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Organometallic Chemistry of Reactive Organic Compounds. 41.[1] Metal-Induced Carbyne/Carbene Coupling with Buchner's Diazo Compound[†]

Wolfgang A. Herrmann,*[2a,3] Manfred L. Ziegler,[2b] and Orhan Serhadli[2b]

Institut für Anorganische Chemie der Johann Wolfgang Goethe-Universität, Niederurseler Hang, D-6000 Frankfurt am Main 50, Germany, and Anorganisch-chemisches Institut der Universität, Im Neuenheimer Feld 270, D-6900 Heidelberg 1, Germany

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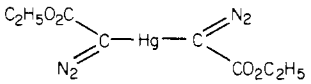
An example of a transition-metal-centered carbon–carbon coupling reaction between a carbyne and a carbene fragment has been encountered through an unexpected diazoalkane fragmentation process: Buchner's prototypal mercuriodiazoalkanes, bis[(alkoxycarbonyl)diazomethyl]mercury, $Hg[C(=N_2)CO_2R]_2$ ($R = C_2H_5$, **2a**; t-C_4H_9, **2b**), react with bromopentacarbonylmanganese, $(CO)_5MnBr$ (**1**), in boiling diethyl ether to yield the previously described dinuclear μ-carbyne complexes of composition $[(\mu\text{-}CCO_2R)Mn(CO)_4]_2$ (**7a,b**) as well as the mononuclear carbyne/carbene coupling products $(CO)_4MnC(CO_2R)=C(HgBr)C(OR)=O$ (**8a,b**), the molecular structure of which latter compounds has been established by means of X-ray crystallography: space group C_{2h}^5 ($P2_1/c$); $a = 1468.9$ (2) pm, $b = 686.2$ (5) pm, $c = 1759.4$ (3) pm, $\beta = 91.04°$. Important bond parameters: Hg—Br = 242.9 (4) pm, C═C = 138 (4) pm, Mn—O = 207.4 (17) pm; ∠Br,Hg,C = 176.5 (8)°. The characteristic structural element is a five-membered metallacyclic frame that arises from [2 + 3] cycloaddition of the (bromomercurio)carbene $|C(HgBr)CO_2R$ upon the intermediate carbyne complex $(CO)_4Mn\equiv CCO_2R$. This novel mode of cyclization implies the formation of a carbon–carbon double bond between carbene and carbyne carbon atoms [cf. C(5)–C(6)]. From a formalistic point of view, compounds **8a** and **8b** might also be described as to result from homolytic trans addition ("metallamercuration") of $(CO)_5MnHgBr$ across the triple bond of preformed acetylenedicarboxylates, $RO_2CC\equiv CCO_2R$, with subsequent decarbonylation and concomitant cyclization of the vinyl-type derivative $(CO)_5Mn-C(CO_2R)=C(HgBr)CO_2R$. This latter mechanistic alternative was, however, ruled out by negative parallel experiments using authentic $(CO)_5MnHgBr$ and the respective alkynes.

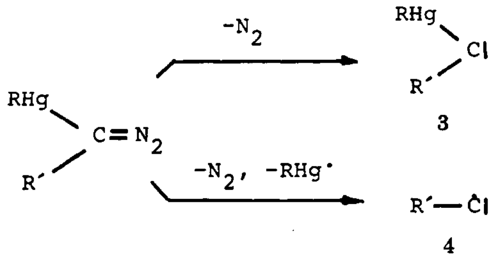
Introduction

Aliphatic diazoalkanes have been used in various branches of organic chemistry for many decades as convenient and exceedingly useful synthetic precursors for a plethora of otherwise not easily accessible compounds as well as for the generation of carbenes.[4,5] Their metal-substituted congeners of types $L_xM-C(=N_2)R$ and $(L_xM)_2C=N_2$, however, have hardly participated in the rapid development of diazoalkane chemistry which fact is even more surprising in view of Buchner's early discovery of the easy-to-make prototypal α-mercuriodiazoalkane **2a**.[6,7] During the past decade many novel metalated diazoalkanes became accessible through straightforward synthetic approaches mainly elaborated by the research groups of Regitz,[8,9] Schöllkopf,[10] and Lorberth.[11] Derivatives having metals such as lithium, silver, mercury, and tin directly attached to the diazo carbon center proved particularly useful as isolable intermediates for the purpose of diazoalkane homologation.



2a

The most spectacular issue of heavy-metal-substituted diazoalkanes, however, came from the old Buchner compound **2a** when Skell and Strausz performed their pioneering short wavelength photolysis study which revealed the generation of both the heterocarbene **3** and the (ethoxycarbonyl)carbyne **4** according to generalized eq 1.[12–16] The occurrence of carbyne species R'–$\dot{C}$:,[17] following nitrogen elimination and mercury–carbon bond cleavage, was inferred by trapping experiments using cyclohexene, *cis*-2-butene, and *trans*-2-butene. These results promised to



(1)

[†] Dedicated to Professor Ulrich Wannagat on the occasion of his 60th birthday.

[1] Part 40: Herrmann, W. A.; Weichmann, J.; Ziegler, M. L.; Pfisterer, H. *Angew. Chem.* **1982**, *94*, 545; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 551; *Angew. Chem. Suppl.* **1982**, 1223–1245.

[2] (a) Universität Frankfurt. (b) Universität Heidelberg.

[3] Karl Winnacker Fellow; to whom all correspondence should be addressed.

[4] See, for example: (a) Eistert, B.; Regitz, M.; Heck, G.; Schwall, H. "Methoden der organischen Chemie (Houben-Weyl-Müller)", 4th ed.; Thieme Verlag: Stuttgart, 1968; vol. X/4, p 482 ff. (b) W. Kirmse, "Carbene Chemistry", 2nd ed.; Academic Press: New York, London, 1971.

[5] Patai, S., Ed. "The Chemistry of Diazo and Diazonium Groups"; Wiley: New York, 1978; Vols. I and II.

[6] Buchner, E. *Ber. Deutsch. Chem. Ges.* **1895**, *28*, 215. For a slightly modified preparation of **2a**, see: Regitz, M. *Synthesis* **1972**, 351.

[7] X-ray structure of compound **2a**: Smith, R. A.; Torres, M.; Strausz, O. P. *Can. J. Chem.* **1977**, *55*, 3527.

[8] Review: Regitz, M. *Synthesis* **1972**, 351.

[9] For a recent monograph covering the syntheses of diazoalkanes, see: Regitz, M. "Diazoalkane – Synthesen und Eigenschaften"; Thieme Verlag: Stuttgart, 1977.

[10] Cf.: Schöllkopf, U.; Bânhidai, B.; Frasnelli, H.; Meyer, R.; Beckhaus, H. *Liebigs Ann. Chem.* **1974**, 1767. Schöllkopf U.; Rieber, N. *Chem. Ber.* **1969**, *102*, 488. Schöllkopf, U.; Bânhidai, B.; Schulz, H.-U. *Liebigs Ann. Chem.* **1972**, *761*, 137.

[11] Cf.: Lorberth, J. *J. Organomet. Chem.* **1971**, *27*, 303. Lorberth, J.; Schmock, F.; Lange, G. *Ibid.* **1973**, *54*, 23. Grüning, R.; Lorberth, J. *Ibid.* **1974**, *69*, 213; **1974**, *78*, 221. Glozbach E.; Lorberth, J. *Ibid.* **1974**, *132*, 359. Krommes, R.; Lorberth, J. *Ibid.* **1975**, *93*, 339; **1975**, *97*, 59; **1976**, *120*, 131. Grüning, R.; Lorberth, J. *Ibid.* **1974**, *71*, 159.

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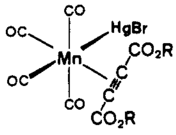
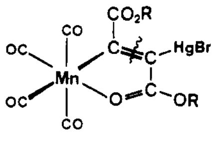
open a new and ostensibly rich field of chemistry and, hence, initiated early attempts to utilize Buchner's compound in organometallic chemistry as well.[18] Clean addition of the bis(carbene)mercury fragment $Hg(\text{-}\ddot{C}\text{-}CO_2C_2H_5)_2$ upon a metal-to-metal double bond occurred when **2a** was reacted with the rhodium complex $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CO)]_2$ under quite mild conditions.[19] On the other hand, treatment of the α-mercuriodiazoalkane with bromopentacarbonylmanganese (**1**) yielded, among other products, the dinuclear μ-carbyne complex of composition $[(\mu\text{-}CCO_2C_2H_5)Mn(CO)_4]_2$ (**7a**) in which latter compound the carbyne group derived from **2a** is stabilized by acting as a bridging three-electron ligand.[20] The second carbyne-derived product **8a** of this reaction was shown to obey the stoichiometry $(CO)_4Mn(HgBr)(CCO_2C_2H_5)_2$, and all spectroscopic data proved fully consistent with a rather trivial-looking alkyne complex of proposed structure A



A



B

$R = C_2H_5$

having the two independent ligands HgBr and $C_2H_5O_2C\text{-}C{\equiv}CCO_2C_2H_5$ in cis positions to each other.[21] In order to convey an unambiguous structural assignment, we have now subjected this compound to an X-ray diffraction study that not only established the surprising geometry of structure B resulting from an heretofore unknown carbyne/heterocarbene coupling process but also shed some light on the initial products of this reaction.

Experimental Section

The manganese compound **8a** was synthesized according to the procedure published elsewhere.[21] The spectroscopic data (IR, ^1H NMR, mass spectra) were in agreement with the characterization given in the original account,[21] except that the infrared absorptions occurring in the 1500–1700 cm^{-1} range (KBr) can now correctly be assigned to the coordinated carbonyl ester group [C(7)–O(5), 1576 cm^{-1} (m)] and the free carbonyl ester group, respectively [C(10)–O(7), 1672 cm^{-1} (m)].[22] Anal. Calcd for $C_{12}H_{10}BrHgMnO_8$ (617.65): C, 23.34; H, 1.64; Mn, 8.90; Hg, 32.47; Br, 12.93. Found: C, 23.40; H, 1.71; Mn, 9.00; Hg, 32.55; Br, 13.03. Large quadrangular-shaped single crystals of compound **8a** were grown from a *n*-pentane/diethyl ether solution (1/2) at +25 to −30 °C and had to be cut down to a convenient size for the purpose of a single-crystal X-ray diffraction study. Rotation and Weissenberg photographs (Cu Kα radiation) showed the crystal of **8a** to be monoclinic and provided rough lattice constants. Exact lattice parameters were calculated by least squares[23a] from diffractometrically determined θ values of 60 selected reflections. Intensity measurements[23b] were performed on a computer-controlled single-crystal diffractometer (AED-Siemens, Mo Kα, θ–2θ scans, five value method). Reflections with $I < 2.56\sigma(I)$ were not considered. A total of 2550 independent intensities remained for calculation. These were corrected for Lorentz and polarization factors. Absorption corrections were omitted. The crystal data are listed in Table I.

Table I. Crystallographic Data of the Vinyl Ketone Complex 8a

formula	$C_{12}H_{10}BrHgMnO_8$
mol wt	647.2 amu
cryst size	0.2 × 0.3 × 0.2 mm
density	$\rho = 2.424\ Mg \cdot m^{-3}$
space group	monoclinic; $C_{2h}^5\text{-}P2_1/c$ $Z = 4$
cell const	
a	1468.9 (2) pm
b	686.2 (5) pm
c	1759.4 (3) pm
β	91.04 (2)°
cell vol	$1773.1 \times 10^6\ pm^3$
linear abs coeff μ	115.96 cm^{-1}
systematic absences	$0k0\ (k = 2n + 1)$; $h0l\ (l = 2n + 1)$
irradiation	Mo Kα (λ = 71.069 ppm)
scan range	$2° \leqslant 2\theta \leqslant 54°$
no. of independent nonzero reflctns	2550
agreement factor	R(anisotropic) = 0.088

The positions of the heavy atoms (Hg and Br) were found by means of a three-dimensional Patterson synthesis while the remaining non-hydrogen atoms came from three-dimensional Fourier and difference Fourier methods. The hydrogen atoms were put into fixed positions by means of the "H-FIX" program.[24a] The isotropic refinement process of the hydrogen atoms was carried out in a way that the U value of each atom ($U = B/8\pi^2$) corresponded to the value of the carbon atoms attached to it. The methyl groups were considered to be rigid groups (C–H = 96 pm). The standard deviations of the hydrogen positions are identical with those of the corresponding carbon positions. The refinement of the structure was carried out by least-squares methods. All calculations were performed on a Data General Nova 3 computer with the SHELXTL program;[24a] scattering factors were those of Hanson, Herman, Lea, and Skillman.[24b] The atom numbering scheme corresponds to the one used in Figure 1. Isotropic refinement converged to $R = 0.16$ while anisotropic refinement gave $R = 0.088$. The goodness of fit value amounts to 8.327 ($\{[\sum w(|F_o| - |F_c|)^2]/(n - p)\}^{1/2}$; $n = 2481$, $p = 211$). Bonding distances and angles are summarized in Table III, and data for least-squares planes in Table IV. The fractional atomic coordinates are listed in Table II. Table V lists the U_{ij} and U(equiv) data.

Molecular Structure of the Carbene/Carbyne Coupling Product 8a

The structure of the mononuclear manganese compound **8a** is depicted in Figure 1 which shows that the molecule exhibits a slightly distorted octahedral overall geometry. The four carbonyl ligands are cis-oriented with respect to C(1) and C(3), with the interligand angles being close to what one might expect for an ideal polyhedron of this type

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(12) DoMinh, T.; Gunning, H. E.; Strausz, O. P. *J. Am. Chem. Soc.* **1967**, *89*, 6785.

(13) Strausz, O. P.; DoMinh, T.; Font, J. *J. Am. Chem. Soc.* **1968**, *90*, 1930.

(14) Skell, P. S.; Valenty, S. J. *J. Am. Chem. Soc.* **1973**, *95*, 5042.

(15) Valenty, S. J.; Skell, P. S. *J. Org. Chem.* **1973**, *38*, 3937.

(16) Strausz, O. P.; Kennepohl, G. J. A.; Garneau, F. X.; DoMinh, T.; Kim, B.; Valenty, S.; Skell, P. S. *J. Am. Chem. Soc.* **1974**, *96*, 5723.

(17) A theoretical treatment (ab initio electronic structure theory) of the related species carbohydroxycarbyne, $HOC(=O)\dot{C}$, has recently been reported: Kim, K. S.; So, S. P.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1982**, *104*, 1457.

(18) Reviews: (a) Herrmann, W. A. *Angew. Chem.* **1978**, *90*, 855; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 800. (b) Herrmann, W. A. *Adv. Organomet. Chem.* 1982, *20*, 159.

(19) Herrmann, W. A.; Huggins, J. M. *Chem. Ber.* **1982**, *115*, 396.

(20) Herrmann, W. A. *Angew. Chem.* **1974**, *86*, 895; *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 812.

(21) Herrmann, W. A. *J. Organomet. Chem.* **1975**, *97*, 1.

(22) The same assignment logically applies for the *tert*-butyl derivative **8b** [1567 (m) and 1696 cm^{-1} (m, s), respectively][21] which has a cyclic structure (B) analogous to that found for **8a** and is thus formulated as *cis*-$(CO)_4\overline{Mn[CO_2\text{-}t\text{-}C_4H_9)=C(HgBr)C(O\text{-}t\text{-}C_4H_9)=O}]$ rather than *cis*-$(CO)_4Mn(HgBr)(t\text{-}C_4H_9O_2CC{\equiv}CCO_2\text{-}t\text{-}C_4H_9)$.

(23) (a) Berdesinski W.; Nuber, B. *Neues Jahrb. Mineral., Abh.* **1966**, *104*, 113. (b) Weiss, J. "Data Collection Program Odysseus"; Anorganisch-chemisches Institut, Universität Heidelberg: West Germany, 1980.

(24) (a) Sheldrick, G. M. "SHELXTL Version"; Anorganisch-chemisches Institut, Universität Göttingen; West Germany, 1980. (b) Hanson, H.; Herman, F.; Lea, J. D.; Skillman, S. *Acta Crystallogr.* **1964**, *17*, 1040.

Table II. Fractional Atomic Coordinates of the Manganese Complex 8a[a]

atom	*x/a*	*y/b*	*z/c*
Hg	−0.0814 (1)	0.2308 (2)	0.5254 (1)
Br	0.0493 (3)	0.2768 (5)	0.4446 (2)
Mn	−0.3682 (3)	0.0559 (6)	0.6459 (2)
C(1)	−0.4466 (21)	0.0731 (44)	0.7262 (16)
C(2)	−0.4085 (20)	0.2842 (39)	0.6036 (14)
C(3)	−0.4546 (20)	−0.0770 (43)	0.5933 (14)
C(4)	−0.3184 (22)	−0.1848 (44)	0.6718 (15)
C(5)	−0.1875 (20)	0.1810 (39)	0.5857 (15)
C(6)	−0.2658 (20)	0.0778 (35)	0.5687 (12)
C(7)	−0.2007 (17)	0.2399 (38)	0.6706 (13)
C(8)	−0.1324 (23)	0.4070 (45)	0.7764 (14)
C(9)	−0.0598 (31)	0.5505 (55)	0.7870 (17)
C(10)	−0.2660 (21)	−0.0188 (42)	0.4880 (14)
C(11)	−0.3257 (38)	−0.2726 (53)	0.4074 (19)
C(12)	−0.2697 (54)	−0.4258 (61)	0.4069 (25)
O(1)	−0.4973 (22)	0.0778 (42)	0.7747 (13)
O(2)	−0.4304 (17)	0.4271 (32)	0.5730 (11)
O(3)	−0.5118 (17)	−0.1583 (32)	0.5614 (11)
O(4)	−0.2833 (18)	−0.3239 (35)	0.6848 (14)
O(5)	−0.2679 (12)	0.2043 (26)	0.7070 (8)
O(6)	−0.1303 (18)	0.3419 (28)	0.6970 (9)
O(7)	−0.2242 (19)	0.0598 (40)	0.4369 (10)
O(8)	−0.3157 (18)	−0.1790 (34)	0.4834 (11)
H(8A)	−0.1224 (24)	0.2982 (45)	0.8098 (13)
H(8B)	−0.1903 (24)	0.4652 (45)	0.7867 (13)
H(9A)	−0.0392 (31)	0.5601 (55)	0.8390 (17)
H(9B)	−0.0945 (31)	0.6644 (55)	0.7737 (17)
H(9C)	−0.0082 (31)	0.5408 (55)	0.7545 (17)
H(11A)	−0.3089 (38)	−0.1827 (53)	0.3683 (19)
H(11B)	−0.3876 (38)	−0.3136 (53)	0.3900 (19)
H(12A)	−0.2299 (54)	−0.4826 (85)	0.3703 (25)
H(12B)	−0.3036 (54)	−0.5269 (85)	0.4313 (25)
H(12C)	−0.2342 (54)	−0.3562 (85)	0.4444 (25)

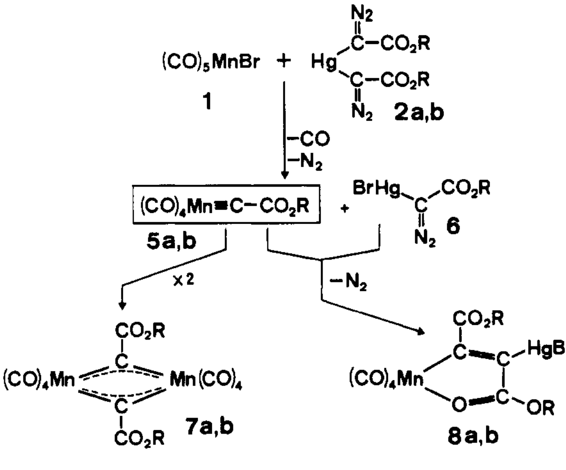
[a] The standard deviations given in parentheses correspond to the least significant digits.

(Table III). The two remaining coordination sites are occupied by the chelating C,O ligand resulting from the diazo precursor **2a** and the HgBr moiety. The original (ethoxycarbonyl)carbyne fragment $|\dot{C}(6)-CO_2Et$ is attached to the metal center through a manganese–carbon single bond (205.1 (26) pm).[25-30] At the same time, this unit forms a conventional carbon–carbon double bond to the (bromomercurio)carbene moiety (*d*(C(5)–C(6)) = 137.9 pm; Table III), the keto group C(7)–O(5) of which latter species in turn being coordinated to the metal atom (*d*(O(5)–Mn) = 207.4 (17) pm). The five-membered metallacycle thus formed hardly deviates from planarity (plane A; Table IV). This plane also includes the atoms C(10), Hg, and O(6) directly attached to the ring carbon atoms since the latter ones are essentially sp^2 hybridized. The ethoxy and ethoxycarbonyl groups associated with the metallacyclic backbone do not show any unusual intramolecular parameters nor does the bromomercurio ligand represent an exception of the commonly observed geometry of typical divalent organomercurials (Br,Hg,C(5) = 176.5 (8)°; *d*(Hg–Br) = 242.9 (4) pm).[30,31]

The bonding pattern derived from the aforementioned structural details suggests the classification of compounds **8a** and **8b** as vinyl ketone complexes. Such compounds, albeit not bearing heavy-metal substituents, have previously been synthesized by the reactions of methyl- and acetylpentacarbonylmanganese with dialkyl acetylenedicarboxylates.[31,32] However, no structural description of these derivatives is available.

Acetylene Insertion vs. Carbene/Carbyne Coupling

The final structural elucidation of compounds 8 presented the intruiging question as to how these molecules can form from the diazomercury precursors **2**. Let us approach this problem from both the known chemistry of Buchner's compound **2a** and the structural features of our manganese complex **8a**. The chelating ligand of **8a** represents the connectivity pattern of diethyl acetylenedicarboxylate which, from a formalistic point of view, has been inserted into a Mn–HgBr bond. Both substrates required for such a reaction could possibly be generated from $(CO)_5MnBr$ (**1**) and $Hg[C(=N_2)CO_2Et]_2$ (**2a**) under the conditions employed for the synthesis of **8a**.[21] The diazo precursor could decompose under elimination of nitrogen to give the symmetrical carbyne/carbyne coupling product $EtO_2C{\equiv}CCO_2Et$,[33,34] whereas the extruded metal then very likely will insert into the manganese–bromine bond of 1 yielding the well-documented bromomercury derivative of composition $(CO)_5MnHgBr$.[21,35] Since the latter compound in fact appears as an isolated side product in 21% yield,[21] its subsequent addition across the carbon–carbon triple bond of the preformed diethyl acetylenedicarboxylate had to be taken into serious considera-



(2)

a : R = C_2H_5; b: R = $^tC_4H_9$

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[25] As expected, the carbon(sp^2)–manganese distance found in this compound is shorter than those reported for heterocycles belonging to the same structural type but having metal-bound sp^3-hybridized carbon atoms instead, cf.: $(CO)_4Mn-P(C_6H_5)_2OCH_2CH_2CH_2$, 221.0 (3) pm;[26] $(CO)_4Mn-P(C_6H_5)_2CH_2CH_2CH_2CH_2$, 222.2 (10) pm;[27] $(CO)_4Mn-P(C_6H_5)_2CH_2CH_2CHCH_3$, 223.7 (9) pm;[27] $(CO)_5MnCH_3$, 218.5 (11) pm.[28]

[26] Lindner, E.; Eberle, H.-J. *J. Organomet. Chem.* **1980**, *191*, 143.

[27] Lindner, E.; Funk, G.; Hoehne, S. *Chem. Ber.* **1981**, *114*, 3855.

[28] Seip, H. M.; Seip, R. M. *Acta Chem. Scand.* **1970**, *24*, 3431.

[29] Bromomethylmercury, $Br-Hg-CH_3$, having a bromine–mercury distance of 241 pm may be quoted as typical example. The observed shortening of the Hg–C(5) bond of **8a** (192.2 (29) pm) compared with the corresponding distance in $Br-Hg-CH_3$ (207 pm) is due to the different carbon hybridization in these compounds (**8a**, sp^2; $Br-Hg-CH_3$, sp^3).[30] Consistently, the Hg–C(sp^2) distance of the diazo precursor **2a** amounts to 201 (1) pm.[7]

[30] Wells, A. F. "Structural Inorganic Chemistry", 4th ed.; Clarendon Press: Oxford, 1975; p 918.

[31] Booth, B. L.; Hargreaves, R. G. *J. Chem. Soc. A* **1970**, 308.

[32] Booth, B. L.; Lewis, E. J. R. *J. Chem. Soc., Dalton Trans.* **1982**, 417.

[33] For a brief discussion of metal-mediated linkage of carbenes and carbynes, see: Hoffmann, R.; Wilker, Ch. N.; Eisenstein, O. *J. Am. Chem. Soc.* **1982**, *104*, 632.

[34] A unique coupling of two carbynes to an acetylene unit within the coordination core of a metal has been described: Fischer, E. O.; Ruhs, A.; Friedrich, P.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 465.

[35] Bower, L. M.; Stiddard, M. H. B. *J. Chem. Soc. A* **1968**, 706. The same compound was originally synthesized by Hieber et al. (*Chem. Ber.* **1960**, *93*, 455) but erroneously formulated as the dimeric species "$Hg[Mn(CO)_5]_2 \cdot HgBr_2$".

Table III. Intramolecular Parameters of the Manganese Compound 8a[a]

(A) Bond Lengths (pm)

Hg-Br	242.9 (4)	Mn-C(6)	205.1 (26)	C(6)-C(10)	156.6 (34)
Hg-C(5)	193.2 (29)	Mn-O(5)	207.4 (17)	C(10)-O(8)	132.1 (38)
Mn-C(1)	184.2 (29)	O(5)-C(7)	121.2 (30)	C(10)-O(7)	122.3 (36)
Mn-C(2)	182.8 (27)	C(7)-C(5)	156.2 (35)	O(8)-C(11)	148.9 (40)
Mn-C(3)	180.5 (28)	C(5)-C(6)	137.9 (39)	C(11)-C(12)	133.5 (31)
Mn-C(4)	186.0 (30)				
C(1)-O(1)	114.2 (40)	C(4)-O(4)	110.7 (40)	O(6)-C(8)	146.6 (30)
C(2)-O(2)	116.2 (35)	C(7)-O(6)	132.7 (32)	C(8)-C(9)	146.2 (53)
C(3)-O(3)	114.7 (36)				

(B) Bond Angles (deg)

Mn-C(6)-C(5)	120.8 (17)	C(10)-O(8)-C(11)	117.4 (25)	Mn-C(4)-O(4)	175.1 (28)
C(6)-C(5)-C(7)	102.9 (22)	O(7)-C(10)-O(8)	127.3 (25)	C(1)-Mn-C(2)	93.2 (13)
C(5)-C(7)-O(5)	124.7 (22)	O(8)-C(11)-C(12)	107.0 (36)	C(1)-Mn-C(3)	89.0 (12)
C(7)-O(5)-Mn	113.7 (15)	C(7)-O(6)-C(8)	117.7 (21)	C(1)-Mn-C(4)	96.8 (13)
O(5)-Mn-C(6)	77.6 (8)	O(6)-C(8)-C(9)	107.4 (24)	C(2)-Mn-C(4)	169.6 (12)
C(6)-C(5)-Hg	130.4 (20)	O(5)-C(7)-O(6)	124.0 (21)	C(1)-Mn-C(6)	168.4 (11)
C(5)-Hg-Br	176.5 (8)	C(5)-C(7)-O(6)	111.2 (21)	C(3)-Mn-O(5)	179.0 (10)
C(5)-C(6)-C(10)	113.8 (23)	C(7)-C(5)-Hg	126.5 (19)	C(3)-Mn-C(6)	102.3 (11)
Mn-C(6)-C(10)	125.4 (19)	Mn-C(1)-O(1)	177.2 (21)	C(4)-Mn-C(6)	86.4 (12)
C(6)-C(10)-O(7)	119.1 (26)	Mn-C(2)-O(2)	175.7 (25)	C(2)-Mn-C(6)	84.5 (11)
C(6)-C(10)-O(8)	113.6 (22)	Mn-C(3)-O(3)	177.4 (28)		

[a] The standard deviations (pm) given in parentheses correspond to the least significant digit(s).

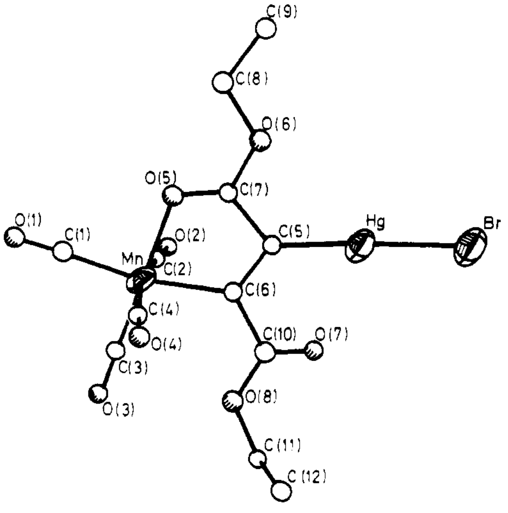

Figure 1.

Table IV. Definitions of Best Planes and Dihedral Angles

(A) Best Planes[a]

plane A	Mn	O(5)	C(7)	C(5)	C(6)
[2.23σ]	(−2.12)	(1.49)	(0.09)	(−2.73)	(3.27)
plane B	C(1)	C(3)	C(6)	O(5)	
[2.94σ]	(−3.06)	(2.85)	(−2.82)	(3.02)	
plane C	Mn	C(3)	C(4)		
plane D	Mn	C(3)	C(2)		
plane E	Mn	C(2)	C(1)		
plane F	Mn	C(3)	C(6)	O(5)	
[0.65σ]	(1.06)	(0.57)	(0.00)	(0.49)	
plane G	C(5)	C(7)	Hg		

(B) Dihedral Angles (deg)

	B	C	D	E	F	G
A	2.7	92.9	82.8	89.9	1.2	1.3
B		95.5	85.4	90.3	1.5	3.2
C			10.0	91.0	94.0	92.4
D				91.0	83.9	82.3
E					90.4	91.0
F						1.7

[a] Standard deviations (σ) are given in brackets while the distances of the atoms from the corresponding planes (pm) appear in parentheses.

tion. However, a parallel experiment employing authentic materials ($EtO_2CC{\equiv}CCO_2Et$ and $(CO)_5MnHgBr$) failed to afford the vinyl ketone complex **8a** described above. Hence, these substrates are clearly not responsible for the formation of **8a** from $Hg[C(=N_2)CO_2Et]_2$ (**2a**) and bromopentacarbonylmanganese (**1**).

The second mechanistic alternative considers the fact that the carbyne fragment $|\dot{C}{-}CO_2Et$ of **2a** shows up in the dinuclear compound $[(\mu\text{-}CCO_2Et)Mn(CO)_4]_2$ (**7a**) as outlined in eq 2. This molecule was suggested to arise from dimerization of the mononuclear species $(CO)_4Mn{\equiv}CCO_2Et$ (**5a**),[36] a possibility that appears all the more likely now that the modified carbyne unit has been found once more as a structural moiety in compound **8a**. The mononuclear carbyne complex **5** was originally expected as the final product but has so far escaped isolation due to rapid subsequent reactions which take place at the reactive metal–carbon triple bond. Apart from the obvious [2 + 2] cyclization pathway affording the stable carbyne-bridged derivative **7a**,[20,21,37] the bromomercury diazo species **6** generated through nucleophilic cleavage of one of the mercury–carbon bonds of the precursor **2a** is available for carbene addition to the five-coordinate $Mn{\equiv}CCO_2Et$ moiety of **5a** (eq 2). This type of reaction is reminiscent of the well-explored carbene transfer from diazoalkanes to metal–metal triple bonds yielding dinuclear addition products.[38-43]

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[36] Herrmann, W. A. "Habilitationsschrift"; Universität Regensburg: West Germany, 1977; p 115. This interpretation receives support from the lack of stable carbyne complexes of type $(CO)_4Mn{\equiv}CR'$ of which there is still not a single example known in the literature.

[37] Dimerization of the mononuclear carbyne species **5a** appears formally analogous to the first step of alkyne addition reactions to $M{\equiv}CR$ units, cf.; Wengrovius, J. H.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 3932.

[38] Messerle L.; Curtis, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 7789.

[39] Herrmann, W. A.; Kriechbaum, G.; Bauer, Ch.; Guggolz, E.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 815.

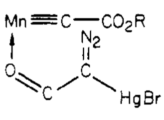
[40] Reviews: (a) Curtis, M. D.; Messerle, L.; Fotinos, N. A.; Gerlach, R. F. *ACS Symp. Ser.* **1981**, *No. 155*, 221. (b) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159. (c) Herrmann, W. A. *J. Organomet. Chem.*, in press.

Table V. Thermal Parameters of Compound **8a**[a]

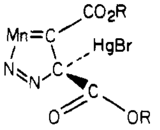
atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U(equiv)
Hg	637	489	331	−24	132	11	484
	7	6	5	5	4	6	3
Br	929	590	671	−83	411	31	725
	25	20	19	17	17	19	12
Mn	625	374	229	19	55	4	409
	27	21	16	15	16	19	13
C(1)	665	518	438	40	129	35	539
	199	172	149	130	140	148	101
C(2)	709	373	369	−44	0	65	484
	188	140	126	13	121	137	39
C(3)	612	574	283	82	116	−57	488
	182	171	122	117	119	145	93
C(7)	526	378	368	−105	39	−121	423
	150	136	115	115	104	130	78
C(5)	667	432	498	−227	−468	180	538
	188	150	150	120	140	133	95
C(6)	745	296	195	0	24	174	412
	190	121	104	90	111	126	83
C(4)	710	542	425	158	−97	96	560
	203	179	146	129	139	153	103
C(8)	999	537	219	−116	−41	42	585
	251	171	117	117	135	174	108
C(9)	1525	770	346	−152	−231	−286	883
	397	259	164	161	199	258	167
C(10)	736	466	307	−59	118	72	502
	210	159	131	117	132	149	098
C(12)	3493	1147	591	−357	−285	368	1747
	989	450	269	282	414	561	373
C(11)	2252	388	546	0	0	0	1062
	548	184	197				203
O(1)	1590	1005	608	41	558	−53	1061
	261	206	153	146	172	204	122
O(2)	1264	584	454	101	−118	176	769
	207	138	116	104	124	142	91
O(3)	1027	633	492	28	−241	−202	720
	179	142	119	104	118	130	86
O(4)	1086	580	865	224	0	149	844
	210	152	176	132	153	143	104
O(5)	640	443	232	−34	45	−5	438
	116	101	73	72	73	90	57
O(6)	730	556	312	−81	69	66	532
	135	119	89	83	88	103	67
O(7)	1277	1015	244	−116	229	−245	843
	211	192	98	109	117	169	101
O(8)	1309	681	349	−268	235	−164	777
	213	151	102	99	118	145	93

[a] Data are multiplied by the factor 10^4. The standard deviations are listed in the second rows.

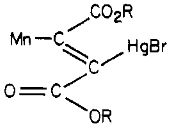
It is not yet known, however, as to whether the final carbyne/carbene coupling process takes place before or after the keto group has attacked the metal center nor can we conclusively prove the existence of one of the plausible intermediates C–E. Further related work concerning this latter problem is aimed at reactivity studies of isolable, coordinatively unsaturated metal carbynes with diazoalkanes.



C



D



E

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Registry No. **1**, 14516-54-2; **2a**, 20363-85-3; **2b**, 22085-17-2; **7a**, 53352-70-8; **7b**, 57219-96-2; **8a**, 85506-87-2; **8b**, 85506-88-3.

Supplementary Material Available: A listing of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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(41) Reductive coupling of cationic mononuclear carbyne complexes to yield α,α'-dicarbene-bridged derivatives is somewhat related to the mechanism proposed for the formation of the vinyl ketone complexes **8a** and **8b**, cf.; Fischer, E. O.; Wittmann, D.; Himmelreich, D.; Neugebauer, D. *Angew. Chem., Int. Ed. Engl.* **1982**, *21* 444; *Angew. Chem. Suppl.* **1982**, 1036–1049.

(42) Reaction of diazoalkanes, $N_2{=}CHR$ (e.g., R = H) with the triosmium complex of composition $Os_3(CO)_9(NCMe)$ (μ-CO)(μ-CH_2) results in the formation of the corresponding alkenyl derivatives $HOs_3(CO)_{10}$-(μ-CH=CHR) in which compounds an overall carbyne/carbene coupling reaction has also occurred. However, carbon–carbon bond formation was shown to *precede* scission of the carbon–hydrogen bond. Therefore, this reaction is to be classified as a carbene/carbene coupling process, cf.: Shapley, J. R.; Sievert, A. C.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* 1981, *103*, 6975.

(43) Two reviewers have pointed out the possibility that the final compounds **8** might arise from attack of **6** upon the dinuclear derivatives **7** rather than upon **5**. Since authentic **6** is not available, we have used closely related diazo compounds such as CH_2N_2, $N_2{=}C(H)CO_2C_2H_5$, $N_2{=}C(CO_2CH_3)_2$ neither of which reacted with compound **7a**. Therefore, the above-mentioned mechanism seems unlikely.