Preliminary communication

Organotransition-metal complexes of multidentate ligands

VIII *. Convenient syntheses and structure of the paramagnetic 16-electron molybdenum(II) carbonyl derivatives, [Mo(CO)₂Br₂(N–N)] (N–N = nitrogen bidentate ligands)

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Abstract

The paramagnetic 16-electron metal carbonyl derivatives of molybdenum(II), $[Mo(CO)_2Br_2(N–N)]$ (N–N = H_2CPz_2 (**1**), $H_2CPz'_2$ (**2**), $H_2CPz''_2$ (**3**); Pz = pyrazol-1-yl; Pz′ = 3,5-dimethylpyrazol-1-yl; Pz″ = 3,4,5-trimethylpyrazol-1-yl) are obtained either by bromination of $[Mo(CO)_4(N–N)]$ in CH_2Cl_2 at $-20°C$ or by reaction of $[Mo(CO)_3Br_2(MeCN)_2]$ with N–N in MeCN at room temperature. These electron-deficient species have been characterized by elemental analyses, IR, NMR, and magnetic moments. The monomeric nature of the complexes is further supported by the solid-state structure of **2**.

Numerous metal carbonyl derivatives of both Mo^0 and Mo^{II} obey the effective atomic number rule [2]. In view of the premise that the 16-electron species are common intermediates in homogeneous catalysis or related stoichiometric reactions [3], the synthesis ** and reactivity [4] of electron-deficient molybdenum carbonyl compounds are of fundamental importance. Previously [1d], we presented a concept of how bulky multidentate ligands probably help to stabilize the 17-electron

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* For Parts I–VII, see ref. 1.

** (a) $[Mo(CO)_2X_2Py_2]$ (X = Cl, Br; Py = pyridine) [5]; (b) $[Mo(CO)_2I_2(Diars)]$ (Diars = *o*-$C_6H_4(AsMe_2)_2$) [6]; (c) $[Mo(CO)_2Cl_2(PPh_3)_2]$ [7]; (d) $[Mo(CO)_2Br_2(PPh_3)_2]$ [8,9]; (e) $[Mo(CO)_2(S_2CNPr^i_2)_2]$ [10,11,12]; (f) $[Mo(CO)_2(OBu^t)_2Py_2]$ [13]; $[Mo(CO)_2(Ph_2BPz_2)(2\text{-methyl-allyl})]$ [14].
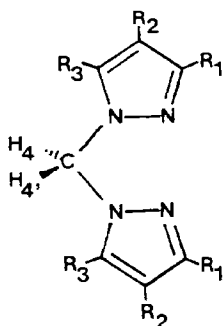
Fig. 1. Structure of the neutral N–N bidentates. H_2CPz_2: $R^1 = R^2 = R^3 = H$; $H_2CPz'_2$: $R^1 = R^3 = Me$, $R^2 = H$; $H_2CPz''_2$: $R^1 = R^2 = R^3 = Me$.

compounds and why the larger hydridotris(3,5-dimethylpyrazol-1-yl)borate, (Tp′) relative to hydridotris(pyrazol-1-yl)borate (Tp), causes $[Tp'Mo(CO)_3]$ to be more stable in air than $[TpMo(CO)_3]$. Now we report that an extension of the same concept by using it to stabilize a series of paramagnetic 16-electron compounds. However, use of all neutral pyrazole-derived bidentate ligands, N–N, leads to the facile formation of $[Mo(CO)_2Br_2(N-N)]$ (N–N = H_2CPz_2 (1), $H_2CPz'_2$ (2), $H_2CPz''_2$ (3); Pz = pyrazol-1-yl; Pz′ = 3,5-dimethylpyrazol-1-yl; Pz″ = 3,4,5-trimethylpyrazol-1-yl (Fig. 1)) without the usual dependence on the methyl groups in the 3, 4, or 5 position of the pyrazolyl ring.

Bromination of $[Mo(CO)_4(N-N)]$ [1b] in CH_2Cl_2 at $-20°C$, or substitution of the neutral N–N bidentate ligands in $[Mo(CO)_3Br_2(MeCN)_2]$ [15] in MeCN at room temperature readily afforded the paramagnetic, six-coordinate, 16-electron monomers, 1–3, which are air-stable solids, in 64–74% yield after recrystallization from $CH_2Cl_2/MeOH$ (eq. 1). These complexes were characterized by elemental analysis, IR and NMR * spectroscopy. The monomeric nature of complexes 1–3 is supported by a complete structural characterization of 2 **. The magnetic moments of 3.32 μBM for 1, 4.07 μB for 2, and 4.14 μB for 3 in acetone-d_6 at 294 K,

$$[Mo(CO)_4(N-N)] \xrightarrow[-2\,CO]{+Br_2\ at\ -20°C} [Mo(CO)_2Br_2(N-N)] \qquad (1)$$

$$[Mo(CO)_3Br_2(MeCN)_2] \xrightarrow[-2MeCN,\,-CO]{+N-N\ at\ room\ temp.}$$

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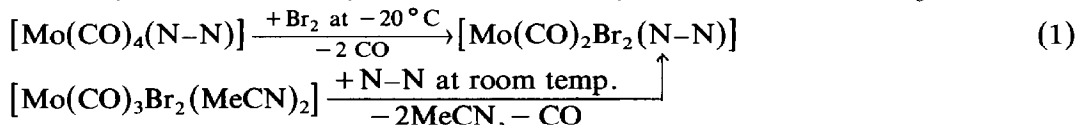
* 1: Anal. Found: C, 23.41; 23.44; H, 1.76, 1.77; N, 12.29, 12.27. $C_9H_8Br_2MoN_4O_2$ calcd.: C, 23.50; H, 1.75; N, 12.19%. IR(KBr): ν(CO), 2016, 1947 cm^{-1}. ^{1}H NMR (acetone-d_6, 294 K, 400 MHz): δ -24.00 (s, 2 H, R^1), 9.46 (s, 2 H, R^2), -31.27 (s, 2 H, R^3) ppm. 2: Anal. Found: C, 30.66, 30.63; H, 3.25, 3.24; N, 10.59, 10.60. $C_{13}H_{16}Br_2MoN_4O_2$ calcd.: C, 30.26; H, 3.13; N, 10.86%. IR(KBr): ν(CO), 2007, 1933 cm^{-1}. ^{1}H NMR (acetone-d_6, 294 K, 400 MHz): δ 44.30 (s, 6 H, R^1), 7.31 (s, 2 H, R^2), 40.60 (s, 6 H, R^3), 16.0 (s, 1 H, H^4), 0.1 (s, 1 H, $H^{4'}$) ppm. 3: Anal. Found: C, 32.63, 32.61; H, 3.71, 3.70; N, 10.21, 10.16. $C_{15}H_{20}Br_2MoN_4O_2$ calcd.: C, 33.03; H, 3.70; N, 10.27%. IR(KBr): ν(CO), 2013, 1934 cm^{-1}. ^{1}H NMR (acetone-d_6, 294 K, 400 MHz): δ 45.21 (s, 6 H, R^1), 4.55 (s, 6 H, R^2), 43.01 (s, 6 H, R^3), 17.8 (s, 1 H, H^4 or $H^{4'}$) ppm.

** Compound 2 crystallizes in the triclinic space group $P\bar{1}$ with a 8.198(2) Å, b 9.130(2) Å, c 12.291(3) Å, α 81.57(2)°, β 89.50(2)°, γ 83.94(2)°, V 905.0(4) Å^3, $Z = 2$, and d_{calcd} 1.89 g/cm^3. A total of 1619 reflections with $I > 2.5\ \sigma(I)$ were considered observed. The Mo atom was first solved by the Patterson-superposition method. The remaining non-hydrogen atoms were subsequently located from a Fourier difference map and all atoms were then refined anisotropically by full-matrix least-squares methods. The positions of all hydrogen atoms were calculated and refined isotropically to give residuals, R and R_w, of 0.032 and 0.029, respectively.
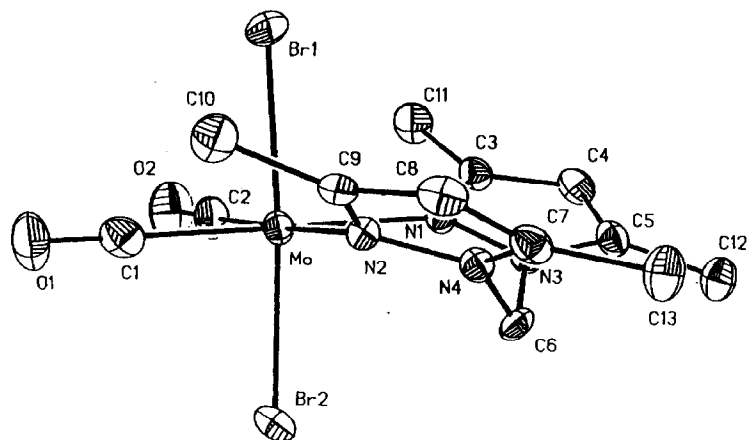
Fig. 2. Structure of $[Mo(\eta^2-H_2CPz'_2)(CO)_2Br_2]$ (2) with atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths and bond angles are: Mo–Br(1), 2.537(1); Mo–Br(2), 2.538(1); Mo–N(1), 2.252(5); Mo–N(2), 2.234(5); Mo–C(1) 2.018(9); Mo–C(2), 2.004(9); C(1)–O(1), 1.088(8); C(2)–O(2), 1.123(8) Å; and Br(1)–Mo–Br(2), 175.5(1); N(1)–Mo–N(2), 84.6(2); and C(1)–Mo–C(2), 83.1(3) °.

measured by use of a published method [16], are consistent with the ground state triplet expected for the complexes. That the values are larger than the spin-only value of 2.83 μBM may be due to a g value greater than 2.

Figure 2 shows the solid-state structure of 2, the first of the paramagnetic 16-electron metal carbonyl derivatives of Mo^{II} to have been crystallographically characterized. The complex is monomeric with a quasi-octahedral geometry which is compatible with the observed paramagnetism for this d^4 transition metal complex [17]. The six-membered $\overline{C(6)N(4)N(2)MoN(1)N(3)}$ metallacycle adopts a shallow boat form in contrast to the nearly planar five-membered $\overline{MoNCCN}$ metallacycle of the Mo(bipy) fragment which is observed in the $[Mo(CO)_2(bipy)(SO_2)_2]$ (bipy = 2,2'-bipyridine) structure [18] and which is probably maintained in $[Mo(CO)_4(bipy)]$ [19]. Hence, that there is no apparent difference among the rate of formation of 1–3 and that the bromination of $[Mo(CO)_4(bipy)]$ gives the 18-electron $[Mo(CO)_3Br_2(bipy)]$ [19] leads us to believe that the boat metallacycle is responsible for converting the possible $[Mo(CO)_3Br_2(N-N)]$ intermediate in eq. 1 into the 16-electron complexes, 1–3. Unexpectedly, Br(1)–Mo–Br(2) the angle is not 180° but 175.5(1)° in 2. This observation supports the steric congestion present in this six-coordinate complex and reflects the much larger nonbonded interactions in the unknown seven-coordinate complexes, $[Mo(CO)_3Br_2(N-N)]$. Thus, if these complexes are formed at all, they lose CO as rapidly as they are formed into 1–3.

Iodination of $[Mo(CO)_4(N-N)]$, halogenation of $[W(CO)_4(N-N)]$, and the reactivity of 1–3 are currently under investigation.

Supplementary material available. Tables of crystal data and collection parameters, positional and thermal parameters, and bond distances and angles for 2 (6 pages) are available from the authors.

Acknowledgement

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