \AA}^2$, $R = 11.7\%$) and thermal ellipsoids for two tin atoms were quite elongated. Nonetheless, a most interesting fact was clear, that the sequestering of Na^+ by en was incomplete and several short Na-Sn distances remained. The resulting cluster arrangement can be described approximately in terms of a nominal tricapped trigonal prism of tin in which two sodium ions with only three bonded nitrogen (from en) also bridge two of the three long edges of the trigonal prism ($\bar{d}(\text{Na-Sn}) = 3.53 \text{ \AA}$) and thereby elongate these edges by over 0.5 \AA relative to the third. (This distortion is not along the pathway associated with $D_{3h} \rightleftharpoons C_{4v}$ interconversion of nine-atom polyhedra.⁸) However, these Na-Sn distances appear relatively ($\sim 0.2 \text{ \AA}$) long compared with those found here (with higher symmetry and much less distortion) when it is noted that the difference in crystal radius of the two cations is 0.36 \AA .

Also, in $\text{Rb}_3\text{As}_7\cdot 3\text{en}$,¹⁹ the rubidium atoms all bridge between the two-coordinate atoms in the As_7^{3-} anion, with the ethylene-

diamine molecules coordinated to the alkali metal only on the outside of the " Rb_3As_7 " complex. A similar mode of coordination also occurs in $\text{Na}_4\text{P}_{14}\cdot 6\text{en}$. Also of note is the ternary compound Rb_7NaGe_8 (and the isotopic K_7NaGe_8) in which tetrahedra of Ge_4^{4-} are linked in pairs by sodium to give a "linear" $[(\text{Ge}_4)\text{-Na}(\text{Ge}_4)]$ unit, the sodium having six equivalent germanium neighbors in a trigonal-antiprismatic arrangement through coordination to two faces of the opposed tetrahedra.²⁰ The Ge-Ge distances in these faces are notably greater than the other distances in the tetrahedron (2.62 vs. 2.53 \AA), while the Na-Ge and Rb-Ge bond distances are in the usual ranges found in their respective binary alloys that also contain tetrahedra.

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Supplementary Material Available: Listings of thermal parameters, interbond angles for the nonastannide unit, bond distances and angles in the 2,2,2-crypt-K⁺ cations, and structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

(18) Diehl, L.; Khodadadeh, K.; Kummer, D.; Strähle, J. *Chem. Ber.* 1976, 109, 3404.

(19) Hönlé, W.; von Schnering, H.-G. to be submitted for publication. Quoted in: von Schnering, H.-G. *ACS Symp. Ser.* 1983, No. 232, 69.

(20) Llanos, J.; Nesper, R.; von Schnering, H.-G. *Angew. Chem., Int. Ed. Engl.* 1983, 22, 998.

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Complex Chemistry of Reactive Organic Compounds. 48.¹ σ -Alkyl, π -Allyl, and π -Olefin Coordination of Diphenylketene: Neutron Diffraction Studies of the Carbonyliron Complexes $\text{Fe}(\text{CO})_3[\eta^3:\eta^1\text{-}(\text{C}_6\text{H}_5)_2\text{CCO}]$ and $\text{Fe}_2(\text{CO})_6[\text{CH}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)]$

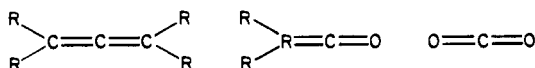
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Photolysis of pentacarbonyliron in the presence of diphenylketene yields the novel $\eta^1:\eta^3$ -diphenylketene complex of composition $\text{Fe}(\text{CO})_3[(\text{C}_6\text{H}_5)_2\text{C}_2\text{O}]$ (1). This compound, according to a single-crystal neutron diffraction study, exhibits the heterocumulene precursor in a π -allyl/ σ -acyl coordination: One phenyl ring engages in π bonding of this ligand to the transition-metal center. Crystallographic data: triclinic, space group $P\bar{1}$; $a = 8.852(2)$, $b = 11.571(4)$, $c = 14.558(6) \text{ \AA}$; $\alpha = 106.94(2)$, $\beta = 89.76(2)$, $\gamma = 91.94(2)^\circ$; $V = 1425.6(2) \text{ \AA}^3$; $Z = 4$; $R(F^2) = 0.078$ for all 5206 reflections measured at $T = 15 \text{ K}$. Upon treatment of compound 1 with excess enneacarbonyldiiron, the dinuclear complex $\text{Fe}_2(\text{CO})_6[\text{CH}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)]$ (3) is formed in 77% yield. This molecule was shown by neutron diffraction techniques to contain a bridging hydrocarbon ligand related to the original ketene ligand in 1 by decarbonylation and 1,3-hydrogen shift. Crystal data: monoclinic, space group $P2_1/n$; $a = 8.298(3)$, $b = 12.463(6)$, $c = 17.380(3) \text{ \AA}$; $\beta = 97.95(1)^\circ$; $V = 1780(1) \text{ \AA}^3$; $Z = 4$; $R(F^2) = 0.111$ for 2622 neutron reflections with $F_o^2 > 1.5\sigma(F_o^2)$ measured at $T = 230 \text{ K}$.

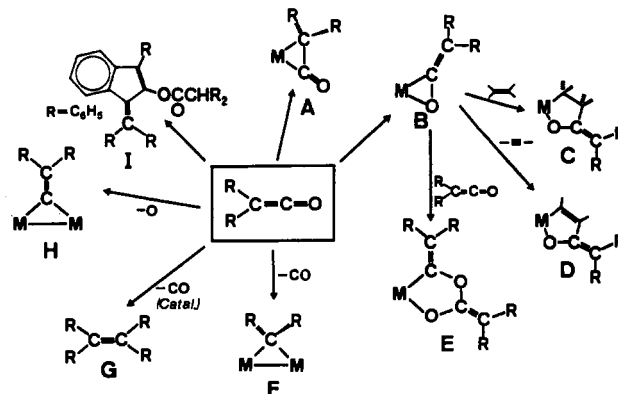
Introduction

The coordination chemistry of ketenes evidences an amazing array of metal fixation, fragmentation, and coupling reactions. The cumulene structure of ketenes effectively interlinks allenes and carbon dioxide and results in behavior similar to reactions of these latter well-studied species with transition-metal complexes.³



- (1) Part 47. Herrmann, W. A.; Plank, J.; Kriechbaum, G. W.; Ziegler, M. L.; Pfisterer, H.; Atwood, J. L.; Rogers, R. D. *J. Organomet. Chem.* in press.
- (2) (a) Brookhaven National Laboratory. (b) Permanent address: University of Paris VI, Laboratory of Systematical Chemistry, F-Paris 75005, France. (c) Permanent address: Department of Chemistry, University of Southern Maine, Portland, ME 04103. (d) Universität Frankfurt am Main.
- (3) For a brief review, see: Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* 1978, 17, 800-812.

Scheme I



If the integrity of the ketene cumulene framework is retained upon complexation, two major coordination modes, A and B, occur: Electron-rich metal centers such as manganese(I) and platinum(0)

usually favor the η^2 -C,C bonding **A**^{1,4-6} while typical electron-poor, oxophilic metals (e.g., titanium and vanadium) prefer the alternative η^2 -C,O fixation **B**.⁷⁻¹⁰ This latter type of system may undergo consecutive insertion reactions, either with another ketene ligand or simple olefins and acetylenes. In any case, ring-expanded five-membered metallacycles C-D and E, respectively, have been isolated^{8,9} and structurally characterized.⁸ In addition, more complicated metal-mediated coupling and isomerization processes have been established, with carbocyclic species like that of the indene derivative **I** being the final result, in which case three ketene units are coupled together in the presence of octacarbonyldicobalt¹¹ (Scheme I). While the proposed vinylidene intermediate escaped isolation,¹¹ a stable (μ -diphenylvinylidene)iron complex of type **H** does form upon cophotolysis of pentacarbonyliron with diphenylketene.¹² Here, deoxygenation of the heterocumulene has occurred. Finally, ketenes are subject to metal-induced decarbonylation when they form alkylidene complexes **F**¹³ or, if these species or their mononuclear analogues are not sufficiently stable, undergo carbon-carbon coupling reactions to olefins **G** (e.g., diphenylketene \rightarrow tetraphenylethylene).¹⁴ Related results also fit into the basic reactivity pattern outlined in Scheme I.¹⁵ Other workers have emphasized the intermediacy of transition-metal ketene complexes in catalytic and stoichiometric reductions of carbon monoxide.¹⁶

Our renewed interest in organometallic ketene reactions stemmed from the reported deoxygenation of diphenylketene in the presence of $\text{Fe}(\text{CO})_5$; the diphenylvinylidene complex $[\mu\text{-(C}_6\text{H}_5)_2\text{C}=\text{C}]\text{Fe}_2(\text{CO})_8$ was the only product isolated, in less than 3% yield.¹² Closer examination demonstrated that this well-known compound¹⁷ does not reflect the typical reaction pathway of this system. Rather, the mononuclear diphenylketene derivative **1** was recognized as the dominating product,¹⁸ which exhibits some

Table I. Experimental Details and Refinement Parameters

	compd 1	compd 3
cryst wt, mg	2.10	2.38
V , mm ³	1.35	1.46
cryst boundary faces	{001}, {001}, {110}, {110}	{111}, {001}, {021}
calcd transmissn range	0.848-0.941	0.875-0.923
no. of reflns measd	5509	7428
no. of indep reflns	5206	4979
no. of reflns used in struct anal., m	5206	2622 [$F_o^2 > 1.5\sigma(F_o^2)$]
no. of variable parameters, n	578	335
$R_c = \sum \sum_i F_o - F_c / \sum \sum_i (F_o^2)^{1/2}$	0.039	0.077
$R(F^2) = \sum F_o^2 - k^2 F_c^2 / \sum F_o^2$	0.078	0.111
$R_w(F^2) = [\sum w(F_o^2 - k^2 F_c^2)^2 / \sum w F_o^4]^{1/2}$	0.084	0.072
$S = [\sum w(F_o^2 - k^2 F_c^2)^2 / (m - n)]^{1/2}$	1.48	1.27

unique chemistry due to an activated C-C bond.^{18,19} Following a preliminary paper,¹⁸ it is the purpose of the present paper to describe the structures of the compounds synthesized during this work. Since the X-ray diffraction studies¹⁸ showed these compounds to possess unexpected features, neutron diffraction techniques were applied in order to characterize them more precisely, especially with regard to the hydrogen positions.

Experimental Section

Single crystals of $\text{Fe}(\text{CO})_5[\eta^2\text{-}\eta^1\text{-(C}_6\text{H}_5)_2\text{CCO}]$ (**1**) and $\text{Fe}_2(\text{CO})_8[\text{C-H(C}_6\text{H}_5)_2(\text{C}_6\text{H}_4)]$ (**3**) were obtained by methods previously reported.¹⁸ A large single crystal of each was affixed to an aluminum pin, sealed in an aluminum can under a helium atmosphere, and placed in a closed-cycle helium refrigerator²⁰ mounted on a four-circle diffractometer^{21,22} at the Brookhaven High Flux Beam Reactor.

Compound 1. A red crystal of hexagonal prismatic habit with a volume of 1.35 mm³ was oriented along the crystallographic (001) direction. A germanium (220) single-crystal monochromator was employed to select a neutron beam of wavelength 1.1617 (1) Å based on KBr ($a_0 = 6.6000$ Å at $T = 295$ K).²³ A sample temperature of 15.0 (5) K²⁴ was maintained during the experiment, and unit-cell dimensions at this temperature were determined by a least-squares fit of the observed $\sin^2 \theta$ values of 30 reflections ($40^\circ < 2\theta < 63^\circ$). Crystal data for $\text{Fe}(\text{CO})_5[\eta^2\text{-}\eta^1\text{-(C}_6\text{H}_5)_2\text{CCO}]$: mol wt 334.1; triclinic, space group $P\bar{1}$; $a = 8.852$ (2), $b = 11.571$ (4), $c = 14.558$ (6) Å; $\alpha = 106.94$ (2), $\beta = 89.76$ (2), $\gamma = 91.94$ (2) $^\circ$; $V = 1425.6$ (2) Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.557$ g cm⁻³. Further experimental details are given in Table I.

Three-dimensional intensity data were obtained over one hemisphere of reciprocal space ($\pm h, \pm k, +l$) with $2\theta \leq 86^\circ$ ($(\sin \theta)/\lambda \leq 0.59$ Å⁻¹) in $\theta/2\theta$ step scans. Selected strong reflections (536) were sampled out to $2\theta = 107^\circ$ ($(\sin \theta)/\lambda = 0.69$ Å⁻¹). The scan range was varied according to $\Delta(2\theta) = (2.19 + 1.49 \tan \theta)^\circ$ for the high-angle data ($55^\circ \leq 2\theta \leq 107^\circ$) and $\Delta(2\theta) = 3.0^\circ$ for low-angle data. The step size was adjusted to give between 65 and 97 steps per scan, and counts were accumulated for approximately 2 s at each step, the exact time interval being determined by monitoring the incident beam intensity. The intensities of two monitor reflections were measured every 200 reflections and showed no significant variation during the course of data collection.

- Schorpp, K.; Beck, W. Z. *Naturforsch. B: Anorg. Chem., Org. Chem.* **1973**, *28B*, 738-740.
- (a) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 335-336. (b) Redhouse, A. D.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 615-616.
- This coordination mode is also accessible via carbonylation of the corresponding metal carbene precursors; cf.: (a) Herrmann, W. A.; Plank, J. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 525-526. (b) Herrmann, W. A.; Plank, J.; Ziegler, M. L.; Weidenhammer, K. *J. Am. Chem. Soc.* **1979**, *101*, 3133-3135. (c) Miyashita, A.; Grubbs, R. H. *Tetrahedron Lett.* **1981**, *22*, 1255-1256.
- Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi Villa, A.; Guastini, C. *Inorg. Chem.* **1978**, *17*, 2995-3002.
- Gambarotta, S.; Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 1173-1178 and references therein.
- Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5499-5500.
- The dimeric ketene complex of composition $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrOCC(C}_6\text{H}_5)_2]_2$ has been obtained by carbonylation of the dialkyl precursor complexes $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}[\text{CH(C}_6\text{H}_5)_2\text{R}]$ ($\text{R} = \text{CH}_3, \text{CH}_2\text{SiMe}_3$): Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1982**, 462-464.
- Hong, P.; Sonogashira, K.; Hagihara, N. *Tetrahedron Lett.* **1971**, *16*, 1105-1108.
- Mills, O. S.; Redhouse, A. D. *J. Chem. Soc., Chem. Commun.* **1966**, 444-445; *J. Chem. Soc. A* **1968**, 1282-1292.
- (a) Hong, P.; Nishii, N.; Sonogashira, K.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1972**, 993. (b) Yamamoto, T.; Garber, A. R.; Wilkinson, J. R.; Boss, C. B.; Streib, W. E.; Todd, L. J. *J. Chem. Soc., Chem. Commun.* **1974**, 354-356.
- Hong, P.; Sonogashira, K.; Hagihara, N. *Nippon Kagaku Zasshi*, **1968**, *89*, 74-77.
- (a) Baba, A.; Ohshiro, Y.; Agawa, T. *J. Organomet. Chem.* **1976**, *110*, 121-127. (b) Young, D. A. *Inorg. Chem.* **1973**, *12*, 482-483. (c) Sato, M.; Ichibori, K.; Sato, F. *J. Organomet. Chem.* **1971**, *26*, 267-270. (d) Churchill, M. R.; DeBoer, B. G.; Hackbarth, J. J. *Inorg. Chem.* **1974**, *13*, 2098-2105. (e) Hong, P.; Sonogashira, K.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1821. (f) Hoberg, H.; Korff, J. *J. Organomet. Chem.* **1978**, *152*, C39-C41; *Ibid.* **1978**, *152*, 255-264.
- (a) Blyholder, G.; Emmett, P. H. *J. Phys. Chem.* **1960**, *64*, 470-472. (b) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121-127.
- Fehlhammer, W. P.; Stolzenberg, H. In Wilkinson, G.; Stone, F. G. A., Abel, E., Eds. "Comprehensive Organometallic Chemistry"; Pergamon Press: Oxford, 1982; Vol. 4, Chapter 31.4, p 544.

- Herrmann, W. A.; Gimeno, J.; Weichmann, J.; Ziegler, M. L.; Balbach, B. *J. Organomet. Chem.* **1981**, *213*, C26-C30.
- Herrmann, W. A.; Weichmann, J.; Balbach, B.; Ziegler, M. L. *J. Organomet. Chem.* **1982**, *231*, C69-C72.
- Air Products and Chemicals, Inc., DISPLEX Model CS-202.
- McMullan, R. K.; (in part) Andrews, L. C.; Koetzle, T. F.; Reiding, F.; Thomas, R.; Williams, G. J. B. "NEXDAS, Neutron and X-Ray Data Acquisition System", unpublished work.
- Dimmler, D. G.; Greenlaw, N.; Kelley, M. A.; Potter, D. W.; Rankowitz, S.; Stubblefield, F. W. *IEEE Trans. Nucl. Sci.* **1976**, *NS-23*, 398-405.
- Donnay, J. D. H.; Ondik, H. M., Eds., "Crystal Data Determinative Tables", 3rd ed.; U. S. Department of Commerce and Joint Committee on Powder Diffraction Standards: Washington, DC, 1973; Vol. 2, p C-164.
- Temperature readings were calculated with reference to a magnetic phase transition in FeF_2 at $T_N = 78.38$ (1) K: Hutchings, M. T.; Schulhof, M. P.; Guggenheim, H. *J. Phys. Rev. B: Solid State* **1972**, *5*, 154-168.

Table II. Positional Parameters^a for Fe(CO)₃[η³:η¹-(C₆H₅)₂CCO] (1) and Fe₂(CO)₆[CH(C₆H₅)(C₆H₄)] (3)

atom	x	y	z	atom	x	y	z
Compound 1							
Fe(1)	0.4334 (1)	0.3278 (1)	0.6410 (1)	Fe(2)	-0.0084 (2)	0.0660 (1)	0.3149 (1)
O(11)	0.3393 (3)	0.4907 (2)	0.5258 (2)	O(21)	0.0818 (3)	0.3052 (2)	0.4541 (2)
O(12)	0.3173 (3)	0.0934 (2)	0.5168 (2)	O(22)	0.0699 (3)	-0.1086 (2)	0.4170 (2)
O(13)	0.7448 (3)	0.3138 (2)	0.5714 (2)	O(23)	-0.3210 (3)	0.0980 (2)	0.3806 (2)
O(14)	0.5394 (3)	0.1911 (2)	0.7722 (2)	O(24)	-0.1293 (3)	-0.1480 (2)	0.1626 (2)
C(11)	0.3779 (2)	0.4304 (2)	0.5699 (2)	C(21)	0.0491 (2)	0.2150 (2)	0.4006 (2)
C(12)	0.3614 (2)	0.1854 (2)	0.5628 (2)	C(22)	0.0425 (2)	-0.0372 (2)	0.3806 (2)
C(13)	0.6235 (2)	0.3194 (2)	0.5990 (2)	C(23)	-0.1990 (2)	0.0846 (2)	0.3539 (2)
C(14)	0.4881 (2)	0.2725 (2)	0.7477 (1)	C(24)	-0.0670 (2)	-0.0509 (2)	0.1981 (2)
C(15)	0.4727 (2)	0.4031 (2)	0.7914 (1)	C(25)	-0.0274 (2)	0.0556 (2)	0.1670 (1)
C(111)	0.3304 (2)	0.4456 (2)	0.6787 (1)	C(211)	0.1200 (2)	0.1081 (2)	0.1996 (1)
C(112)	0.2161 (2)	0.3560 (2)	0.7254 (2)	C(212)	0.2174 (2)	0.0392 (2)	0.2402 (1)
C(113)	0.0845 (2)	0.3918 (2)	0.6848 (2)	C(213)	0.3530 (2)	0.0950 (2)	0.2888 (2)
C(114)	0.0648 (2)	0.5104 (2)	0.6898 (2)	C(214)	0.3923 (2)	0.2127 (2)	0.2950 (2)
C(115)	0.1754 (2)	0.6003 (2)	0.7377 (2)	C(215)	0.2992 (2)	0.2800 (2)	0.2510 (2)
C(116)	0.3034 (2)	0.5706 (2)	0.7761 (2)	C(216)	0.1676 (2)	0.2304 (2)	0.2045 (2)
C(121)	0.5944 (2)	0.4762 (2)	0.8529 (2)	C(221)	-0.1350 (2)	0.1004 (2)	0.1091 (1)
C(122)	0.7454 (2)	0.4425 (2)	0.8382 (2)	C(222)	-0.2916 (2)	0.0868 (2)	0.1202 (2)
C(123)	0.8590 (2)	0.5062 (2)	0.9012 (2)	C(223)	-0.3929 (2)	0.1225 (2)	0.0616 (2)
C(124)	0.8226 (2)	0.6041 (2)	0.9791 (2)	C(224)	-0.3391 (2)	0.1716 (2)	-0.0098 (2)
C(125)	0.6733 (2)	0.6382 (2)	0.9939 (2)	C(225)	-0.1838 (2)	0.1861 (2)	-0.0213 (2)
C(126)	0.5592 (2)	0.5742 (2)	0.9316 (2)	C(226)	-0.0818 (2)	0.1496 (2)	0.0368 (2)
H(112)	0.2085 (5)	0.2712 (4)	0.7433 (4)	H(212)	0.2125 (5)	-0.0591 (4)	0.2152 (3)
H(113)	-0.0003 (5)	0.3231 (4)	0.6508 (4)	H(213)	0.4266 (5)	0.0410 (4)	0.3178 (4)
H(114)	-0.0360 (5)	0.5365 (4)	0.6593 (4)	H(214)	0.4955 (5)	0.2543 (4)	0.3323 (4)
H(115)	0.1577 (5)	0.6945 (4)	0.7426 (4)	H(215)	0.3314 (5)	0.3724 (4)	0.2540 (4)
H(116)	0.3874 (5)	0.6405 (4)	0.8098 (4)	H(216)	0.0963 (5)	0.2833 (4)	0.1736 (4)
H(122)	0.7754 (5)	0.3663 (4)	0.7772 (4)	H(222)	-0.3357 (5)	0.0473 (4)	0.1752 (3)
H(123)	0.9755 (5)	0.4800 (4)	0.8882 (4)	H(223)	-0.5128 (5)	0.1122 (4)	0.0717 (3)
H(124)	0.9102 (6)	0.6538 (4)	1.0273 (4)	H(224)	-0.4158 (5)	0.1983 (4)	-0.0570 (3)
H(125)	0.6452 (5)	0.7114 (4)	1.0548 (3)	H(225)	-0.1408 (5)	0.2267 (4)	-0.0752 (3)
H(126)	0.4420 (5)	0.5977 (4)	0.9453 (3)	H(226)	0.0383 (5)	0.1576 (4)	0.0242 (3)
Compound 3							
Fe(1)	-0.1260 (2)	0.7505 (1)	0.65556 (9)	C(12)	0.1892 (5)	0.9432 (3)	0.5846 (2)
Fe(2)	0.0512 (2)	0.7175 (1)	0.79060 (9)	C(13)	0.0541 (4)	0.9607 (2)	0.6189 (2)
O(1)	-0.3790 (4)	0.6559 (3)	0.7233 (2)	C(14)	-0.1198 (3)	0.8751 (2)	0.7980 (1)
O(2)	-0.3369 (5)	0.8459 (3)	0.5240 (2)	C(15)	0.0254 (3)	0.8916 (2)	0.8484 (1)
O(3)	-0.0132 (6)	0.5851 (3)	0.5546 (2)	C(16)	0.0259 (4)	0.8889 (2)	0.9297 (1)
O(4)	0.1318 (5)	0.5149 (3)	0.7236 (2)	C(17)	-0.1152 (4)	0.8714 (2)	0.9604 (2)
O(5)	0.3739 (5)	0.7334 (3)	0.8830 (2)	C(18)	-0.2628 (4)	0.8572 (2)	0.9112 (2)
O(6)	-0.1321 (5)	0.6009 (3)	0.8993 (2)	C(19)	-0.2657 (3)	0.8583 (2)	0.8316 (2)
C(1)	-0.2771 (3)	0.6791 (2)	0.6983 (1)	H(7)	-0.2243 (7)	0.9525 (4)	0.6915 (3)
C(2)	-0.2539 (3)	0.8076 (2)	0.5750 (1)	H(10)	0.3328 (8)	0.7131 (6)	0.6777 (4)
C(3)	-0.0553 (4)	0.6463 (2)	0.5955 (1)	H(11)	0.3984 (10)	0.8393 (7)	0.5766 (5)
C(4)	0.0966 (3)	0.5944 (2)	0.7488 (1)	H(12)	0.2207 (11)	0.9971 (6)	0.5397 (4)
C(5)	0.2480 (3)	0.7278 (2)	0.8491 (2)	H(13)	-0.0232 (9)	1.0296 (5)	0.6028 (4)
C(6)	-0.0631 (3)	0.6486 (2)	0.8587 (1)	H(15)	0.1294 (7)	0.9254 (4)	0.8251 (3)
C(7)	-0.1316 (3)	0.8948 (2)	0.7138 (1)	H(16)	0.1400 (9)	0.9030 (6)	0.9675 (3)
C(8)	0.0157 (3)	0.8899 (2)	0.6786 (1)	H(17)	-0.1130 (11)	0.8691 (6)	1.0230 (3)
C(9)	0.1145 (3)	0.7973 (2)	0.7006 (1)	H(18)	-0.3732 (9)	0.8455 (6)	0.9354 (5)
C(10)	0.2547 (4)	0.7814 (2)	0.6621 (2)	H(19)	-0.3801 (7)	0.8480 (6)	0.7938 (4)
C(11)	0.2907 (4)	0.8528 (3)	0.6065 (2)				

^a Esd's in parentheses.

Integrated intensities were obtained with the first and last tenth of each scan taken as background. Absorption corrections ($\mu = 1.247 \text{ cm}^{-1}$) were applied to the observed intensities by means of numerical integration over a Gaussian grid of 960 sampling points²⁵ and converted to squared structure factors, $F_o^2 = I \sin 2\theta$. A total of 5509 observations including multiple observations of the same reflection was reduced to 5206 independent values of F_o^2 .

Initial atomic coordinates for all atoms were taken from the room-temperature X-ray model.¹⁸ Least-squares refinement was carried out with a modified version of the program by Busing, Martin, and Levy,²⁶ minimizing the quantity $\sum w(F_o^2 - k^2 F_c^2)^2$. Weights were taken as $w = 1/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma_{\text{count}}^2(F_o^2) + (0.01F_o^2)^2]$. The model included positional and anisotropic thermal parameters for all atoms, a

scale factor k , and a type I isotropic extinction parameter.²⁷ The most significant extinction correction factor was 0.77 dividing F_o^2 for reflection 110. Neutron scattering lengths were taken to be $b_{\text{Fe}} = 0.954 \times 10^{-12}$, $b_{\text{O}} = 0.5803 \times 10^{-12}$, $b_{\text{C}} = 0.6648 \times 10^{-12}$, and $b_{\text{H}} = -0.3741 \times 10^{-12}$ cm.²⁸ Parameters were blocked into groups of approximately 200 variables that were refined alternately to convergence. The refinement was terminated when the maximum shift/esd for any parameter was less than 0.1σ . A difference synthesis computed at this stage was essentially featureless. Final agreement factors are included in Table I, while positional parameters for all atoms are given in Table II.

Compound 3. A black single crystal with a volume of 1.46 mm³ was selected for the neutron diffraction measurements. The experimental procedure was the same as for compound 1 except for the wavelength which was determined to be 1.1615 (1) Å when calibrated with the KBr

- (25) (a) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 180-182.
 (b) Coppens, P.; Leiserowitz, L. L.; Rabinovich, D. *Acta Crystallogr.* **1965**, *18*, 1035-1038.
 (26) Busing, W. R.; Martin, K. O.; Levy, H. A. "ORFLS", Report ORNL-TM-306; Oak Ridge National Laboratory: Oak Ridge, TN, 1962.

- (27) Becker, P. J.; Coppens, P. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* **1975**, *A31*, 417-425.
 (28) Koester, L. In "Neutron Physics"; Springer-Verlag: Berlin, Heidelberg, New York, 1977; pp 36-37.

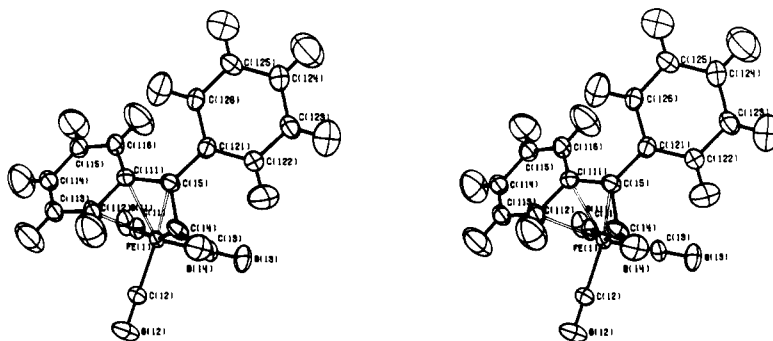


Figure 1. Stereoview of molecule 1 of compound 1 with thermal ellipsoids drawn to enclose 97% probability.

crystal as described above. Prior to data collection, the behavior of sample crystals during cooling was monitored and a reversible phase transition with peak splitting was observed at 209 (1) K; therefore, data were collected at 230 K. Unit-cell dimensions at this temperature were determined by a least-squares fit of the averaged $\sin^2 \theta$ values for reflections belonging to 12 different forms ($40^\circ < 2\theta < 67^\circ$).

Crystal data for $\text{Fe}_2(\text{CO})_6[\text{CH}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)]$: mol wt 446.0; monoclinic, space group $P2_1/n$; $a = 8.298$ (3), $b = 12.463$ (6), $c = 17.380$ (3) Å; $\beta = 97.95$ (1)°; $V = 1780$ (1) Å³; $Z = 4$, $\rho_{\text{calc}} = 1.664$ g cm⁻³. Further experimental details are given in Table I.

Intensities were measured in the same fashion as for compound 1, with scan widths of 2.4 or 2.8° for $2\theta < 60^\circ$ ($\sin \theta/\lambda < 0.43$ Å⁻¹) and $\Delta(2\theta) = (0.85 + 3.4 \tan \theta)^\circ$ for the range $60^\circ < 2\theta < 106^\circ$ ($0.43 < (\sin \theta)/\lambda < 0.69$ Å⁻¹). The step size was adjusted so that there were between 60 and 90 steps in each scan, with background representing about 10% at each end of the scan. Absorption corrections ($\mu = 0.985$ cm⁻¹) were calculated by numerical integration over a Gaussian grid of 1440 sampling points. A total of 7428 observations was reduced to 4979 independent values of F_o^2 , of which the 2622 reflections with $F_o^2 > 1.5\sigma(F_o^2)$ were used in the structure analysis.

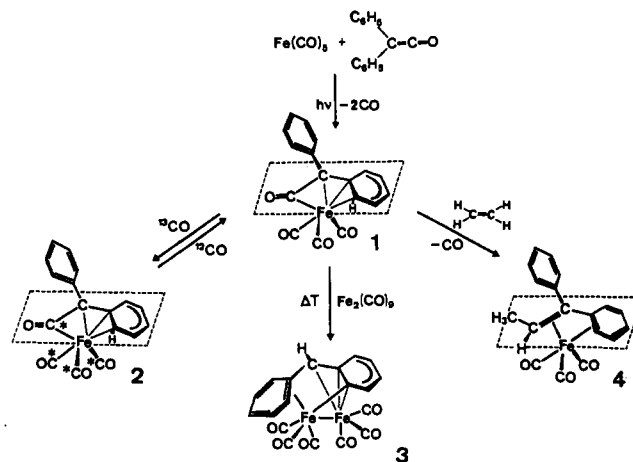
The structural model found by X-rays at room temperature¹⁸ provided starting values for all atomic positions. Least-squares refinement was carried out in a manner identical with that for compound 1, using the same weighting scheme and neutron scattering lengths. The most important extinction correction factor was 0.76 dividing F_o^2 for reflection 002. A final difference synthesis was essentially featureless. Final agreement factors are included in Table I while positional parameters are given in Table II.

Thermal parameters (Table I-S) and lists of F^2 values for compounds 1 and 3 are available as supplementary material.

Results and Discussion

Synthesis. Irradiation with a mercury high-pressure lamp of solutions of pentacarbonyliron and diphenylketene in diethyl ether at +15 °C results in elimination of carbon monoxide and formation of the red, air-stable compound 1, which was assigned the empirical formula $\text{C}_{17}\text{H}_{10}\text{FeO}_4$ by elemental analysis and mass spectrometry. An X-ray analysis has revealed a structure containing the *intact* diphenylketene ligand.¹⁸ This compound forms as the main product (isolated yield 38%), while the previously reported dinuclear μ -vinylidene complex $[\mu-(\text{C}_6\text{H}_5)_2\text{C}=\text{C}]\text{Fe}_2(\text{CO})_8$ ¹² occurs in less than 3% yield (cf., ref 18). Crossover and labeling experiments showed the $(\text{O}=\text{C})-\text{C}$ bond of the metal-attached ketene to be reversibly open and reclose so that it should also be available for carbon-carbon coupling reactions.¹⁸ Actually, ethylene reacts under mild conditions (boiling *n*-hexane (1 atm)) to give the crystallographically characterized 1,3-diene complex 4.¹⁹ Structurally, 4 derives from the ketene compound 1 in that the labile C-C bond is broken up (CO elimination) while the entering ethylene ligand undergoes 1,2-hydrogen shift, ending up as a methylcarbene unit attached to the η^3 -alkylidene ligand $\text{C}(\text{C}_6\text{H}_5)_2$. Carbon-carbon bond cleavage likewise is observed when a solution of 1 in benzene is treated at 75 °C with $\text{Fe}_2(\text{CO})_9$, a frequently used effective source of $\text{Fe}(\text{CO})_3$ and/or $\text{Fe}(\text{CO})_4$ fragments. Here, the dinuclear species 3 of composition $\text{C}_{19}\text{H}_{10}\text{Fe}_2\text{O}_6$ with its unusually coordinated hydrocarbon ligand $\text{CH}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)$ is formed as black air-stable crystals in 77% yield.¹⁹ Scheme II summarizes these unexpected but nevertheless readily occurring coupling reactions that always retain the di-

Scheme II



phenylcarbene unit or its tautomeric structure (e.g., 3) as part of the molecule.

Structure. (a) η^3 : η^1 -Diphenylketene Complex 1. The two crystallographically independent molecules in the unit cell have very similar structures. A stereoview²⁹ of one molecule is presented in Figure 1, using the same atom-numbering scheme as in the original paper (Figure 1a in ref 18), while bond distances and angles are presented in Table III. The only distances that differ by more than 3σ between the two molecules are $\text{Fe}(1)-\text{C}(14) = 1.914$ (2) Å and $\text{Fe}(2)-\text{C}(24) = 1.900$ (2) Å.

On the basis of the structural parameters and the electron count at the metal center, it is evident that the ketene entity is still intact in terms of the atom connectivity and that this unit acts overall as a four-electron ligand. The carbon atoms C(112), C(111), and C(15) form a π -allylic array attached to the tricarbonyliron core in the usual η^3 mode. In addition, the ketene carbonyl group now acts as an acyl-type ligand toward the metal, with the corresponding $\text{Fe}(1)-\text{C}(14)$ σ bond being relatively short (1.914 (2) Å). This twofold metal fixation of the entire ligand ($\eta^3 + \eta^1$) entails a moderately strained system ($\angle\text{C}(15)-\text{C}(14)-\text{Fe}(1) = 76.9$ (1)°). Approximate sp^2 hybridization at C(14) is supported by the observed value of 135.8 (2)° for the angle $\text{C}(15)-\text{C}(14)-\text{O}(14)$. Furthermore, the $\text{Fe}(1)-\text{C}(14)$ separation of 1.914 (2) Å is significantly shorter than one should expect for an olefinic interaction of the heterocumulene ligand and rather falls within the well-documented range of σ bonds between iron(0) and sp^2 -hybridized carbon atoms.³⁰ This acyl-type ligand has a trans influence upon the opposite terminal Fe-CO bond ($\angle\text{C}(14)-\text{Fe}(1)-\text{C}(11) = 160.7$ (1)°); thus, the corresponding bond length $\text{Fe}(1)-\text{C}(11)$ clearly is longer (1.866 (2) Å) than the other two (cf., $\text{Fe}(1)-\text{C}(12) = 1.806$ (2) Å and $\text{Fe}(1)-\text{C}(13) = 1.784$ (2)

(29) Johnson, C. K. "ORTEP-II"; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(30) Koerner von Gustorf, E. A., Grevels, F. W., Fischer, I., Eds. "The Organic Chemistry of Iron"; Academic Press: New York, 1978; Vol. 1.

Table III. Interatomic Distances (Å)^a and Bond Angles (deg)^a for Fe(CO)₃[η³:η¹-(C₆H₅)₂CCO] (1) and Fe₂(CO)₆[CH(C₆H₅)(C₆H₄)] (3)

Distances for 1			
Fe(1)-C(11)	1.866 (2)	Fe(2)-C(21)	1.866 (2)
Fe(1)-C(12)	1.806 (2)	Fe(2)-C(22)	1.802 (2)
Fe(1)-C(13)	1.784 (2)	Fe(2)-C(23)	1.778 (2)
Fe(1)-C(14)	1.914 (2)	Fe(2)-C(24)	1.900 (2)
Fe(1)-C(15)	2.133 (2)	Fe(2)-C(25)	2.128 (2)
Fe(1)-C(111)	2.177 (2)	Fe(2)-C(211)	2.184 (2)
Fe(1)-C(112)	2.260 (2)	Fe(2)-C(212)	2.258 (2)
C(11)-O(11)	1.138 (3)	C(21)-O(21)	1.135 (3)
C(12)-O(12)	1.136 (3)	C(22)-O(22)	1.138 (3)
C(13)-O(13)	1.143 (3)	C(23)-O(23)	1.146 (3)
C(14)-O(14)	1.204 (3)	C(24)-O(24)	1.207 (3)
C(111)-C(112)	1.432 (3)	C(211)-O(212)	1.432 (3)
C(112)-C(113)	1.434 (3)	C(212)-C(213)	1.430 (3)
C(113)-C(114)	1.371 (3)	C(213)-C(214)	1.372 (3)
C(114)-C(115)	1.429 (3)	C(214)-C(215)	1.426 (3)
C(115)-C(116)	1.364 (3)	C(215)-C(216)	1.372 (3)
C(116)-C(111)	1.446 (3)	C(216)-C(211)	1.444 (3)
C(121)-C(122)	1.403 (3)	C(221)-C(222)	1.403 (3)
C(122)-C(123)	1.400 (3)	C(222)-C(223)	1.393 (3)
C(123)-C(124)	1.395 (3)	C(223)-C(224)	1.398 (3)
C(124)-C(125)	1.398 (3)	C(224)-C(225)	1.394 (3)
C(125)-C(126)	1.393 (3)	C(225)-C(226)	1.397 (3)
C(126)-C(121)	1.400 (3)	C(226)-C(221)	1.407 (3)
C(14)-C(15)	1.470 (3)	C(24)-C(25)	1.463 (3)
C(15)-C(111)	1.441 (3)	C(25)-C(211)	1.442 (3)
C(15)-C(121)	1.478 (3)	C(25)-C(221)	1.478 (3)
C(112)-H(112)	1.086 (5)	C(212)-H(212)	1.089 (4)
C(113)-H(113)	1.084 (4)	C(213)-H(213)	1.085 (5)
C(114)-H(114)	1.088 (5)	C(214)-H(214)	1.088 (4)
C(115)-H(115)	1.088 (5)	C(215)-H(215)	1.085 (4)
C(116)-H(116)	1.087 (4)	C(216)-H(216)	1.079 (5)
C(122)-H(122)	1.093 (5)	C(222)-H(222)	1.097 (5)
C(123)-H(123)	1.085 (5)	C(223)-H(223)	1.078 (5)
C(124)-H(124)	1.078 (5)	C(224)-H(224)	1.081 (5)
C(125)-H(125)	1.086 (5)	C(225)-H(225)	1.087 (5)
C(126)-H(126)	1.083 (5)	C(226)-H(226)	1.084 (4)
av C-H	1.086 (5)		
Angles for 1			
C(11)-Fe(1)-C(12)	99.6 (1)	C(21)-Fe(2)-C(22)	101.7 (1)
C(11)-Fe(1)-C(13)	93.5 (1)	C(21)-Fe(2)-C(23)	91.0 (1)
C(11)-Fe(1)-C(14)	160.7 (1)	C(21)-Fe(2)-C(24)	159.7 (1)
C(11)-Fe(1)-C(15)	118.6 (1)	C(21)-Fe(2)-C(25)	117.7 (1)
C(11)-Fe(1)-C(111)	90.4 (1)	C(21)-Fe(2)-C(211)	91.2 (2)
C(11)-Fe(1)-C(112)	92.4 (1)	C(21)-Fe(2)-C(212)	94.3 (1)
C(12)-Fe(1)-C(13)	98.1 (1)	C(22)-Fe(2)-C(23)	97.4 (1)
C(12)-Fe(1)-C(14)	98.0 (1)	C(22)-Fe(2)-C(24)	97.8 (1)
C(12)-Fe(1)-C(15)	136.2 (1)	C(22)-Fe(2)-C(25)	135.1 (1)
C(12)-Fe(1)-C(111)	128.7 (1)	C(22)-Fe(2)-C(211)	126.7 (1)
C(12)-Fe(1)-C(112)	91.5 (1)	C(22)-Fe(2)-C(212)	89.6 (1)
C(13)-Fe(1)-C(14)	91.6 (1)	C(23)-Fe(2)-C(24)	91.9 (1)
C(13)-Fe(1)-C(15)	99.9 (1)	C(23)-Fe(2)-C(25)	102.2 (1)
C(13)-Fe(1)-C(111)	131.5 (1)	C(23)-Fe(2)-C(211)	134.2 (1)
C(13)-Fe(1)-C(112)	167.7 (1)	C(23)-Fe(2)-C(212)	170.2 (1)
C(14)-Fe(1)-C(15)	42.2 (1)	C(24)-Fe(2)-C(25)	42.1 (1)
C(14)-Fe(1)-C(111)	72.4 (1)	C(24)-Fe(2)-C(211)	72.6 (1)
C(14)-Fe(1)-C(112)	79.4 (1)	C(24)-Fe(2)-C(212)	80.3 (1)
C(15)-Fe(1)-C(111)	39.1 (1)	C(25)-Fe(2)-C(211)	39.1 (1)
C(15)-Fe(1)-C(112)	67.8 (1)	C(25)-Fe(2)-C(212)	68.0 (1)
C(111)-Fe(1)-C(112)	37.6 (1)	C(211)-Fe(2)-C(212)	37.6 (1)
Fe(1)-C(11)-O(11)	177.6 (2)	Fe(2)-C(21)-O(21)	178.5 (2)
Fe(1)-C(12)-O(12)	176.9 (2)	Fe(2)-C(22)-O(22)	175.2 (2)
Fe(1)-C(13)-O(13)	179.5 (2)	Fe(2)-C(23)-O(23)	178.7 (2)
Fe(1)-C(14)-O(14)	145.6 (2)	Fe(2)-C(24)-O(24)	145.3 (2)
Fe(1)-C(14)-C(15)	76.9 (1)	Fe(2)-C(24)-C(25)	77.3 (1)
C(15)-C(14)-O(14)	135.8 (2)	C(25)-C(24)-O(24)	136.0 (2)
C(14)-C(15)-C(111)	112.8 (2)	C(24)-C(25)-C(211)	113.4 (2)
C(14)-C(15)-C(121)	120.4 (2)	C(24)-C(25)-C(221)	120.3 (2)
C(111)-C(15)-C(121)	126.7 (2)	C(211)-C(25)-C(221)	126.3 (2)
av ring C-C-C	120.0 (2) ^b	av ring C-C-C	120.0 (2) ^b

Table III (Continued)

Distances for 3			
Fe(1)-Fe(2)	2.624 (2)	Fe(2)-C(4)	1.760 (3)
Fe(1)-C(1)	1.781 (3)	Fe(2)-C(5)	1.805 (3)
Fe(1)-C(2)	1.784 (3)	Fe(2)-C(6)	1.829 (3)
Fe(1)-C(3)	1.814 (3)	Fe(2)-C(9)	1.985 (3)
Fe(1)-C(7)	2.068 (3)	Fe(2)-C(14)	2.437 (3)
Fe(1)-C(8)	2.105 (3)	Fe(2)-C(15)	2.413 (3)
Fe(1)-C(9)	2.122 (3)	C(7)-C(8)	1.442 (4)
C(1)-O(1)	1.138 (4)	C(7)-C(14)	1.472 (3)
C(2)-O(2)	1.149 (4)	C(8)-C(9)	1.436 (3)
C(3)-O(3)	1.131 (4)	C(9)-C(10)	1.434 (4)
C(4)-O(4)	1.138 (4)	C(10)-C(11)	1.375 (4)
C(5)-O(5)	1.129 (4)	C(11)-C(12)	1.427 (5)
C(6)-O(6)	1.137 (4)	C(12)-C(13)	1.358 (5)
		C(13)-C(8)	1.431 (4)
		C(14)-C(15)	1.404 (3)
		C(15)-C(16)	1.413 (2)
		C(16)-C(17)	1.369 (4)
		C(17)-C(18)	1.404 (5)
		C(18)-C(19)	1.380 (4)
		C(19)-C(14)	1.431 (4)
C(7)-H(7)	1.085 (6)	C(16)-H(16)	1.089 (8)
C(10)-H(10)	1.082 (9)	C(17)-H(17)	1.087 (7)
C(11)-H(11)	1.107 (8)	C(18)-H(18)	1.070 (8)
C(12)-H(12)	1.089 (7)	C(19)-H(19)	1.085 (8)
C(13)-H(13)	1.085 (8)	av C-H	1.087 (3)
C(15)-H(15)	1.087 (6)		
Angles for 3			
C(1)-Fe(1)-C(2)	98.6 (1)	C(4)-Fe(2)-C(5)	93.7 (1)
C(1)-Fe(1)-C(3)	100.7 (1)	C(4)-Fe(2)-C(6)	91.0 (1)
C(1)-Fe(1)-C(7)	99.5 (1)	C(4)-Fe(2)-C(9)	90.9 (1)
C(1)-Fe(1)-C(8)	137.7 (1)	C(4)-Fe(2)-C(14)	152.1 (1)
C(1)-Fe(1)-C(9)	131.6 (1)	C(4)-Fe(2)-C(15)	172.7 (1)
C(2)-Fe(1)-C(3)	92.2 (1)	C(5)-Fe(2)-C(6)	100.3 (1)
C(2)-Fe(1)-C(7)	89.2 (1)	C(5)-Fe(2)-C(9)	95.2 (1)
C(2)-Fe(1)-C(8)	94.4 (1)	C(5)-Fe(2)-C(14)	113.7 (1)
C(2)-Fe(1)-C(9)	127.4 (1)	C(5)-Fe(2)-C(15)	80.1 (1)
C(3)-Fe(1)-C(7)	159.3 (1)	C(6)-Fe(2)-C(9)	164.2 (1)
C(3)-Fe(1)-C(8)	118.9 (1)	C(6)-Fe(2)-C(14)	89.2 (1)
C(3)-Fe(1)-C(9)	92.6 (1)	C(6)-Fe(2)-C(15)	94.0 (1)
C(7)-Fe(1)-C(8)	40.4 (1)	C(9)-Fe(2)-C(14)	81.8 (1)
C(7)-Fe(1)-C(9)	70.4 (1)	C(9)-Fe(2)-C(15)	85.8 (1)
C(8)-Fe(1)-C(9)	39.7 (1)	C(14)-Fe(2)-C(15)	33.6 (1)
Fe(1)-C(1)-O(1)	176.8 (3)	Fe(2)-C(4)-O(4)	177.2 (3)
Fe(1)-C(3)-O(2)	178.7 (3)	Fe(2)-C(5)-O(5)	177.2 (3)
Fe(1)-C(3)-O(3)	176.2 (3)	Fe(2)-C(6)-O(6)	176.4 (3)
C(8)-C(7)-C(14)	118.1 (2)	C(7)-C(14)-C(19)	119.1 (2)
C(7)-C(8)-C(13)	124.7 (2)	C(7)-C(14)-C(15)	121.9 (2)
C(7)-C(8)-C(9)	114.0 (2)	C(14)-C(15)-C(16)	120.3 (2)
C(8)-C(9)-C(10)	117.2 (2)	C(15)-C(16)-C(17)	120.5 (3)
C(9)-C(10)-C(11)	120.5 (3)	C(16)-C(17)-C(18)	120.3 (3)
C(10)-C(11)-C(12)	121.4 (3)	C(17)-C(18)-C(19)	120.1 (3)
C(11)-C(12)-C(13)	120.1 (3)	C(14)-C(19)-C(18)	120.8 (3)
C(12)-C(13)-C(8)	120.0 (3)	C(15)-C(14)-C(19)	117.9 (2)
C(9)-C(8)-C(13)	120.8 (2)	C(14)-C(7)-H(7)	114.4 (4)
C(8)-C(7)-H(7)	118.4 (4)		

^a Esd's in parentheses. ^b Standard deviations of mean values are given as the larger of the individual esd's or $\sigma(\chi_{av}) = [\sum^n (\chi_i - \chi_{av})^2 / n(n-1)]^{1/2}$, where χ_{av} is the mean value and χ_i are individual values.

Å). Considering both the relatively short length and the observed trans influence, the partial multiple-bond character of Fe(1)-C(14) seems evident.³⁰⁻³³

The distances between the metal center and the π -bonded hydrocarbon unit are much longer than the acyl interaction Fe(1)-C(14). Separated by 2.133-2.260 Å from the metal, the carbon atoms C(15), C(111), and C(112) form a typical η^3 -allyl skeleton wherein the C-C distances are similar (ca. 1.44 Å) and

perfectly fit in the range found for a plethora of related tricarbonyl (η^3 -allyl) iron complexes.³⁰⁻³⁴

It is clear that the loss of cumulene conjugation upon metal fixation of a heterocumulene such as the present diphenylketene ligand changes the backbone of this ligand from linear to bent ($\angle C(15)-C(14)-O(14) = 135.8(2)^\circ$). The same effect is observed for π complexation of allenes where angles between 142 and 152° occur. As a further inevitable consequence of metal attachment, the C(14)-C(15) bond length becomes much longer (1.470(3) Å) than in free ketenes (e.g., 1.271 Å for dimethylketene³⁵) and

- (31) Dettlaf, G.; Behrens, U.; Weiss, E. *Chem. Ber.* **1978**, *111*, 3019-3028.
 (32) Mitsudo, T.-A.; Sasaki, T.; Watanabe, Y.; Takegami, Y.; Nishigaki, S.; Nakatsu, K. *J. Chem. Soc., Chem. Commun.* **1978**, 252-253.
 (33) Newton, M. G.; Pantaleo, N. S.; King, R. B.; Chu, C.-K. *J. Chem. Soc., Chem. Commun.* **1979**, 10-12.

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

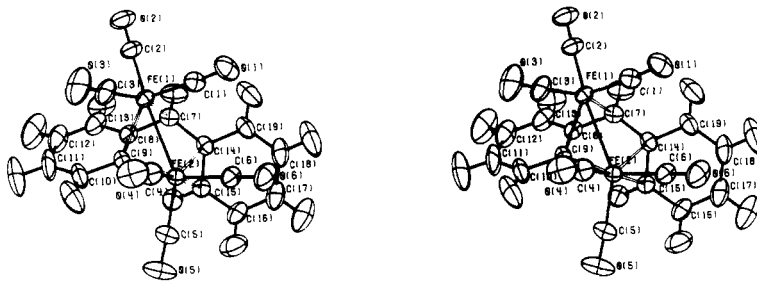


Figure 2. Stereoview of molecule 3 with ellipsoids as in Figure 1.

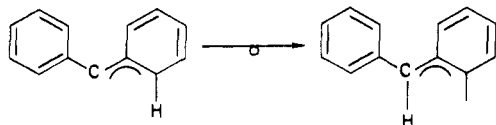
even exceeds the value recorded for the η^2 -C,C-diphenylketene complex $(\eta^2\text{-C}_6\text{H}_5)_2\text{Mn}(\text{CO})_2[(\text{C}_6\text{H}_5)_2\text{C}_2\text{O}]$ (1.350 (2) Å^{5b}). On the other hand, no substantial lengthening of the C–O bond length (1.204 (3) Å) is observed (cf., dimethylketene 1.179 Å³⁵). Opposite effects are of course expected and found if a ketene employs η^2 -C,O bonding to a transition metal.⁸

One striking structural feature of compound 1 is partial involvement of a phenyl ring in the π -allyl-type bonding via the ipso and ortho carbon sites C(111) and C(112), respectively. Consequently, aromaticity of the respective π system is highly disturbed as evidenced by alternating bond lengths (C(112)–C(113) = 1.434 (3), C(113)–C(114) = 1.371 (3), C(114)–C(115) = 1.429 (3), C(115)–C(116) = 1.364 (3), C(116)–C(111) = 1.446(3) Å). As a result, the ortho hydrogen atom at C(112) resonates upfield at δ 4.43 (CDCl₃).¹⁸ By way of contrast, C–C distances typical of ordinary benzene derivatives are observed for the uncomplexed phenyl substituent (C(121)–C(126): mean C–C = 1.398 (3) Å).

The π -allylic bonding of the hydrocarbon system seems to be fairly strong because it is retained in most reactions of 1 (see structure of compound 3). On the other hand, the central C(14)–C(15) bond adjacent to the former ketene CO group is highly activated. An elegant proof of this bond lability has been provided by ¹³C-labeling experiments: When a solution of 1 in benzene is stirred under an atmosphere of ¹³C carbon monoxide (room temperature, 3 days), statistical incorporation of the labeled ligand in all four CO positions (2) is observed,¹⁸ while free diphenylketene is absolutely unreactive under the same and even under more severe conditions (boiling benzene, 3 days). CO equilibration is a strictly intramolecular process as shown by double-labeling crossover experiments.¹⁸ It is thus evident that intramolecular CO exchange occurs via a η^3 -diphenylmethene intermediate that builds up after preceding decarbonylation. Transfer of neither the intact diphenylketene ligand nor the diphenylmethylene unit to another tricarbenyliron fragment is feasible.

(b) σ -Alkyl/ π -Olefin/ π -Allyl Complex 3. The labile C(14)–C(15) bond of the mononuclear η^3 : η^1 -diphenylketene complex 1 undergoes irreversible cleavage at elevated temperatures in the absence of carbon monoxide to form the dinuclear compound 3. A stereoview of 3 is shown in Figure 2; again, the original numbering scheme¹⁸ has been used.

The most unusual feature of this compound is the novel hydrocarbon ligand. Having the same net composition (C₁₃H₁₀) as its immediate precursor (the diphenylmethylene unit derived from diphenylketene), it represents a tautomer in which one ortho hydrogen atom (H(112) of compound 1) is shifted to the methylene carbon atom C(15) to appear in 3 as the group C(7)–H(7) that terminates an allyl system.



This strangely constructed hydrocarbon ligand is found to bridge an iron–iron bond via five different carbon atoms, thus demonstrating three different coordination modes of hydrocarbon ligands:

(i) π -allyl complexation toward Fe(1) via the assembly C(7),C(8),C(9); (ii) π -olefin-type fixation to Fe(2) using the C(14)–C(15) bond of a phenyl ring; (iii) σ -alkyl bonding from C(9) (the position that has lost its hydrogen substituent) to the metal center Fe(2). We do not attempt to speculate in any detail about the certainly very complex sequence of reactions that might rationalize the final structural outcome, but a metal-induced cleavage ("activation") of the C(112)–H(112) bond in 1 is likely to represent an early step of this reaction.

With the caveat that metal–metal bond lengths do not reliably correlate with bond orders, at least in the presence of bridging ligands, the recorded iron–iron distance of 2.624 (2) Å and the EAN rule imply a single bond between the metal centers. Authentic or formal iron–iron single bonds range between 2.40 and 2.80 Å in length.³⁰ These relatively broad variations show that the coordination core of the metals as well as the number and stereochemistry of bridging ligands do in fact strongly influence the respective metal-to-metal separation.

The π -allyl system formed by the carbon backbone C(7),C(8),C(9) compares well with that of the precursor molecule 1 (C(15),C(111),C(112); see discussion above), although the Fe(1)–C(7,8,9) bond lengths are on the average 0.1 Å shorter. Since C(9) forms bonds to both metals, an internal comparison is possible: While its distance to Fe(2) is clearly indicative of a single bond (1.985 (3) Å), the much longer C(9)–Fe(1) bond (2.122 (3) Å) is typical of metal-coordinated π -allyl groups. Finally, the π -coordinated C(14)–C(15) bond belonging to one phenyl ring is much further away from Fe(2) (2.437 (3) and 2.413 (3) Å, respectively) than one must expect for an ordinary olefin-type complexation (ca. 2.10–2.20 Å^{36–39}). Steric strain may, in part, be responsible for this feature. Since both phenyl systems are now involved in the metal fixation of the entire hydrocarbon ligand, alternating carbon–carbon bond distances result (cf., Table III).

Precise location of all hydrogen atoms in the neutron diffraction work presented here confirms the previously postulated hydrogen shift that is also evident from NMR studies.¹⁸ Compound 3 has two unique hydrogen substituents, namely H(7) (δ 4.93 (s) in CDCl₃) and H(15) (δ 4.39 (mc) in CDCl₃) that no longer participate in aromatic π systems. However, these C–H bonds are not found to differ significantly in length from the other C–H linkages in the molecule.

This paper supports the impression that conventional μ -methylene complexes are not generally obtained along the ketene route.⁴⁰ Rather, unusual isomerization phenomena may occur (e.g., tautomerism, C(C₆H₅)₂ → CH(C₆H₅)(C₆H₄)) in order to avoid electronically unsaturated structures such as that of the originally expected molecule of composition [μ - η^1 -C(C₆H₅)₂]-Fe₂(CO)₆. Complex 3 neatly exemplifies how the basic three coordination modes of hydrocarbon ligands, π -allyl, π -olefin, and σ -alkyl, build up in one and the same molecule. To our knowledge, there are only two comparable precedents of such structures.^{31,41}

(35) Sutter, D.; Charpentier, L.; Dreizler, H. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1972**, *27A*, 597–600.

(36) Baikie, P. E.; Mills, O. S. *Inorg. Chim. Acta* **1967**, *1*, 55–60.

(37) Bennett, M. J.; Graham, W. A. G.; Stewart, R. P., Jr.; Tuggle, R. M. *Inorg. Chem.* **1973**, *12*, 2944–2949.

(38) Cotton, F. A.; Lahuerta, P. *Inorg. Chem.* **1975**, *14*, 116–119.

(39) Behrens, U. *J. Organomet. Chem.* **1976**, *107*, 103–111.

(40) Review: Herrmann, W. A. *J. Organomet. Chem.* **1983**, *250*, 319–343.

(41) Aumann, R.; Averbek, H.; Krüger, C. *Chem. Ber.* **1975**, *108*, 3336–3348.

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Supplementary Material Available: Listings of thermal parameters (Table I-S) and phenyl-ring least-squares planes (Table II-S), stereoviews showing the packing in one unit cell (Figures 1-S and 2-S), and listings of observed and calculated F^2 values (50 pages). Ordering information is given on any current masthead page.

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Synthesis, Electrochemistry, and Crystal and Molecular Structure of $[(C_5H_5)_2Ti(SCH_2CH_2P(C_6H_5)_2)_2Cu]BF_4$: A Heterobimetallic Species with a Copper to Titanium Dative Bond

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The bifunctional dissymmetric ligand $(C_6H_5)_2PCH_2CH_2SH$ (PSH) was used in the synthesis of a new early-transition-metal/late-transition-metal heterobimetallic species. Initially the Ti complex $(C_5H_5)_2Ti(SCH_2CH_2P(C_6H_5)_2)_2$ (**1**) was prepared. The reaction of **1** with methyl iodide confirms the dangling nature of the phosphine groups. Compound **1** is capable of acting as a tetradentate "metalloid ligand". The preparation and spectroscopic and electrochemical properties of a copper(I) complex of **1** are reported. The results of an X-ray structural study of this complex are presented. The compound $[(C_5H_5)_2Ti(SCH_2CH_2P(C_6H_5)_2)_2Cu]BF_4$ (**3**) crystallizes in the monoclinic space group $P2_1/c$ with $a = 16.853$ (3) Å, $b = 15.297$ (1) Å, $c = 15.575$ (3) Å, $\beta = 108.90^\circ$, and $Z = 4$. Cyclic voltammetry shows that compound **3** exhibits an electrochemically reversible reduction at -0.99 V vs. SCE. The novel reversibility of this formally Ti(IV)-Ti(III) couple is attributed to the Cu-Ti interaction present in **3**. The details of the structure of this heterobimetallic species are discussed, and the implications of its chemistry are considered.

Introduction

Many studies involving binuclear transition-metal complexes have appeared in the literature.¹ The relevance of bimetallic compounds to bioinorganic systems is one cause for interest.^{2,3} Another reason for this interest is the potential application of binuclear organometallic species in catalysis. In this vein, the chemistry associated with water-gas shift catalysis by homonuclear bimetallic rhodium, platinum, and iridium complexes has been studied extensively by the research groups of Eisenberg,⁴ Puddephatt,⁵ Balch,⁶ and Cowie.⁷ More recently attention has focused on the activation of small molecules by heterobimetallic systems.⁸⁻²¹ Compounds containing early-transition-metal/late-

transition-metal combinations are expected to exhibit unique reactivity patterns and thus polarize and activate substrates such as CO. This notion is supported by recent work in which early-transition-metal species (i.e., Ti, Zr) act as Lewis acids toward metal carbonyl complexes.¹¹⁻¹³ Despite the potential for applications in catalysis, few early-transition-metal/late-transition-metal species have been synthesized.¹

We recently reported a monometallic system containing the ligand $(C_6H_5)_2PCH_2CH_2SH$ (PSH).²² We felt that this bifunctional dissymmetric ligand could be used to link two metal centers together, thus providing a new synthetic route to heterobimetallic species. The use of PSH is attractive for several reasons: group 4³³ metals form stable thiolato complexes, group 8³³ and coinage metals have a well-established phosphine chemistry, and the possibility of sulfur bridges between metal centers offer conceivable metal-metal interactions that could lead to species with new and unique reactivity patterns. In this paper we report our initial work in this area. The preparation of the titanium complex $(C_5H_5)_2Ti(SCH_2CH_2P(C_6H_5)_2)_2$ (**1**) is described. The reaction product of **1** with methyl iodide confirms the nature of this species. Compound **1** is capable of acting as a tetradentate "metalloid ligand". The preparation and spectroscopic and electrochemical properties of a copper(I) complex of **1**, i.e. $[(C_5H_5)_2Ti(SCH_2CH_2P(C_6H_5)_2)_2Cu]BF_4$ (**3**), are presented. An

- (1) Bruce, M. I. *J. Organomet. Chem.* **1983**, *242*, 147.
- (2) Holm, R. H.; Ibers, J. A.; *Science (Washington, D.C.)* **1980**, *209*, 223.
- (3) Coucouvanis, D. *Acc. Chem. Res.* **1981**, *14*, 201.
- (4) Kubiak, C. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 3637 and references therein.
- (5) Brown, M. P.; Cooper, S. J.; Frew, A. A.; Muir, L. M.; Muir, K. W.; Puddephatt, R. J.; Seddon, K. R.; Thomson, M. A. *Inorg. Chem.* **1981**, *20*, 1500 and references therein.
- (6) Balch, A. L.; Olmstead, M. M.; Lee, C. L. *Inorg. Chem.* **1982**, *21*, 2712 and references therein.
- (7) Cowie, M.; Dickson, R. S. *Inorg. Chem.* **1981**, *20*, 2682 and references therein.
- (8) Roberts, D. A.; Mercer, W. C.; Zahurak, S. M.; Geoffroy, G. L.; Debrosse, C. W.; Cass, M. E.; Pierpont, C. G. *J. Am. Chem. Soc.* **1982**, *104*, 910.
- (9) Marsella, J. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 5596.
- (10) Hamilton, D. M.; Willis, W. S.; Stucky, G. D. *J. Am. Chem. Soc.* **1981**, *103*, 4255.
- (11) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 665.
- (12) Longato, B.; Norton, J. R.; Huffman, J. C.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 209.
- (13) Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6360.
- (14) Finke, R. G.; Gaughan, G.; Pierpont, C.; Cass, M. E. *J. Am. Chem. Soc.* **1981**, *103*, 1394.

- (15) Bars, O.; Braunstein, P. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 308.
- (16) Carlton, L.; Lindsell, W. E.; McCullough, K. J.; Preston, P. N. *J. Chem. Soc., Chem. Commun.* **1982**, 1001.
- (17) Farr, J. P.; Olmstead, M. M.; Rutherford, N. M.; Wood, F. E.; Balch, A. L. *Organometallics* **1983**, *2*, 1758.
- (18) Hutton, A. T.; Pringle, P. G.; Shaw, B. L. *Organometallics* **1983**, *2*, 1889.
- (19) Breen, M. J.; Shulman, P. M.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Organometallics* **1984**, *3*, 782.
- (20) Regragui, R.; Dixneuf, P. H.; Taylor, N. J.; Carty, A. J. *Organometallics* **1984**, *3*, 814.
- (21) Arndt, L.; Delord, T.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1984**, *106*, 456.
- (22) Stephan, D. W. *Inorg. Chem.* **1984**, *23*, 2207.