A Novel Homoscorpionate Ligand and its Unusual Bonding in a Molybdenum Complex

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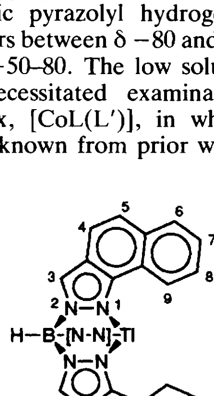
The new ligand, hydrotris(2*H*-benz[G]indazol-2-yl)borate, (L) forms octahedral and mixed octahedral [CoL_2] and [CoL(L′)] [L′ = HB(3-neopentylpyrazolyl)]; an unusual complex [$MoL(CO)_2(\eta^3\text{-}CH_2CMeCH_2)$], the structure of which is established by X-ray crystallography shows L acting in a bidentate manner.

As part of an ongoing study of novel homoscorpionate (trispyrazolylborate) ligands L^x,[1] we explored ways of constraining their 3-phenyl substituents so that they would be predominantly either orthogonal or parallel to the pyrazoyl (pz) plane, aiming for closer control of the steric environment around the coordinated metal. Examples of orthogonal constraint involved placing methyl substituents in the phenyl 2,4,6-positions, [$HB(3\text{-mesityl-pz})_3$],[2] or placing benzo rings on each of its sides, {$HB[3\text{-}(9\text{-anthryl})\text{-pz}]_3$}.[3] Indeed, for both of these ligands the 3-substituents displayed only small deviations from orthogonality to the pz plane.

Conversely, aiming at coplanarity of the phenyl and pyrazolyl rings, we had tethered the phenyl group through its *ortho* position to the pyrazolyl 4-position with either a methylene, or ethylene link.[4] The ethylene tether imparted a twist angle of *ca.* 22° to the phenyl group. The methylene tether, while making the two rings essentially coplanar, pulled the phenyl group away from the metal, and did not provide the desired steric hindrance.[4]

In order to enforce coplanarity of the phenyl and pyrazolyl rings, we changed the tether from ethylene to ethyne, making the ligand based on 2*H*-benz[G]indazole,[5] (which may be viewed as naphthopyrazole). This ligand, hydrotris(2*H*-benz[G]indazol-2-yl)borate (L) was synthesized from benz[G]indazole and KBH_4, and was characterized as the Tl salt, **1**, mp 286–289 °C (decomp.). Its NMR spectrum indicated a single product of C_{3v} symmetry, but did not indicate which nitrogen was bonded to boron: either N^2 (as in the structure above) or N^1 could bind. This was a non-trivial issue, since a number or reports had been published claiming that indazole in various polyindazolylborate ligands bonds to boron through the more hindered N^1.[6] While this assertion was questioned in a review,[7] it was also cautiously supported,[8] and the issue remained unresolved.

Some indication for N^2-bonding was elicited from the broadening of the 9-H proton, which has in prior examples been associated with proximity to ^{205}Tl. A better probe for symmetry and regiochemistry in homoscorpionate ligands is the proton NMR spectrum of homo-, or heteroleptic paramagnetic octahedral cobalt(II) complexes {[$CoL^x{}_2$] or [$CoL^x(L')$][L′ = $HB(\text{neopentyl-pz})_3$]} where the widely separated (>200 ppm) chemical shifts can be uniquely assigned to specific pyrazolyl hydrogens.[9] Typically, the pyrazole 3-H appears between δ −80 and −100, while the 5-H is in the range δ +50–80. The low solubility of the readily formed [CoL_2] necessitated examination of the mixed octahedral complex, [CoL(L′)], in which the location of protons of L′ was known from prior work.[10] The pyrazolyl proton peak of L was at δ *ca.* 70, again supporting the B–N^2 bond assignment. Unequivocal conformation of the ligand structure came from X-ray crystallography (see below).



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An unusual result was obtained in the reaction of TlL with [$Mo(CO)_2(MeCN)_2Cl(\eta^3\text{-}CH_2CMeCH_2)$]. The complex [$MoL(CO_2)(\eta^3\text{-}CH_2MeCH_2)$] was obtained as yellowish-orange crystals, contrasting with the usually bright yellow [$MoL^x(CO)_2(\eta^3\text{-}CH_2CMeCH_2)$] species. Its IR spectrum displayed weak BH bands around 2100 cm^{-1} and CO at 1954 and 1870 cm^{-1}. The NMR spectrum indicated a total lack of symmetry, with each naphthopyrazolyl group unique, as seen best in the case of the 3-H singlets which were at δ 8.46, 8.30 and 8.17, and for the widely spaced 9-H doublets (δ 10.21, 9.46 and 8.85). In addition, each of the η^3-methallyl *syn*- and *anti*-protons was unique. This was totally at odds with the NMR spectra of all known [$MoL^x(CO)_2(\eta^3\text{-}CH_2CMeCH_2)$] complexes, which exhibit either a dynamic C_{3v} symmetry arising from rotation around the B–Mo axis[11] or static C_s symmetry. Two possible structures were compatible with the observed NMR spectrum. (*i*) one containing a bidentate ligand, with an agostic B–H–Mo bond, in which the η^3-methallyl group would be in the least hindered position, *i.e.* not between the benzindazolyl groups. Thus, looking down the Mo–B axis, we would have one uncoordinated naphthopyrazolyl far from the metal, one of the coordinated naphthopyrazolyl moieties close to the η^3-methyallyl group, and the other one distant from it. In this structure each of the *syn*- and

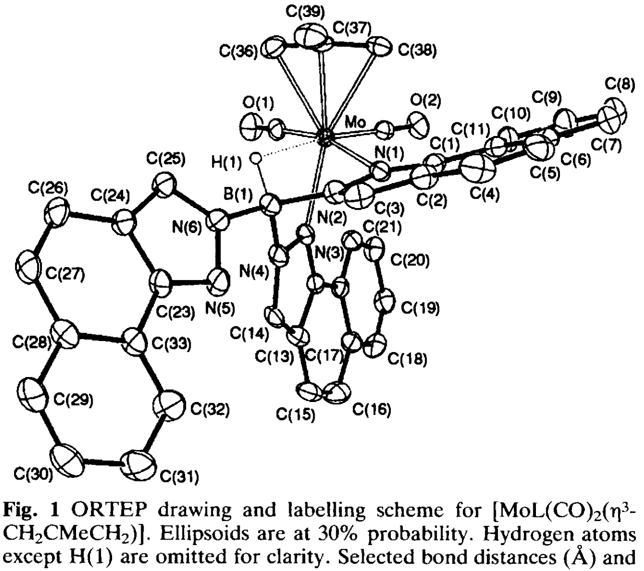

Fig. 1 ORTEP drawing and labelling scheme for [$MoL(CO)_2(\eta^3\text{-}CH_2CMeCH_2)$]. Ellipsoids are at 30% probability. Hydrogen atoms except H(1) are omitted for clarity. Selected bond distances (Å) and angles (°): Mo–H(1) 2.163(8), Mo–N(1) 2.304(5), Mo–N(3) 2.212(5), Mo–C(34) 1.960(6), Mo–C(35) 1.917(5), Mo–C(36) 2.317(8), Mo–C(37) 2.244(7), Mo–C(38) 2.363(7), N(1)–Mo–N(3) 81.2(2), N(1)–Mo–H(1) 74.9(4), N(3)–Mo–H(1) 72.7(4), N(1)–Mo–C(34) 166.9(2), N(3)–Mo–C(34) 85.9(2), N(1)–Mo–C(35) 102.3(2), N(3)–Mo–C(35) 100.8(2), H(1)–Mo–C(34) 99.9(4), H(1)–Mo–C(35) 173.2. Selected bond distances (Å) and angles (°) for the second molecule in the unit cell: Mo′–H′ 2.107(8), Mo′–N′ 2.226(5), Mo′–N(3′) 2.298(4), Mo′–C(34′) 1.960(6), Mo′–C(35′) 1.937(7), Mo′–C(36′) 2.357(7), Mo′–C(37′) 2.241(6), Mo′–C(38′) 2.306(6), N′–Mo′–N(3′) 81.2(2), N′–Mo′–H′ 72.3(4), N(3′)–Mo′–H′ 76.4(4), N′–Mo′–C(34′) 85.7(2), N′–Mo′–C(35′) 101.7(2), N(3′)–Mo′–C(34′) 166.6(2), N(3′)–Mo′–C(35′) 103.4(2), H′–Mo′–C(34′) 96.9(4), H′–Mo′–C(35′) 173.9(4).

anti-protons in the methallyl group would be in a different magnetic environment. (*ii*) An alternative structure would involve η^3-bonding, but of a rearranged ligand with one naphthopyrazolyl group reversed, such rearrangements having been found to occur in 3-isopropyl-,[12] 4-bromo-3-isopropyl-,[12] 3-neopentyl-[10] and 3-mesityl-pyrazolylborate[2] complexes. Again, the η^3-methallyl group would avoid being between the naphthopyrazolyl groups, and the same lack of symmetry would prevail.

X-ray crystallography† (Fig. 1) established the former of these structures, containing a bidentate and unrearranged ligand, and an agostic B–H–Mo bond such as has been found in $H_2B(pz^X)_2$ complexes.[13] The H–Mo distance is *ca.* 2.1 Å, and thus very similar to that found in the complex $[Mo\{H_2B(3,5Me_2\text{-}pz)_2\}(CO)_2(\eta^3\text{-}CH_2CMeCH_2)]$.[14]

The reason for the non-formation of the usual type of complex is the extended intrusion of the 9-CH into the coordination sphere of Mo. While two of the naphthopyrazolyl groups can be accommodated, the third one is rebuffed by the η^3-methallyl group. An agostic B–H bond is formed in order to provide an 18-electron configuration for Mo. This is the first such finding among complexes $[MoL^x(CO)_2(CH_2CMeCH_2)]$, and it reflects on the very large cone angle [av. 276°, compared with 199° for the parent $HB(pz)_3$] associated with L. Although the wedge angle is also large [average 87°, *vs.* 91° for $HB(pz)_3$] permitting side-entry to the metal, it is of no help in accommodating fairly bulky groups, such as η^3-methallyl, at the metal, which would be in direct collision with the tricyclic ring system protruding far along the boron–metal axis. The large wedge angle in L also facilitates the formation of octahedral $[ML_2]$ complexes, at the same time destabilizing tetrahedral complexes such as [ML(X)].

What is unique about L, is that it is the first homoscorpionate to contain a totally rigid 3-substituent. All the hitherto known L^x ligands had 3-R substituents capable of either complete rotation, or at least oscillation around the pyrazolyl 3-carbon; L is also the first homoscorpionate to yield the abnormal, and yet stable $[Mo(CO)_2(\eta^3\text{-}CH_2CMeCH_2)]$ derivative in which the ligand is bidentate.

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Footnotes

† *Crystal data* for $[MoL(CO)_2(\eta^3\text{-}CH_2CMeCH_2)]\cdot 0.5CH_2Cl_2$: $C_{39.5}H_{30}BClMoN_6O_2$, triclinic, $P\bar{1}$, $a = 10.892(3)$, $b = 14.597(4)$, $c = 23.467(5)$ Å, $\alpha = 71.93(2)$, $\beta = 77.84(2)$, $\gamma = 82.66(2)°$, $V = 3459.5(15)$ Å^3, $Z = 4$, $D_c = 1.465$ g cm^{-3}, μ(Mo-Kα) = 5.02 cm^{-1}, $T = 297$ K. Preliminary photographic characterization showed P1 Laue symmetry allowing the possibility for the space group to be $P1$ or $P\bar{1}$. *E*-statistics suggested the centrosymmetric alternative and the chemically sensible results of refinement proved this choice to be correct. Of 12466 reflections collected ($4 \leq 2\theta \leq 50°$), 12142 were independent and 8158 were considered observed ($4\sigma F$). A semiempirical absorption correction was applied to the data set. The asymmetric unit contains two independent but chemically identical molecules and one molecule of methylene chloride. The structure was solved by direct methods which located the heavy atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included as idealized isotropic contributions (C–H = 0.960 Å, U was fixed at 0.0800 Å^2). The agostic hydrogen was located and refined. At convergence: $R(F) = 0.0545$, $R_w(F) = 0.0646\%$, $s = 1.27$, $\Delta\rho = 0.82$ e Å^{-3}. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ Correct analytical results were obtained for all new compounds.

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