A theoretical and experimental study of the fluxional behaviour of molybdenum dihydrobis- and hydrotris-pyrazolylborates‡†§

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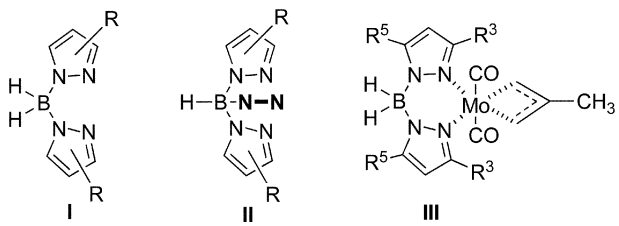
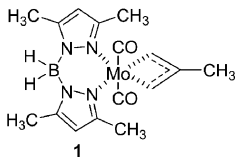
The fluxional barrier of (dicarbonyl)[dihydrobis(3,5-dimethylpyrazol-1-yl)borato][η-(1,2,3)-2-methylpropen-1-yl]-molybdenum (1) has been measured and a complete assignment of its ^{1}H, ^{13}C and ^{15}N NMR signals has been carried out. Theoretical calculations at the B3LYP/LANL2DZ level including GIAO absolute shieldings (σ) have allowed to analyze the molecular contributions to the barrier as well as to assign some signals involved in the fluxional process.

Introduction

Trofimenko's scorpionates are one of the most popular ligands in coordination chemistry.[1] Both dihydrobis- **I** and hydrotris-pyrazolyl-borates **II** (**N–N** is the third, hidden, pyrazolyl group) have been used as ligands for preparing Mo complexes.[2] Some of us have carried crystallography, mass spectrometry and NMR spectroscopy studies on these ligands but with other metals.[3–10] We will describe in this paper the fluxional behaviour of complexes **III**. The Mo metal bears two CO groups and one methallyl molecule. The conclusions reached from the experimental study of **1** will be extended by means of theoretical calculations to other related complexes. Note that Mo(η^3-allyl) $(CO)_2$ complexes are very popular in organometallic chemistry and that most of them are fluxional in solution.[11–19]

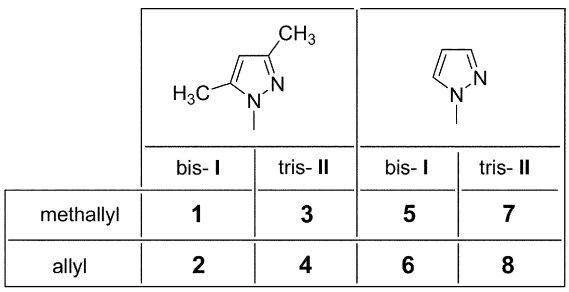


Molybdenum complexes based on scorpionates **II** are much more common than those based on **I**. For instance, see references20–28 for **II** while only two papers[26,29] report Mo complexes of **I**. In the 1970 paper,[29] two complexes one with allyl and the other with methallyl **1** were described together with their IR and ^{1}H NMR data at variable temperature. In the 2002 paper,[26] the X-ray structure of compound **1** and that of a perbromopyrazolyl derivative were reported.



1

In the present paper we will report the experimental study of the fluxionality of the molybdenum dihydrobispyrazolylborate **1** using DNMR, as well as its theoretical study comparatively to seven more Mo scorpionates summarised in Scheme 1.



X-ray structures: **1** (EFUFOA), **3** (NIBWUZ), **4** (NIBWOK), **8** (ZIRTEZ).

Scheme 1 The eight studied Mo scorpionates (all having two CO groups) with the ref. codes of the X-ray structures reported in the CSD.[30]

Results and discussion

Static part

The X-ray structure of compound **1** has been reported (EFUFOA).[26,30] We have recorded the ^{1}H, ^{13}C and ^{15}N NMR spectra in $CDCl_3$ solution at 300, 330 and 213 K (Table 1). Bidimensional experiments were performed in order to assign the ^{1}H, ^{13}C and ^{15}N signal.§

Due to the presence of the molybdenum atom in **1**, we have used the LANL2DZ basis set for the theoretical calculations.[31] The optimized geometry is almost identical to the X-ray structure (EFUFOA) including the B–H_{en}-Mo intramolecular hydrogen bond. The absolute shieldings have been calculated at the GIAO/B3LYP/LANL2DZ level and compared with the experimental values at 213 K (Table 1). With the help of the previously commented bidimensional experiments, this allowed to identify the **A** and **B** pyrazole rings as well as the diastereotopic carbonyl groups and the methallyl protons and carbon atoms (Fig. 1).

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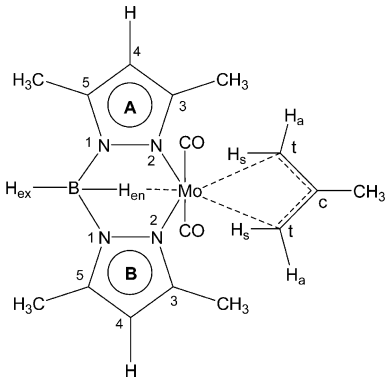
† The HTML version of this article has been enhanced with colour images.

‡ Dedicated to Professor Vicente Gotor on the occasion of his 60th birthday.

§ Electronic supplementary information (ESI) available: Experimental NMR spectroscopy in solution and in the solid state, bidimensional experiments; tables of energetic data and absolute shieldings (σ, ppm) calculated values and statistical details of the presence–absence matrix. See DOI: 10.1039/b705703b

Table 1 ^{1}H, ^{13}C and ^{15}N chemical shifts (ppm) and ^{1}H-^{1}H coupling constants (Hz) in $CDCl_3$ and ^{13}C and ^{15}N chemical shifts (ppm) in solid state (CPMAS)



^{1}H NMR T/K	Hen	Hex	3-Me pz	H4 pz	5-Me pz	Hs methallyl	Ha methallyl	Me methallyl
300	−2.00 (vbq) $^{1}J_{BH} = 91$	~3.0 (vbs)	2.44 (bs) 2.61 (bs)	5.70 (s)	2.10 (s)	3.26 (bs) 3.65 (bs)	1.27 (bs) 1.59 (bs)	1.73 (s)
330	−2.00 (bq) $^{1}J_{BH} = 87$	~3.0 (bq)	2.52 (bs)	5.70 (s)	2.10 (s)	3.47 (bs)	1.44 (bs)	1.76 (s)
213	−1.99 (bs)	3.01 (vbs)	2.35 (s) 2.65 (s)	5.65 (s) 5.76 (s)	2.08 (s) 2.07 (s)	3.20 (dd) 3.68 (d) $^{4}J = 3.5$	1.20 (d) $^{2}J = 2.1$ 1.61 (s)	1.66 (s)

^{13}C NMR T/K	C3 pz	C4 pz	C5 pz	C_t methallyl	C_c methallyl	Me methallyl	CO	3-Me pz	5-Me pz
300	149.7 (bs) 152.0 (bs)	105.4	142.7 (bs) 144.2 (bs)	50.0 (bs) 66.4 (bs)	92.2	22.1	225.8 (bs) 232.9 (bs)	13.7 (bs)	10.4
330	n.o.	105.5	n.o.	n.o.	92.3	22.0	n.o.	13.6 (bs)	10.4
CPMAS	150.8 151.9	105.6 106.7	142.7 143.2	49.3 68.9	93.2	21.9	227.8 233.5	15.3 13.1	13.1 10.2
213	149.0 151.7	104.9 105.1	144.1 142.3	49.8 66.4	91.8	22.2	225.7 233.5	14.0 13.6	10.7 10.5

^{15}N NMR T/K	N1	N2
CPMAS	−146.1 −149.8	−124.0
213	−151.1 −150.1	−130.3 −126.9

s = singlet; d = doublet; dd = double doublet; bs = broad signal; vbs = very broad signal; bq = broad quartet; vbq = very broad quartet; n.o. = not observed.

The three nuclei, for which we have δ experimental data, correlate fairly well with the calculated shieldings (see Table 2). These empirical equations relating σ and δ involve an intercept that should be close to the corresponding reference and a scaling factor that should be close to 1. They are absolutely necessary to assign the signals of the dynamic part of **1**.

The σ absolute shieldings of the remaining atoms of compound **1** are (all values in ppm): $^{11}B = 120.68$, $^{17}O = -75.32$ and -60.97, $^{95}Mo = -310.89$. In the case of ^{11}B, we have calculated at the same level BH_4^- (exp. −38.0, calc. 161.02) and Me_3B (exp. 86.2, calc. 23.19).[32] Using these two points, to $\sigma = 120.68$ corresponds $\delta = -1.65$ for **1**, which is reasonable considering that experimental data for other scorpionates range between −3 to −10.[33,34] In the case of ^{17}O, we have used H_2O (δ exp. 0.00, σ calc. 398.33) and $H_2C{=}O$ (δ exp. 656.5, σ calc. −563.38) to predict for both CO groups 351 and 322,[26] which are reasonable values taking into account that the ^{17}O signal appears at 373 for $Mo(CO)_6$.[35]

Dynamic part. We have determined the barrier corresponding to the dynamic process present in compound **1**. In $CDCl_3$, at the concentration of 18.2 mg 0.75 mL^{-1}, the spectra were recorded at 330, 307, 301, 293, 288, 258 and 243 K and the rates calculated using the Bruker Win Dynamics program.[36]

$T_c = 288$ K, $k = 93.8\ s^{-1}$, $\Delta G^{\ddagger}_{288} = 59.6$ kJ mol^{-1}

With all the points, $r^2 = 0.9995$, $\Delta H^{\ddagger} = 66.4$ kJ mol^{-1}, $\Delta S^{\ddagger} = 221.3$ J mol^{-1} K^{-1}

Without the extreme points (330 and 243 K), $r^2 = 0.99998$, $\Delta H^{\ddagger} = 68.7$ kJ mol^{-1}, $\Delta S^{\ddagger} = 229.3$ J mol^{-1} K^{-1}.

In 1970 Trofimenko discussed the fluxional behaviour of **1** and related compounds on the basis of variable temperature ^{1}H NMR studies in $CDCl_3$ at 60 MHz.[29] According to him, the stereochemical nonrigidity of these scorpionates, that affect both the bidentate ligand and π-methallyl protons, could be explained in two ways (see Scheme 2): **A**) rotation of π-methallyl group around its centre of gravity thus averaging the environments of

Table 2 Linear relationships relating experimental δ values in ppm to calculated σ absolute shieldings in ppm

Nucleus	Added compounds	n	r^2	Intercept	Slope
$^{1}H^{a}$	TMS, HC≡CH, $H_2C{=}O$, CH_4	16	0.985	28.3 ± 0.8	$-(0.86 \pm 0.03)$
^{13}C	TMS, HC≡CH, $H_2C{=}O$, CH_4 $MeNO_2$, Me_3B	21	0.993	176.3 ± 2.2	$-(0.92 \pm 0.02)$
^{15}N	$MeNO_2$, NH_3	6	0.999	$-(161.9 \pm 2.2)$	$-(0.83 \pm 0.02)$

[a] H_{en} has to be removed (exp. −1.99, predicted with the first regression −0.82).

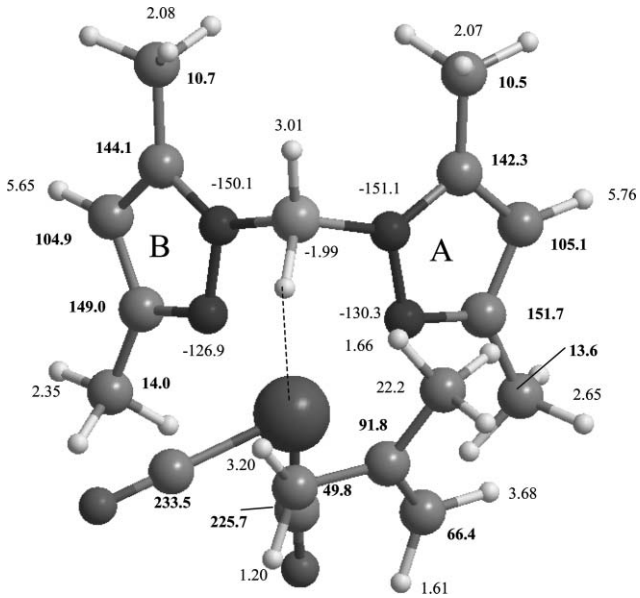
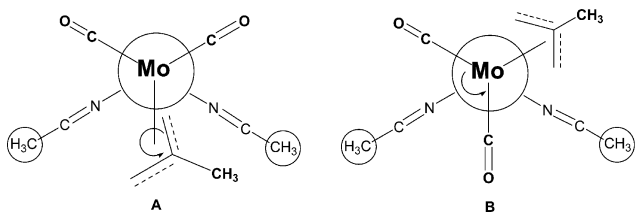


Fig. 1 The optimized structure of compound **1** showing the B–H · · · Mo hydrogen bond. The ^{1}H, ^{13}C and ^{15}N experimental chemical shifts were assigned as reported later.



Scheme 2 The two mechanisms proposed by Trofimenko in his 1970 paper.[29]

the 3-methyl and the π-allyl termini and resulting in dynamic C_s symmetry of the molecule (in the original paper, Trofimenko mistakenly assign it a C_{2v} symmetry),[29] or **B**) the same type of dynamic C_{2v} symmetry can be achieved by rotation of the $Mo(CO)_2$-π-C_4H_7 group around the B–Mo axis. The **B** process was preferred on several grounds one of them being that HB(3,5-dimethylpyrazol-1-yl)$_3$Mo(CO)$_2$-π-allyl **4** is stereochemically rigid over 100 °C (see later on).[29] We will first discuss Trofimenko's preferred mechanism **B**.

Transition State (TS) geometries for mechanism B. For dihydrobispyrazolyl-borate derivatives, the TS has a C_s symmetry with the symmetry plane going through the B, the Mo and the central C atom of the η^3-allyl group (see Fig. 2 for the case of **1**). In the case of the hydrotrispyrazolylborates, the symmetry is also C_s with the same atoms belonging to the plane, besides all the non-hydrogen atoms of one of the pyrazole rings being also on the symmetry plane, see Fig. 3 for the TS of compound **3**.

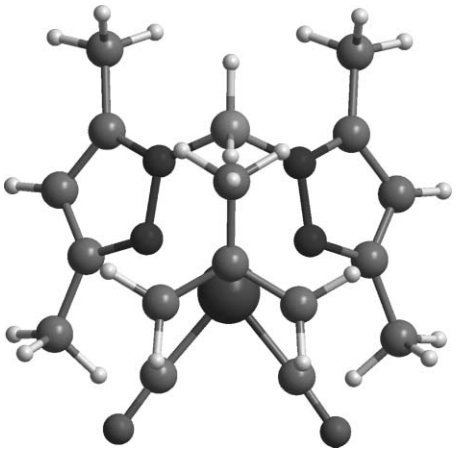


Fig. 2 The TS corresponding to compound **1**.

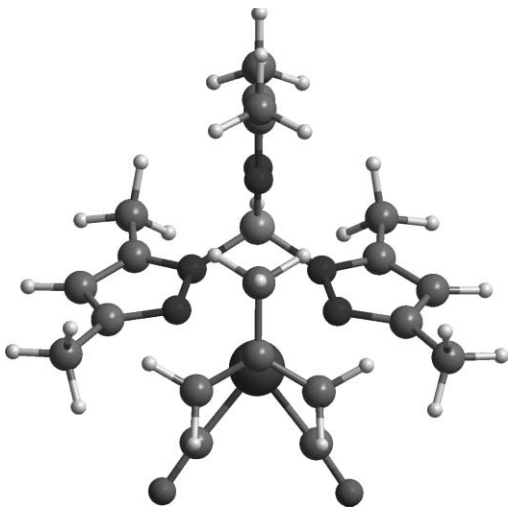
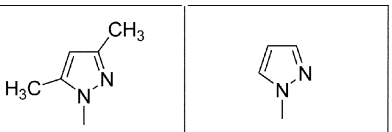


Fig. 3 The TS corresponding to compound **3**.

TS barriers for mechanism B. We have calculated the barriers corresponding to compounds **1–8** and reported them in Scheme 3. There are $\Delta H^{\ddagger}$ values with ZPE correction in kJ mol^{-1} (see ESI).

Note the excellent agreement for compound **1** (experimental 66–69 kJ mol^{-1} depending on the points used) and the considerable increase of the barrier for compounds **3** and **4** that also agrees with Trofimenko's observation reported above[29] and with two papers that describe only conformational isomerism of the allyl substituent in non-symmetric *C*-methyl terminal substituted allyl derivatives.[23,24]



	bis- I	tris- II	bis- I	tris- II
methallyl	**1** 67.9	**3** 150.4	**5** 29.0	**7** 124.3
allyl	**2** 61.8	**4** 111.5	**6** 29.4	**8** 81.9

Scheme 3 Calculated fluxional barriers (in kJ mol^{-1}) for compounds **1–8**.

We have analyzed the data of Scheme 3 using a presence-absence matrix (0 absent, 1 present, see ESI) corresponding to a full-factorial design with the purpose of having an estimation of the factors that contribute to these barriers. A first attempt leads to the following contributions: the presence of methyl groups on the pyrazoles increases the barrier by 32 kJ mol^{-1}; the presence of a methyl group on the π-allyl increases the barrier by 21 kJ mol^{-1}; with regard to dihydrobis derivatives (ring), the hydrotris derivatives (cage) have an increase of the barrier of 69 kJ mol^{-1}. Since the r^2 value of the correlation was poor (0.95) we tried another model which takes into account the interaction between the main factors: the presence of methyl groups on the pyrazoles increases the barrier by 35 kJ mol^{-1}; the presence of a methyl group on the π-allyl increases the barrier by 3 kJ mol^{-1}; with regard to dihydrobis derivatives (ring), the hydrotris derivatives (cage) have an increase of the barrier of 55 kJ mol^{-1}; the presence of a methyl group on the π-allyl in the case of hydrotris derivatives produces a further increase of 36 kJ mol^{-1}, finally, in the case of dihydrobis derivatives, the presence of methyl groups on the pyrazole rings decrease the barrier by 7 kJ mol^{-1}. To this model corresponds $r^2 = 0.999$.

Discussion of mechanism A. We have calculated the minima and the TSs of the four dihydrobispyrazolyl borates complexes **1**, **2**, **5** and **6** (Table 3) since mechanism **A** is not able to explain the equivalence of the three pyrazole substituents in hydrotrispyrazolyl-borates **3**, **4**, **7** and **8** (only two would became equivalent, the third one will remain different).

Table 3 deserves two comments: (i) the minima of Table 3 are always much higher in energy than the minima of mechanism **B** (this was already hinted by Trofimenko);[29] (ii) the **A1** minimum, (Figure 4 left) more stable than the **A2** one (Fig. 4 right) in three cases, cannot explain the dynamic NMR behaviour because nothing will happen (remember that increasing the temperature transform a C_1 into a C_s averaged structure). This aspect of the problem was also commented by Trofimenko when he wrote "structure **A1** would also be expected to have the π-allyl group symmetrically disposed with regard to the 3-methyl groups".[29] Therefore, mechanism **A** should be rejected.

Table 3 Values in kJ mol^{-1} with regard to the absolute minima of mechanism **B**

Complex	**A1** Min (C_s)	**A2** Min (C_1)*	TS (**A1**/**A2**)	TS (**A2**/**A2***)
1	47.6	46.6	91.0 [44.4]	66.8 [20.2]
2	40.7	54.5	74.0 [33.3]	75.5 [21.0]
5	25.4	36.4	65.2 [39.8]	45.3 [8.9]
6	24.8	43.7	65.2 [40.4]	53.4 [9.7]

*The **A2** minimum has an enantiomer **A2***. In brackets, differences between TSs and the minima of lower energy

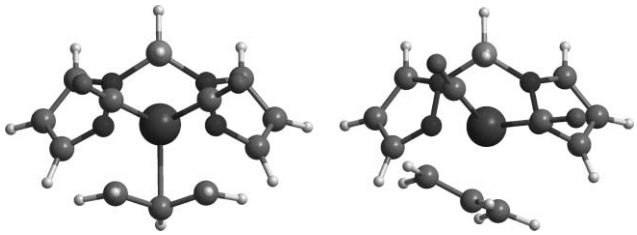


Fig. 4 The **A1** and **A2** minima of compound **6**.

Conclusion

In conclusion, the combined use of variable temperature multinuclear magnetic resonance and DFT calculations has allowed understanding the fluxional processes present in scorpionates confirming Trofimenko's proposal that it occurs through mechanism **B** (rotation about the B–Mo bond). Moreover, it has been established that B3LYP/LANL2DZ calculations provide accurate energies and NMR shieldings.

Experimental

Compound **1**, (dicarbonyl)[dihydrobis(3,5-dimethylpyrazol-1-yl)borato][η-(1,2,3)-2-methylpropen-1-yl]-molybdenum, was reported by Trofimenko.[29]

NMR Spectroscopy. Solution and Solid State (see ESI§).

GIAO calculations. The geometry of the systems has been optimized with the B3LYP/LANDL2DZ computational level within the Gaussian 03 package.[31,37,38] The geometry of the X-ray structures has been used as starting point for those cases where they where available. In all the cases, the energetic minimum or TS nature of the structures have been confirmed by frequency calculation at the same computational level. The chemical shielding have been calculated with the GIAO method at the B3LYP/LANDL2DZ computational level.[39]

Acknowledgements

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