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Organotransition-Metal Complexes of Multidentate Ligands. 10.[1] Steric vs Electronic Control on Formation of Six- and Seven-Coordinate Carbonyl Halides of Molybdenum(II) and Tungsten(II)

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Halogenation of the complexes (N-N)$M(CO)_4$ gives either the six- or seven-coordinate compounds (N-N)$M(CO)_mX_2$ (N-N = H_2CPz_2, $H_2CPz'_2$, $H_2CPz''_2$, $PhHCPz_2$, or $PhHCPz'_2$; Pz = pyrazol-1-yl; Pz′ = 3,5-dimethylpyrazol-1-yl; Pz″ = 3,4,5-trimethylpyrazol-1-yl; M = Mo or W; m = 2 or 3; X = Br or I). Formation of these stable carbonyl halides with one specific coordination number is explainable in terms of the interplay of the steric and electronic effects. The explanation is further supported by the structural details of the crystal structures of the paramagnetic compounds $(H_2CPz'_2)Mo(CO)_2Br_2$ (**2**) and $(PhHCPz'_2)Mo(CO)_2I_2$ (**9**) and the diamagnetic compound $(H_2CPz''_2)W(CO)_3Br_2$ (**7**). **2**: triclinic; $P\bar{1}$; a = 8.198 (2) Å, b = 9.130 (3) Å, c = 12.291 (4) Å; α = 81.57 (2)°, β = 89.50 (2)°, γ = 83.94 (2)°; V = 905.0 (5) Å^3; Z = 2; ρ = 1.894 g cm^{-3}; R = 0.033, R_w = 0.031 based on 1619 reflections with $I > 2.5\sigma(I)$. **7**: monoclinic; $P2_1/c$; a = 13.255 (5) Å, b = 9.956 (4) Å, c = 16.315 (7) Å; β = 109.28 (4)°; V = 2032.2 (14) Å^3; Z = 4; ρ = 2.157 g cm^{-3}; R = 0.047, R_w = 0.051 based on 1803 reflections with $I > 3.0\sigma(I)$. **9**: orthorhombic; $Pnma$; a = 16.438 (4) Å, b = 14.600 (4) Å, c = 9.515 (3) Å; V = 2283.5 (11) Å^3; z = 4; ρ = 1.996 g cm^{-3}; R = 0.037, R_w = 0.040 based on 1426 reflections with $I > 3\sigma(I)$.

Introduction

In a previous communication,[1h] we briefly reported the synthesis and structure of the paramagnetic 16-electron compounds (N-N)$Mo(CO)_2Br_2$, either from bromination of (N-N)$Mo(CO)_4$ or from reaction of $(MeCN)_2Mo(CO)_3Br_2$ with N-N, where N-N is H_2CPz_2, $H_2CPz'_2$, or $H_2CPz''_2$ (Pz = pyrazol-1-yl; Pz′ = 3,5-dimethylpyrazol-1-yl; Pz″ = 3,4,5-trimethylpyrazol-1-yl) (eq 1). The intramolecular decarbonylation of the presumed unstable intermediate (N-N)$Mo(CO)_3Br_2$ into the six-coordinated (N-N)$Mo(CO)_2Br_2$ is probably induced by the sterically demanding conformation of the Mo(N-N) fragment. To investigate in more depth the influence of the nature of the metal and the ligands on the formation of either six- or seven-coordinate dihalides, we directed our attention to a more detailed study of bromination and iodination of (N-N)$M(CO)_4$ (N-N = H_2CPz_2, $H_2CPz'_2$, $H_2CPz''_2$, $PhHCPz_2$, or $PhHCPz'_2$ as shown in Figure 1; M = Mo or W). Now we wish to give here a full account of this subject.

$$\begin{tikzcd}
(N{-}N)M(CO)_4 + X_2 \arrow[r, "-CO"] & (N{-}N)M(CO)_3X_2 \arrow[r, "-CO"] & (N{-}N)M(CO)_2X_2 \\
(MeCN)_2M(CO)_3X_2 + N{-}N \arrow[ru, "-2MeCN"'] & &
\end{tikzcd} \tag{1}$$

Results and Discussion

The same halocarbonyl complexes are frequently observed as products either from halogenation of substituted metal carbonyls or from rection of the carbonyl halides with mono- or multidentate ligands.[2] The formation of the six-coordinate (N-N)$Mo(CO)_2Br_2$ and the seven-coordinate (N-N)$W(CO)_3Br_2$ and (N-N)$M(CO)_3I_2$ followed in this manner, where N-N is H_2CPz_2, $H_2CPz'_2$, or $H_2CPz''_2$ and M is Mo or W. The identical compounds can be obtained either by halogenation of (N-N)$M(CO)_4$ or from reaction of $(MeCN)_2M(CO)_3X_2$ with the bidentate N-N ligand (eq 1). However, in contrast to the monomeric and dimeric forms of the halogenation products of (bpy)$M(CO)_4$ (bpy = 2,2′-bipyridine),[2a] the solid-state structures of $(H_2CPz'_2)Mo(CO)_2Br_2$ and $(H_2CPz''_2)W(CO)_3Br_2$ and the similarity of the physical data for these two compounds to those of relevant (N-N)$M(CO)_mX_2$ complexes (m = 2 or 3; X = Br or I)[3] establish that all of the halogenation products of (N-N)$M(CO)_4$ have similar monomeric structures in either the six- or the seven-coordinate category. The monomeric form probably reflects the steric effects of the bulky N-N ligand.

The magnetic moments (Evans's method) of 3.32 μ_B for $(H_2CPz_2)Mo(CO)_2Br_2$ (**1**), 4.07 μ_B for $(H_2CPz'_2)Mo(CO)_2Br_2$ (**2**), and 4.14 μ_B for $(H_2CPz''_2)Mo(CO)_2Br_2$ (**3**) are consistent with the ground-state triplet expected for the complexes. That the values are larger than the spin-only value of 2.83 μ_B may be due to a g value greater than 2.[4]

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[1] (a) Part 1: Shiu, K.-B.; Vong, W.-J. *J. Chin. Chem. Soc. (Taipei)* **1987**, *34*, 195. (b) Part 2: Shiu, K.-B.; Chang, C.-J. *Ibid.* **1987**, *34*, 297. (c) Part 3: Shiu, K.-B.; Liou, K.-S.; *Ibid.* **1988**, *35*, 187. (d) Part 4: Shiu, K.-B.; Lee, L.-Y. *J. Organomet. Chem.* **1988**, *348*, 357. (e) Part 5: Shiu, K.-B.; Chang, C.-J.; Wang, Y.; Cheng, M.-J. *J. Chin. Chem. Soc. (Taipei)* **1989**, *36*, 25. (f) Part 6: Shiu, K.-B.; Lee, L.-Y. *Ibid.* **1989**, *36*, 31. (g) Part 7: Shiu, K.-B.; Liou, K.-S.; Cheng, C. P.; Fang, B.-R.; Wang, Y.; Lee, G.-H.; Vong, W.-J. *Organometallics* **1989**, *8*, 1219. (h) Part 8: Shiu, K.-B.; Liou, K.-S.; Wang, S.-L.; Cheng, C. P.; Wu, F.-J. *J. Organomet. Chem.* **1989**, *359*, C1. (i) Part 9: Shiu, K.-B.; Shen, F.-M.; Wang, S.-L.; Wei, S.-C. *Ibid.* **1989**, *372*, 251.

[2] (a) Stiddard, M. H. B. *J. Chem. Soc.* **1962**, 4712. (b) Colton, R.; Tomkins, I. B. *Aust. J. Chem.* **1967**, *20*, 13. (c) Colton, R. *Coord. Chem. Rev.* **1971**, *6*, 269. (d) Lippard, S. J. *Prog. Inorg. Chem.* **1976**, *21*, 91. (e) Drew, M. G. B. *Ibid.* **1977**, *23*, 67. (f) Baker, P. K.; Fraser, S. G.; Keys, E. M. *J. Organomet. Chem.* **1986**, *309*, 319.

[3] The seven-coordinate $(H_2CPz_2)Mo(CO)_3I_2$, $(H_2CPz'_2)Mo(CO)_3I_2$, $(H_2CPz''_2)Mo(CO)_3I_2$, and $(H_2CPz_2)W(CO)_3I_2$ show a doublet, instead of a triplet, in the CO stretching region probably due to the accidental overlap of the two lower-frequency ν(CO) bands. This argument can find supporting evidence from the ν(CO) bands observed for these compounds in KBr disks: 2024 (s), 1966 (s), 1616 (s) for $(H_2CPz_2)Mo(CO)_3I_2$; 2016 (s), 1948 (s), 1928 (s) for $(H_2CPz'_2)Mo(CO)_3I_2$; 2010 (s), 1929 (s), 1919 (s) for $(H_2CPz''_2)Mo(CO)_3I_2$; and 2020 (s), 1948 (s), 1902 (s) cm^{-1} for $(H_2CpZ_2)W(CO)_3I_2$.

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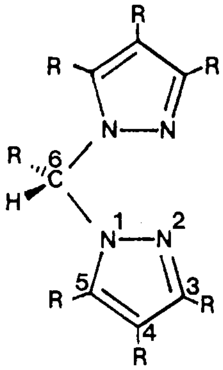

Figure 1. Structure and numbering scheme for N-N ligands: (i) 3-C-R = 4-C-R = 5-C-R = 6-C-R = H; N-N = H_2CPz_2. (ii) 3-C-R = 5-C-R = Me, 4-C-R = 6-C-R = H; N-N = $H_2CPz'_2$. (iii) 3-C-R = 4-C-R = 5-C-R = Me, 6-C-R = H; N-N = $H_2CPz''_2$. (iv) 3-C-R = 4-C-R = 5-C-R = H, 6-C-R = Ph; N-N = $PhHCPz_2$. (v) 3-C-R = 5-C-R = Me, 4-C-R = H, 6-C-R = Ph; N-N = $PhHCPz'_2$.

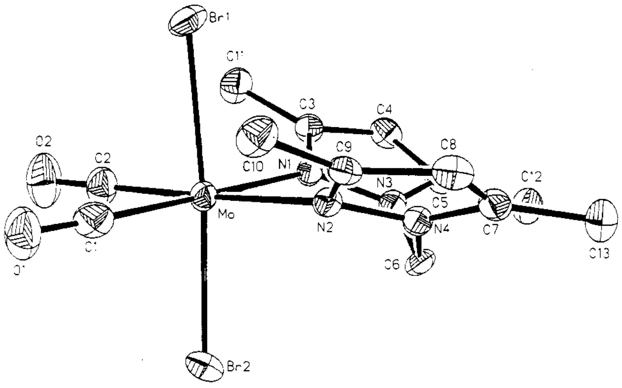

Figure 2. Structure of $(H_2CPz'_2)Mo(CO)_2Br_2$ (**2**), showing the atomic numbering scheme. Thermal ellipsoids correspond to 50% probability.

It is also evident that the monomeric form of **1-3** is maintained in solution and these compounds are, to the best of our knowledge, the first paramagnetic six-coordinate monomers with bidentate nitrogen ligands.[2,5]

The chemical shifts in the ^1H NMR spectra of **1-3** can be assigned by the integrated intensity ratios and line widths of the resonances.[1d] Hence, the 3-C-R and 5-C-R protons (Figure 1) in **2** and **3** show chemical shifts downfield from TMS, whereas those in **1** exhibit the upfield values. Coincidently, a similar pattern was previously reported for those of the 17-electron radicals, $TpMo(CO)_3$ (**4**) and $Tp'Mo(CO)_3$ (**5**) (Tp = hydridotris(pyrazol-1-yl)borato; Tp' = hydridotris(3,5-dimethylpyrazol-1-yl)borato).[1d,6] The pattern may indicate that the contact interaction through spin polarization is the principal factor in the paramagnetic shifts of **1-5** so that the downfield or upfield chemical shifts are reminiscent of the sign reversal of the hyperfine coupling constants of hydrogen and methyl substituents of a π radical.[6b,7,8]

Table I. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2

	x	*y*	*z*	*U*(eq)[a]
Mo	2996 (1)	3096 (1)	2625 (1)	44 (1)
Br(1)	532 (1)	2098 (1)	1871 (1)	74 (1)
Br(2)	5305 (1)	4243 (1)	3440 (1)	62 (1)
N(1)	4194 (8)	764 (7)	3131 (5)	46 (3)
N(2)	4285 (7)	2929 (7)	1036 (5)	43 (2)
N(3)	5652 (7)	297 (7)	2685 (5)	45 (3)
N(4)	5638 (7)	1920 (7)	990 (6)	42 (2)
O(1)	1255 (9)	6305 (8)	2037 (7)	99 (4)
O(2)	992 (11)	3387 (9)	4778 (6)	115 (4)
C(1)	1885 (12)	5198 (12)	2188 (8)	65 (4)
C(2)	1743 (12)	3233 (10)	4023 (9)	71 (4)
C(3)	3746 (10)	−425 (9)	3790 (7)	50 (3)
C(4)	4919 (11)	−1627 (9)	3759 (7)	57 (4)
C(5)	6130 (11)	−1169 (9)	3074 (7)	50 (3)
C(6)	6511 (9)	1317 (9)	1973 (7)	47 (3)
C(7)	6067 (10)	1798 (9)	−70 (7)	49 (3)
C(8)	4960 (10)	2764 (9)	−711 (7)	53 (3)
C(9)	3881 (10)	3442 (9)	−18 (7)	44 (3)
C(10)	2446 (10)	4564 (9)	−341 (7)	61 (4)
C(11)	2232 (11)	−420 (10)	4450 (8)	73 (4)
C(12)	7710 (10)	−1943 (9)	2754 (9)	65 (4)
C(13)	7502 (10)	793 (10)	−356 (7)	66 (4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table II. Selected Bond Lengths and Bond Angles for 2

	Bond Lengths, Å		
Mo–Br(1)	2.537 (1)	Mo–Br(2)	2.538 (1)
Mo–N(1)	2.251 (6)	Mo–N(2)	2.231 (6)
Mo–C(1)	2.035 (10)	Mo–C(2)	2.006 (11)
N(1)–N(3)	1.364 (9)	N(1)–C(3)	1.338 (10)
N(2)–N(4)	1.372 (8)	N(2)–C(9)	1.343 (10)
N(3)–C(5)	1.371 (9)	N(3)–C(6)	1.421 (10)
N(4)–C(6)	1.418 (10)	N(4)–C(7)	1.363 (11)
O(1)–C(1)	1.077 (12)	O(2)–C(2)	1.127 (14)
C(3)–C(4)	1.385 (11)	C(3)–C(11)	1.477 (12)
C(4)–C(5)	1.356 (12)	C(5)–C(12)	1.487 (12)
C(7)–C(8)	1.364 (11)	C(7)–C(13)	1.487 (12)
C(8)–C(9)	1.385 (12)	C(9)–C(10)	1.492 (11)
	Bond Angles, deg		
Br(1)–Mo–Br(2)	175.5 (1)	Br(1)–Mo–N(1)	90.7 (2)
Br(2)–Mo–N(1)	92.7 (2)	Br(1)–Mo–N(2)	89.5 (2)
Br(2)–Mo–N(2)	93.8 (2)	N(1)–Mo–N(2)	84.5 (2)
Br(1)–Mo–C(1)	88.9 (3)	Br(2)–Mo–C(1)	87.6 (3)
N(1)–Mo–C(1)	179.1 (3)	N(2)–Mo–C(1)	96.4 (3)
Br(1)–Mo–C(2)	88.1 (3)	Br(2)–Mo–C(2)	88.7 (3)
N(1)–Mo–C(2)	96.1 (3)	N(2)–Mo–C(2)	177.4 (3)
C(1)–Mo–C(2)	83.0 (4)	Mo–N(1)–N(3)	120.6 (4)
Mo–N(1)–C(3)	133.6 (5)	N(3)–N(1)–C(3)	105.7 (6)
Mo–N(2)–N(4)	120.4 (4)	Mo–N(2)–C(9)	133.3 (5)
N(4)–N(2)–C(9)	105.1 (6)	N(1)–N(3)–C(5)	111.0 (6)
N(1)–N(3)–C(6)	120.3 (6)	C(5)–N(3)–C(6)	128.6 (6)
N(2)–N(4)–C(6)	119.3 (6)	N(2)–N(4)–C(7)	111.4 (6)
C(6)–N(4)–C(7)	128.7 (6)	Mo–C(1)–O(1)	174.4 (9)
Mo–C(2)–O(2)	175.9 (8)	N(1)–C(3)–C(4)	109.6 (7)
N(1)–C(3)–C(11)	124.1 (7)	C(4)–C(3)–C(11)	126.2 (7)
C(3)–C(4)–C(5)	108.0 (7)	N(3)–C(5)–C(4)	105.6 (7)
N(3)–C(5)–C(12)	122.2 (7)	C(4)–C(5)–C(12)	132.2 (7)
N(3)–C(6)–N(4)	113.3 (6)	N(4)–C(7)–C(8)	105.8 (7)
N(4)–C(7)–C(13)	122.6 (7)	C(8)–C(7)–C(13)	131.6 (8)
C(7)–C(8)–C(9)	107.7 (7)	N(2)–C(9)–C(8)	110.0 (7)
N(2)–C(9)–C(10)	122.7 (7)	C(8)–C(9)–C(10)	127.3 (7)

Figure 2 shows the solid-state structure of $(H_2CPz'_2)Mo(CO)_2Br_2$ (**2**) with the atomic numbering scheme. Atomic positional parameters and selected bond lengths and bond angles are given in Tables I and II, respectively. This

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(4) Two relevant paramagnetic compounds, $Py_2Mo(CO)_2Cl_2$ and $Py_2Mo(CO)_2Br_2$, were reported earlier.[5] The chloride and the bromide have the magnetic moments of 2.71 and 2.76 μ_B, respectively. Both compounds gave an ESR signal at room temperature, and each gave a *g* value of 1.94. On the basis of this value, the calculated magnetic moment is 2.66 μ_B.

(5) Colton, R.; Rix, C. J. *Aust. J. Chem.* **1968**, *21*, 1155.

(6) (a) Shiu, K.-B.; Curtis, M. D. *Organometallics* **1983**, *2*, 936. (b) Curtis, M. D.; Shiu, K.-B.; Butler, W. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3335.

(7) For a π-radical,[8] the hyperfine coupling constants (A_H, A_{Me}) follow the McConnall's equation $A_H = Q_H\rho_C$, $A_{Me} = Q_{Me}\rho_C$, where ρ_C is the spin density at the carbon atom that the proton or the methyl group is bonded. Q_H and Q_{Me} are constants; Q_H is about −23.5 G while Q_{Me} is close to +27 G.

(8) (a) Carrington, A.; McLachlan, A. D. *Introduction to Magnetic Resonances*; Harper and Row: New York, 1967. (b) LaMar, G. N.; Horrocks, W. DeW. Jr.; Holm, R. H., Eds.; *NMR of Paramagnetic Molecules*; Academic Press: New York, 1973.

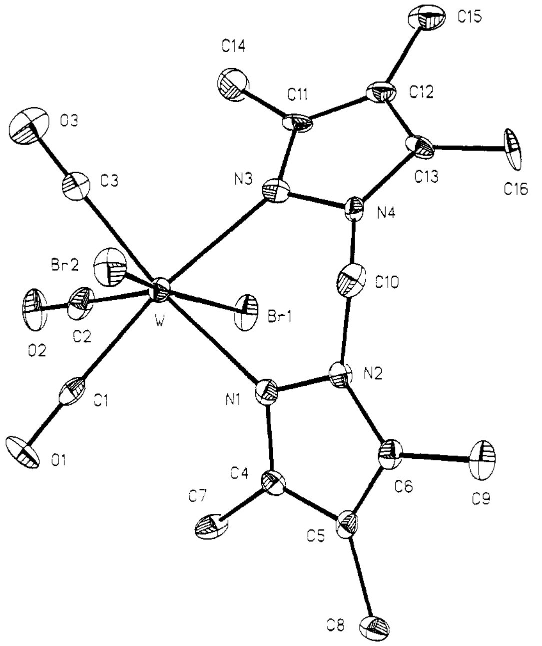

Figure 3. Structure of $(H_2CPz''_2)W(CO)_3Br_2$ (**7**) showing the atomic numbering scheme and 50% probability thermal ellipsoids.

complex has a quasi-octahedral structure with two trans bromine atoms, Br(1) and Br(2), which appear to be bent away from the bulky $H_2CPz'_2$ ligand to form an angle (u) ∠Br(1)-Mo-Br(2) = 175.5 (1)°. According to the EHMO calculations[9] on the Mo(II) compounds of the $MoA_2B_2C_2$ type (A = monobasic anion such as Br^-, Me^-, or RO^-; B, C = neutral ligands such as CO, pyridine (Py), Pr_3), this and two other angles, υ and w (υ = ∠N(1)-Mo-N(2) = 84.5 (2)°; w = ∠C(1)-Mo-C(2) = 83.0 (4)°), are very important in determining the relative energy levels of the $d_{x^2-y^2}$, d_{xz}, and d_{yz} orbitals, the t_{2g} set in octahedral or near octahedral molecular structures as well as the resultant magnetism after d^4 electron occupation in the Mo(II) compounds. The calculated u, υ, and w angles are 192, 83, and 86°, respectively, for a diamagnetic $Py_2Mo(CO)_2(OMe)_2$ compound,[10] adopting a similar ligand disposition around the central metal atom to **2**. Thus, it is quite obvious that the large difference in the u angle is the predominant factor for a change from diamagnetic to paramagnetic properties in **2**, although the different π-donating ability between the bromides and the methoxides cannot be completely excluded.[12]

The six-membered $\overline{\mathrm{C(6)N(4)N(2)MoN(1)N(3)}}$ metallacycle of the $Mo(H_2CPz'_2)$ fragment in **2** adopts a shallow boat form in contrast to the nearly planar five-membered $\overline{\mathrm{MoNCCN}}$ metallacycle of the Mo(bpy) fragment observed in the $(bpy)Mo(CO)_2(SO_2)_2$ structure[13] and probably maintained in $(bpy)Mo(CO)_4$.[2a] Thus, that the facile formation of **1**–**3** without the usual dependence on the methyl groups in the 3, 4, or 5 positions of the pyrazolyl ring (Figure 1)[1f] and that bromination of $(bpy)Mo(CO)_4$ gives the seven-coordinate $(bpy)Mo(CO)_3Br_2$[2] lead us to believe that the boat metallacycle is responsible for converting the possible $(N\text{-}N)Mo(CO)_3Br_2$ intermediate, following any of the synthetic routes used, into the six-coordinate compounds **1**–**3**. Unexpectedly, the angle ∠Br(1)-Mo-Br(2) is not 180° but 175.5 (1)° in **2**. This observation supports the steric congestion present in this six-coordinate compound and reflects the much larger nonbonded interactions in the unknown or unstable seven-coordinate compounds $(N\text{-}N)Mo(CO)_3Br_2$. Thus, the intramolecular decarbonylation occurs as rapidly as they are formed to produce **1**–**3** at room temperature.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^{-3}) for 7

	x	y	z	U(eq)[a]
W	7350 (1)	−39 (1)	1982 (1)	30 (1)
Br(1)	8238 (1)	1428 (2)	1034 (1)	51 (1)
Br(2)	6731 (1)	−945 (2)	3266 (1)	53 (1)
O(1)	8276 (9)	−2946 (12)	2416 (7)	62 (5)
O(2)	7033 (9)	−1529 (10)	227 (6)	66 (5)
O(3)	4932 (9)	−670 (15)	1127 (8)	86 (6)
N(1)	8906 (8)	576 (12)	2979 (6)	33 (4)
N(2)	8995 (7)	1433 (11)	3659 (5)	33 (4)
N(3)	6889 (8)	2086 (12)	2227 (7)	43 (4)
N(4)	7426 (7)	2769 (12)	2990 (5)	31 (4)
C(1)	7924 (9)	−1895 (20)	2240 (8)	42 (6)
C(2)	7165 (10)	−957 (15)	877 (8)	50 (6)
C(3)	5814 (9)	−459 (19)	1445 (9)	51 (6)
C(4)	9918 (11)	120 (12)	3134 (8)	33 (5)
C(5)	10592 (9)	655 (14)	3898 (7)	32 (5)
C(6)	9989 (9)	1492 (14)	4202 (6)	34 (5)
C(7)	10213 (9)	−816 (16)	2506 (8)	49 (5)
C(8)	11786 (11)	331 (15)	4318 (9)	48 (5)
C(9)	10337 (13)	2344 (17)	4994 (9)	60 (6)
C(10)	8045 (10)	2010 (15)	3738 (7)	43 (5)
C(11)	6293 (10)	3005 (16)	1704 (8)	40 (5)
C(12)	6384 (10)	4223 (16)	2109 (8)	41 (6)
C(13)	7128 (9)	4065 (15)	2938 (8)	36 (5)
C(14)	5550 (13)	2654 (18)	803 (9)	72 (7)
C(15)	5845 (11)	5531 (17)	1693 (11)	63 (7)
C(16)	7566 (14)	4984 (11)	3639 (8)	46 (6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

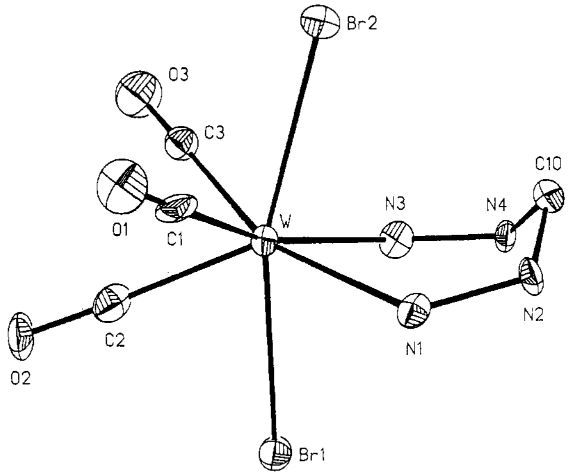

Figure 4. Central part of **7** showing the boat conformation of the six-membered metallacycle $C(N\text{-}N)_2W$ of the $(H_2CPz''_2)W$ fragment and the distorted capped octahedral geometry of the central W atom with one carbonyl, C(2)O(2), in the unique capping position.

The structure of $(H_2CPz''_2)W(CO)_3Br_2$ (**7**) was determined by X-ray crystallography. The atomic positional parameters and the important bond lengths and bond angles are listed in Table III and IV, respectively. An

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(9) Kubacek, P.; Hoffman, R. *J. Am. Chem. Soc.* **1981**, *103*, 4320.

(10) In fact, a similar diamagnetic compound, $Py_2Mo(CO)_2(OBu^t)_2$, was characterized structurally to find u = 204°, υ = 85°, and w = 72°.[11]

(11) Chisholm, M. H.; Huffman, J. C.; Kelly, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 7615.

(12) The electron-donating and/or -accepting capability of N-N (N-N = H_2CPz_2, $H_2CPz'_2$, or $H_2CPz''_2$) is probably similar to those of two pyridine ligands, based on the similar ν(CO) bands: 2025, 1945 for $Py_2Mo(CO)_2Br_2$;[5] 2028, 1948 for $(H_2CPz_2)Mo(CO)_2Br_2$; 2024, 1942 for $(H_2CPz'_2)Mo(CO)_2Br_2$; and 2000, 1924 cm^{-1} for $(H_2CPz''_2)Mo(CO)_2Br_2$ measured in CH_2Cl_2 solution (Table VIII).

(13) Kubas, G. J.; Ryan, R. R.; McCarty, V. *Inorg. Chem.* **1980**, *19*, 3003.

Table IV. Selected Bond Lengths and Bond Angles for 7

Bond Lengths, Å			
W-Br(1)	2.667 (2)	W-Br(2)	2.648 (2)
W-N(1)	2.250 (9)	W-N(3)	2.274 (12)
W-C(1)	1.990 (19)	W-C(2)	1.963 (14)
W-C(3)	1.977 (12)	O(1)-C(1)	1.143 (22)
O(2)-C(2)	1.166 (17)	O(3)-C(3)	1.131 (16)
N(1)-N(2)	1.373 (14)	N(1)-C(4)	1.358 (17)
N(2)-C(6)	1.325 (12)	N(2)-C(10)	1.428 (17)
N(3)-N(4)	1.392 (13)	N(3)-C(11)	1.320 (17)
N(4)-C(10)	1.439 (15)	N(4)-C(13)	1.344 (19)
C(4)-C(5)	1.379 (15)	C(4)-C(7)	1.530 (20)
C(5)-C(6)	1.357 (19)	C(5)-C(8)	1.536 (17)
C(6)-C(9)	1.486 (18)	C(11)-C(12)	1.367 (22)
C(11)-C(14)	1.516 (17)	C(12)-C(13)	1.395 (15)
C(12)-C(15)	1.531 (22)	C(13)-C(16)	1.429 (17)
Bond Angles, deg			
Br(1)-W-Br(2)	163.1 (1)	Br(1)-W-N(1)	78.2 (3)
Br(2)-W-N(1)	88.3 (3)	Br(1)-W-N(3)	77.8 (3)
Br(2)-W-N(3)	90.4 (3)	N(1)-W-N(3)	81.7 (4)
Br(1)-W-C(1)	114.8 (4)	Br(2)-W-C(1)	73.3 (4)
N(1)-W-C(1)	84.5 (5)	N(3)-W-C(1)	158.9 (5)
Br(1)-W-C(2)	70.6 (5)	Br(2)-W-C(2)	126.1 (5)
N(1)-W-C(2)	126.7 (5)	N(3)-W-C(2)	129.4 (5)
C(1)-W-C(2)	71.6 (6)	Br(1)-W-C(3)	116.5 (5)
Br(2)-W-C(3)	74.6 (5)	N(1)-W-C(3)	160.4 (6)
N(3)-W-C(3)	88.7 (6)	C(1)-W-C(3)	99.3 (6)
C(2)-W-C(3)	72.3 (6)	W-N(1)-N(2)	124.5 (7)
W-N(1)-C(4)	131.1 (8)	N(2)-N(1)-C(4)	104.0 (8)
N(1)-N(2)-C(6)	111.6 (10)	N(1)-N(2)-C(10)	118.7 (8)
C(6)-N(2)-C(10)	129.4 (10)	W-N(3)-N(4)	121.6 (7)
W-N(3)-C(11)	132.0 (9)	N(4)-N(3)-C(11)	105.1 (11)
N(3)-N(4)-C(10)	118.8 (11)	N(3)-N(4)-C(13)	111.0 (9)
C(10)-N(4)-C(13)	129.2 (10)	W-C(1)-O(1)	177.5 (12)
W-C(2)-O(2)	178.0 (11)	W-C(3)-O(3)	178.3 (15)
N(1)-C(4)-C(5)	110.2 (12)	N(1)-C(4)-C(7)	122.3 (9)
C(5)-C(4)-C(7)	127.4 (12)	C(4)-C(5)-C(6)	106.4 (10)
C(4)-C(5)-C(8)	126.0 (12)	C(6)-C(5)-C(8)	127.6 (10)
N(2)-C(6)-C(5)	107.7 (10)	N(2)-C(6)-C(9)	124.1 (12)
C(5)-C(6)-C(9)	128.2 (11)	N(2)-C(10)-N(4)	114.1 (11)
N(3)-C(11)-C(12)	111.3 (11)	N(3)-C(11)-C(14)	121.7 (14)
C(12)-C(11)-C(14)	126.8 (13)	C(11)-C(12)-C(13)	106.8 (12)
C(11)-C(12)-C(15)	125.9 (11)	C(13)-C(12)-C(15)	127.0 (13)
N(4)-C(13)-C(12)	105.6 (11)	N(4)-C(13)-C(16)	122.0 (10)
C(12)-C(13)-C(16)	132.4 (14)		

Table V. Atomic Coordinatines ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for 2

	x	y	z	U(eq)[a]
I(1)	3855 (1)	7500	284 (1)	62 (1)
I(2)	6946 (1)	7500	2248 (1)	81 (1)
Mo	5454 (1)	7500	959 (1)	49 (1)
O(1)	4921 (4)	8851 (5)	3343 (7)	100 (3)
N(1)	5903 (3)	6480 (4)	−632 (6)	44 (2)
N(2)	6115 (3)	6680 (4)	−1996 (5)	41 (2)
C	5844 (6)	7500	−2686 (10)	42 (3)
C(1)	5113 (5)	8402 (7)	2441 (8)	69 (3)
C(11)	6082 (6)	5118 (6)	924 (9)	78 (4)
C(12)	6171 (4)	5619 (5)	−441 (8)	52 (3)
C(13)	6528 (5)	5282 (6)	−1638 (9)	60 (3)
C(14)	6489 (4)	5953 (5)	−2613 (8)	49 (2)
C(15)	6763 (5)	5963 (6)	−4126 (8)	71 (3)
C(21)	4940 (6)	7500	−3041 (9)	40 (3)
C(22)	4542 (5)	6697 (6)	−3264 (8)	59 (3)
C(23)	3735 (5)	6675 (8)	−3677 (9)	80 (4)
C(24)	3359 (8)	7500	−3848 (13)	93 (7)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VI. Selected Bond Lenghts and Bond Angles for 9

Bond Lengths, Å			
I(1)-Mo	2.706 (1)	I(2)-Mo	2.742 (1)
Mo-N(1)	2.249 (6)	Mo-C(1)	2.009 (9)
Mo-N(1A)	2.249 (6)	Mo-C(1A)	2.009 (9)
O(1)-C(1)	1.125 (11)	N(1)-N(2)	1.376 (7)
N(1)-C(12)	1.344 (10)	N(2)-C	1.436 (8)
N(2)-C(14)	1.359 (9)	C-C(21)	1.523 (13)
C-N(2A)	1.436 (8)	C(11)-C(12)	1.497 (11)
C(12)-C(13)	1.372 (11)	C(13)-C(14)	1.352 (11)
C(14)-C(15)	1.509 (11)	C(21)-C(22)	1.360 (10)
C(21)-C(22A)	1.360 (10)	C(22)-C(23)	1.383 (11)
C(23)-C(24)	1.364 (12)	C(24)-C(23A)	1.364 (12)
Bond Angles, deg			
I(1)-Mo-I(2)	167.2 (1)	I(1)-Mo-N(1)	99.1 (1)
I(2)-Mo-N(1)	90.4 (1)	I(1)-Mo-C(1)	84.0 (2)
I(2)-Mo-C(1)	86.3 (2)	N(1)-Mo-C(1)	176.7 (3)
I(1)-Mo-N(1A)	99.1 (1)	I(2)-Mo-N(1A)	90.4 (1)
N(1)-Mo-N(1A)	83.0 (3)	C(1)-Mo-N(1A)	97.5 (3)
I(1)-Mo-C(1A)	84.0 (2)	I(2)-Mo-C(1A)	86.3 (2)
N(1)-Mo-C(1A)	97.5 (3)	C(1)-Mo-C(1A)	81.9 (5)
N(1A)-Mo-C(1A)	176.7 (3)	Mo-N(1)-N(2)	125.3 (4)
Mo-N(1)-C(12)	129.5 (5)	N(2)-N(1)-C(12)	104.1 (5)
N(1)-N(2)-C	122.0 (6)	N(1)-N(2)-C(14)	110.8 (6)
C-N(2)-C(14)	126.4 (6)	N(2)-C-C(21)	113.9 (5)
N(2)-C-N(2A)	112.9 (7)	C(21)-C-N(2A)	113.9 (5)
Mo-C(1)-O(1)	174.5 (8)	N(1)-C(12)-C(11)	122.8 (7)
N(1)-C(12)-C(13)	111.3 (7)	C(11)-C(12)-C(13)	125.9 (7)
C(12)-C(13)-C(14)	106.8 (7)	N(2)-C(14)-C(13)	107.0 (7)
N(2)-C(14)-C(15)	122.6 (7)	C(13)-C(14)-C(15)	130.4 (7)
C-C(21)-C(22)	120.3 (5)	C-C(21)-C(22A)	120.3 (5)
C(22)-C(21)-C(22A)	119.2 (10)	C(21)-C(22)-C(23)	121.7 (9)
C(22)-C(23)-C(24)	116.6 (10)	C(23)-C(24)-C(23A)	124.1 (12)

overall view of **7** is presented in Figure 3, while Figure 4 presents only the central part of the molecule, showing clearly the boat conformation of the $W(H_2CPz''_2)$ fragment and the geometry of the tungsten atom, which is a distorted capped octahedron with one carbonyl in the unique capping position (W-C(2) = 1.963 (14) Å). The capped face contains one bromine atom (W-Br(2) = 2.648 (2) Å) and two carbonyl groups (W-C(1) = 1.990 (19) Å, W-C(3) = 1.977 (12) Å). The remaining bromine atom (W-Br(1) = 2.667 (2) Å) with two nitrogen atoms of $H_2CPz''_2$ (W-N(1) = 2.250 (9) Å, W-N(3) = 2.274 (12) Å) make up the uncapped face.

Interestingly, although in the structures of **2** and **7** the bites of the N-N ligand are similar (**2**, $\angle$N(1)-Mo-N(2) = 84.6 (2)°; **7**, $\angle$N(1)-W-N(3) = 81.7 (4)°) and the M-N bond lengths are similar (**2**, 2.251 (5), 2.235 (5) Å; **7**, 2.274 (12), 2.250 (9) Å), the angles $\angle$Br(1)-M-Br(2) are quite different. The two bromine atoms in **2** appear to be pushed out from $H_2CPz'_2$ with $\angle$Br(1)-Mo-Br(2) = 175.5 (1)° whereas those in **7** seem to represent the conformation of least intraligand repulsion. Thus, they bend toward $H_2CPz''_2$ with $\angle$Br(1)-W-Br(2) = 163.1 (1)°, although this ligand seems similar in the steric bulk to $H_2CPz'_2$ (Figure 1). The different values for the angle $\angle$Br-M-Br raise a question for us to answer: why does the intramolecular decarbonylation occur for the unknown (N-N)$Mo(CO)_3Br_2$ intermediates while it does not happen for the carbonyl halides (N-N)$W(CO)_3Br_2$ and (N-N)$M(CO)_3I_2$? We suggest that the intramolecular decarbonylation or the stability of the known and the unknown seven-coordinate compounds is determined by the relative importance of the electronic and steric effects. Apparently, the metal-to-CO bonding interaction is rather weak in the unknown seven-coordinate (N-N)$Mo(CO)_3Br_2$, so that the steric effect dictates decarbonylation into the six-coordinate (N-N)$Mo(CO)_2Br_2$. Although the W(II) and Mo(II) atoms are of similar size, the more diffuse 5d orbitals compared with the 4d orbitals overlap better the carbonyl π^* orbitals, leading the formation of the stable seven-coordinate (N-N)$W(CO)_3Br_2$. Sine I^- is a better electron donor than Br^-, more metal-to-CO back bonding is expected for (N-N)$M(CO)_3I_2$ than (N-N)$M(CO)_3Br_2$. Thus, the general ease of CO loss follows the trend (N-N)$Mo(CO)_3Br_2$ > (N-N)$Mo(CO)_3I_2$, (N-N)$W(CO)_3Br_2$ > (N-N)$W(CO)_3I_2$. When the bulky N-N ligand is replaced by the two small MeCN ligands, the

Table VII. Analytical Data for the Six- and Seven-Coordinated Carbonyl Halides

compound (formula)	anal. found (calcd), % C	H	N	color	yield, % method 1	method 2
$(H_2CPx_2)Mo(CO)_2Br_2$ ($C_9H_8Br_2MoN_4O_2$)	23.44 (23.50)	1.77 (1.75)	12.27 (12.19)	red-brown	68	65
$(H_2CPz'_2)Mo(CO)_2Br_2$ ($C_{13}H_{16}Br_2MoN_4O_2$)	30.66 (30.26)	3.26 (3.13)	10.59 (10.86)	yellow-brown	76	72
$(H_2CPz''_2)Mo(CO)_2Br_2$ ($C_{15}H_{20}Br_2MoN_4O_2$)	32.64 (33.03)	3.70 (3.70)	10.16 (10.27)	yellow-brown	74	70
$(H_2CPz_2)W(CO)_3Br_2$[a] ($C_{10}H_8Br_2N_4O_3W$)	20.84 (20.85)	1.40 (1.40)	9.62 (9.73)	yellow-brown	70	65
$(H_2CPz'_2)W(CO)_3Br_2$ ($C_{14}H_{16}Br_2N_4O_3W$)	26.48 (26.60)	2.57 (2.53)	8.87 (8.87)	red-brown	68	66
$(H_2CPz''_2)W(CO)_3Br_2$ ($C_{16}H_{20}Br_2N_4O_3W$)	29.06 (29.11)	3.05 (3.05)	8.41 (8.49)	red-brown	72	70
$(H_2CPz_2)Mo(CO)_3I$ ($C_{10}H_8I_2MoN_4O_3$)	20.65 (20.64)	1.44 (1.39)	9.62 (9.63)	dark orange-yellow	78	62
$(H_2CPz'_2)Mo(CO)_3I_2$ ($C_{14}H_{16}I_2MoN_4O_3$)	26.13 (26.35)	2.55 (2.53)	8.75 (8.78)	dark orange-yellow	76	68
$(H_2CPz''_2)Mo(CO)_3I_2$ ($C_{16}H_{20}I_2MoN_4O_3$)	28.75 (28.85)	3.02 (3.03)	8.39 (8.41)	dark orange-yellow	81	75
$(H_2CPz_2)W(CO)_3I_2$ ($C_{10}H_8I_2N_4O_3W$)	17.90 (17.93)	1.25 (1.20)	8.25 (8.37)	dark orange-yellow	75	78
$(H_2CPz'_2)W(CO)_3I_2$ ($C_{14}H_{16}I_2N_4O_3W$)	23.13 (23.16)	2.23 (2.22)	7.70 (7.72)	dark orange-yellow	78	82
$(H_2CPz''_2)W(CO)_3I_2$ ($C_{16}H_{20}I_2N_4O_3W$)	25.00 (25.48)	2.69 (2.67)	7.14 (7.43)	dark orange-yellow	78	85
$(PhHCPz_2)Mo(CO)_3I_2$ ($C_{16}H_{12}I_2MoN_4O_3$)	28.89 (29.20)	1.87 (1.84)	8.44 (8.52)	dark orange-yellow	63	
$(PhHCPz'_2)Mo(CO)_2I_2$ ($C_{19}H_{20}I_2MoN_4O_2$)	33.26 (33.25)	2.93 (2.94)	8.17 (8.17)	dark orange-yellow	73	

[a] This compound is slightly air sensitive even in the solid state.

resultant seven-coordinate $(MeCN)_2M(CO)_3X_2$ should be stable, for the unfavorable steric effect is removed. Indeed, these compounds were prepared and found to be stable thermally.[2f] The reported stability of $(MeCN)_2M(CO)_3X_2$ parallels the following trend: $(MeCN)_2W(CO)_3I_2$ is more stable than $(MeCN)_2Mo(CO)_3I_2$, and both are more stable than $(MeCN)_2M(CO)_3Br_2$.

By comparing the angle ∠OC–Mo–CO formed from the two cis-carbonyls and the central Mo atom in the structures of $(H_2CPz'_2)Mo(CO)_4$[1e] and $(PhHCPz'_2)Mo(CO)_4$ (**8**),[14] we have recently recognized that the $PhHCPz'_2$ ligand is bulkier than the $H_2CPz'_2$ ligand. To gain further support that the more important steric effect may help to induce decarbonylation of the seven-coordinated carbonyl iodides, we also carried out the iodination of **8**. Fortunately, the iodination product is the expected six-coordinate compound $(PhHCPz'_2)Mo(CO)_2I_2$ (**9**), which is paramagnetic with a magnetic moment of 2.86 μ_B and monomeric with a solid-state structure (Figure 5) containing features similar to those of **2** except that **9** has an imposed mirror plane including Mo, I(1), I(2), C, C(21), and C(24) atoms. This result then led us to perform the iodination of $(PhHCPz_2)Mo(CO)_4$. To our surprise, the product is a seven-coordinate compound, $(PhHCPz_2)Mo(CO)_3I_2$. Apparently, there is not a net increase in the steric bulk of the bidentate ligand by simultaneous replacement of the H atom and two methyl groups of $H_2CP'_2$ (Figure 1) with the Ph group and two H atoms, respectively. Thus, iodination of either $(H_2CPz'_2)Mo(CO)_4$ or $(PhHCPz_2)Mo(CO)_4$ gives a seven-coordinate product. The atomic positional parameters of **9** are given in Table V. Selected bond lengths and bond angles are presented in Table VI.

Experimental Section

All operations were performed by the usual Schlenk techniques,[15] using deoxygenated, dry solvents and gases. IR spectra, calibrated with polystyrene, were recorded on a Hitachi Model 260-30 or 270-30 instrument; NMR spectra were obtained on a Bruker WP-100 (^1H, 100 MHz) or AM-400 (^1H, 400 MHz) FT NMR spectrometer. Proton chemical shifts (δ in ppm, J in hertz) are positive downfield or negative upfield relative to internal $SiMe_4$ (TMS) standard. The magnetic moments were measured by the Evans' method in d_6-acetone at 294 K.[16] Elemental analysis results were obtained by the staff of the Microanalytical Service of the Department of Chemistry, National Cheng Kung University.

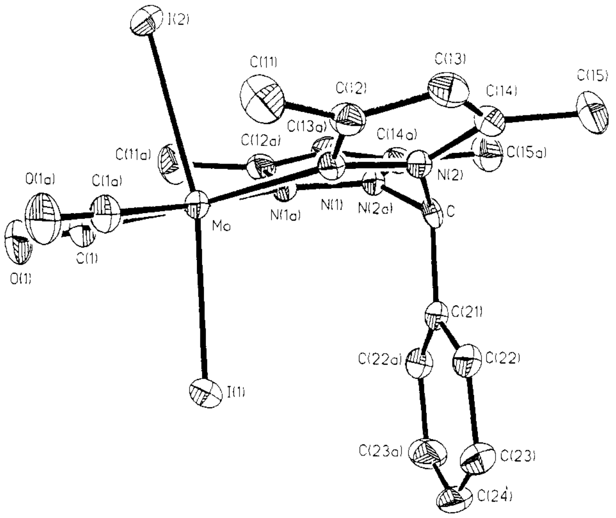

Figure 5. Structure of $(PhHCPz'_2)Mo(CO)_2I_2$ (**9**) showing the atomic numbering scheme. The thermal ellipsoids are drawn at 50% probability level.

The ligands H_2CPz_2, $H_2CPz'_2$, $H_2CPz''_2$, $PhHCPz_2$, and $PhHCPz'_2$ were prepared as described previously.[14,17-19] The complexes $(H_2CPz_2)M(CO)_4$, $(H_2CPz'_2)M(CO)_4$, $(H_2CPz''_2)M(CO)_4$, $(PhHCPz_2)Mo(CO)_4$, $(PhHCPz'_2)Mo(CO)_4$, and $(MeCN)_2M(CO)_3X_2$ were prepared by literature methods.[1b,2f,14,19]

Since the preparations of $(N\text{-}N)M(CO)_mX_2$ (N-N = H_2CPz_2, $H_2CPz'_2$, $H_2CPz''_2$, $PhHCPz_2$, or $PhHCPz'_2$; M = Mo or W; m = 2 or 3; X = Br or I) are all similar and straightforward, only a typical preparation is described. Other products and the analytical data are shown in Table VII. The IR and NMR data are listed in Table VIII.

$(H_2CPz'_2)Mo(CO)_2Br_2$. Method 1. A stirred solution of $(H_2CPz'_2)Mo(CO)_4$ (0.41 g, 1.0 mmol) in CH_2Cl_2 (20 mL) was treated dropwise with a solution of Br_2 (0.16 g of Br_2 in 20 mL of CH_2Cl_2) at room temperature. After the addition of Br_2 was complete, 10 mL of MeOH was added, and the CH_2Cl_2 solvent was then removed under vacuum, giving an orange–yellow precipitate. This solid was collected and recrystallized from CH_2Cl_2/MeOH to give 0.41 g (76%) of product.

Method 2. The ligand $H_2CPz'_2$ (0.20 g, 1.0 mmol) was added to 20 mL of MeCN in which was dissolved 0.42 g (1.0 mmol) of $(MeCN)_2Mo(CO)_3Br_2$ at room temperature. The mixture was stirred at the temperature for 2 h. The solvents were removed under vacuum, giving an orange–yellow residue. The product is

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Table VIII. Spectroscopic Data for the Six- and Seven-Coordinated Carbonyl Halides

compound	IR[a] ν(CO), cm^{-1}	^{1}H NMR,[b] ppm 3-C–R	5-C–R	4-C–R	6-C–R/6-C–H
$(H_2CPz_2)Mo(CO)_2Br_2$	2028 (s), 1948 (s)	−24.00 (2 H, s)	−31.27 (2 H, s)	9.46 (2 H, s)	*(2 H)
$(H_2CPz'_2)Mo(CO)_2Br_2$	2024 (s), 1942 (s)	44.30 (6 H, s)	40.60 (6 H, s)	7.31 (2 H, s)	16.00 (1 H, s), 0.10 (1 H, s)
$(H_2CPz''_2)Mo(CO)_2Br_2$	2020 (s), 1940 (s)	45.21 (6 H, s)	43.01 (6 H, s)	4.55 (6 H, s)	17.80 (1 H, s), *(1 H)
$(PhHCPz'_2)Mo(CO)_2I_2$	2000 (s), 1924 (s)	47.84 (6 H, s)	53.18 (6 H, s)	10.07 (2 H, s)	19.53 (1 H, s),[c] 6.94 (2 H, s),[c] 5.55 (2 H, s),[c] 0.40 (1 H, s)
$(H_2CPz_2)W(CO)_3Br_2$	2024 (s), 1958 (s), 1938 (sh)	8.26 (4 H, d)(2.6)[d]		6.66 (2 H, t)	6.83 (2 H, s)
$(H_2CPz'_2)W(CO)_3Br_2$	2028 (s), 1940 (s), 1920 (s)	2.61 (6 H, s), 2.41 (6 H, s)		6.26 (2 H, s)	6.85 (2 H, s)
$(H_2CPz''_2)W(CO)_3Br_2$	2028 (s), 1930 (sh), 1920 (s)	2.53 (6 H, s), 2.34 (6 H, s)		1.97 (6 H, s)	6.85 (2 H, s)
$(H_2CPz_2)Mo(CO)_3I_2$	2028 (s), 1944 (vs)	7.98 (2 H, d), 7.74 (2 H, d)		6.54 (2 H, t)	6.75 (2 H, s)
$(H_2CPz'_2)Mo(CO)_3I_2$	2024 (s), 1934 (vs)	2.47 (6 H, s), 2.41 (6 H, s)		6.06 (2 H, s)	6.55 (2 H, s)
$(H_2CPz''_2)Mo(CO)_3I_2$	2008 (s), 1930 (vs)	2.39 (6 H, s), 2.32 (6 H, s)		1.92 (6 H, s)	6.54 (2 H, s)
$(H_2CPz_2)W(CO)_3I_2$	2020 (s), 1924 (vs)	8.22 (2 H, d)(2.4), 8.01 (2 H, d)(3.0)		6.55 (2 H, t)	6.58 (2 H, s)
$(H_2CPz'_2)W(CO)_3I_2$	2020 (s), 1926 (sh), 1916 (s)	2.49 (6 H, s), 2.45 (6 H, s)		6.09 (2 H, s)	6.60 (2 H, s)
$(H_2CPz''_2)W(CO)_3I_2$	2016 (s), 1928 (s), 1916 (s)	2.40 (6 H, s), 2.35 (6 H, s)		1.92 (6 H, s)	9.59 (2 H, s)
$(PhHCPz_2)Mo(CO)_3I_2$	2032 (s), 1974 (s), 1941 (s)	8.59 (2 H, d)(2.1), 8.50 (2 H, d)(2.4)		6.79 (2 H, t)	8.55 (1 H, s), 7.46 (3 H, m),[c] 6.40 (2 H, m)[c]

[a] In CH_2Cl_2 solution. Abbreviations: s, strong; vs, very strong; sh, shoulder. [b] The chemical shifts are not assigned for the 3-C–R and the 5-C–R protons of the diamagnetic seven-coordinated compounds. The asterisks represent the signal not observed at 294 K. Solvents used for the NMR spectra: $(CD_3)_2CO$ for the carbonyl bromides, $(PhHCPz'_2)Mo(CO)_2I_2$, and $(PhHCPz_2)Mo(CO)_3I_2$; CD_3CN for $(H_2CPz_2)W(CO)_3I_2$; $CDCl_3$ for the other compounds. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. [c] The phenyl protons. [d] The coupling constant in hertz.

Table IX. Crystal, Data Collection, and Refinement Parameters for 2, 7, and 9

	2	7	9
		Crystal Parameters	
formula	$C_{13}H_{16}Br_2MoN_4O_2$	$C_{16}H_{20}Br_2N_4O_3W$	$C_{19}H_{20}I_2MoN_4O_2$
cryst system	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$Pnma$ (no. 62)
a, Å	8.198 (2)	13.255 (5)	16.438 (4)
b, Å	9.130 (3)	9.956 (4)	14.600 (4)
c, Å	12.291 (4)	16.315 (7)	9.515 (3)
α, deg	81.57 (2)		
β, deg	89.50 (2)	109.28 (4)	
γ, deg	83.94 (2)		
V, Å^3	905.0 (5)	2032.2 (14)	2283.5 (11)
Z	2	4	4
ρ_{calcd}, g cm^{-3}	1.894	2.157	1.996
T, K	295	296	298
μ, cm^{-1}	50.9	97.3	32.6
cryst dimens, mm	0.75 × 0.37 × 0.25	0.62 × 0.68 × 0.70	0.41 × 0.23 × 0.21
orientatn rflns, range	18, $9° \le 2\theta \le 21°$	13, $15° \le 2\theta \le 30°$	17, $9° \le 2\theta \le 26°$
		Data Collection	
diffractometer		Nicolet R3m/V	
radiation		Mo Kα (λ = 0.71073 Å)	
monochromator		graphite cryst	
scan type		$\theta/2\theta$	
2θ scan range	$3° \le 2\theta \le 45°$	$2.5° \le 2\theta \le 50°$	$2.5° \le 2\theta \le 50°$
data collected	$+h,\pm k,\pm l$	$\pm h,+k,+l$	$+h,+k,+l$
scan speed, deg min^{-1}	variable, 2–15	variable, 3–15	variable, 4–15
rflns collected	2399	2988	2488
independent data	2379	2387	2115
independent data obsd	1619 ($2.5\sigma(I)$)	1803 ($3\sigma(I)$)	1426 ($3\sigma(I)$)
std rflns		3 std/50 rflns	
decay, %		≤1	
		Refinement	
R, %	3.71	4.60	3.72
R_w, %	3.66	5.13	3.96
$\Delta(\rho)$, e Å^{-3}	0.49	2.02[b]	0.94
Δ/σ	0.007	0.033	0.002
GOF	1.53	0.64	1.48
data/parameter	8.1	7.6	10.5
weighing factor,[a] g	0.0003	0.0109	0.0004

[a] $w^{-1} = \sigma^2(F) + g(F^2)$. [b] Ghost peak.

then recrystallized from CH_2Cl_2/MeOH to give 0.31 g (64%).

Crystallographic Studies. The crystals of **2**, **7**, and **9** were grown from CH_2Cl_2/hexane at room temperature. General operating procedures and listings of programs were previously given.[1i] Absorption correction was performed on the three compounds (the calculated transmission range is 0.91–0.72 for **2**, 0.92–0.74 for **7**, and 0.94–0.87 for **9**) using ψ scans. Pertinent crystallographic information is summarized in Table IX.

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Registry No. **1**, 120170-13-0; **2**, 120170-14-1; **3**, 120170-15-2; **7**, 125108-55-6; **8**, 124225-84-9; **9**, 125108-63-6; $(H_2CPz_2)W(CO)_3Br_2$, 125108-53-4; $(H_2CPz'_2)W(CO)_3Br_2$, 125108-54-5; $(H_2CPz_2)Mo(CO)_3I_2$, 125108-56-7; $(H_2CPz'_2)Mo(CO)_3I_2$, 125108-57-8; $(H_2CPz''_2)Mo(CO)_3I_2$, 125108-58-9; $(H_2CPz_2)W(CO)_3I_2$, 125108-59-0; $(H_2CPz'_2)W(CO)_3I_2$, 125108-60-3; $(H_2CPz''_2)W(CO)_3I_2$, 125108-61-4; $(PhHCPz_2)Mo(CO)_3I_2$, 125108-62-5; $(H_2CPz'_2)Mo(CO)_4$, 119268-12-1; $(MeCN)_2Mo(CO)_3Br_2$, 105059-20-9; $(H_2CPz_2)Mo(CO)_4$, 119578-37-9; $(H_2CPz_2)W(CO)_4$, 123543-51-1; $(H_2CPz'_2)W(CO)_4$, 119268-13-2; $(H_2CPz''_2)Mo(CO)_4$, 119578-38-0; $(H_2CPz''_2)W(CO)_4$, 125108-64-7; $(PhHCPz_2)Mo(CO)_4$, 125108-65-8; $(PhHCPz'_2)Mo(CO)_4$, 124225-84-9; $(MeCN)_2Mo(CO)_3I_2$, 102349-56-4; $(MeCN)_2W(CO)_3Br_2$, 105059-21-0; $(MeCN)_2W(CO)_3I_2$, 102382-37-6.

Supplementary Material Available: Tables of fractional coordinates of hydrogen atoms and U_{ij} values for non-hydrogen atoms (3 pages); a listing of F_o vs F_c values for **2**, **7**, and **9** (25 pages). Ordering information is given on any current masthead page.

Aspects of the Cleavage of Phosphines with Potassium: Synthesis and Reactivity of Lithium and Potassium Bis(*p*-(dimethylamino)phenyl)phosphide

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The cleavage of the triarylphosphines $P(p\text{-}C_6H_4NMe_2)_3$ and $PhP(p\text{-}C_6H_4NMe_2)_2$ with potassium in ether solvents was found to occur at room temperature. Cleavage of the mixed phosphine $PhP(p\text{-}C_6H_4NMe_2)_2$ was found to give a mixture of products that reflects the relative stability of the phosphides $KP(Ph)(p\text{-}C_6H_4NMe_2)$ and $KP(p\text{-}C_6H_4NMe_2)_2$. Cleavage with lithium resulted in the scrambling of the aryl groups so that the products $LiPPh_2$ and $P(Ph)_2(p\text{-}C_6H_4NMe_2)$ also were obtained. Comparison with the cleavage of PPh_3 shows that $MP(p\text{-}C_6H_4NMe_2)_2$ (M = Li, K) is more nucleophilic than the corresponding phenylphosphide $MPPh_2$. The preparation of the chlorophosphine $ClP(p\text{-}C_6H_4NMe_2)_2$ and its reaction with lithium or potassium is an alternate path to the phosphides. The reaction of $ClP(p\text{-}C_6H_4NMe_2)_2$ with lithium yielded both $LiP(p\text{-}C_6H_4NMe_2)_2$ and $(p\text{-}C_6H_4NMe_2)_2PP(p\text{-}C_6H_4NMe_2)_2$. The amino-substituted potassium phosphide $KP(p\text{-}C_6H_4NMe_2)_2$ is conveniently prepared from $P(p\text{-}C_6H_4NMe_2)_3$ and is a useful intermediate for the synthesis of phosphines that contain amine functional groups.

Introduction

The preparation of water-soluble phosphines for use in aqueous-phase and two-phase catalytic reactions is an area of current interest.[1-7] One goal of two-phase reactions is to achieve catalytic systems in which the products can be easily separated from the homogeneous catalyst. Applications are found in the homogeneous hydrogenation and hydroformylation of olefins. The most successful approach to date is the sulfonation of phenyl groups bonded to phosphorus in tertiary and ditertiary phosphines.[2] For example, sulfonated derivatives of triphenylphosphine[2,3] and of several chiral phosphines such as (*S*,*S*)-2,3-bis(diphenylphosphino)butane[1a] have been reported. Water-soluble phosphines with cationic and neutral polar groups also are of interest.[4-7] Examples of phosphines with quaternary amine functional groups are limited to one such group per phosphorus atom, which limits the water solubility of this type of modified phosphines.[5,7]

Recently we have sought phosphines that contain two or more cationic groups per phosphorus atom for use in aqueous and supported aqueous phase catalysis.[8] The systematic introduction of (dimethylamino)phenyl groups into phosphines and their subsequent quaternization would satisfy this purpose.[9] Tertiary phosphines typically are synthesized by one of two routes, nucleophilic substitution of a chlorophosphine with an organolithium or Grignard reagent or nucleophilic substitution of an alkyl halide or tosylate with a phosphide anion.[10] Furthermore, chlorophosphines may be converted to phosphides through re-

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