[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 $NaHFe_2(CO)_8$ (2.521 (1) Å).[12] An appropriate value for silver is the Pauling tetrahedral radius of 1.44 Å.

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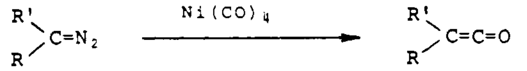
Carbene Addition to Metal Carbonyls—a Novel Reaction in Organometallic Chemistry. Direct Synthesis of η^2-Ketene Complexes from Diazoalkanes[1]

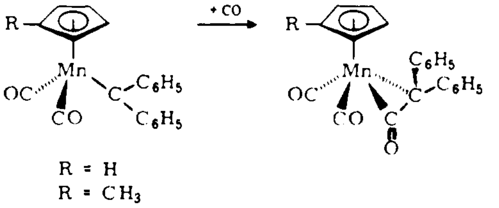
Sir:

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]



$$\mathrm{R'(R)C{=}N_2} \xrightarrow{\mathrm{Ni(CO)_4}} \mathrm{R'(R)C{=}C{=}O} \qquad (1)$$

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)

R = H
R = CH_3

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° ≥ 2θ ≥ 4.47°; Mo Kα 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)		

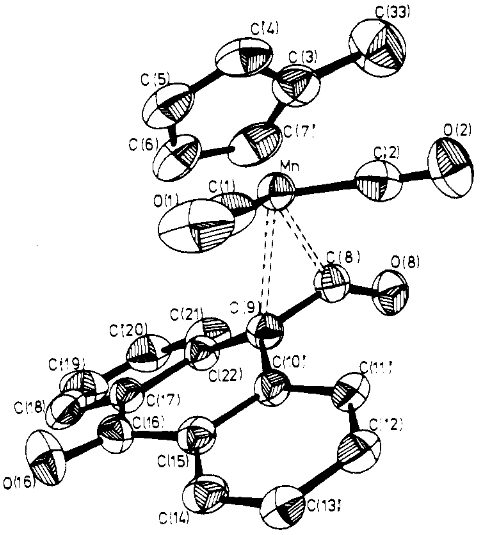


Figure 1. ORTEP representation of dicarbonyl (η^5-methylcyclopentadienyl)(η^2-anthronylketene)manganese (**5b**). The thermal ellipsoids correspond to 50% probability.

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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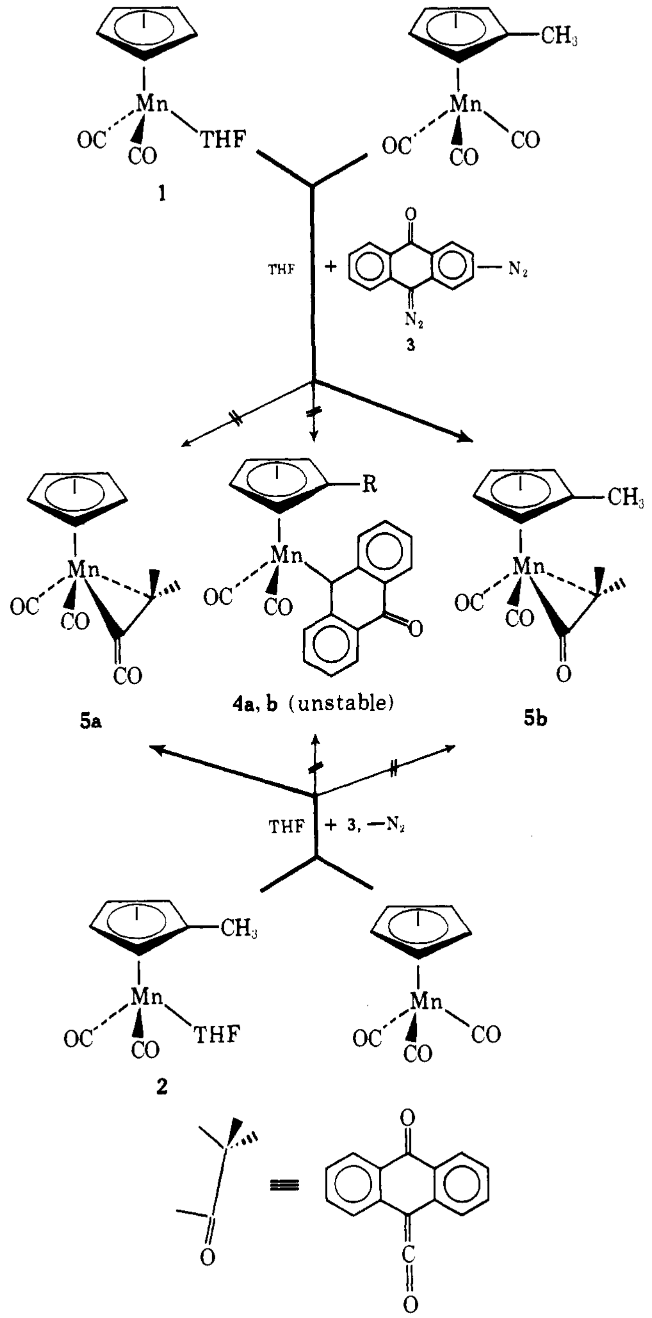
Scheme I



plexes **1** or **2**, respectively, seems to play a pivotal role in the formation of the η^2-ketene complexes **5**. (3) Yields up to a maximum of ~20% for **5** are obtained when a fourfold excess of **1** or **2** acts upon the diazo compound **3** in a CO atmosphere at 20 °C. However, varying amounts of organic byproducts (see above) are found, the yields of which increase with the temperature and the carbon monoxide concentration. (4) Addition of possible CO transfer reagents such as $Ni(CO)_4$[3] do not improve the production of **5** but rather inhibit the formation of the desired η^2-ketene complexes, no matter what reaction conditions are employed. (5) Clean reactions occur only in systems containing approximately equimolar ratios of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, $(\eta^5\text{-}C_5H_5)Mn(CO)_2THF$ (**1**), and 9-diazoanthrone(10) (**3**) in the absence of carbon monoxide (N_2 atmosphere!). The yields thus obtained for **5a** range between 65 and 76%, based on **3**. Only small amounts of anthrone and bisanthronyl are found. This is also true for the corresponding mixture of $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_3$, $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2THF$ (**2**), and 9-diazoanthrone(10) (**3**). The yields of **5** are not strongly dependent upon the temperature, but they turned out to reach a maximum when the reactions are conducted for 20 h at 10 °C. (6) ^{13}CO-labeling experiments prove that CO exchange does not take place between $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ and $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2THF$. There is no sign of CO exchange between $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_3$ and $(\eta^5\text{-}C_5H_5)Mn(CO)_2THF$ (**1**) either. (7) $(\eta^5\text{-}C_5H_4R)Mn(CO)_2THF$ reacts with CO (1 atm, 20 °C) to yield ~90% $(\eta^5\text{-}C_5H_4R)Mn(CO)_3$ after 1 day in THF solution. (8) Once formed, the η^2-ketene complexes **5a** and **5b** do not exchange their ketene ligands with **2** and **1**, respectively. On the basis of about 65 experiments, especially those performed as described in observation 5, we suspected that the formation of η^2-ketene complexes from a diazoalkane precursor might proceed via carbene addition to one of the CO ligands of the intact $(\eta^5\text{-}C_5H_4R)Mn(CO)_3$ components. To check whether this is true or not, we ran the crucial crossing experiments as depicted in Scheme I. Starting with the THF complex **1**, for instance, we obtained *exclusively* the "wrong" η^2-ketene complex **5b** when we added a mixture of $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_3$ and **3**! In turn, *only* **5a** is formed from $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2THF$ (**2**), $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, and **3**.

We consider this to be the striking proof that the carbene derived from 9-diazoanthrone(10) is transferred to the parent carbonyl complexes $(\eta^5\text{-}C_5H_4R)Mn(CO)_3$ (R = H, CH_3). Taking into account that, in the systems described here, diazoalkanes usually form (stable) carbene complexes of type $(\eta^5\text{-}C_5H_4R)Mn(CO)_2(CRR')$,[5-7] we have good reasons to assume the initial formation of anthronylcarbene-manganese species. As can be seen from on-scale models, the anthronylcarbene ligand does not fit into a $(\eta^5\text{-}C_5H_4R)Mn(CO)_2$ fragment because of extreme steric interactions with the η^5-cyclopentadienyl groups, thus accounting for the instability of these particular carbene complexes.[9,10] Also, the observation that **5** is not formed in the absence of $(\eta^5\text{-}C_5H_4R)Mn(CO)_2THF$ is in agreement with the formation of manganese-carbene complexes prior to carbene transfer. The predominant occurrence of anthrone and bisanthronyl from 1:1 mixtures of **1** (or **2**) and **3** is consistent with a weak metal coordination of anthronylcarbene, the latter being converted upon decomposition into these organic products if there is no other substrate present.[11] Finally, the yield-improving influence of carbon monoxide (observation 3) is due to slow formation of $(\eta^5\text{-}C_5H_4R)Mn(CO)_3$ from $(\eta^5\text{-}C_5H_4R)Mn(CO)_2THF$ and not a result of CO addition to the intermediate manganese-carbene complexes (see observation 7).[12]

Apart from having established a novel type of organometallic reaction, our experiments point to a promising new synthetic entry to the class of η^2-ketene complexes, of which only scattered examples were previously known.[13] The preparative route outlined in this communication is under active investigation in our laboratories.

Supplementary Material Available: List of atomic parameters of **5b** and procedure for the preparation of the η^2-ketene complexes **5a** and **5b** and for a crossing experiment (4 pages). Ordering information is given on any current masthead page.

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(7) For a recent review, see W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 17, 800 (1978).

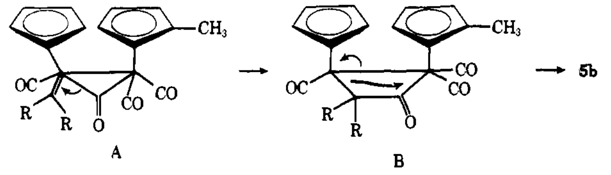
(8) Anal. Found for **5a:** C, 66.60; H, 3.48; Mn, 13.58; O, 16.37; mol wt, 379 (osmometrically in $CHCl_3$). Calcd for $C_{21}H_{13}MnO_4$ (396.3): C, 66.68; H, 3.31; Mn, 13.86; O, 16.15. Found for **5b:** C, 67.30; H, 3.87; Mn, 13.32; O, 15.46; mol wt, 402 (osmometrically in $CHCl_3$), 410 (field desorption mass spectroscopy). Calcd for $C_{23}H_{15}MnO_4$ (410.3): C, 67.33; H, 3.68; Mn, 13.40; O, 15.59. IR spectra (ν_{CO}, cm^{-1}; KBr): **5**a, 2000 (s–vs), 1939 (vs), 1758 (s, ketene), 1644 (s, ketone); **5b**, 2000 (s–vs), 1960 (vs), 1747 (s, ketene), 1648 (s, ketone). Physical properties: air-stable, red, refracting rhombs; dec pt 120 °C (**5**a), 129 °C (**5b**).

(9) In contrast, diphenylcarbene and (benzoyl)phenylcarbene complexes of this type can avoid steric interactions with the metal carbonyl fragment by noncoplanar arrangements of both carbene substituents. $(\eta^5\text{-}C_5H_5)\text{-}Mn(CO)_2\{C[C(=O)C_6H_5]C_6H_5\}$: A. D. Redhouse, *J. Organomet. Chem.*, **99**, C29 (1975). $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$: B. L. Haymore, personal communication. A similar structure has been reported for $(CO)_5\text{-}W[C(C_6H_5)_2]$ in which the planes of the phenyl rings are twisted ~42° from the plane defined by the carbene carbon atom and the atoms directly bonded to it: C. P. Casey, T. J. Burkhardt, Ch. A. Bunnell, and J. C. Calabrese, *J. Am. Chem. Soc.*, **99**, 2127 (1977).

(10) Note that in $(\eta^5\text{-}C_5H_4R)Mn(CO)_2(CRR')$ complexes the plane defined by Mn, C(carbene), and the atoms directly attached to C(carbene) is a mirror plane of the $cpMn(CO)_2$ fragment: G. Huttner and D. Regler, *Chem. Ber.*, **105**, 1230 (1972); E. Hädicke and W. Hoppe, *Acta Crystallogr., Sect. B*, **27**, 760 (1971). This is in agreement with MO calculations on compounds of this type containing single-faced π-acceptor ligands (P. Hofmann, Universität Erlangen—Nürnberg, personal communication; B. E. R. Schilling, R. Hoffmann, and D. L. Lichtenberger, *J. Am. Chem. Soc.*, **101**, 585 (1979)).

(11) This route of diazoalkane decomposition is well established in metal-catalyzed reactions; see S. Patai, "The Chemistry of Diazonium and Diazo Groups", Parts 1 and 2, Wiley, New York, 1978.

(12) At present, it is hard to say how this carbene transfer proceeds. As one referee suggested, one could think of a mechanism initiated by CO dissociation from the intermediate carbene complex which, in turn, should be open to attack by the parent carbonyl $(\eta^5\text{-}RC_5H_4)Mn(CO)_3$ forming the binuclear intermediates A and B. However, *stable* carbene complexes of type $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CRR')$ (e.g., R, R′ = C_6H_5) do not show any sign of ^{13}CO exchange (THF or THF–benzene, 25 °C), nor do they react with $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, even under prolonged heating in THF. Thus, the stability of carbene complexes seems to be one of the factors which govern carbene transfer capability.



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Direct Observation of the Methyl Diazonium Ion in Fluorosulfuric Acid

Sir:

Alkyl diazonium ions have been observed in solution in strongly acidic media only when substituted with strongly electron-withdrawing groups.[1,2] Recent kinetic studies on the hydrolysis of diazomethane have shown that in acidic aqueous tetrahydrofuran the methyl diazonium ion **1** may have an appreciable lifetime, half-life of 0.3 s at 25 °C.[3] We now report that protonation of diazomethane by a fluorosulfuric acid–sulfuryl chlorofluoride solution at −120 °C yields two unstable species, considered to be the methyl diazonium ion and the isomeric methylene diazenium ion **2**[4] on the basis of their NMR spectra at −106 °C.

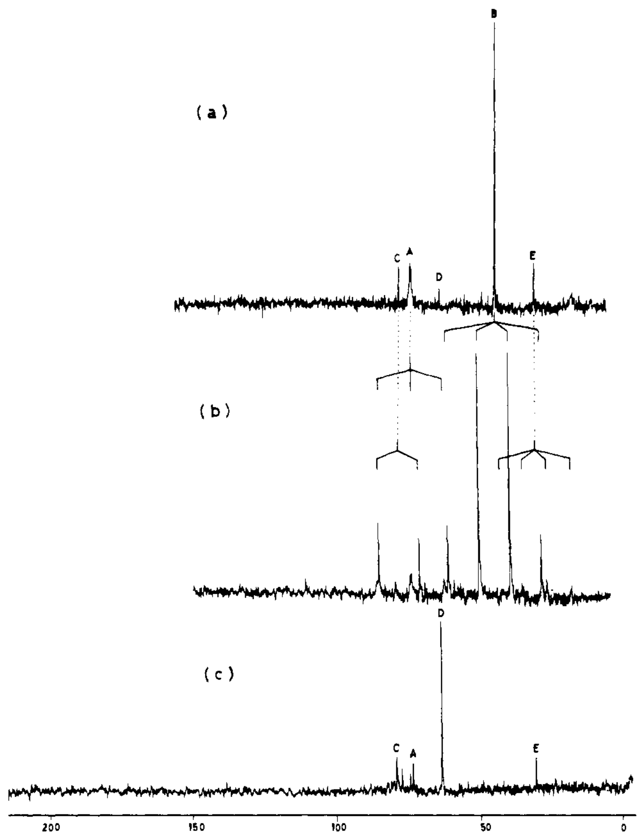

Figure 1. ^{13}C spectra of species formed by reaction of CH_2N_2 with $HFSO_3$: (a) at −106 °C, proton decoupled; (b) at −106 °C, proton coupled; (c) at −85 °C, proton coupled (peak A, $CH_2N_2H^+$; peak B, $CH_3N_2^+$; peak C, $CHCl_3$ (reference); peak D, CH_3OSO_2F; peak E, byproduct.

$$\begin{aligned} &CH_2N_2 + HFSO_3 \\ &\quad \rightarrow \underset{\mathbf{1}\ (80\%)}{CH_3{-}{}^{+}N{\equiv}N} + \underset{\mathbf{2}\ (20\%)}{CH_2{=}{}^{+}N{=}N{-}H} + FSO_3^{\,-} \qquad (1) \end{aligned}$$

Samples were prepared by passage of a nitrogen stream containing gaseous diazomethane into the acid solution at −120 °C. This method avoids high local concentrations of substrate, thus preventing the polymer formation which was consistently observed in attempts to extract the diazomethane into the acid solution from a matrix of dichloromethane at −120 °C.

The proton decoupled ^{13}C spectrum of the $HFSO_3$ sample at −106 °C (Figure 1a) showed two major peaks, one broad at 73.28 (peak A) and one fine at 43.78 ppm (peak B), in the ratio 1:4 (relative integral intensity), and two minor peaks (<5%), one of which corresponds to methyl fluorosulfate, δ 63.20 ppm (lit.[5] δ 62.5 ppm in CCl_4). As the sample was heated to −85 °C both the principal peaks diminished in intensity, while the methyl fluorosulfate peak increased to finally comprise 85% of the sample, accompanied by 15% of unidentified material. The disappearance of peak A was less rapid than that of peak B indicating that they belong to different species.

In the proton coupled ^{13}C spectrum (Figure 1b) peak A was split into a triplet while peak B became a quadruplet, corresponding to CH_2 and CH_3 groups. When the sample was prepared with $DFSO_3$ instead of $HFSO_3$, peak B appeared as a triplet in the proton decoupled spectrum instead of the singlet previously observed, implying monodeuteration on carbon; in contrast peak A remained a broad singlet (no protonation on carbon). A similar pattern was observed in the ^1H spectrum of the deuterated sample where the major resonance was a triplet (J = 2.2 Hz), indicating H-D coupling, and the remaining one was a broad singlet. The methyl fluorosulfate

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