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Preliminary communication

Synthesis, structure and properties of stereochemically non-rigid molybdenum pyrazolylborato complexes containing a *dihapto*-thiocarboxamido ligand

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Abstract

Pyrazolylboratomolybdenum complexes containing the η^2-CSNMe$_2$ ligand have been prepared by treating the appropriate carbonylmetallate anion with Me$_2$NCSCl. The structure of pzB(pz)$_3$Mo(CO)$_2$(η^2-CSNMe$_2$) (IIIb) has been established by X-ray crystallographic methods. The ^{1}H and ^{13}C NMR spectra of IIIb show evidence for two separate intramolecular dynamic processes in solution. Complex IIIb can be alkylated at the sulphur atom and forms 1/1 complexes with mercuric halides.

The tendency of the pyrazolylborate ligands [RBpz$_3$]$^-$ (pz = 1-pyrazolyl; R = H, pz) to favor octahedral coordination geometry over 7-coordination in their complexes has been exploited in the synthesis of the unusual *dihapto*-acyl complexes RBpz$_3$Mo(CO)$_2$(η^2-COR^1) (I, R^1 = alkyl, aryl) [1] which have recently been shown to have interesting chemical properties [2]. Here we report the chemical and structural properties of the first examples of pyrazolylborate complexes containing the related *dihapto-N,N*-dimethylthiocarboxamido ligand.

Although inert to reaction with *N,N*-dimethylcarbamoyl chloride, Me$_2$NCOCl, the molybdenum tricarbonyl complex [PhCH$_2$NEt$_3$][RBpz$_3$Mo(CO)$_3$] (IIa, R = H; IIb, R = pz) reacts readily with the thioacyl analogue, Me$_2$NCSCl, in MeCN at room temperature to yield the η^2-thiocarboxamido complexes RBpz$_3$Mo(CO)$_2$(η^2-CSNMe$_2$), (IIIa, IIIb) in ca. 57% yield. The new complexes are dark red air-stable

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crystalline solids [*] with IR spectra in the carbonyl region which are very similar to that of the related cyclopentadienide complex $(\eta\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CSNMe_2)$ (IV) [3]. The structure of IIIb has been determined by X-ray crystallographic methods [**] and is shown in Fig. 1. The coordination about molybdenum is distorted octahedral with the tridentate ligand and two CO groups occupying five sites and the η^2-$CSNMe_2$ ligand in the sixth position. The structure is qualitatively similar to those of the analogous *dihapto*-acyl complexes II except for the respective orientations of the acyl O–C and S–C vectors. In complexes of type II the η^2-COR^1 group is oriented between the two CO ligands and close to one of them [1]. In IIIb the S–C vector lies between pyrazolyl nitrogen N(21) and carbonyl ligand C(5)O(5) but is closer to the latter (torsion angles: N(21)–Mo–S–C(1) 74.9°, C(5)–Mo–S–C(1) −42.3°). The rotational preferences of the *dihapto*-acyl ligand in octahedral complexes $L_5M(\eta^2\text{-}COR)$ have been analyzed by Curtis et al. [1b]. These authors have noted that depression of a pair of *trans* ligands in the equatorial plane of the O_h L_5Mo fragment in a direction away from the η^2-COR ligand tends to increase overlap of the fragment orbitals with the latter ligand which aligns itself with -or close to- the axis of distortion. Comparison of the angles N(21)–Mo–C(4) (170.89(9)°) and N(31)–Mo–C(5) (155.64(9)°) suggests that a similar effect may operate in IIIb. However the stereochemical non-rigidity shown by IIIb in solution (see below) suggests a low barrier to rotation of the η^2-$CSNMe_2$ ligand so that the observed orientation may owe as much to crystal packing as it does to electronic effects. The bond lengths within the η^2-$CSNMe_2$ ligand are in accord with previous determinations [4] and suggest significant carbenoid character for the Mo–C(1) bond.

The ^{1}H NMR spectra of IIIa and IIIb and the ^{13}C NMR spectra of IIIb reveal that there is no rotation about the N–C bond of the *dihapto*-thiocarboxamido ligands. Four inequivalent pyrazolyl groups and two inequivalent CO ligands are to be expected if the solid-state structure persists in solution. The observed ^{1}H and ^{13}C NMR spectra show that all three coordinated pyrazolyl groups and both CO ligands

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[*] Physical and spectroscopic data for IIIa: Found: C, 37.40; H, 3.70; N, 21.93. $C_{14}H_{16}BMoN_7O_2S$ calcd.: C, 37.11; H, 3.56; N, 21.64%. IR (thin film): ν(CO) 1930, 1830 (s) cm^{-1}. ν(CN) 1560 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 7.68 (d, J 2.0 Hz, 3H, H(3/5)), 7.58 (d, J 2.0 Hz, 3H, H(5/3)), 6.17 (apparent t, 3H, H(4)), 3.80, 3.70 (s, 2×3H, NMe_2) ppm. IIIb: Found: C, 39.13; H, 3.28; N, 24.28. $C_{17}H_{18}BMoN_9O_2S$ calcd.: C, 39.32; H, 3.49; N, 24.29%. IR (CH_2Cl_2): ν(CO) 1938, 1839(s) cm^{-1} ν(CN) 1560 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 7.96 (d, J 2.4 Hz, 1H, H(3/5) of uncoordinated pz), 7.93 (d, J 1.5 Hz, 1H, H(5/3) of uncoordinated pz), 7.82 (d, J 1.6 Hz, 3H, H(3/5) of coordinated pz), 7.67 (d, J 2.2 Hz, 3H, H(5/3) of coordinated pz), 6.58 (apparent t, 1H, H(4) of uncoordinated pz), 6.18 (apparent t, 3H, H(4) of coordinated pz), 3.82, 3.71 (s, 2×3H, NMe_2) ppm. ^{13}C NMR ($CDCl_3$, Me_4Si): 251.23 ($\mathit{C}SNMe_2$), 242.62 ($\mathit{C}O$), 145.47 (C(3), coordinated), 141.97 (C(3), uncoordinated), 136.19 (C(5), uncoordinated), 135.34 (C(5), coordinated), 107.08 (C(4), uncoordinated), 105.84 (C(4), coordinated), 50.64, 45.41 (η^2-$CSN\mathit{Me}_2$) ppm.

[**] Crystal data for IIIb: $C_{17}H_{18}BMoN_9O_2S$, $M = 519.2$, monoclinic, space group $P2_1/n$, a 13.242(2), b 13.462(4), c 12.082(2) Å, β 99.67(1)°, U 2123.0 Å^3, D_c 1.62 g cm^{-3} for $Z = 4$, $F(000) = 1048$, λ (Mo-K_α) 0.71073 Å, $\mu = 7.3$ cm^{-1}, T 21°C, crystal size 0.60×0.20×0.10 mm. Three-dimensional data collected on a CAD4 diffractometer and corrected for Lorentz, polarisation and absorption factors. All hydrogen atoms were located from difference maps, and allowed for but not refined in the full-matrix least-squares calculations. At convergence, $R = 0.027$ ($R_w = 0.037$) for 3521 observed reflections with $2 < 2\theta < 54°$. Full details of molecular geometry have been deposited with the Cambridge Crystallographic Data Centre, and are also available from one of us (GF).

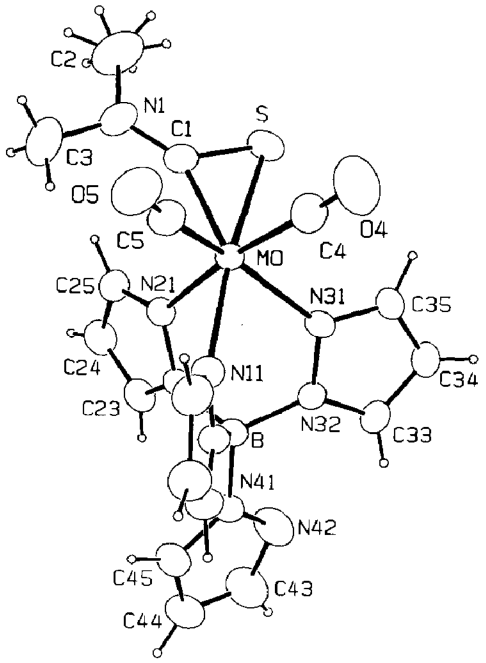

Fig. 1. A view of the structure of IIIb. The three hydrogen atoms on methyl carbon C(2) are disordered over two sites as shown. Selected bond lengths (Å) and angles (°) are: Mo–C(1) 2.076(3), Mo–C(4) 1.942(3), Mo–C(5) 1.952(2), Mo–S 2.550(1), Mo–N(11) 2.192(2), Mo–N(21) 2.266(2), Mo–N(31) 2.236(2), C(1)–S 1.673(2), C(1)–N(1) 1.307(3), N(1)–C(2) 1.476(5), N(1)–C(3) 1.457(4), S–Mo–C(1) 40.80(7), Mo–S–C(1) 54.18(9), Mo–C(1)–S 85.0(1).

are equivalent on the NMR time-scale. A "windscreen-wiper" motion of the η^2-CSNMe$_2$ ligand across the equatorial plane of the L$_5$M fragment coupled with pairwise bending of *trans* ligands (illustrated schematically in Fig. 2) is sufficient to account for the equivalence of CO ligands. A similar oscillatory motion of the η^2-COR^1 ligand in I has been proposed by Curtis [1b] but the amplitude of oscillation of the dihapto ligand in IIIb is wider than in the former case and it may be that the η^2-CSNMe$_2$ ligand is effectively rotating about the axis joining Mo to the centre of gravity of the C–S bond. A second dynamic process, rotation of the pyrazolylborate ligand about the B...Mo axis [5], must be involved to rationalise the equivalence of all three coordinated pyrazolyl groups. In contrast the *dihapto*-acyl complexes I show ^{1}H NMR spectra consistent with a 1/2 ratio of coordinated

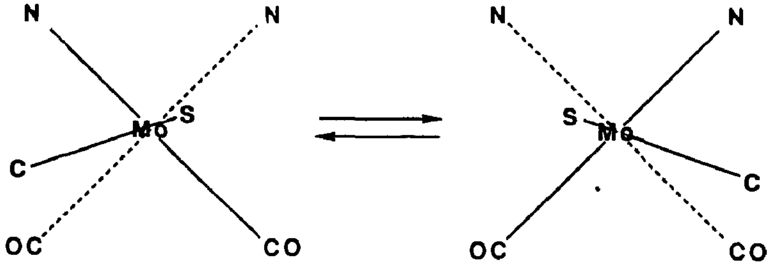

Fig. 2. Schematic representation of L$_5$M fragment with coupling of *trans*-ligands.

pyrazolyl groups and the tridentate ligand is therefore stereochemically rigid [1]. The manner in which the change in structure of the *dihapto* ligand alters the barrier to pyrazolylborate rotation is not clear at this point of our investigation.

Triphenylphosphine in boiling toluene does not abstract sulphur from the thiocarboxamido ligand in IIIb, nor is there any indication of CO substitution. However the complex is readily alkylated by Me_3OBF_4 and the similarity of $\nu(CO)$ in the ionic product * to that of the product of alkylation of the η-cyclopentadienide analogue IV [3] allows us to formulate the former as the *S*-methylated species $[pzBpz_3Mo(CO)_2(\eta^2\text{-}C(SMe)NMe_2)]BF_4$ (V). Stable 1/1 adducts are formed between IIIb and HgX_2 (VIa, X = Cl; b, X = Br) in which we believe the sulphur atom to be acting as the donor site to mercury. Apart from the differences in $\nu(CO)$ and $\nu(CN)$ (and the presence of a strong band due to BF_4^- in the spectrum of V) the IR spectra of V and VI in the fingerprint region are virtually superimposable. The fact that the HgX_2 adducts VI exhibit $\nu(CO)$ bands at a higher wavenumber than those in the cationic S-methylated species V is unexpected and suggests that the former should be formulated as the ionic species $[pzB(pz)_3Mo(CO)_2(\eta^2\text{-}CS(HgX)NMe_2)]X$. We have been unable to record satisfactory ^1H NMR spectra for VI because of their low solubility. The ^1H NMR spectrum of V shows that, like IIIb, it is stereochemically non-rigid in solution but differs significantly from the latter in that the process, or processes, involved are in the slow-exchange region at room temperature. All of the new complexes described here are currently receiving further study.

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* Physical and spectroscopic data: V: Found: C, 34.52; H, 3.22; N, 19.81. $C_{18}H_{21}B_2F_4MoN_9O_2S$ calcd.: C, 34.81; H, 3.41; N, 20.30%. IR (KBr): $\nu(CO)$ 2010, 1921(s) cm^{-1}, $\nu(CN)$ 1602, 1568 (m) cm^{-1}. ^1H NMR ($CDCl_3$, Me_4Si): δ ca. 7.93 (broad apparent singlet, 8H, H(3) and H(5) of coordinated and uncoordinated pz), 6.67 (apparent t, 1H, H(4) of uncoordinated pz), 6.40 (apparent t, 3H, H(4) of coordinated pz), 4.22, 4.14 (s, 3H, NMe_2), 2.23 (s, 3H, SMe) ppm. VIa: Found: C, 25.69, H, 2.16; N, 15.60; Cl, 8.73. $C_{17}H_{18}BCl_2HgMoN_9O_2S$ calcd.: C, 25.82; H, 2.29; N, 15.94; Cl, 8.97%. IR (KBr): $\nu(CO)$ 2050, 1985(s) cm^{-1}, $\nu(CN)$ 1615(s) cm^{-1}. VIb: Found: C, 22.10; H, 2.11; N, 13.33. $C_{17}H_{18}BBr_2HgMoN_9O_2S$ calcd.: C, 23.21; H, 2.06; N, 14.33%. IR (thin film): $\nu(CO)$ 2025, 1980(s) cm^{-1}, $\nu(CN)$ 1625 cm^{-1}. Although the IR spectrum of VIb is virtually identical to that of VIa, the microanalytical data for the former suggest contamination with the excess $HgBr_2$ which cannot be removed by recrystallisation.

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