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Preparation and Properties of Dinitrogen-Molybdenum Complexes. 6.¹ Syntheses and Molecular Structures of a Five-Coordinate $\text{Mo}(0)$ Complex $\text{Mo}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$ and a Related Six-Coordinate Complex $\text{Mo}(\text{CO})(\text{N}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$

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Abstract: The reaction of *trans*- $\text{Mo}(\text{N}_2)_2(\text{dpe})_2$ ($\text{dpe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) with benzyl propionate at reflux in benzene under dinitrogen yielded *trans*- $\text{Mo}(\text{CO})(\text{N}_2)(\text{dpe})_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$. On bubbling argon gas into a solution of the latter complex, a stable five-coordinate complex $\text{Mo}(\text{CO})(\text{dpe})_2$ was obtained and this reaction was reversible. The structures of those two complexes have been determined from three-dimensional x-ray counter data. The complex $\text{Mo}(\text{CO})(\text{dpe})_2$ crystallizes in the monoclinic system with the space group $P2_1/n$, with the following cell dimensions: $a = 17.849$ (3), $b = 24.295$ (4), $c = 10.939$ (2) Å; $\beta = 99.117$ (4)°, $V = 4683.5$ (13) Å³, and $Z = 4$. The molybdenum atom has square-pyramidal coordination with four phosphorus atoms as a basal plane and an axial linear carbonyl ligand (average Mo-P = 2.452 (2) Å, Mo-C = 1.903 (9) Å, and C-O = 1.192 (12) Å). The nearest hydrogen is 2.98 (11) Å from molybdenum, suggesting van der Waals contact of the ortho hydrogen atom of one of the dpe phenyl groups with the metal. The complex $\text{Mo}(\text{CO})(\text{N}_2)(\text{dpe})_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$ crystallizes in the monoclinic system with the space group $C2/c$, with the following cell dimensions: $a = 48.50$ (6), $b = 11.07$ (1), $c = 18.25$ (2) Å; $\beta = 97.98$ (3)°, $V = 9699$ (22) Å³, and $Z = 8$. The molybdenum atom has octahedral coordination with average Mo-P = 2.448 (4) Å, Mo-C = 1.973 (16) Å, Mo-N = 2.068 (12) Å, C-O = 1.127 (20) Å, and N-N = 1.087 (18) Å. Bond distances in two complexes are compared and discussed.

In a previous communication,³ we briefly reported that a stable five-coordinate $\text{Mo}(0)$ complex, $\text{Mo}(\text{CO})(\text{dpe})_2$ ($\text{dpe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) (**1**), was obtained on bubbling argon gas into a benzene solution of *trans*- $\text{Mo}(\text{CO})(\text{N}_2)(\text{dpe})_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$ (**2**) and this reaction was reversible. Since structural information on metal sites which have the capacity to bind dinitrogen as a ligand is strongly desirable, it seems of special interest to determine the molecular structure of **1**. Furthermore, the five-coordinate $\text{M}(0)$ complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{or} \text{W}$) are frequently postulated as the intermediates in $\text{S}_{\text{N}}1$ processes of six-coordinate group 6 metal complexes⁴ and the structures of such species have been extensively studied by trapping them in low-temperature solid matrices.⁵ Although a few examples of five-coordinate d^6 complexes of $\text{Ru}(\text{II})$ and $\text{Rh}(\text{III})$ have been established by x-ray diffraction studies,⁶ none is, to the best of our knowledge, known for group 6 transition metal complexes.⁷ We wish here to report the synthesis

and the molecular structure of the first example of a stable five-coordinate d^6 molybdenum complex **1**, as well as of the dinitrogen complex **2**.

Experimental Section

All reactions were carried out under an atmosphere of pure dinitrogen or argon using purified dioxygen-free solvents and standard Schlenk-tube techniques. The complex *trans*- $\text{Mo}(\text{N}_2)_2(\text{dpe})_2$ was prepared by the published method.⁸ Infrared spectra were recorded from KBr pellets using a Nihon-bunko IRA1 double-beam spectrometer.

Preparation of *trans*- $\text{Mo}(\text{CO})(\text{N}_2)(\text{dpe})_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$ (2**). Method A.** Dimethylformamide (DMF) (19.0 g, 0.26 mol) was added to a solution of *trans*- $\text{Mo}(\text{N}_2)_2(\text{dpe})_2$ (2.0 g, 2.1 mmol) in benzene (80 mL) under dinitrogen. The mixture was heated under reflux for 20 min, during which the orange solution had become dark red. After cooling, *n*-hexane (100 mL) was added and the precipitate formed was filtered off, washed with ether and *n*-hexane, and dried in vacuo to yield dark

Table I. Summary of Crystal Data

compd	Mo(CO)(dpe) ₂	Mo(CO)(N ₂)(dpe) ₂ · ½C ₆ H ₆
formula	C ₅₃ H ₄₈ OP ₄ Mo	C ₅₆ H ₅₁ N ₂ OP ₄ Mo
formula wt	920.81	987.88
<i>a</i> , Å	17.849 (3)	48.50 (6)
<i>b</i> , Å	24.295 (4)	11.07 (1)
<i>c</i> , Å	10.939 (2)	18.25 (2)
β, deg	99.117 (4)	97.98 (3)
<i>V</i> , Å ³	4683.5 (13)	9699 (22)
<i>Z</i>	4	8
density, g/cm ³ (calcd)	1.31	1.35
systematic absences	<i>h</i> 0 <i>l</i> , <i>h</i> + <i>l</i> odd 0 <i>k</i> 0, <i>k</i> odd	<i>hkl</i> , <i>h</i> + <i>k</i> odd <i>h</i> 0 <i>l</i> , <i>l</i> odd
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>F</i> (000)	1904	4088
crystal dimensions	0.3 × 0.3 × 0.7 mm	0.1 × 0.7 × 0.6 mm
μ, cm ⁻¹	4.5	4.4
maximum absorption effects	27%	27%

red crystals of Mo(CO)(DMF)(dpe)₂ (1.6 g, 76%).⁹ Anal. Calcd for C₅₆H₅₅NO₂P₄Mo: C, 67.7; H, 5.6; N, 1.4. Found: C, 67.1; H, 5.7; N, 1.3.

When Mo(CO)(DMF)(dpe)₂ (1.6 g) was recrystallized from benzene/*n*-hexane under a dinitrogen atmosphere, dinitrogen replaced the DMF ligand from the complex to give orange crystals, which were separated, washed with *n*-hexane, and dried in vacuo to yield **2** (1.0 g, 63%). Anal. Calcd for C₅₆H₅₁N₂OP₄Mo: C, 68.1; H, 5.2; N, 2.8. Found: C, 67.9; H, 5.4; N, 3.2. The presence of benzene in **2** was checked by gas chromatographic analysis of a toluene solution of **2**.

Method B. Benzyl propionate (3.4 g, 21 mmol) was added to a solution of *trans*-Mo(N₂)₂(dpe)₂ (2.0 g, 2.1 mmol) in benzene (60 mL). The mixture was heated under reflux for 30 min, during which the solution had become dark brown. On cooling under dinitrogen, the dark brown solution changed rapidly to orange. Addition of *n*-hexane (80 mL) deposited orange crystals, which were filtered off, washed with *n*-hexane, and dried in vacuo to yield **2** (1.1 g, 53%).

When toluene was used as solvent instead of benzene, **2** was obtained similarly in a moderate yield (54%); however, in this case orange crystals of **2** were mixed with a small amount (3%) of yellow crystals of *cis*-Mo(CO)₂(dpe)₂.¹⁰ Gas chromatographic analysis of the reaction system disclosed the formation of ethylene, ethane, and benzene as decarbonylated products.

Preparation of Mo(CO)(dpe)₂ (1). Argon gas was bubbled through a solution of **2** (99 mg, 0.10 mmol) in benzene (10 mL) at 50 °C for 3 min. The original orange color changed rapidly to dark brown. On addition of *n*-hexane (15 mL) to the resulting solution under an argon atmosphere, black crystals were formed, which were filtered off, washed with *n*-hexane, and dried in vacuo to yield **1** (48 mg, 52%). Anal. Calcd for C₅₃H₄₈OP₄Mo: C, 69.1; H, 5.2; N, 0.0. Found: C, 68.7; H, 5.3; N, 0.0.

Reaction of Mo(CO)(dpe)₂ (1) with Dinitrogen. Under a dinitrogen atmosphere benzene (5 mL) was added to crystals of **1** (46 mg, 0.05 mmol). The moment the complex dissolved, the solution became orange. Addition of *n*-hexane (10 mL) deposited orange crystals of *trans*-Mo(CO)(N₂)(dpe)₂·½C₆H₆ (**2**, 37 mg, 75%).

Reaction of Mo(CO)(dpe)₂ (1) with Carbon Monoxide. Carbon monoxide was bubbled through a solution of **1** (95 mg, 0.10 mmol) in benzene (10 mL) at room temperature. The color of the solution immediately changed to yellowish orange and after a few minutes *n*-hexane (15 mL) was added to deposit yellowish-orange crystals, which were filtered off, washed with *n*-hexane, and dried in vacuo to yield *trans*-Mo(CO)₂(dpe)₂ (29 mg, 30%) (*ν* (C≡O) 1812 cm⁻¹). Anal. Calcd for C₅₄H₄₈O₂P₄Mo: C, 68.4; H, 5.1, N, 0.0. Found: C, 68.9; H, 5.0; N, 0.0.

When the above reaction solution was allowed to stand for several hours and then *n*-hexane was added, the well-known compound *cis*-Mo(CO)₂(dpe)₂¹⁰ was exclusively isolated as yellow crystals.

Crystal Preparation. Dark red crystals of **1** and orange crystals of **2** were precipitated in the form of plates from benzene/*n*-hexane under argon and dinitrogen atmosphere, respectively, and were sealed in

Table II. Summary of Intensity Collection and Refinement

	Mo(CO)(dpe) ₂	Mo(CO)(N ₂)- (dpe) ₂ ·½C ₆ H ₆
used data (<i>F</i> _o ≥ 3σ <i>F</i> _o)	7122	3606
total data	13 341	5496
2θ limits	2θ ≤ 60°	2θ ≤ 42.5°
scan speed (2θ)	2°/min	2°/min
scan length, min	1 + 0.45 tan θ	1 + 0.45 tan θ
background	measd for 10 s at each end of the scan	measd for 10 s at each end of the scan
weighting scheme ^a	<i>w</i> = 0.7 for <i>F</i> _o < 19 <i>w</i> = 1.0 for 19 ≤ <i>F</i> _o ≤ 76 <i>w</i> = (76/ <i>F</i> _o) ² for 76 < <i>F</i> _o	<i>w</i> = 0.7 for <i>F</i> _o < 38 <i>w</i> = 1.0 for 38 ≤ <i>F</i> _o ≤ 76 <i>w</i> = (76/ <i>F</i> _o) ² for 76 < <i>F</i> _o
<i>R</i> ^b (isotropic)	0.108	0.110
<i>R</i> _w ^c (isotropic)	0.135	0.146
<i>R</i> (anisotropic)	0.091	0.088
<i>R</i> _w (anisotropic)	0.108	0.120
<i>R</i> (final)	0.076	0.084
<i>R</i> _w (final)	0.087	0.120

^a The scale of *F*_o is approximately equal to absolute scale. ^b *R* = Σ||*F*_o| - |*F*_c||/Σ|*F*_o|. ^c *R*_w = [Σ*w*(|*F*_o| - |*F*_c||)²/Σ*w*|*F*_o|²]^{1/2}.

Pyrex glass capillaries under the same atmosphere for x-ray data collection.

Crystallographic Data. The crystals of **2** belonged to the monoclinic system with the absent spectra: *hkl*, *h* + *k* odd; *h*0*l*, *l* odd, that were characteristic of the centrosymmetric space group *C*2/*c* or the non-centrosymmetric space group *Cc*. The centrosymmetric space group was shown to be the correct one on the basis of the following results: (a) the acceptable positional parameters, thermal parameters, and agreement indexes in the successful refinements; (b) the clear and distinct location of all the 48 unique hydrogen atoms except solvent hydrogens in a difference Fourier map. Lattice parameters of both crystals were determined by a least-squares fit to the setting angles for 12 hand-centered reflections with 20° < 2θ < 32° for the complex **1** and 16° < 2θ < 31° for the complex **2** using the average of positive and negative 2θ angles for Mo Kα. Because of air sensitivity and good solubility of the complexes, only approximate densities, values of which were between those of chloroform (*d* = 1.49) and glycerol (*d* = 1.26), could be observable by flotation. Table I shows the pertinent crystal information for both crystals.

Data collection was carried out with LiF-monochromatized Mo Kα (λ = 0.7107 Å) radiation, using a Rigaku automated four-circle diffractometer by 2θ-ω scan technique. Four standard reflections for each complex were monitored every 50 measurements to check any unfavorable effects. The systematic changes in the intensities were not observed. The variation of their intensities was within 2.3% for the crystal of **1** and 5.5% for the crystal of **2**, respectively. Lorentz and polarization corrections were applied in the usual manner, but no absorption correction was made since maximum absorption effects (μ*R*) are 0.63 and 0.62 for **1** and **2**, respectively. Table II shows the details of intensity collections and refinements of both crystals.

Structure Refinement.¹¹ The Patterson synthesis was used to locate the molybdenum atom for each complex. Subsequent Fourier syntheses revealed the positions of all the nonhydrogen atoms except the carbon atoms of the solvated benzene of the complex **2** because of the disorder of it. The structures were refined by block-diagonal least-squares technique for nonhydrogen atoms first with isotropic thermal parameters, then with anisotropic thermal parameters. The quantity minimized was Σ*w*(|*F*_o| - |*F*_c||)² where in the case of **2**, disordered benzene was neglected in *F*_c. The atomic scattering factors were taken from the International Tables^{12a} and the anomalous terms for Mo and P were those of Cromer and Liberman^{12b} and were included in *F*_c. At this stage, difference Fourier syntheses showed clear peaks of hydrogen atoms of both complexes except those of the solvated molecule in the complex **2**. Then we carried out block-diagonal least-squares calculations including the positional parameters of the hydrogen atoms.

Table IIIa. Positional and Thermal Parameters for the Nonhydrogen Atoms of Mo(CO)(dpe)₂

Atom	x ^a	y	z	U ₁₁ ^b	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Mo	2375 (1)	1705 (1)	3352 (1)	247 (2)	367 (2)	294 (2)	10 (3)	19 (2)	16 (3)
P (1)	1338 (1)	1031 (1)	2855 (2)	335 (9)	415 (11)	436 (10)	4 (7)	25 (7)	-22 (8)
P (2)	1296 (1)	2320 (1)	2778 (2)	298 (8)	430 (10)	312 (8)	34 (7)	-12 (6)	-30 (7)
P (3)	3346 (1)	2383 (1)	4055 (2)	316 (8)	430 (10)	350 (9)	-15 (7)	0 (7)	-3 (7)
P (4)	3426 (1)	1086 (1)	4065 (2)	308 (8)	426 (10)	420 (10)	36 (7)	32 (7)	65 (8)
O	1875 (4)	1683 (3)	6170 (6)	1194 (57)	845 (49)	560 (36)	127 (46)	415 (37)	147 (37)
C (5)	2058 (4)	1694 (4)	5169 (7)	546 (47)	565 (47)	424 (37)	127 (42)	111 (32)	100 (39)
C (1)	403 (4)	1362 (3)	2955 (7)	329 (35)	488 (45)	566 (46)	37 (32)	45 (31)	67 (36)
C (2)	360 (4)	1922 (3)	2289 (7)	286 (32)	471 (41)	504 (41)	36 (29)	-37 (29)	-62 (33)
C (3)	4189 (4)	2037 (4)	4957 (7)	334 (36)	651 (54)	493 (43)	1 (35)	-77 (31)	10 (38)
C (4)	4341 (4)	1492 (3)	4298 (8)	306 (35)	546 (47)	641 (50)	45 (32)	-17 (33)	-11 (39)
C (11)	1214 (5)	875 (3)	1165 (7)	597 (48)	420 (44)	453 (42)	45 (37)	-12 (35)	-29 (34)
C (12)	1841 (6)	988 (6)	579 (10)	655 (64)	1384 (109)	686 (65)	147 (67)	271 (53)	-137 (68)
C (13)	1771 (8)	948 (7)	-720 (11)	1315 (115)	1716 (142)	608 (68)	215 (105)	485 (73)	-118 (80)
C (14)	1105 (9)	779 (6)	-1425 (11)	1469 (123)	1192 (107)	587 (69)	163 (92)	101 (73)	-86 (69)
C (15)	507 (8)	651 (6)	-868 (11)	1243 (111)	1293 (118)	770 (80)	-306 (93)	-313 (74)	-162 (77)
C (16)	533 (6)	721 (5)	454 (10)	781 (68)	970 (83)	667 (61)	-400 (62)	-128 (51)	-78 (57)
C (12)	1218 (4)	359 (3)	3600 (7)	409 (38)	526 (48)	491 (43)	-21 (34)	45 (32)	-9 (36)
C (12)	1364 (6)	-140 (4)	3069 (9)	856 (70)	590 (60)	675 (60)	30 (32)	105 (51)	-24 (47)
C (12)	1306 (7)	-645 (4)	3725 (11)	1228 (98)	463 (59)	948 (82)	-159 (61)	-6 (71)	-102 (54)
C (12)	1109 (6)	-642 (4)	4885 (10)	870 (75)	667 (68)	828 (73)	-43 (57)	31 (58)	114 (56)
C (12)	966 (6)	-154 (5)	5412 (10)	921 (77)	665 (66)	861 (73)	-65 (58)	245 (60)	196 (56)
C (12)	1027 (6)	359 (4)	4788 (10)	834 (68)	516 (54)	784 (66)	-7 (49)	255 (54)	139 (48)
C (21)	919 (4)	2888 (3)	3739 (7)	312 (32)	484 (42)	389 (35)	88 (29)	48 (27)	-9 (33)
C (21)	300 (5)	3204 (4)	3257 (8)	560 (48)	824 (69)	476 (43)	221 (47)	-48 (36)	-203 (46)
C (21)	22 (5)	3608 (4)	3967 (9)	544 (52)	866 (74)	718 (61)	259 (51)	35 (44)	-238 (54)
C (21)	366 (5)	3678 (4)	5203 (9)	643 (56)	721 (64)	658 (57)	59 (48)	183 (45)	-249 (49)
C (21)	984 (6)	3358 (4)	5682 (7)	862 (66)	811 (70)	379 (40)	100 (56)	35 (40)	-159 (45)
C (21)	1263 (4)	2912 (3)	4955 (7)	495 (43)	486 (46)	436 (40)	2 (35)	-3 (32)	-48 (34)
C (22)	1173 (4)	2719 (3)	1357 (6)	311 (33)	627 (49)	280 (32)	24 (32)	-2 (25)	39 (31)
C (22)	1620 (6)	3264 (4)	1454 (8)	944 (70)	580 (55)	544 (48)	-133 (55)	178 (46)	20 (47)
C (22)	1774 (8)	3556 (5)	428 (10)	1175 (105)	742 (74)	716 (69)	-144 (71)	240 (68)	162 (58)
C (22)	1685 (7)	3292 (5)	-711 (9)	916 (76)	1094 (90)	606 (57)	-98 (74)	93 (52)	252 (65)
C (22)	1471 (7)	2757 (5)	-839 (8)	948 (79)	1201 (96)	354 (45)	-107 (70)	72 (47)	-33 (53)
C (22)	1314 (5)	2462 (4)	2167 (6)	525 (47)	724 (59)	426 (42)	-118 (43)	35 (35)	-11 (41)
C (31)	3769 (4)	2614 (3)	2708 (7)	408 (37)	427 (41)	433 (38)	48 (31)	138 (30)	-3 (31)
C (31)	4468 (5)	2878 (4)	2776 (9)	484 (47)	694 (61)	702 (58)	-69 (43)	170 (42)	24 (48)
C (31)	4792 (6)	2959 (5)	1665 (12)	637 (61)	778 (74)	1299 (99)	-39 (54)	538 (65)	178 (68)
C (31)	4402 (7)	2787 (5)	550 (11)	1066 (91)	925 (84)	945 (83)	207 (71)	625 (72)	116 (67)
C (31)	3731 (7)	2520 (6)	465 (9)	1025 (88)	1321 (106)	480 (56)	173 (80)	255 (56)	114 (63)
C (31)	3364 (6)	2435 (5)	1526 (8)	738 (61)	923 (74)	392 (43)	167 (55)	75 (41)	-22 (45)
C (32)	3314 (4)	3012 (3)	4998 (7)	317 (34)	612 (50)	471 (41)	-6 (33)	38 (29)	-152 (37)
C (32)	3235 (5)	2947 (4)	6255 (8)	548 (48)	707 (60)	491 (46)	-50 (43)	87 (37)	-219 (42)
C (32)	3193 (6)	3409 (5)	7011 (9)	640 (59)	1050 (91)	693 (60)	49 (58)	59 (47)	-322 (60)
C (32)	3209 (7)	3296 (5)	6524 (11)	831 (76)	1139 (99)	807 (74)	115 (69)	8 (59)	-519 (69)
C (32)	3267 (7)	4005 (4)	5294 (12)	968 (84)	523 (61)	1173 (97)	-16 (57)	96 (72)	-123 (61)
C (32)	3324 (6)	3545 (4)	4518 (9)	786 (65)	550 (55)	675 (58)	77 (48)	128 (49)	-89 (46)
C (41)	3364 (4)	588 (3)	2833 (7)	409 (37)	388 (38)	434 (38)	62 (30)	113 (29)	28 (31)
C (41)	3786 (5)	783 (4)	1725 (8)	519 (45)	585 (52)	532 (46)	-20 (39)	191 (37)	20 (40)
C (41)	3796 (6)	424 (4)	927 (8)	713 (60)	877 (73)	523 (51)	-46 (54)	245 (45)	9 (48)
C (41)	3590 (7)	-114 (5)	810 (10)	1270 (100)	724 (72)	658 (63)	-3 (69)	214 (64)	-166 (55)
C (41)	3375 (10)	-311 (5)	1885 (11)	1984 (153)	568 (70)	816 (80)	-223 (83)	340 (89)	27 (59)
C (41)	3362 (8)	41 (4)	2890 (9)	1466 (107)	568 (61)	504 (53)	-89 (66)	156 (60)	4 (46)
C (42)	3559 (4)	619 (3)	5438 (6)	545 (43)	474 (44)	311 (34)	105 (35)	47 (30)	50 (31)
C (42)	2955 (5)	514 (4)	6051 (9)	592 (53)	696 (63)	795 (64)	180 (47)	219 (47)	399 (52)
C (42)	3041 (7)	134 (5)	7048 (12)	989 (85)	949 (88)	1064 (90)	321 (72)	441 (71)	545 (74)
C (42)	3703 (7)	-141 (5)	7379 (9)	1275 (96)	806 (74)	510 (52)	403 (70)	255 (57)	273 (52)
C (42)	4312 (6)	-36 (6)	6796 (10)	811 (73)	1353 (113)	808 (74)	576 (76)	38 (58)	422 (74)
C (42)	4237 (5)	350 (5)	5836 (9)	593 (55)	1201 (97)	592 (56)	344 (59)	129 (44)	342 (58)

^aThe quantities given in the table are the positional and thermal coefficients × 10⁴.^bThe form of the anisotropic thermal ellipsoid is exp[-2π²(h²a²U₁₁ + k²b²U₂₂ + l²c²U₃₃ + 2hka²U₁₂ + 2hla²U₁₃ + 2klb²U₂₃).

while their isotropic thermal parameters were fixed at 6.0 Å². After the final refinement, the standard deviations of observations of unit weight [Σw(|F_o| - |F_c|)²/(m - n)]^{1/2} were 3.41 and 10.7, respectively, where the numbers of reflections (*m*) were 7122 and 3606 and the numbers of refined parameters (*n*) were 725 and 743, respectively. In the final cycle, no parameter shifted by more than 0.3 of its estimated standard deviation. Analyses of w(|F_o| - |F_c|)² as functions of setting angles, *F*_o, and Miller indexes revealed that agreement was not good at low angles of the complex **2**. This is to be expected in view of our inadequate treatment for the rather ill-defined solvent molecule. The maximum densities in the final difference Fourier syntheses were 0.7 and 0.8 e/Å³ for **1** and **2**, respectively.

The positional and thermal parameters obtained from the last cycle of refinement are listed in Tables IIIa,b and IVa,b with the associated standard deviations estimated from the inverse matrix. A listing of the observed and calculated structure amplitudes used in the refinements is available.

Results and Discussion

Synthesis of a Five-Coordinate Molybdenum(0) Complex Mo(CO)(dpe)₂ (1) from trans-Mo(N₂)₂(dpe)₂. The molybdenum bis(dinitrogen) complex *trans*-Mo(N₂)₂(dpe)₂ (**3**) reacts with

Table IVa. Positional and Thermal Parameters for the Nonhydrogen Atoms of Mo(CO)(N₂)(dpe)₂·1/2C₆H₆

Atom	x ^a	y	z	U ₁₁ ^b	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Mo	1350 (1)	1717 (1)	542 (1)	348 (1)	215 (5)	323 (6)	-9 (6)	46 (5)	16 (5)
P (1)	1801 (1)	2000 (3)	1325 (2)	374 (21)	309 (21)	344 (20)	11 (16)	39 (17)	17 (16)
P (2)	1197 (1)	2469 (3)	1680 (2)	428 (23)	353 (22)	312 (21)	27 (18)	101 (17)	-11 (17)
P (3)	892 (1)	1694 (3)	-195 (2)	414 (22)	289 (19)	456 (22)	-6 (18)	34 (18)	48 (18)
P (4)	1464 (1)	851 (3)	-616 (2)	396 (21)	296 (20)	343 (20)	-4 (17)	69 (16)	-6 (16)
C (5)	1358 (3)	89 (12)	985 (7)	719 (106)	332 (80)	254 (76)	50 (77)	31 (70)	8 (67)
O	1382 (2)	-833 (10)	1249 (7)	761 (82)	550 (72)	763 (82)	55 (64)	-26 (60)	154 (64)
N (1)	1382 (2)	3405 (11)	-74 (7)	347 (69)	449 (74)	586 (81)	-76 (62)	-27 (56)	-188 (66)
N (2)	1405 (2)	4271 (9)	-193 (7)	618 (84)	148 (58)	714 (90)	-50 (58)	99 (69)	156 (59)
C (1)	1784 (3)	2352 (15)	2388 (8)	436 (91)	633 (103)	334 (83)	166 (82)	-8 (70)	-140 (76)
C (2)	1460 (3)	1964 (14)	2442 (8)	498 (94)	579 (104)	362 (83)	55 (78)	102 (70)	89 (75)
C (3)	942 (3)	1702 (14)	-1170 (8)	501 (94)	440 (88)	418 (84)	73 (80)	-44 (70)	-4 (75)
C (4)	1143 (3)	711 (15)	-1282 (8)	359 (86)	637 (107)	451 (90)	-71 (78)	23 (69)	21 (80)
C (11)	2056 (3)	756 (12)	1480 (8)	399 (83)	249 (73)	399 (82)	-57 (63)	-38 (65)	-80 (63)
C (12)	2256 (3)	674 (7)	2102 (9)	562 (108)	625 (114)	626 (110)	-53 (89)	69 (86)	-167 (91)
C (13)	2440 (3)	-274 (16)	2378 (9)	449 (98)	675 (116)	649 (113)	36 (88)	21 (83)	67 (94)
C (14)	2438 (3)	-1133 (17)	1653 (10)	397 (96)	745 (118)	747 (118)	208 (85)	208 (85)	-32 (99)
C (15)	2247 (4)	-1033 (17)	1044 (9)	790 (125)	656 (116)	546 (106)	289 (102)	244 (93)	-54 (91)
C (16)	2057 (3)	-1161 (13)	962 (7)	697 (108)	352 (92)	295 (79)	-52 (73)	-61 (68)	16 (68)
C (12)	2019 (3)	3253 (11)	1139 (8)	387 (81)	311 (74)	434 (81)	28 (71)	38 (65)	-54 (69)
C (12)	2281 (3)	3125 (13)	862 (9)	600 (102)	348 (86)	526 (94)	-91 (77)	55 (78)	-34 (75)
C (12)	2423 (3)	4089 (16)	683 (10)	526 (109)	563 (109)	800 (131)	-155 (90)	95 (94)	87 (98)
C (12)	2323 (4)	2582 (18)	748 (10)	1067 (157)	706 (126)	354 (112)	-367 (118)	-87 (106)	69 (98)
C (12)	2059 (4)	5444 (15)	985 (10)	840 (132)	440 (100)	720 (122)	-270 (97)	38 (101)	62 (90)
C (12)	1919 (3)	4392 (16)	1195 (10)	364 (91)	703 (129)	696 (115)	-20 (85)	-77 (82)	5 (95)
C (21)	879 (3)	3947 (15)	204 (10)	422 (95)	533 (103)	734 (113)	62 (79)	201 (83)	50 (87)
C (21)	802 (4)	489 (20)	1902 (12)	603 (117)	104 (160)	786 (132)	-99 (114)	301 (101)	-22 (114)
C (21)	569 (4)	253 (21)	2147 (11)	790 (139)	1040 (165)	756 (134)	-87 (125)	255 (109)	103 (124)
C (21)	417 (4)	1041 (27)	2531 (13)	801 (153)	1807 (256)	988 (166)	-592 (169)	596 (133)	-43 (173)
C (21)	493 (6)	2115 (30)	2685 (22)	1188 (233)	1625 (286)	1662 (204)	-466 (204)	1365 (268)	-875 (279)
C (21)	722 (5)	2652 (23)	2402 (18)	967 (182)	950 (181)	2161 (315)	-265 (149)	840 (197)	-742 (199)
C (21)	1185 (3)	4090 (14)	1858 (8)	576 (102)	380 (90)	452 (90)	23 (76)	88 (76)	17 (73)
C (22)	1292 (4)	4588 (15)	2546 (9)	660 (111)	467 (99)	651 (112)	-62 (86)	161 (90)	-144 (85)
C (22)	1287 (4)	5842 (16)	2658 (11)	1033 (151)	455 (108)	789 (131)	-2 (106)	-3 (113)	-171 (107)
C (22)	1178 (4)	6574 (17)	2069 (12)	909 (146)	501 (115)	959 (149)	137 (108)	32 (116)	-95 (107)
C (22)	1071 (4)	6079 (18)	1407 (10)	962 (151)	687 (144)	655 (121)	135 (117)	-410 (107)	48 (110)
C (22)	1083 (3)	4842 (13)	1302 (8)	729 (131)	336 (84)	473 (93)	45 (81)	-58 (82)	-13 (74)
C (31)	675 (3)	3012 (15)	-112 (9)	549 (104)	629 (115)	540 (102)	-210 (85)	-98 (82)	-198 (87)
C (31)	698 (4)	4050 (16)	-508 (11)	600 (115)	568 (109)	870 (133)	215 (96)	-254 (99)	3 (99)
C (31)	539 (4)	5096 (15)	-397 (

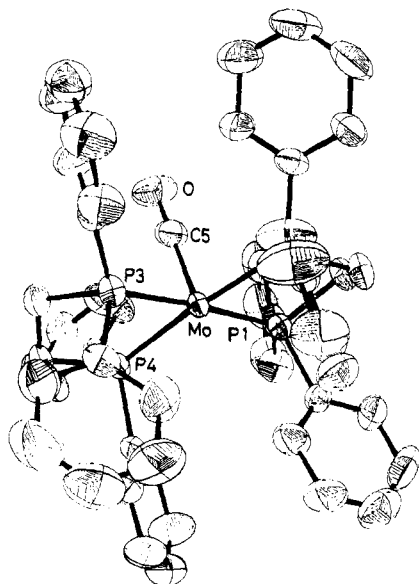


Figure 1. Perspective view of Mo(CO)(dpe)_2 . The shapes of the atoms in this drawing represent 50% probability contours of thermal motions.

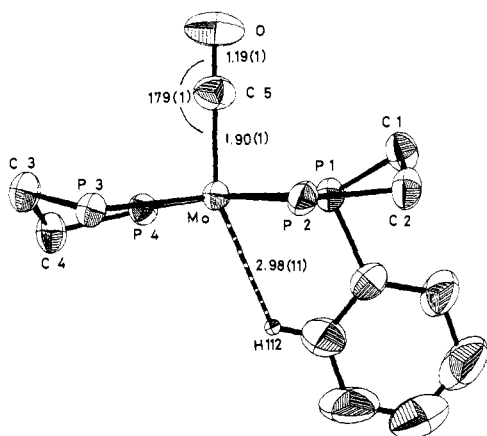
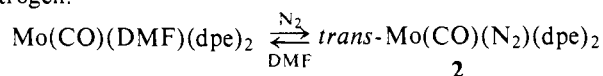


Figure 2. Perspective view of Mo(CO)(dpe)_2 . The shapes of the atoms in this drawing represent 50% probability contours of thermal motions.

the strong σ -donor property of dpe ligands and the strong π -donor property of the DMF ligand.¹⁶ This complex can be recrystallized from benzene under an argon atmosphere, but is completely converted to **2** on recrystallization under dinitrogen.



On the other hand, **2** can be directly obtained from the reaction of **3** with benzyl propionate in toluene at reflux under dinitrogen. In this reaction, ethylene, ethane, and benzene are detected as decarbonylated products.¹⁷ The infrared spectrum of **2** shows medium bands at 2110 and 2080 cm^{-1} , which change position to 2036 and 2009 cm^{-1} upon ^{15}N substitution and are therefore associated with $\nu(\text{N}\equiv\text{N})$, and strong bands at 1812 and 1789 cm^{-1} assignable to $\nu(\text{C}\equiv\text{O})$. The splitting of $\nu(\text{N}\equiv\text{N})$ and $\nu(\text{C}\equiv\text{O})$ is due to a crystal effect since such splitting was not observed in solution ($\nu(\text{C}\equiv\text{O})$ 1799 cm^{-1} and $\nu(\text{N}\equiv\text{N})$ 2128 cm^{-1} in benzene). A sharp singlet observed at -69 ppm (relative to 85% H_3PO_4) in the ^{31}P NMR spectrum indicates a trans configuration of **2**. The dinitrogen ligand of **2** is very labile in solution, which is consistent with the high $\nu(\text{N}\equiv\text{N})$ caused by the presence of a strong π -acceptor CO ligand in the trans position. Thus, on removing dinitrogen in vacuo or with a stream of argon, the original orange color of

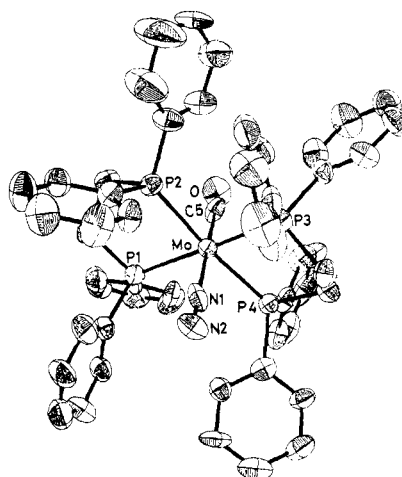
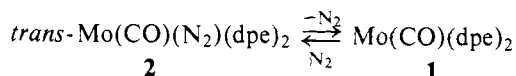


Figure 3. Perspective view of $\text{Mo(CO)(N}_2\text{)(dpe)}_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$. The shapes of the atoms in this drawing represent 50% probability contours of thermal motions.

a benzene solution of **2** changes rapidly to dark brown. From this solution, an unsaturated complex **1** is isolated as black crystals. The infrared spectrum of **1** exhibits a band at 1807 cm^{-1} assignable to $\nu(\text{C}\equiv\text{O})$. This reaction is reversible and, dissolved in benzene under dinitrogen, **1** is easily reconverted to **2**.



Structures of Mo(CO)(dpe)_2 (1**) and $\text{Mo(CO)(N}_2\text{)(dpe)}_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$ (**2**).** The structure of **1** consists of discrete, well-separated monomers. A perspective view of the complex, showing the numbering scheme, is shown in Figures 1 and 2. The carbon ring atoms are labeled as $\text{C}(xyz)$, x being the first ring index [(1)–(4)], y the second index [(1)–(2)], and z the position of the atom [(1)–(6)]. The carbon $\text{C}(xyz)$ attaches $\text{P}(x)$. The hydrogen atom of phenyl group $\text{H}(xyz)$ bonds to $\text{C}(xyz)$, and the methylene hydrogen atom $\text{H}(xy)$ bonds to $\text{C}(x)$. This five-coordinate complex has a nearly square-pyramidal structure with four phosphorus atoms as a basal plane and a linear carbonyl ligand in the axial position. The minimum angle between the vector from Mo to C(5) and the four phosphorus atoms' least-squares plane¹⁸ is 87.4° and it may be regarded as perpendicular.

The structure of the complex **1** is not unexpected, because substantial evidence has been presented that five-coordinate group 6 metal(0) carbonyls and their derivatives exhibit square-pyramidal rather than trigonal bipyramidal geometry.^{4b,c,5,19} Furthermore the predominant square-pyramidal intermediates of $\text{S}_{\text{N}}1$ processes have been shown to contain the best π -accepting ligand in the axial position.^{4c,5b} As expected, the complex **1** has an axial carbonyl ligand, which is compatible with the finding that the reaction of **1** with carbon monoxide results in the formation of $\text{trans-Mo(CO)}_2(\text{dpe})_2$, followed by isomerization to the thermodynamically more stable cis isomer.²⁰

The molybdenum atom of the five-coordinate complex **1** is displaced 0.13 Å out of the least-squares plane¹⁸ defined by the four coordinated phosphorus atoms toward the carbon atom of the carbonyl ligand, indicating that the molybdenum atom and the four phosphorus atoms lie nearly in the same plane. This is consistent with Hoffmann's prediction²¹ that the conformation of an ML_5 molecule, if it is a square pyramid, will clearly depend upon the number of the d electrons and d^6 systems will favor a "flat" square pyramid. In the case of another d^6 square-pyramidal complex, $\text{RuCl}_2(\text{PPh}_3)_3$,^{6a} the

Table V. Selected Distances (Å) and Angles (deg)

	$\text{Mo}(\text{CO})(\text{dpe})_2$	$\text{Mo}(\text{N}_2)(\text{CO})\text{-(dpe)}_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$
Bond Distances		
Mo-C(5)	1.903 (9)	1.973 (16)
Mo-N(1)		2.068 (12)
Mo-P(1)	2.438 (2)	2.459 (4)
Mo-P(2)	2.448 (2)	2.447 (4)
Mo-P(3)	2.453 (2)	2.435 (4)
Mo-P(4)	2.468 (2)	2.452 (4)
C(5)-O	1.192 (12)	1.127 (20)
N(1)-N(2)		1.087 (18)
P(1)-C(1)	1.871 (8)	1.852 (17)
P(1)-C(111)	1.865 (9)	1.847 (14)
P(1)-C(121)	1.851 (8)	1.805 (14)
P(2)-C(2)	1.891 (8)	1.840 (16)
P(2)-C(211)	1.864 (8)	1.829 (18)
P(2)-C(221)	1.866 (8)	1.825 (16)
P(3)-C(3)	1.865 (9)	1.829 (16)
P(3)-C(311)	1.846 (8)	1.817 (17)
P(3)-C(321)	1.849 (9)	1.831 (15)
P(4)-C(4)	1.892 (9)	1.845 (17)
P(4)-C(411)	1.856 (7)	1.842 (15)
P(4)-C(421)	1.867 (8)	1.854 (16)
C-C (phenyl)	av 1.394 (25)	av 1.377 (32)
C-H (phenyl)	av 0.97 (10)	av 1.01 (11)
nonbonded distance		
Mo...H(112)	2.98 (11)	
Bond Angles		
C(5)-Mo-N(1)		174.61 (59)
C(5)-Mo-P(1)	90.36 (27)	85.05 (48)
C(5)-Mo-P(2)	92.15 (27)	87.30 (48)
C(5)-Mo-P(3)	95.05 (27)	100.37 (48)
C(5)-Mo-P(4)	95.04 (27)	90.16 (48)
N(1)-Mo-P(1)		90.78 (36)
N(1)-Mo-P(2)		95.29 (36)
N(1)-Mo-P(3)		84.07 (36)
N(1)-Mo-P(4)		87.64 (36)
P(1)-Mo-P(2)	79.81 (7)	79.29 (13)
P(3)-Mo-P(4)	79.75 (7)	79.48 (13)
P(1)-Mo-P(3)	174.60 (7)	172.89 (14)
P(2)-Mo-P(4)	172.81 (7)	174.60 (14)
P(1)-Mo-P(4)	99.83 (7)	105.26 (13)
P(2)-Mo-P(3)	99.92 (7)	96.28 (13)
Mo-C(5)-O	178.6 (8)	175.0 (14)
Mo-N(1)-N(2)		177.0 (12)

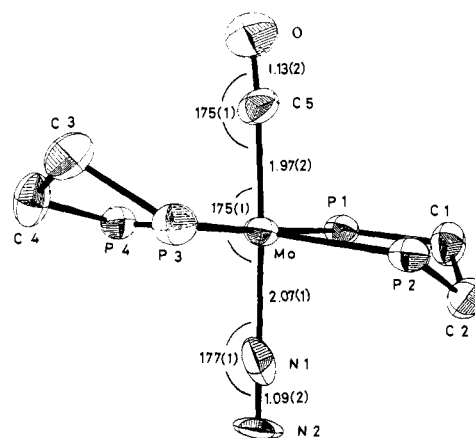
displacement from the basal plane is 0.456 Å, which may be ascribed to the bulkiness of the axial phosphine ligand.

In the complex **1**, the nearest hydrogen, H(112), is 2.95 (11) Å from molybdenum, suggesting van der Waals contact of the ortho hydrogen of one of the dpe phenyl groups with the metal.

Table VI. Distances and IR Spectra of Carbonyl Ligands

complex ^e	$\nu(\text{C}\equiv\text{O}), \text{cm}^{-1}$	distances, Å ^f		
		Mo-C	C-O	
$\text{Mo}(\text{CO})(\text{dpe})_2^a$	1807	1.903 (9)	1.192 (12)	
$\text{Mo}(\text{CO})(\text{N}_2)(\text{dpe})_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6^a$	1812	1.973 (16)	1.127 (20)	
	1791			
$\text{Mo}(\text{CO})_3(\text{cot})^b$	1887	* 1.99 (1)	* 1.15 (1)	Carbonyls trans to the C=C
	1734			
$\text{Mo}(\text{CO})_4(\text{dpm})^c$	2020	* 1.93 (1)	* 1.18 (2)	Carbonyls trans to the phosphorus atoms
	1919			
	1907	* 2.05 (3)	* 1.12 (1)	Two mutually trans carbonyls
	1881			
$\text{Mo}(\text{CO})_3(\text{trien})^d$	1898	* 1.943 (6)	* 1.152 (9)	Carbonyls trans to the nitrogen atoms
	1758			

^a This work. ^b J. S. McKechnie and I. C. Paul, *J. Am. Chem. Soc.*, **88**, 5927 (1966); S. Winstein, H. D. Kaesz, C. G. Kreter, and E. C. Friedrich, *ibid.*, **87**, 3267 (1965). ^c K. K. Cheung, T. F. Lai, and K. S. Mok, *J. Chem. Soc. A*, 1644 (1971); J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961). ^d F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 314 (1965); ref 15. ^e dpe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$; cot = cyclooctatetraene; dpm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$; trien = diethylenetriamine. ^f *, average value.

**Figure 4.** Perspective view of $\text{Mo}(\text{CO})(\text{N}_2)(\text{dpe})_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$. The shapes of the atoms in this drawing represent 50% probability contours of thermal motions.

Any other significant intra- and intermolecular contacts are not observed. The maximum and minimum C-C bond distances are 1.450 (19) and 1.347 (21) Å, respectively, while the C-H bond distances are 1.18 (11) and 0.77 (11) Å, respectively. We conclude that the complex **1** has a five-coordinate, 16-electron molybdenum atom, and therefore can readily combine with gaseous dinitrogen or other two-electron donating species to form six-coordinate 18-electron systems. The reversibility of the dinitrogen coordination is probably due to the tendency of the ortho hydrogen of one of the dpe phenyl groups to block this unused octahedral site, as well as the nitrogen ligand being weakly bound. Various substrates other than dinitrogen such as amines, pyridines, olefins, and amides react with **1** to yield complexes of the type *trans*- $\text{Mo}(\text{CO})\text{-L}(\text{dpe})_2$. In these reactions, the bulkiness of the substrate has a large effect in its reactivity toward **1**.^{3,22}

The structure of **2** also consists of discrete, well-separated monomer and solvent molecules. A perspective view of the complex, showing the numbering scheme, is shown in Figures 3 and 4. The carbon and hydrogen atoms are named in the same way. This six-coordinate complex has octahedral geometry, with four phosphorus atoms as a basal plane and dinitrogen and carbonyl ligands in the trans axial positions. There are no significant intra- and intermolecular contacts. The maximum and minimum C-C bond distances are 1.428 (26) and 1.264 (50) Å, respectively, while the C-H bond distances are 1.44 (22) and 0.83 (20) Å, respectively. The solvent molecule exists near the C2 axis, but we cannot refine the position of the molecule because of its disorder. There is a high electron density sphere (1.0–2.2 e/Å³) (radius ca. 1.7 Å) at the center

($x = 1/2, y = 0.16, z = 1/4$), but there are not suitable peaks for carbon atoms.

Selected bond distances and angles are shown in Table V. The average Mo–P distances of 2.452 (2) and 2.448 (4) Å found in the complexes **1** and **2**, respectively, are nearly equal to that of 2.454 (1) Å found in the complex **3**,²³ but shorter than that of 2.541 (4) Å found in [MoF(N₂H₂)(dpe)₂][BF₄]²⁴ and 2.559 (5) Å in MoBr₂(CO)₃(dpe).²⁵ The average P–Mo–P angles of 79.79 (7) and 79.39 (13)° found in the complexes **1** and **2**, respectively, are essentially equal to those found in the other three complexes. Transition metal–phosphorus bonds are usually considered to have some double bond character presumably through back-donation ($d\pi-d^*\pi$) from the metal, which greatly depends upon the electron density of the metal. The shorter average Mo–P distances of the molybdenum zerovalent complexes **1** and **2** compared with those of high-valent molybdenum complexes reflect the greater back-donation from the metal to phosphorus ligands, which results in the shortening of the metal–phosphorus distances.

The Mo–C(5) distance of 1.903 (9) Å found in the complex **1** is one of the shortest Mo–C distances and the C–O distance of 1.192 (12) Å is one of the longest C–O distances, as shown in Table VI. On the other hand, the complex **2**, which has dinitrogen in the trans position of the carbonyl ligands, shows the longer Mo–C distance of 1.973 (16) Å and the shorter C–O distance of 1.127 (20) Å.

Goldberg and Raymond applied the "constrained model" to the polycarbonyl tungsten complex, W(CO)₅(O=PPh₂CHPh₃),²⁶ in which they assumed a constant C–O distance since four equatorial carbonyl ligands are chemically equivalent. However, their constrained model could not be applied in this work, since both complexes **1** and **2** are monocarbonyl complexes. Insofar as this work, the differences of C–O or Mo–C distances of **1** and **2** are significant. These facts suggest that, in the complex **1**, the carbonyl ligand accepts a considerable back-donation from the molybdenum atom and the shorter Mo–C distance and the longer C–O distance are presumably ascribable to the absence of any ligand in the trans position competing for bonding electrons. In the complex **2**, however, the Mo–C distance becomes longer, since both dinitrogen and carbonyl ligands have to compete for bonding electrons.

The Mo–N–N linkage in the complex **2** is essentially linear and the Mo–N distance and the N–N distance are 2.068 (12) and 1.087 (18) Å, respectively. The C–Mo–N linkage is also nearly linear and the N–Mo–P angles are within the range of 84.1 (4)–95.3 (4)°. The N–N distance of the complex **2** is shorter by 0.038 Å than the N–N distance of the complex **3**,²³ and the Mo–N distance is longer by 0.054 Å than that of the complex **3**. Since the carbonyl ligand is a much stronger π acceptor compared with the dinitrogen ligand, the back-donation from the molybdenum atom to the dinitrogen ligand in the complex **2** does not occur as much as in the complex **3**, which is substantiated by the Mo–N and N–N distances observed and the higher $\nu(\text{N}\equiv\text{N})$ at 2110 and 2080 cm⁻¹ of the complex **2** compared with $\nu(\text{N}\equiv\text{N})$ at 2020 and 1970 cm⁻¹ of the complex **3**.⁸

Supplementary Material Available: Tables IIIb and IVb, positional parameters for the hydrogen atoms of Mo(CO)(dpe)₂ and Mo(CO)(N₂)(dpe)₂·1/2C₆H₆, respectively, and the table of observed and calculated structure amplitudes (18 pages). Ordering information is given on any current masthead page.

References and Notes

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