6.22 (t, 1, J = 7 Hz, olefinic H), 7.1–7.4 (m, 15, aromatic H's); mass spectrum, m/e 270 (M^+, 8%), 192 (65), 179 (40), 178 (42), 165 (43), 115 (93), 91 (base).

The catalyzed reaction afforded a 77% yield of **1n** in 8 h reaction time.

1,3-Diphenyl-1(*E*)-butene (1i). A catalyzed reaction with 3-methoxy-1-phenyl-1-butene (**1q**) (vide infra) for 5 h, chromatography on silica gel impregnated with 15% silver nitrate, and elution with hexane led to a 58% yield of oily styrene **1i**:[22] ^{1}H NMR δ 1.40 (d, 3, J = 6 Hz, Me), 3.60 (m, 1, CH), 6.2–6.4 (m, 2, olefinic H's), 7.0–7.3 (m, 10, aromatic H's).

General Procedure for the Reactions of Methylmagnesium Bromide. An ethereal solution of methylmagnesium bromide, 7 mL (17.5 mmol) of 2.5 M, was poured into 10 mL of dry benzene and most of the ether removed by distillation. The acetal, 5.0 mmol, was added and the mixture refluxed under argon. Upon conclusion of the reaction the mixture was worked up as in the above Grignard reactions.

An ethereal solution of methylmagnesium bromide, 7 mL (17.5 mmol) of 2.5 M, was poured into a solution of 320 mg (0.5 mmol) of bis(triphenylphosphine)nickel dichloride in 10 mL of dry benzene, the mixture stirred at room temperature for 15 min, and most of the ether removed by distillation. The acetal, 5.0 mmol, was added and the mixture refluxed under argon.[26] Workup as before yielded the product.

Reactions with Cinnamaldehyde Dimethyl Acetal (1m). An uncatalyzed reaction for 27 h, chromatography on silica gel impregnated with 15% silver nitrate, and elution with hexane led to liquid 3-methyl-1-phenyl-1-butene (**1o**)[20] (40% yield): IR C=C 1610 (w) cm^{-1}; ^{1}H NMR δ 1.03 (d, 6, J = 6 Hz, Me_2), 2.40 (5-line m, 1, J = 6 Hz, CH), 6.1–6.3 (m, 2, olefinic H's), 7.1–7.4 (m, 5, aromatic H's). Further elution gave liquid 4-phenyl-2-pentene (**1p**)[21] (40% yield): IR C=C 1600 (w) cm^{-1}; ^{1}H NMR δ 1.32 (d, 3, J = 6 Hz, Me), 1.59 (d, 3, J = 6 Hz, olefinic Me), 3.3–3.6 (m, 1, CH), 5.4–5.7 (m, 2, olefinic H's), 7.20 (s, 5, aromatic H's).

The catalyzed reaction for 4 h, chromatography on basic alumina (activity I), and elution with hexane gave **1o**[20] in 78% yield.

An ethereal solution of methylmagnesium bromide, 4 mL (6 mmol) of 1.5 M, was added to 10 mL of dry benzene and most of the ether removed by distillation. Acetal, 5 mmol, was added and the mixture refluxed for 2 h. The usual workup, chromatography on basic alumina (activity I), and elution with hexane led to a 92% yield of liquid 3-methoxy-1-phenyl-1(*E*)-butene (**1q**):[18] IR C=C 1600 (w) cm^{-1}; ^{1}H NMR δ 1.31 (d, 3, J = 6 Hz, Me), 3.28 (s, 3, OMe), 3.85 (5-line m, 1, J = 6 Hz, CH), 6.02 (dd, 1, J = 13, 6 Hz, H-2), 6.48 (d, 1, J = 13 Hz, H-1), 7.1–7.4 (m, 5, aromatic H's).

Reactions with Benzaldehyde Dimethyl Acetal (5a). The uncatalyzed reaction for 2 h, chromatography on basic alumina (activity I), and elution with hexane afforded an 89% yield of liquid α-phenylethyl methyl ether (**5b**):[24] ^{1}H NMR δ 1.39 (d, 3, J = 6 Hz, Me), 3.18 (s, 3, OMe), 4.25 (q, 1, J = 6 Hz, CH), 7.30 (s, 5, aromatic H's).

The catalyzed reaction also lasted 2 h. Its workup as above led to an 80% yield of **5b**.[24]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. **1a**, 6044-68-4; (*E*)-**1b**, 18318-79-1; **1c**, 31525-65-2; **1d**, 3542-14-1; (*E*)-**1e**, 3412-44-0; (*E*)-**1f**, 60053-38-5; **1g**, 22665-13-0; (*E*)-**1h**, 4416-96-0; (*E*)-**1i**, 7302-01-4; (*E*)-**1j**, 83605-30-5; **1k**, 51507-36-9; **1l**, 83605-31-6; (*E*)-**1m**, 63511-93-3; (*E*)-**1n**, 18916-14-8; (*E*)-**1o**, 15325-61-8; (*E*)-**1p**, 42461-65-4; (*E*)-**1q**, 24808-74-0; (*E*)-**2**, 56763-59-8; **3a**, 61967-21-3; **3b**, 83605-32-7; **4**, 83605-33-8; **5a**, 1125-88-8; **5b**, 4013-34-7; bis(triphenylphosphine)nickel dichloride, 14264-16-5; phenyl bromide, 108-86-1; methyl bromide, 74-83-9.

Transition Metal Methylene Complexes. 36.[1] Chelate-Type Bridging α-Diazo Ketones through Cleavage of a Metal–Metal Triple Bond[†]

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Received August 18, 1982

Cleavage of the metal–metal triple bond of bis[dicarbonyl(η^5-pentamethylcyclopentadienyl)molybdenum](*Mo≡Mo*) (**1a**) is effected by the α-ketodiazoalkanes **2a–d** resulting in the formation of the chelate-type dinuclear insertion products **3a–d**. An X-ray crystallographic study of the key compound **3a** revealed the central structural frame $\mathrm{Mo{=}N\overline{NC(R){=}C(CH_3)OMo}}$ [$\mathrm{R = C({=}O)CH_3}$] to be composed of an essentially planar five-membered metallacyclic unit that coordinates to the second metal atom via a terminal nitrogen group (Mo(2)–N(2) = 183.6 (17) pm; N(1)–N(2) = 124.4 (24) pm). No molybdenum–molybdenum bond is present after α-diazo ketone addition to the unsaturated organometallic precursor **1a**, with the nonbonding MoMo distance being longer than 380 pm. Metal–metal bond cleavage appears to be prevalent in the reactions of metal–metal triple bonds with carbonyl-flanked diazoalkanes capable of chelating mononuclear organometallic fragments.

Introduction

Organometallic compounds having metal–metal double bonds offer a straightforward route to μ-alkylidene complexes of type $\mathrm{L_x\overline{MCRR'M}L_x}$ when treated with various diazoalkanes.[4–6] These reactions normally proceed rapidly even under very mild conditions, and not one case is known in which intermediates containing the intact diazo pre-

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[†] In memoriam of Rowland Pettit.

(1) Communication 35: Xiang, S. F.; Chen, H. W.; Eyermann, C. F.; Jolly, W. L.; Smit, S. P.; Theopold, K. H.; Bergman, R. G.; Herrmann, W. A.; Pettit, R. *Organometallics* **1982**, *1*, 1200. Communication 34: Herrmann, W. A.; Bauer, Ch.; Mayer, K. K. *J. Organomet. Chem.* **1982**, *236*, C18.

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cursor have been detected unambiguously. High reactivity toward diazoalkanes is also observed for the dinuclear organometallic compounds having metal-to-metal bond orders greater than 2. Apart from clean addition of diphenyldiazomethane to the $Mo{\equiv}Mo$ triple bond of Chisholm's hexaalkoxydimolybdenum compounds $Mo_2(OR)_6$,[7] the reactions of the prototypal metal–metal triple-bonded compounds $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$ (**1b**) with the same and closely related diazo derivatives has been studied in greater detail by Curtis and co-workers,[8-10] who observed the remarkable stability of 1/1 diazoalkane addition products to the metal–metal triple bond. Since it appeared that this particular metal–metal bond does not obey a uniform reactivity pattern in the sense that the nature of the diazoalkanes bears a decisive influence upon the final products,[8-14] we have entered a systematic investigation by using a broad variety of diazo precursors as we had done before with the related rhodium compound $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CO)]_2$.[4,5] Continuing this work, we have now found that the unusual insertion reaction of α-diazo ketones into the metal–metal triple bond of **1b** as reported recently[13] appears to be of general applicability.

Experimental Section

All operations were performed under air-free conditions by using absolutely dry solvents; for further details regarding the general working technique, the reader is referred to previous papers of this series.[15-17] The molybdenum complex **1a** was prepared according to the procedure published by King and Bisnette[18] from hexacarbonylmolybdenum[17] and distilled pentamethylcyclopentadiene[19] in boiling *n*-decane and was purified by means of column chromatography and subsequent recrystallization from CH_2Cl_2/diethyl ether. Elemental analyses were performed in the Mikroanalytische Laboratorien (vorm. A. Bernhardt), Gummersbach, West Germany, and in the microanalytical laboratory of the Universität Frankfurt am Main. Field-desorption mass spectra were recorded by Dr. K. K. Mayer and E. Fischer at the Universität Regensburg.

1. Reactions of 1a with 3-Diazo-2,4-dioxopentane (Diacetyldiazomethane, 2a). A solution of 574 mg (1 mmol) of **1a** in 25 mL of tetrahydrofuran (THF) was cooled to −30 °C and stirred while 140 mg of (1.1 mmol) of the α-ketodiazoalkane **2a** was added as a solid. The solution was then allowed to warm up to room temperature with continued stirring, and after approximately 1 h the solution was deep pink. The solvent was removed under reduced pressure and the solid residue washed three times with cold *n*-hexane. The product was extracted from this residue with diethyl ether. Low-temperature crystallization of this ether extract from dichlormethane/diethyl ether mixtures gave **3a** as a crystalline, dark pink solid in 78% yield (550 mg). The compound is somewhat air sensitive both in the solid state and in solution. Anal. Calcd for $C_{29}H_{36}Mo_2N_2O_6$ (700.50): C, 49.72; H, 5.18; Mo, 27.39; N, 4.00. Found: C, 49.83; H, 5.16; Mo, 27.45; N, 3.84; molecular weight 692 (field-desorption mass spectrum from toluene solution; ^{92}Mo).

2. Reaction of 1a with 1-Diazo-1-phenyl-2-oxopropane (Acetylphenyldiazomethane, 2b). A solution of 574 mg (1 mmol) of **1a** in 25 mL of THF was cooled to −20 °C and stirred while 160 mg (1 mmol) of the α-diazo ketone **2b** was added. The solution was allowed to warm to room temperature and then stirred for another 2 h after which time the color had changed from red to pinkish brown. The solvent was then removed under reduced pressure. The product was found to be soluble in *n*-hexane and was therefore extracted from the solid residue with the same solvent and then crystallized from *n*-hexane/diethyl ether mixtures giving the desired compound **3b** as a microcrystalline, dark pink-brown solid, yield 500 mg (68%). Like the diacetyldiazomethane derivative **3a**, compound **3b** is also air sensitive both in the solid state and in solution. Anal. Calcd for $C_{33}H_{38}Mo_2N_2O_5$ (734.26): C, 53.98; H, 5.18; Mo, 26.13; N, 3.82. Found: C, 53.68; H, 5.29; Mo, 25.85; N, 3.68; molecular weight 726 (field-desorption mass spectrum from toluene solution; ^{92}Mo).

3. Reaction of 1a with (4-Methoxybenzoyl)(4-methoxyphenyl)diazomethane (2c). Compound **3c** was prepared by adding 300 mg (1.1 mmol) of the α-diazo ketone **2c** to a cooled solution (0 °C) of 574 mg (1 mmol) of **1a** in 25 mL of THF. The solution was allowed to warm to room temperature and then stirred for another 2 h. During this time, the solution changed from red to dark brown. The solvent was removed under reduced pressure and the product subsequently extracted from the solid residue with diethyl ether. Low-temperature crystallization of this extract from dichloromethane/diethyl ether mixtures gave a microcrystalline, dark pink solid in 82% yield (700 mg). This compound is again air sensitive in both the solid state and in solution and, at room temperature, is slowly converted to a brown compound of hitherto unknown structure. Anal. Calcd for $C_{40}H_{44}Mo_2N_2O_7$ (856.69): C, 56.11; H, 5.14; Mo, 22.41; N, 3.27. Found: C, 56.23; H, 4.99; Mo, 22.55; N, 3.01; molecular weight 848 (field-desorption mass spectrum from toluene solution; ^{92}Mo).

4. Reaction of 1a with 3-Oxo-2-diazobutane (Acethylmethyldiazomethane, 2d). A solution of 574 mg (1 mmol) of **1a** in 25 mL of THF was cooled to −20 °C and stirred while 98 mg (1 mmol) of α-ketodiazoalkane **2d** was added as a solid. The solution was allowed to warm to room temperature, and stirring was continued for approximately 30 min before the solvent was removed under reduced pressure. This residue was washed twice with *cold n*-hexane (ca. −10 °C) and the product recrystallized from dichloromethane/diethyl ether mixtures, giving **3d** as a dark pink crystalline solid in 74% yield (500 mg). The compound is also air sensitive both in the solid state and in solution. Anal. Calcd for $C_{28}H_{36}Mo_2N_2O_5$ (672.49): C, 50.01; H, 5.40; N, 4.17. Found: C, 50.00; H, 5.20; N, 4.08; molecular weight 664 (field-desorption mass spectrum from toluene solution; ^{92}Mo).

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(3) (a) Royal Society Fellowship, 1982/1983. (b) Karl Winnacker Fellow, 1979–1984; to whom all correspondence should be addressed.

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Table I. Spectroscopic Characterization of the (μ-Diazo ketone)molybdenum Complexes 3a–d

	IR ν(CO),[a] cm^{-1}	^{1}H NMR[b]
3a[a]	1969 (st), 1928 (st), 1884 (st), 1839 (st) [KBr] 1974 (m), 1933 (st), 1893 (w), 1842 (m) [CH_2Cl_2] 1970 (w), 1940 (st), 1898 (m), 1854 (m) [diethyl ether]	$\delta(C_5(CH_3)_5)$ 1.99 (s, 15 H), 1.79 (s, 15 H) $\delta(C(=O)CH_3)$ 2.27 (s, 3 H), 2.24 (s, 3 H)
3b	1951 (st), 1924 (st), 1871 (st), 1836 (st) [KBr] 1956 (m-st), 1930 (st), 1874 (m-st), 1840 (st) [CH_2Cl_2] 1954 (w), 1933 (st), 1878 (m), 1852 (m) [diethyl ether]	$\delta(C_5(CH_3)_5)$ 1.71 (s, 15 H), 1.84 (s, 15 H) $\delta(C(=O)CH_3)$ 1.96 (s, 3 H), $\delta(C_6H_5)$ 7.3 (m, 5 H)
3c	1955 (st), 1928 (st), 1863 (st), 1848 (st) [KBr]	$\delta(C_5(CH_3)_5)$ 1.77 (s, 15 H), 1.80 (s, 15 H) $\delta(CH_3)$ 3.80 (s, 3 H), 3.73 (s, 3 H) $\delta(C_6H_4)$ 7.0 (m, 8 H)
3d	1956 (st), 1923 (st), 1872 (st), 1832 (st) [KBr] 1951 (m), 1925 (st), 1868 (m), 1838 (m) [CH_2Cl_2] 1954 (m), 1933 (st), 1875 (m), 1850 (m) [diethyl ether]	$\delta(C_5(CH_3)_5)$ 2.00 (s, 15 H), 1.77 (s, 15 H) $\delta(C(=O)CH_3)$ 2.01 (s, 3 H) $\delta(CH_3)$ 1.76 (s, 3 H)

[a] Perkin-Elmer infrared grating spectrophotometer 283 B. [b] 270 MHz, 25 °C, $CDCl_3$, internal $Si(CH_3)_4$. [c] $^{13}C\{^1H\}$NMR spectrum (67.88 MHz, Bruker; 25 °C, $CDCl_3$, internal $Si(CH_3)_4$): $\delta(C_5(CH_3)_5)$ 109.88 and 109.01, $\delta(C_5(CH_3)_5)$ 11.06 and 10.36, $\delta(C(=O)\mathit{C}H_3)$ 25.01 and 32.18, $\delta(\mathit{C}(=O)CH_3)$ 178.02 and 189.94; $\delta(\mathit{C}(COCH_3)_2)$ 104.92; $\delta(Mo\mathit{C}O)$ 264.99, 244.65, 240.68, ~258.

Table II. Atomic Positional Parameters of the (μ-Diazo ketone)molybdenum Complex 3a[a]

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Mo(1)	0.1557	0.4040	0.1285	H(15A)	0.0359	−0.0503	−0.1392
Mo(2)	0.1163	0.0841	−0.0627	H(15B)	0.0258	−0.1840	−0.1460
N(1)	0.1058	0.2929	0.0453	H(15C)	0.0465	−0.1285	−0.2075
N(2)	0.1080	0.2173	−0.0081	C(16)	0.1224	−0.1162	−0.0783
C(1)	0.1895	0.2792	0.1169	C(17)	0.1310	−0.1749	−0.1482
O(1)	0.2113	0.2086	0.1101	H(17A)	0.1100	−0.1890	−0.2037
C(2)	0.1896	0.3672	0.2466	H(17B)	0.1407	−0.2481	−0.1199
O(2)	0.2109	0.3392	0.3175	H(17C)	0.1522	−0.1333	−0.1582
C(3)	0.1622	0.1290	−0.0979	C(18)	0.1487	−0.0873	0.0037
O(3)	0.1900	0.1510	−0.1143	C(19)	0.1941	−0.1030	0.0423
C(4)	0.0856	0.1309	−0.1820	H(19A)	0.1947	−0.1391	−0.0108
O(4)	0.0657	0.1546	−0.2583	H(19B)	0.2006	−0.1600	0.0889
C(5)	0.0687	0.3198	0.0606	H(19C)	0.2131	−0.0405	0.0590
C(6)	0.0283	0.2896	−0.0101	C(20)	0.1339	0.5978	0.0840
O(6)	0.0008	0.2885	0.0182	C(21)	0.0966	0.6485	0.0870
C(7)	0.0234	0.2812	−0.1030	H(21A)	0.1045	0.6885	0.1428
H(7A)	0.0370	0.3239	−0.1348	H(21B)	0.0719	0.6087	0.0771
H(7B)	−0.0011	0.3197	−0.1092	H(21C)	0.0934	0.7040	0.0404
H(7C)	0.0180	0.2034	−0.1263	C(22)	0.1363	0.5459	0.0135
C(8)	0.0743	0.3798	0.1352	C(23)	0.1090	0.5210	−0.0742
O(8)	0.1094	0.4171	0.1835	H(23A)	0.0905	0.4791	−0.1229
C(9)	0.0421	0.4104	0.1717	H(23B)	0.1069	0.6031	−0.0871
H(9A)	0.0196	0.3909	0.1203	H(23C)	0.1030	0.5068	−0.0216
H(9B)	0.0446	0.4939	0.1770	C(24)	0.1738	0.5054	0.0233
H(9C)	0.0385	0.3788	0.2235	C(25)	0.1953	0.4411	−0.0299
C(10)	0.1282	−0.0403	0.0594	H(25A)	0.1729	0.4605	−0.0816
C(11)	0.1449	−0.0012	0.1488	H(25B)	0.2009	0.3592	−0.0306
H(11A)	0.1253	0.0369	0.1674	H(25C)	0.2180	0.4854	−0.0297
H(11B)	0.1680	0.0473	0.1625	C(26)	0.1999	0.5419	0.1133
H(11C)	0.1520	−0.0745	0.1791	C(27)	0.2432	0.5452	0.1632
C(12)	0.0864	−0.0470	0.0053	H(27A)	0.2394	0.4826	0.1214
C(13)	0.0542	−0.0195	0.0410	H(27B)	0.2595	0.5185	0.2209
H(13A)	0.0339	−0.0086	−0.0158	H(27C)	0.2561	0.6093	0.1459
H(13B)	0.0559	0.0490	0.0765	C(28)	0.1734	0.5959	0.1482
H(13C)	0.0477	−0.0858	−0.0697	C(29)	0.1877	0.6575	0.2364
C(14)	0.0846	−0.0947	−0.0742	H(29A)	0.1701	0.7208	0.2362
C(15)	0.0446	−0.1264	−0.1497	H(29B)	0.2099	0.6869	0.2225
				H(29C)	0.1972	0.6219	0.2940

[a] Standard deviations: for x/a, Mo ±0.0001, C, O, N ±0.004–0.006, H ±0.006–0.008; for y/b, Mo ±0.002; C, O, N ±0.0013–0.0024; H ±0.0020–0.0026; for z/c, Mo ±0.0011; C, N, O, H ±0.0010–0.0018.

5. X-ray Structure Determination of Compound 3a. Rotation and Weissenberg photographs (Cu Kα radiation) showed the crystal to be monoclinic and provided rough lattice constants. Exact lattice parameters were derived from the setting angles of 25 machine-centered reflections (Syntex R3, monochromatic Mo Kα radiation, graphite monochromator). Data collection (θ–2θ scans, $2.5° \leq 2\theta \leq 55°$) yielded 1603 independent reflections with $I > 3.0\sigma(I)$. Lorentz and polarization corrections as well as empirical (ψ scans) absorption correction were applied. The crystal data are given in Table V. The positions of the atoms were taken from Patterson and Fourier maps; the position of the H atoms were fixed with the program HFIX.[25] Final refinement by a cascade-matrix procedure with anisotropic temperature factors for the heavy atoms Mo(1) and Mo(2) and with isotropic temperature factors for the other non-hydrogen atoms converged with a weighted $R = 0.061$, the weighting scheme being $W = 1/\sigma^2(F)$. Calculations were carried out on a NOVA 3 computer, the plots being drawn on a Tektronic plotter. The program package was SHELXTL;[25] the scattering factors were those of Hanson, Herman, Lea and Skillman.[26] The atom numbering corresponds to the one used in Figure 1. Atomic coordinates are listed in Table II, bond distances and bond angles are listed in Table III, and data of some least-squares planes are given in Table IV.

Synthetic and Crystallographic Results. The molybdenum complex **1a** reacts in tetrahydrofuran solution with the α-diazo ketones **2a–d** under mild conditions (−30 to +25 °C) to give the

Table III. Structural Parameters of the (μ-Diazo ketone)molybdenum Complex 3a

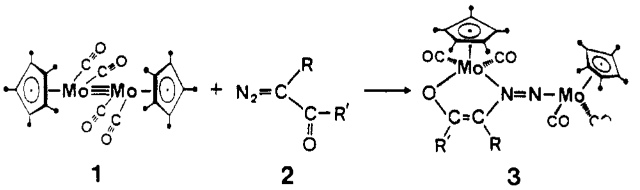
(A) Bond Distances (pm)

Mo(1)-N(1)	224.4 (14)	Mo(1)-C(20)	237.8 (28)	Mo(1)-C(26)	231.1 (25)
Mo(1)-C(1)	192.4 (22)	Mo(1)-C(22)	237.9 (26)	Mo(1)-C(28)	227.8 (24)
Mo(1)-C(2)	191.2 (20)	Mo(1)-C(24)	232.9 (29)	Mo(1)-O(8)	214.5 (15)
Mo(2)-N(2)	183.6 (17)	Mo(2)-C(10)	234.6 (20)	Mo(2)-C(16)	232.6 (22)
Mo(2)-C(3)	199.1 (24)	Mo(2)-C(12)	233.2 (21)	Mo(2)-C(18)	234.1 (23)
Mo(2)-C(4)	192.8 (22)	Mo(2)-C(14)	231.7 (25)		
N(1)-N(2)	124.4 (24)	N(1)-C(5)	146.9 (28)		
C(8)-C(5)	133.7 (28)	C(10)-C(12)	144.9 (25)	C(10)-C(11)	142.5 (28)
C(8)-C(9)	151.0 (32)	C(12)-C(14)	137.7 (30)	C(12)-C(13)	149.5 (35)
C(8)-O(8)	130.1 (20)	C(14)-C(16)	140.1 (31)	C(14)-C(15)	156.4 (27)
C(6)-C(5)	153.7 (26)	C(16)-C(18)	137.1 (25)	C(16)-C(17)	143.6 (41)
C(6)-C(7)	144.8 (31)	C(18)-C(10)	145.2 (33)	C(18)-C(19)	153.7 (27)
C(6)-O(6)	122.8 (35)	C(20)-C(22)	131.3 (39)	C(20)-C(21)	147.5 (49)
C(1)-O(1)	155.9 (28)	C(22)-C(24)	137.7 (38)	C(22)-C(23)	143.9 (41)
C(2)-O(2)	117.6 (25)	C(24)-C(26)	148.6 (30)	C(24)-C(25)	153.0 (49)
C(3)-O(3)	114.7 (31)	C(26)-C(28)	140.5 (35)	C(26)-C(27)	148.1 (31)
C(4)-O(4)	121.9 (28)	C(28)-C(20)	143.5 (25)	C(28)-C(29)	150.8 (31)

(B) Bond Angles (deg)

N(1)-Mo(1)-C(1)	85.3 (0.7)	N(1)-Mo(1)-O(8)	73.3 (0.6)	C(1)-Mo(1)-O(8)	134.2 (0.8)
N(1)-Mo(1)-C(2)	124.9 (0.8)	C(1)-Mo(1)-C(2)	74.4 (0.9)	C(2)-Mo(1)-O(8)	85.3 (0.8)
N(2)-Mo(2)-C(3)	102.3 (0.9)	N(2)-Mo(2)-C(4)	96.7 (0.9)	C(3)-Mo(2)-C(4)	83.2 (1.0)
Mo(2)-N(2)-N(1)	166.1 (1.4)	Mo(1)-N(1)-C(5)	111.3 (1.1)	N(2)-N(1)-C(5)	123.1 (1.5)
Mo(1)-N(1)-N(2)	125.6 (1.3)				
N(1)-C(5)-C(8)	113.7 (1.5)	C(5)-C(6)-O(6)	113.4 (2.0)	C(5)-C(8)-C(9)	125.2 (1.7)
N(1)-C(5)-C(6)	120.0 (1.8)	C(7)-C(6)-O(6)	124.2 (1.9)	C(9)-C(8)-O(8)	113.8 (1.7)
C(6)-C(5)-C(8)	126.1 (2.0)	C(5)-C(8)-O(8)	121.0 (2.0)	C(8)-O(8)-Mo(1)	117.3 (1.2)
C(5)-C(6)-C(7)	121.7 (2.2)				
Mo(1)-C(20)-C(22)	74.0 (1.7)	Mo(1)-C(26)-C(28)	70.9 (1.4)	C(10)-C(12)-C(14)	106.3 (1.8)
Mo(1)-C(20)-C(28)	68.3 (1.4)	C(24)-C(26)-C(28)	103.5 (1.9)	Mo(2)-C(14)-C(12)	73.4 (1.3)
C(22)-C(20)-C(28)	105.6 (2.2)	Mo(1)-C(28)-C(20)	75.9 (1.5)	Mo(2)-C(14)-C(16)	72.8 (1.3)
Mo(1)-C(22)-C(20)	73.9 (1.6)	Mo(1)-C(28)-C(26)	73.4 (1.4)	C(12)-C(14)-C(16)	112.7 (1.6)
Mo(1)-C(22)-C(24)	71.0 (1.5)	C(20)-C(28)-C(26)	110.7 (1.9)	Mo(2)-C(16)-C(14)	72.1 (1.4)
C(20)-C(22)-C(24)	114.4 (2.1)	Mo(2)-C(10)-C(12)	71.4 (1.1)	Mo(2)-C(16)-C(18)	73.5 (1.4)
Mo(1)-C(24)-C(22)	75.0 (1.7)	Mo(2)-C(10)-C(18)	71.8 (1.2)	C(14)-C(16)-C(18)	105.3 (2.0)
Mo(1)-C(24)-C(26)	70.6 (1.5)	C(12)-C(10)-C(18)	104.6 (1.6)	Mo(2)-C(18)-C(10)	72.1 (1.2)
C(22)-C(24)-C(26)	105.8 (2.4)	Mo(2)-C(12)-C(10)	72.5 (1.2)	Mo(2)-C(18)-C(16)	72.3 (1.2)
Mo(1)-C(26)-C(24)	72.0 (1.4)	Mo(2)-C(12)-C(14)	72.2 (1.4)	C(10)-C(18)-C(16)	111.0 (1.8)
C(20)-Mo(1)-C(22)	32.1 (0.9)	C(28)-Mo(1)-C(20)	35.8 (0.7)	C(14)-Mo(2)-C(16)	35.1 (0.8)
C(22)-Mo(1)-C(24)	34.0 (0.9)	C(10)-Mo(2)-C(12)	36.1 (0.6)	C(16)-Mo(2)-C(18)	34.2 (0.6)
C(24)-Mo(1)-C(26)	37.4 (0.8)	C(12)-Mo(2)-C(14)	34.4 (0.7)	C(18)-Mo(2)-C(10)	36.1 (0.8)
C(26)-Mo(1)-C(28)	35.6 (0.8)				
Mo(1)-C(1)-O(1)	176.2 (1.9)	Mo(2)-C(3)-O(3)	176.1 (1.6)	Mo(2)-C(4)-O(4)	176.7 (2.0)
Mo(1)-C(2)-O(2)	176.5 (2.0)				

dinuclear products **3a–d** in 65–82% yield after recrystallization of the crude mixtures (eq 1). These compounds are soluble in most organic solvents except for unpolar ones such as *n*-pentane. Both elemental analyses and field-desorption mass spectra establish compounds **3a–d** to represent 1/1 addition products of the α-diazoketones **2a–d** to the metal–metal triple bond of the organometallic precursor **1a**. It can be concluded from the IR and ^{1}H and ^{13}C NMR spectra (Table I) that two chemically different (η^5-C_5Me_5)Mo$(CO)_2$ fragments are present but no clear-cut information about the coordination mode of the diazo ligands and the arrangement of the respective structural units can be deduced from these data. Since two previous papers[13,14] have shown that great care must be taken with the assignment of structure solely based upon the spectroscopic similarity with apparently analogous derivatives, an X-ray diffraction study of the key compound **3a** was undertaken in order to achieve unambiguous proof of structure (Figure 1).



1 **2** **3**

• = CH_3

(1)

2,3	a	b	c	d
R	C(=O)CH$_3$	C$_6$H$_5$	C$_6$H$_4$-*p*-OCH$_3$	CH$_3$
R′	CH$_3$	CH$_3$	C$_6$H$_4$-*p*-OCH$_3$	CH$_3$

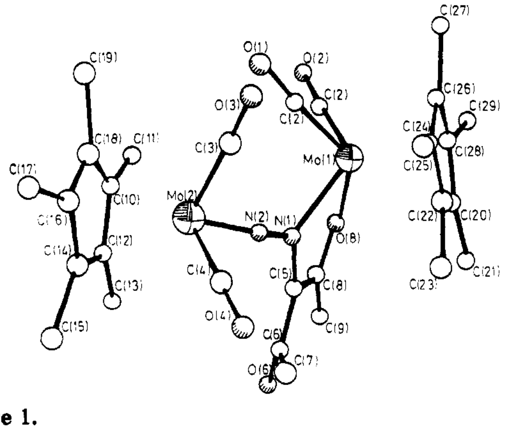


Figure 1.

Compound **3a** crystallizes from dichloromethane/diethyl ether in the monoclinic space group C_{2h}^{6}—$C2/c$ (Table V). The frac-

Table IV. **Best Planes of the (μ-Diazo ketone)molybdenum Complex 3a**[a]

Plane A (std dev 0.0)

Mo(1)*	N(1)*	N(2)*	Mo(2)
0.0	0.0	0.0	42.8

Plane B (0.01)

Mo(2)*	N(1)*	N(2)*	Mo(1)
0.02	−0.02	0.00	187.69

Plane C (6.96)

Mo(1)*	Mo(2)*	N(1)*	N(2)*
−0.15	4.43	6.93	−11.22

Plane D (6.88)

Mo(2)*	N(1)*	N(2)*	C(5)*	Mo(1)
4.32	7.02	−11.01	−0.33	66.6

Plane E (0.0)

Mo(1)*	N(1)*	O(8)*	N(2)	Mo(2)
0.0	0.0	0.0	29.88	114.14

Plane F (8.9)

Mo(1)*	N(1)*	C(5)*	C(8)*	O(8)*	Mo(2)
−8.95	10.89	−7.96	−4.61	10.63	123.05

Plane G (0.0)

N(1)*	N(2)*	C(5)*	Mo(1)	Mo(2)
0.0	0.0	0.0	11.12	42.76

Plane H (9.86)

N(1)*	C(5)*	C(6)*	O(6)*	C(8)*	N(2)
−6.27	−2.78	16.39	−12.15	4.81	−40.85

Plane I (15.21)

N(1)*	C(5)*	C(6)*	C(7)*	C(8)*	C(9)*
−1.05	−11.66	−24.81	20.55	14.38	2.58

Plane K (1.2)

C(10*	C(12)*	C(14)*	C(16)*	C(18)*	Mo(2)
1.25	−0.33	−0.66	1.46	−1.72	199.4

Plane L (1.86)

C(20)*	C(22)*	C(24)*	C(26)*	C(28)*	Mo(1)
0.28	1.49	−2.37	2.46	−1.86	−201.12

Dihedral Angles (deg)

	B	C	D	E	F	G	H	I	K	L
A	90.7	11.4	15.4	16.7	13.7	3.4	162.5	151.9	152.4	149.7
B		98.4	77.9	81.7	88.1	87.3	82.7	72.0	73.0	64.2
C			20.5	28.0	24.2	13.9	155.4	148.3	148.5	149.6
D				22.5	24.0	12.7	148.6	137.0	137.6	134.3
E					6.4	15.1	164.2	152.3	153.3	145.7
F						13.4	170.3	158.1	159.0	151.9
G							160.9	149.6	150.3	146.8
H								12.3	11.5	18.5
I									1.1	9.0
K										10.0

[a] Atoms defining a plane are symbolized by an asterisk. The distances of the atoms from the corresponding plane are given in pm.

tional atomic coordinates are listed in Table II while the bonding parameters and best planes including dihedral angles are summarized in Tables III and IV, respectively.

Figure 1 illustrates the salient structural features and shows that the α-diazo ketones used in the above-mentioned reactions have effected cleavage of the molybdenum–molybdenum triple bond of **1a**, yielding two independent $(\eta^5\text{-}C_5Me_5)Mo(CO)_2$ fragments. The metals are now held together by means of the dinitrogen group of the structurally intact diazoalkane ligands, with each metal center being coordinated to a different nitrogen atom [Mo(1)–N(1) and Mo(2)–N(2)]. Because a metal–metal bond is no longer present [d(Mo–Mo) > 380 pm], both $(\eta^5\text{-}C_5Me_5)Mo(CO)_2$ units require three-electron ligands in order to meet the EAN rule and to maintain their diamagnetic character. Here, the α-diazo ketones **2a–d** once more prove ideal systems for acting as bridging six-electron ligands:

(1) The terminal nitrogen atom N(2) exclusively binds to Mo(2) producing a metal–nitrogen bond which exhibits significant multiple bond character [d(Mo–N(2)) = 183.6 (7) pm]. In spite of the fact that the resulting diazometal core Mo(2)–N(2)–N(1) deviates somewhat from linearity [∠Mo(2)–N(2)–N(1) = 166.1 (14)°], a close analogy between this group and the previously characterized methane diazonium complexes of types $(\eta^5\text{-}C_5H_5)W(CO)_2(N{=}NCH_3)$[20,21] and $(\eta^5\text{-}C_5H_5)W(CO)_2(N{=}\overline{NCH_3)}Cr(CO)_5$[22,23] can be drawn. This comparison is also justified by considering the very similar nitrogen–nitrogen bond lengths recorded in the range of 121-126 pm for all these derivatives [d(N(1)–N(2)) = 124.4 (24) pm], indicating considerable

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(20) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 355. Herrmann, W. A., Biersack, H. *Chem. Ber.* **1977**, *110*, 896.

(21) Hillhouse, G. L.; Haymore, B. L.; Herrmann, W. A. *Inorg. Chem.* **1979**, *18*, 2423.

(22) Herrmann, W. A.; Bistram, S. A. *Chem. Ber.* **1980**, *113*, 2648.

(23) Hillhouse, G. L.; Haymore, B. L.; Bistram, S. A.; Herrmann, W. A. *Inorg. Chem.*, in press.

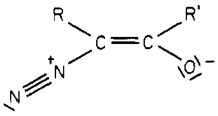
Table V. Crystallographic Data

formula	$C_{29}H_{36}Mo_2N_2O_6$
cryst size	0.3 × 0.5 × 0.2 mm
space group	monoclinic; C^6_{2h}-$C2/c$; $Z = 8$
mol wt	700.496 amu
color	dark red
cell constants	
a, pm	3590.0 (12)
b, pm	1144.4 (4)
c, pm	1613.4 (6)
β, deg	110.56 (3)
density (X-ray)	$\mu = 1.499$ Mg m^{-3}
V, pm^3	6206.23 × 10^6
t_{opt}, cm	0.487
linear abs coeff	$\mu = 4.11$ cm^{-1}
systematic absences	$h0k$ ($l = 2n + 1$), hkl ($h + k = 2n + 1$)
scan range	2.5° ⩽ 2θ ⩽ 55°
irradiation	Mo Kα (λ = 71.069 pm)
no. of nonzero reflctns	1683
R values	$R_{iso} = 0.079$, $R_{aniso} = 0.077$,[a] $R_w = 0.061$

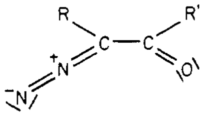
[a] Only the heavy atoms were refined anisotropically.

double-bond character. The metal center Mo(2) is in a distorted tetrahedral environment provided that the π-bonded pentamethylcyclopentadienyl ligand is considered as occupying only a single position.

(2) A completely different geometry is encountered for Mo(1): this metal is part of an essentially planar five-membered ring (Table IV; plane F) which results from the chelating capabilities of carbonyl-flanked diazoalkanes.[24] This behavior is understandable in view of the fact that the enol type form A contributes more to the ground state than the alternative ketonic resonance form B. Accordingly, the carbon–carbon distance in the diazo



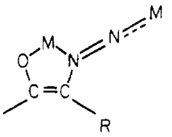
A



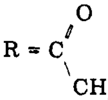
B

skeleton is quite small (*d*(C(5)–C(8)) = 133.7 (28) pm) and very much resembles that of a typical double bond. In addition, a significant lengthening of the adjacent carbonyl group compared with a standard keto functionality is found [*d*(C(8)–O(8)) = 130.1 (20) pm] as should be expected from the structure A.

Note in this context that the uncomplexed keto group C(6)–O(6) exhibits a much smaller bond length (122.8 (35) pm). The Mo(1)–N(1) bond is considerably longer (224.4 (14) pm) than the Mo(2)–N(2) bond (183.6 (17) pm) and approaches a metal-to-nitrogen single bond. Compounds **3a–d** thus turn out to belong to the previously discovered chelate-type bridging α-diazo ketones.[13] It is interesting to note that the structural details of the cyclopentadienyl derivative **4**[13] hardly deviate from those of the

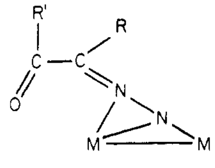


C

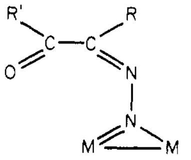
3a, R =  $\mathrm{C}(\overset{\mathrm{O}}{/\!/})\mathrm{CH_3}$, R' = CH_3

4, R = C_6H_5, R' = C_6H_5[13]

pentamethylcyclopentadienyl compound **3a** discussed in this paper. However, it is not trivial that in the present case the structural type C is again verified since the diazo precursor **2a** (diacetyldiazomethane) displays a second α-keto substituent which could equally well coordinate to the metal centers. In light of earlier reports documenting the pronounced tendency of the molybdenum compounds [(η^5-C_5R_5)Mo(CO)$_2$]$_2$ (R = CH_3, **1a**; H, **1b**) to strongly bind diazoalkanes via the terminal nitrogen atoms,[8–10,13,14] it is highly probable that the initial reaction step of eq 1 involves formation of an intermediate having structure D[14] or E.[8] Subsequent rearrangement with concomitant metal–oxygen



D



E

bond making and metal–metal bond cleavage produces the final compounds of type C. The overall reactions are thus best described as insertions of the chelating α-diazo ketones **2a–d** into the metal–metal triple bond of the precursors **1a** and **1b**.

Acknowledgment. This work was generously supported by the Royal Society, London, the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Hoechst Aktiengesellschaft.

Registry No. **1a**, 12132-04-6; **2a**, 29397-21-5; **2b**, 3893-35-4; **2c**, 18627-14-0; **2d**, 14088-58-5; **3a**, 83435-81-8; **3b**, 83435-82-9; **3c**, 83435-83-0; **3d**, 83435-84-1.

Supplementary Material Available: Tables of observed and calculated structure factors, atomic parameters, and thermal parameters (18 pages). Ordering information is given on any current masthead page.

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[24] Similar five-membered metallacycles (M = Co) were obtained from (η^5-C_5H_5)Co(CO)$_2$ and diazo ester precursors: cf. Herrmann, W. A.; Steffl, I.; Ziegler, M. L.; Weidenhammer, K. *Chem. Ber.* **1979**, *112*, 1731.

[25] Sheldrick, G. M. SHELXTL Version 1980, Anorganisch Chemisches Institut der Universität Göttingen.

[26] Hanson, H.; Herman, F.; Lea, J. D.; Skillman, S. *Acta Crystallogr.* **1964**, *17*, 1040–1044.