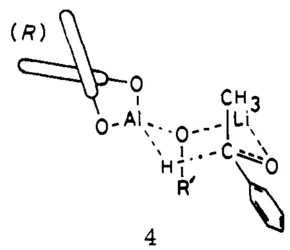

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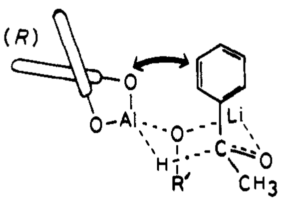

5

state **5**, in accord with the observed enantioselectivity. The origin of the unusual enantioselection with the reagent bearing β,β,β-trifluoroethoxy or a bulky aryloxy group remains unclear.[17] Electronic effects of phenyl group on the stability of the transition state are also to be clarified.

Acknowledgment. Partial financial support from the Ministry of Education, Japanese Government (Grant-in-aid, No. 303023), is acknowledged.

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(4) Upon addition of ethanol and **1**, 1 and 2 molar equiv of H_2 were evolved, respectively.
(5) Aging time (1–10 h) did not affect the enantioselectivity.
(6) The salt was recrystallized repeatedly from acetone–hexane until a constant specific rotation, $[\alpha]^{22}{}_D$ −10.4 (*c* 1.08, ethanol), was obtained.
(7) The synthetic and resolved materials were purified under identical GLC conditions. Both samples were alternately subjected to the measurement of optical rotation under the *same conditions* (solvent source, concentration, temperature, etc.) using a JASCO DIP-SL automatic polarimeter and a 0.1-dm quartz cell. The reported highest $[\alpha]_D$ value (temperature unstated) is given in footnote *n* of Table I. Recorded mp 48–49 °C: Kenyon, J.; Partridge, S. M. *J. Chem. Soc.* **1936,** 128.
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(11) For an enantioselective reduction of benzaldehyde-α-*d*, see Midland, M. M.; Tramontans, A.; Zderic, S. A. *J. Am. Chem. Soc.* **1977,** *99*, 5211.
(12) 2-Octanone formed 2-octanol in 24% ee. Benzyl methyl ketone gave 1-phenyl-2-propanol in 13% ee.
(13) A mixture of **2** (R′O = C_2H_5O) and propiophenone (1:1 ratio) in THF was stirred at 30 °C, and the reaction was monitored by analyzing the aliquots (quenched by dilute HCl) by GLC. After the ratio of the unreacted ketone to ethylphenylcarbinol had become constant (23:77) (the reaction stopped at this stage! (cf. Meyers, A. I.; Kendall, P. M. *Tetrahedron Lett.* **1974,** 1337)), acetophenone was added and the mixture was allowed to stand at 30 °C. Upon quenching of the mixture with CH_3OH, 0.14 equiv of H_2 was evolved. No methylphenylcarbinol was formed, however, indicating the irreversible nature of the reaction. This result was reproducible.
(14) Reaction of acetophenone and a reagent formed from equimolar amounts of $LiAlH_4$ and (*R*)-(+)-**1** without any added R′OH (30 °C, THF) afforded (*R*)-(+)-**3** (R = CH_3) in only 2% ee. In this case, $LiAlH_4$ is probably the major reducing agent.
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(16) Models suggest the existence of severe steric repulsion between the axial group and binaphthoxy oxygen and C-3 hydrogen.
(17) In such cases, owing to the decrease in the basicity of the R′O oxygen and/or steric constraints, the preferred transition state may adopt a binaphthoxy oxygen as the chelating atom, consistent with the experimental results.

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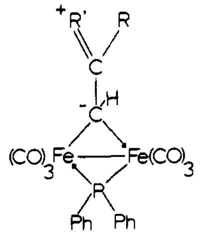
Triangular Iron-Silver Clusters

Sir:

Despite recent activity in the metal cluster field,[1] relatively few systematic methods are available for the introduction of a metal fragment into a bi- or polynuclear framework.[2,3] Thus, for example, mixed metal clusters in which a group 1b element, Cu, Ag, or Au, is part of a cluster polyhedron[4] are rare although there is evidence that these metals, especially gold,[5] have a propensity to form stable clusters. We describe here a simple and possibly versatile route to clusters containing silver and iron group atoms, which involves the addition of hydrocarbon soluble silver salts to neutral binuclear iron carbonyl complexes. In these reactions the d^{10} silver ion can be regarded as a Lewis acid, interacting with an electron-rich metal carbonyl species. This approach is thus the reverse of that recently described by Stone and co-workers[6] where the electronically unsaturated transition metal carbonyl complex $Os_3(CO)_{10}H_2$ was used as an electrophilic center for attack by nucleophilic d^{10} Ni, Pt, and Au compounds.

The compounds I (R = Ph; R′ = NMe_2, NEt_2, $NPr_2{}^n$, NHMe, NHEt, NHC_6H_{11}-c, NC_5H_{10}-c, NHPh) can be synthesized in high yield via the addition of primary or secondary amines across the triple bond of the σ,π-acetylide in II. Treatment of I (R = Ph; R′ = NHMe) in benzene with an equimolar quantity of silver perchlorate in benzene afforded (90%) an immediate crystalline precipitate of an adduct $Fe_2(CO)_6[CHC(R)R'](PPh_2)AgClO_4$ (III, R = Ph; R′ = NHMe): mp 147 °C dec; ν(CO) (THF) 2034 (m), 1991 (s), 1955 (m, br), 1940 (m, br) cm^{-1}. The complex is indefinitely stable in air in the solid state, insoluble in petroleum ether, sparingly soluble in toluene, and very soluble in tetrahydrofuran. Solutions in tetrahydrofuran are stable for several hours under nitrogen. The ^1H NMR spectrum of III (acetone-d_6, 60 MHz) (δ (wrt Me_4Si) 2.75 (s, C–H), 3,05 (d, J = 10 Hz, CH_3), 6,7–7,3 (m, C_6H_5)) was very similar to that of I (C_6D_6) (1,65 (s, C–H), 1.80 (d, J = 6 Hz, CH_3), 6.7–7.3 (m, C_6H_5)) except for a marked downfield shift of the –CH and CH_3 resonances. In neither case was the coupled N-H resonance observable. The ^{31}P spectrum at 183 K showed two doublets (δ (85% H_3PO_4) 173,4 ppm ($^2J_{^{107}Ag\text{-}P}$ = 28,22, $^2J_{^{109}Ag\text{-}P}$ = 32.40 Hz) due to coupling of phosphorus with the magnetic silver nuclei ^{107}Ag and ^{109}Ag of spin ½. At 300 K, a broad doublet, with an average Ag–^{31}P coupling was observable probably owing to solvent exchange processes at the coordinated silver atom. Structural details were revealed by a single-crystal X-ray analysis. Red prisms of $Fe_2(CO)_6[CHC(Ph)NHMe]$-$(PPh_2)AgClO_4 \cdot C_6H_6 \cdot C_6H_5Me$ crystallize in the triclinic space group $P\bar{1}$ with a = 14,101 (3), b = 10,654 (4), c = 15.777 (4) Å; α = 93.68 (4), β = 114,27 (2), γ = 95.03 (3)°. With Z = 2 and a molecular weight of 974,71 the calculated density of



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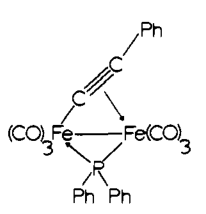

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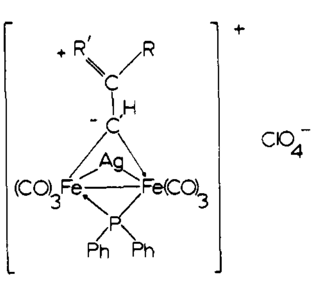

III

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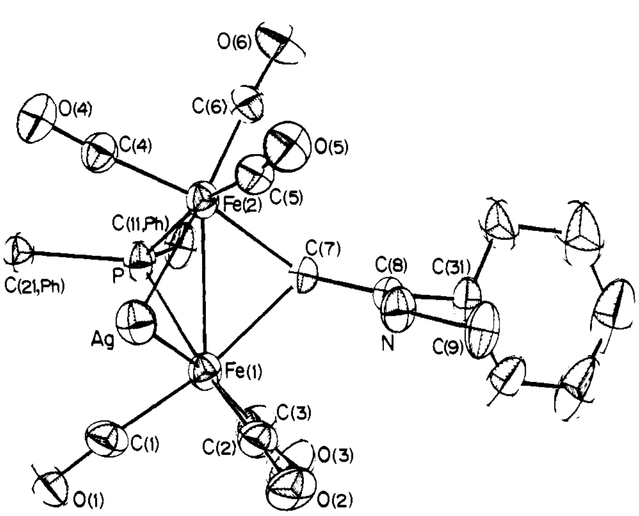

Figure 1. A perspective view of the molecular structure of $Fe_2(CO)_6[CHC(Ph)NHMe](PPh_2)AgClO_4$ showing atomic numbering. For the sake of clarity the molecule of benzene of crystallization, the weakly coordinated toluene molecule, and the perchlorate anion are not shown.

1.511 g cm^{-1} agrees with the value measured by flotation in C_6H_{12}/CCl_4 (1.51 g cm^{-3}). The structure solution and refinement were based on the intensities[8] of 4617 reflections measured on a GE-XRD-6 Datex automated diffractometer. Standard heavy-atom methods were used. At the present state of refinement R and R_w are 0.046 and 0.056, respectively. An ORTEP II plot of the molecular structure is shown in Figure 1. The basic trimetallic skeleton consists of an almost equilateral triangle of two iron atoms and a silver atom with the Fe-Fe bond bridged by a diphenylphosphido group and a single carbon atom of a dipolar iminium ligand $Me(H)^+N{=}C(Ph){-}{}^-CH$.[9] The two Ag-Fe distances (Ag-Fe(1) of 2.685 (1) Å and Ag-Fe(2) of 2.703 (1) Å) are comparable to the Fe(1)-Fe(2) bond length (2.682 (1) Å) despite the difference in covalent radii for iron (1.26 Å) and silver (1.44 Å).[10] It appears that the formation of two Ag-Fe bonds causes a lengthening of ~0.10 Å to the Fe(1)-Fe(2) bond length since the Fe-Fe distances in the closely related species $Fe_2(CO)_6[CHC(Ph)NEt_2](PPh_2)$[13] and $Fe_2(CO)_6[CHC(Ph)NHC_6H_{11}\text{-}c](PPh_2)$[7] average 2.563 Å. The Ag-Fe distances herein are apparently the first values to be reported for silver-iron metal-metal bonds. However, in $Co(CO)_4Ag[Me_2AsC_6H_4As(Me)C_6H_4AsMe_2]$ where there is a direct Co-Ag bond, the metal-metal distance is 2.66 (1) Å.[14] On this basis the observed Ag-Fe bond lengths represent predominantly single bonds. The silver atom is also coordinated weakly to one double bond of a toluene molecule (Ag-C(42), 2.51 (1); Ag-C(43), 2.50 (1) Å) with the anion ClO_4^- occupying interstices in the lattice. An alternative stereochemical description of the molecule emphasizes the structural relationship to $Fe_2(CO)_9$. Thus, in III, there are three bridges (Ag, PPh_2, CHC(Ph)NHMe) as in $Fe_2(CO)_9$ and the Fe(1)-Ag-Fe(2) (59.7 (0)°), Fe(1)-P-Fe(2) (74.1 (0)°), and the Fe(1)-C(7)-Fe(2) (81.0 (0)°) angles are all acute (cf. Fe(1)-C-Fe(2) of 77.4 (0)° in $Fe_2(CO)_9$[11]). In electronic terms the PPh_2 and CHC(Ph)NHMe bridges provide a total of six electrons to the iron atoms in the parent molecule and in III; the same number of electrons are formally contributed by three CO bridges in $Fe_2(CO)_9$. It follows that, while each iron atom is electronically satisfied in $Fe_2(CO)_6[CHC(Ph)NHMe](PPh_2)$, there is a vacant coordination site on each metal atom. Seen in this light the insertion of Ag^+, an electrophile and formal zero electron donor, into a bridging position is not unexpected. The effect of the Ag^+ ion on the charge distribution in the $Fe_2(CO)_6$ fragment is surprisingly small; indeed the ν(CO) spectra of parent and silver adduct in THF are virtually superimposable, although ^{31}P NMR data in the same solvent suggest that the silver ion remains bonded to the Fe_2 framework in this solvent.

The generality of the reaction of I with silver salts has been shown by the characterization of III (R = Ph; R′ = NEt_2, $NPr_2{}^n$, NHEt, $NHC_6H_{11}\text{-}c$, $NC_5H_{10}\text{-}c$)[15] as well as the PF_6^- and NO_3^- salts of III (R = Ph; R′ = NHMe). The reactivity of I toward Ag^+ may imply that other electrophiles such as H^+, Hg^{2+}, Cu^+, Tl^+, and a variety of 14- and 16-electron transition metal substrates should interact in similar fashion. This and the utility of 1,2 and 1,3-dipolar ligands in cluster synthesis are currently under investigation.

Acknowledgments. We are grateful to the National Research Council of Canada for financial support of this work. Partial support of G.N.M. was made available via a graduate student scholarship from the University of Waterloo.

Supplementary Material Available: Structure factors for $Fe_2(CO)_6[CHC(Ph)NHMe](PPh_2)AgClO_4{\cdot}C_6H_6{\cdot}C_6H_5Me$ (25 pages). Ordering information is given on any current masthead page.

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(2) The use of carbonyl metalates in mixed metal cluster synthesis has recently attracted attention. For example reactions of $M(CO)_5^-$ (M = Mn, Re) with $M_3'(CO)_{12}$ (M′ = Fe, Ru, Os), yielded, after acidification, $H_3MOs_3(CO)_{13}$, $H_3MOs_3(CO)_{16}$, $HReOs_3(CO)_{15}$, and $H_2Re_2Ru_2(CO)_{16}$ (J. Knight and M. J. Mays, *J. Chem. Soc., Dalton Trans.*, 1022 (1972)). Geoffroy and Gladfelter have also employed nucleophilic attack by carbonyl metalate anions on neutral carbonyls of the iron triad to synthesize clusters comprising three different metals (G. L. Geoffroy and W. L. Gladfelter, *J. Am. Chem. Soc.*, **99**, 7565 (1977)). For high nuclearity metal carbonyl clusters, one of the most successful synthetic methods is redox condensation, in which one or both reactants may be cluster anions. The elegant work of Chini and co-workers in this area has recently been reviewed: P. Chini, G. Longoni, and V. G. Albano, *Adv. Organomet. Chem.*, **14**, 285 (1976).

(3) Other methods which have been successfully used are the direct reaction of two neutral metal containing species, usually under vigorous conditions or for long periods of time and the pyrolysis of mixtures of carbonyls. Typical examples are the synthesis of mixed Pt–M (M = Fe, Ru, Os) clusters in low yields from zerovalent platinum phosphine derivatives and $M_3(CO)_{12}$ (M. I. Bruce, G. Shaw and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1082, 1781 (1972)) and the preparation of $H_2FeRu_3(CO)_{13}$ from $Fe(CO)_5$ and $[Ru(CO)_3Cl_2]_2$ at 100 °C for 30 h (D. B. W. Yawney and F. G. A. Stone, *J. Chem. Soc. A*, 502 (1969)).

(4) Most of the known compounds containing transition metal copper, silver, or gold bonds are of the types $L_nM{-}M'{-}ML_n$ or $L_nM{-}M'L'_m$ where L_nM represents a typical carbonyl or cyclopentadienyl metal group, M′ is a group 1b metal atom, and L′ is a tertiary phosphine. Some typical examples are $[(Bu_3P)Co(CO)_3Cu]_n$ and $[\eta^5\text{-}C_5H_5W(CO)_3Ag]_n$ (P. Hackett and A. R. Manning, *J. Chem. Soc., Dalton Trans.*, 1606 (1975)) and $[(o\text{-Triars})M]_2Fe(CO)_4$ (M = Cu, Ag; *o*-Triars = bis(*o*-dimethylarsinophenyl)methylarsine) (A.S. Kasenally, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, 5343 (1965)).

(5) Some notable examples of group 1b clusters are the hexanuclear triphenylphosphinecopper(I) hydride, $H_6Cu_6(PPh_3)_6HCONMe_2$ (M. R. Churchill, S. A. Bezman, J. A. Osborn, and J. Wormold, *Inorg. Chem.*, **11**, 1818 (1972)), the homo- and mixed hexanuclear clusters, $R_4Cu_2\ Ag_4X_2$, $R_4Cu_4Ag_2X_2$, and $R_4Ag_4Au_2X_2$ (R = $2\text{-}Me_2NC_6H_4$; X = Cl, Br, I, CF_3SO_3) (G. van Koten, J. T. B. H. Jastrzebski, and J. G. Noltes, *ibid.*, **16**, 1782 (1977)), and the gold clusters of which $[Au_6(PPh_3)_6](BPh_4)_2$ and $Au_{11}(PPh_3)_7(SCN)_3$ are typical (L. Malatesta, *Gold Bull.*, 8 (1975); D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1163 (1976)).

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(7) The compounds I are binuclear with strong Fe–Fe bonds and phosphido and one-carbon, three-electron bridges. Structural features have been described elsewhere; see A. J. Carty, G. N. Mott, N. J. Taylor, and J. E. Yule, *J. Am. Chem. Soc.*, **100**, 3051 (1978).

(8) Intensity data were collected at 298 K with Mo K_α radiation ($\lambda = 0.71069$ Å) using the θ–2θ scan technique with the scan width determined by the equation $\Delta\theta = \pm 0.9 + 0.43 \tan \theta$. The scan time was 2° min^{-1} and background counts of 10 s were taken before and after each scan. From a total of 6722 independent measurements, 4617 with intensities $I \geq 3\sigma(I)$ were counted as observed and used in the solution and refinement. With $\mu = 12.81\ cm^{-1}$ for these atoms, no absorption correction was made.

(9) The iminium ion character of the bridging ligand is shown by the planarity at C(8) (the angles C(7)–C(8)–N, C(7)–C(8)–C(10), and N–C(8)–C(10) are 124.1 (3), 116.3 (3), and 119.6 (3)°, respectively) and the short C(8)–N bond length (1.311 (9) Å). The stereochemistry of C(7) is distorted tetrahedral. The organic ligand is thus very similar to the bridging iminium groups in $Fe_2(CO)_6[CHC(Ph)NEt_2](PPh_2)$[13] and $Fe_2(CO)_6[CHC(Ph)NHC_6H_{11}\text{-}c](PPh_2)$.[7]

(10) An approximate covalent radius of Fe(0) pertinent to the present situation is taken as one half of the average Fe–Fe distance in the triply bridged compounds $Fe_2(CO)_9$ (2.523 (1) Å)[11] and $NaHFe_2(CO)_6$ (2.521 (1) Å).[12] An appropriate value for silver is the Pauling tetrahedral radius of 1.44 Å.

(11) F. A. Cotton and J. M. Troup, *J. Chem. Soc., Dalton Trans.*, 800 (1974).

(12) H. B. Chin, Ph.D. Thesis, University of Southern California, Los Angeles, Calif., 1975.

(13) A. J. Carty, N. J. Taylor, H. N. Paik, W. F. Smith, and J. G. Yule, *J. Chem. Soc., Chem. Commun.*, 41 (1976).

(14) T. L. Blundell and H. M. Powell, *J. Chem. Soc. A*, 1688 (1971).

(15) Microanalyses have been obtained for all compounds prepared; IR and ^{31}P NMR data for III (R = Ph; R′ = NEt_2, $NPr_2{}^n$, NHEt), are essentially identical with those for III (R = Ph; R′ = NHMe).

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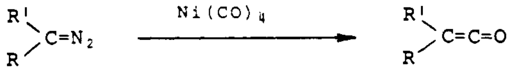
Carbene Addition to Metal Carbonyls—a Novel Reaction in Organometallic Chemistry. Direct Synthesis of η^2-Ketene Complexes from Diazoalkanes[1]

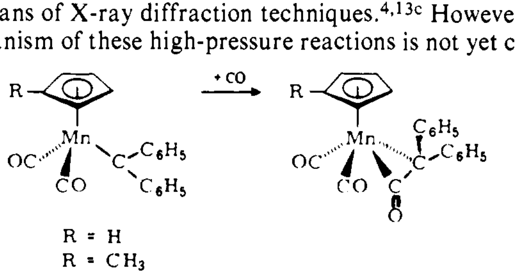
Sir:

The carbonylation of carbenes has remained an unsolved problem since the early days of diazoalkane chemistry, although this process might well be of considerable importance in some catalytic reactions of carbon monoxide, especially those with olefins and hydrogen. Turning their attention to the question of carbonylation of carbenes by metal carbonyls, originally raised by Staudinger[2] as early as in 1916, Rüchardt and Schrauzer examined the action of tetracarbonyl nickel on diphenyldiazomethane and some of its homologues; according to eq 1 they isolated the corresponding free ketenes as final products and postulated unstable carbene complexes as intermediates which are said to be carbonylated via metal centered CO migrations.[3]



$$\begin{matrix}R^1\\ \!\!\!>C=N_2\\ R\end{matrix} \xrightarrow{Ni(CO)_4} \begin{matrix}R^1\\ \!\!\!>C=C=O\\ R\end{matrix} \qquad (1)$$

Recently, we provided the first preparative proof that such a reaction is in fact possible. Diarylcarbene-manganese complexes such as $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$ were shown to undergo carbonylation under extreme pressure conditions to yield the corresponding stable η^2-ketene complexes, e.g., $(\eta^5\text{-}C_5H_5)Mn(CO)_2[O{=}C{=}C(C_6H_5)_2]$ (eq 2); the identity of both compounds was unequivocally established by means of X-ray diffraction techniques.[4,13c] However, the mechanism of these high-pressure reactions is not yet clear.



(2)

Here, we report for the very first time the direct synthesis of η^2-ketene complexes from diazoalkanes via carbene complexes and present clear proof that these products do not result from carbon monoxide addition to the metal–carbene unit but rather from carbene addition to a metal carbonyl.

The reaction of dicarbonyl(η^5-cyclopentadienyl)(tetrahydrofuran)manganese (**1**) or its methyl derivative (**2**), respectively, with 9-diazoanthrone(10) (**3**) does not yield the corresponding anthronyl-carbene complexes (**4**) expected on the basis of our previous results with diazomethane[5] and a series of aryldiazomethanes,[6] but the novel η^2-anthronylketene derivatives (**5**) instead. Since we could not believe the formation of such compounds, both from our experience with the reactivity pattern of diazoalkanes in metal carbonyl chemistry[7] and the analytical and spectroscopic data of **5**,[8] we decided to perform a complete crystal structure analysis of **5b**. This compound crystallizes from diethyl ether–methylene chloride in the triclinic space group $P\bar{1}$ with a = 841.8 (4), b = 1058.7 (5), c = 1179.3 (4) pm; α = 107.59 (3), β = 95.44 (2), γ = 112.18 (3)°; Z = 2. A total of 2557 nonzero reflections ($I > 2.569\,\sigma(I)$) were recorded with an automatic, computer-controlled Siemens diffractometer ($60.09° \geqslant 2\theta \geqslant 4.47°$; Mo K$\alpha$ irradiation). The structure was solved and refined by standard methods (R = 5.9%) and is in perfect agreement with the IR spectroscopic evidence.[8] An ORTEP representation is given in Figure 1. Some relevant bond distances and angles are given in Table I. Both of the phenyl rings of the anthronyl system are significantly bent to each other, the interplanar angle amounting to 157.0 (5)°. The central metal is surrounded by a distorted tetragonal-pyramidal arrangement of the atoms directly bonded to it (Cp, C(1), C(2), C(8), C(9)).

Table I

bond lengths	pm	bond angles	degrees
Mn-C(1)	182.8 (6)	C(1)-Mn-C(2)	91.1 (3)
Mn-C(2)	176.9 (7)	C(8)-Mn-C(9)	39.5 (2)
Mn-C(8)	197.6 (6)	C(8)-C(9)-C(10)	119.4 (5)
Mn-C(9)	224.2 (6)	C(10)-C(9)-C(22)	117.6 (5)
Mn-C(Cp) (av)	215.5	C(8)-C(9)-C(22)	118.2 (4)
		O(8)-C(8)-C(9)	139.8 (6)
C(8)-C(9)	144.8 (8)		
C(8)-O(8)	119.4 (8)		
C(1)-O(1)	113.3 (8)		
C(2)-O(2)	115.0 (10)		

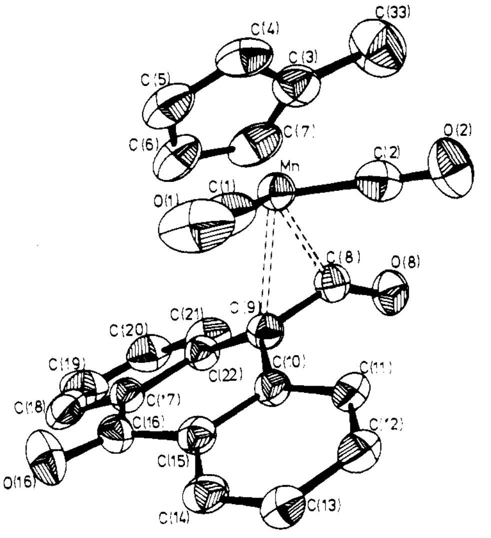


Figure 1. ORTEP representation of dicarbonyl (η^5-methylcyclopentadienyl)(η^2-anthronylketene)manganese (**5b**). The thermal ellipsoids correspond to 50% probability.

How can the formation of the η^2-ketene complexes from 9-diazoanthrone(10) (**3**) be explained? The following observations are of salient mechanistic importance. (1) Regardless of the reaction temperatures (−10 to +30 °C), the yields of **5** are always below ~4% when equimolar ratios of the THF complexes **1** or **2**, respectively, and **3** are employed. Considerable amounts of anthrone and bisanthronyl are formed at the same time. (2) 9-Diazoanthrone(10) (**3**) does not react at all with the parent compounds $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ or $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_3$, respectively, even under more drastic conditions (refluxing THF, 20 h) than used for the reactions between **1** (or **2**) and **3**. Thus, the presence of the THF com-

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