Electronic Supplementary Information for Dalton Transactions

A Theoretical and Experimental Study of the Fluxional Behaviour of Molybdenum Dihydrobis- and Hydrotris-pyrazolylborates

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Electronic supplementary information (ESI)

NMR Spectroscopy. Solution. The spectra were recorded on a Bruker DRX 400 spectrometer (9.4 Tesla, 400.13 MHz for ^{1}H, 100.62 MHz for ^{13}C and 40.56 MHz for ^{15}N) with a 5-mm inverse-detection H-X probe equipped with a z-gradient coil. Chemical shifts (δ in ppm) are given from internal solvent, $CDCl_3$ 7.26 for ^{1}H, 77.0 for ^{13}C, and for ^{15}N nitromethane (0.00) was used as external reference. Parameters for ^{1}H NMR spectra were spectral width 4496 Hz, pulse width 7.5 µs at an attenuation level of 0 dB and resolution 0.27 Hz per point. Parameters for ^{13}C NMR spectra were spectral width 26178 Hz, pulse width 10.6 µs at an attenuation level of -6 dB and resolution 0.80 Hz per point; WALTZ-16 was used for broadband proton decoupling; the FIDS were multiplied by an exponential weighting (lb = 1 Hz) before Fourier transformation. 2D (^{1}H-^{1}H) gs-COSY and inverse proton detected heteronuclear shift correlation spectra, (^{1}H-^{13}C) gs-HMQC, (^{1}H-^{13}C), gs-HMBC and (^{1}H-^{15}N) gs-HMBC were acquired and processed using standard Bruker NMR software in non-phase-sensitive mode and were carried out to assign the ^{1}H, ^{13}C and ^{15}N signals. Gradient selection was achieved through a 5% sine truncated shaped pulse gradient of 1 ms. Selected parameters for (^{1}H-^{1}H) gs-COSY were spectral width 4496 Hz, the acquisition data size was 1024 points and one transient was accumulated per increment, with a 1 s relaxation delay, for a total of 512 experiments, data processing using zero filling in the *F*1 domain and shifted sine-bell apodization of factor 0 in both dimensions. Selected parameters for (^{1}H-^{13}C) gs-HMQC spectra were spectral width 4496 Hz for ^{1}H and 16.34 kHz for ^{13}C, 1024 x 256 data set, number of scans 2 and relaxation delay 1s. Parameters for (^{1}H-^{13}C) gs-HMQC spectra were spectral width 4496 Hz for ^{1}H and 26.18 kHz for ^{13}C, 1024 x 128 data set, number of scans 4, relaxation delay 1s and 60 ms delay for the evolution of the ^{13}C-^{1}H long-range coupling. Parameters for (^{1}H-^{15}N) gs-HMQC spectra were spectral width 4496 Hz for ^{1}H and 12.44 kHz for ^{15}N, 1024 x 512 data set, number of scans 2, relaxation delay 1s and 83 ms delay for the evolution of the ^{15}N-^{1}H long-range coupling. The FIDs were processed using zero filling in the *F*1 domain and a sine-bell window function in both dimensions was applied prior to Fourier transformation. In the gs-HMQC experiments GARP modulation of ^{13}C was used for decoupling. Variable temperature: A Bruker BVT3000 temperature unit was used to control the temperature and an exchanger to reach low temperatures. To avoid problems at low temperatures caused by air moisture, pure nitrogen was used as cooling gas stream.

Solid state. ^{13}C (100.73 MHz) and ^{15}N (40.60 MHz) CPMAS NMR spectra were obtained on a Bruker WB 400 spectrometer at 300 K using a 4 mm DVT probehead and standard CP pulse sequences were employed.. Samples were carefully packed in a 4-mm diameter cylindrical zirconia rotors with Kel-F end-caps. Operating conditions involved 3.2 µs 90° ^{1}H pulses and decoupling field strength of 78.1 kHz by TPPM sequence. ^{13}C spectra were originally referenced to a glycine sample and then the chemical shifts were recalculated to the Me_4Si (for the carbonyl atom δ (glycine) = 176.1 ppm) and ^{15}N spectra to $^{15}NH_4Cl$ and then converted to nitromethane scale using the relationship: $\delta^{15}N$(nitromethane) = $\delta^{15}N$(ammonium chloride) – 338.1 ppm. The typical acquisition parameters for ^{13}C CPMAS were: spectral width, 40 kHz; recycle delay, 5 s; acquisition time, 30 ms; contact time, 2 ms; and spin rate, 12 kHz. In order to distinguish protonated and unprotonated carbon atoms, the NQS (Non-Quaternary Suppression) experiment by conventional cross-polarization was recorded; before the acquisition the decoupler is switched off for a very short time of 25 μs. Typical acquisition parameters for ^{15}N CPMAS were: spectral width, 40 kHz; recycle delay, 5 s; acquisition time, 35 ms; contact time, 5 ms; and spin rate, 6 kHz.

The cross peaks observed between pairs of signals are: (^{1}H-^{1}H) gs-COSY: 1.20 (Ha)↔3.20 (Hs), 1.61 (Ha)↔3.68 (Hs), 3.20 (Hs)↔3.68 (Hs), 2.07 (5-Me)↔5.76 (H4), 2.08 (5-Me)↔5.65 (H4), 2.35 (3-Me)↔5.65 (H4), 2.65 (3-Me)↔5.76 (H4). (^{1}H-^{13}C) gs-HMQC: 1.20 (Ha)↔49.8, 1.61 (Ha)↔66.4, 1.66 (Me methallyl)↔22.2, 2.07&2.08 (5-Me)↔10.5&10.7, 2.35 (3-Me)↔14.0, 2.65 (3-Me)↔13.6, 3.20 (Hs)↔49.8, 3.68 (Hs)↔66.4, 5.65 (H4)↔104.9, 5.76 (H4)↔105.1. (^{1}H-^{13}C) gs-HMBC: 1.20 (Ha)↔22.2 (Me methallyl), 1.20 (Ha)↔66.4 (C_t), 1.20 (Ha)↔225.7 (CO), 1.61 (Ha)↔22.2 (Me methallyl), 1.61 (Ha)↔49.8 (C_t), 1.61 (Ha)↔233.5 (CO), 1.66 (Me methallyl)↔49.8 (C_t), 1.66 (Me methallyl)↔66.4 (C_t), 1.66 (Me methallyl)↔91.8 (C_c), 2.07&2.08 (5-Me)↔104.9&105.1 (C4), 2.07 (5-Me)↔142.3 (C5), 2.08 (5-Me)↔144.1 (C5), 2.35&2.65 (3-Me)↔104.9&105.1 (C4), 2.35 (3-Me)↔144.1 (C5), 2.35 (3-Me)↔149.0 (C3), 2.65 (3-Me)↔151.7 (C3), 3.20 (Hs)↔66.4 (C_t), 3.68 (Hs)↔49.8 (C_t), 5.65 (H4)↔144.1 (C5), 5.65 (H4)↔149.0 (C3), 5.76 (H4)↔142.3 (C5), 5.76 (H4)↔151.7 (C3). (^{1}H-^{15}N) gs-HMBC: 2.07 (5-Me)↔–151.1 (N1), 2.08 (5-Me)↔–150.1 (N1), 2.35 (3-Me)↔–126.9 (N2), 2.65 (3-Me)↔–130.3 (N2), 5.65 (H4) ↔–150.1 (N1), 5.76 (H4)↔–151.1 (N1).

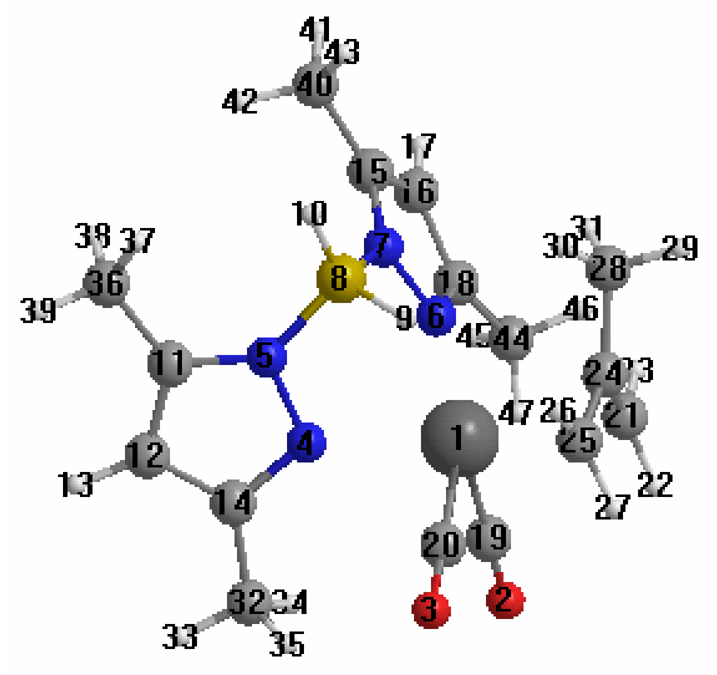
B3LYP/LANL2DZ calculations (absolute energies in hartrees and relative energies in kJ mol^{-1})

Comp.	Minimum	TS	Barrier	Barrier+ZPE
1	–1085.3559	–1085.3301	67.9	67.6
2	–1046.0459	–1046.0224	61.8	61.5
3	–1388.9978	–1388.9406	150.4	148.9
4	–1349.6874	–1349.6450	111.5	111.6
5	–928.0969	–928.0858	29.0	29.3
6	–888.7865	–888.7753	29.4	29.3
7	–1153.1307	–1153.0833	124.3	122.8
8	–1113.8213	–1113.7901	81.9	81.4

Absolute shieldings (*σ*, ppm)

References			B3LYP/LANL2DZ
BH_4_GIAO.log:	1	B	161.0201
BH_4_GIAO.log:	2	H	33.6756
BMe_3_GIAO.log:	1	B	23.1862
BMe_3_GIAO.log:	2	C	177.0135
BMe3_GIAO.log:	3	C	177.0329
BMe3_GIAO.log:	4	C	177.0414
BMe3_GIAO.log:	5	H	31.6551
BMe3_GIAO.log:	6	H	31.6553
BMe3_GIAO.log:	7	H	31.6579
BMe3_GIAO.log:	8	H	31.6551
BMe3_GIAO.log:	9	H	31.6553
BMe3_GIAO.log:	10	H	31.6579
BMe3_GIAO.log:	11	H	31.433
BMe3_GIAO.log:	12	H	31.4322
BMe3_GIAO.log:	13	H	31.4303
C_2H_2_GIAO.log:	1	C	129.1164
C_2H_2_GIAO.log:	3	H	30.6777
CH_2O_GIAO.log:	1	C	–17.0724
CH_2O_GIAO.log:	2	O	–563.3824
CH_2O_GIAO.log:	3	H	21.3584
CH_4_GIAO.log:	1	C	195.5784
CH_4_GIAO.log:	2	H	32.3813
H_2O_GIAO.log:	1	O	298.3304
H_2O_GIAO.log:	2	H	31.8177
$Mo(CO)_6$_GIAO.log:	1	Mo	–97.5837
$Mo(CO)_6$_GIAO.log:	2	C	–35.093
$Mo(CO)_6$_GIAO.log:	3	O	–120.2748
MoO_4_GIAO.log:	1	Mo	–395.3101
MoO_4_GIAO.log:	2	O	–373.802
NH_3_GIAO.log:	1	N	261.5728
NH_3_GIAO.log:	2	H	32.7386
Nitromethane_GIAO.log:	1	C	120.3508
Nitromethane_GIAO.log:	2	H	28.1942
Nitromethane_GIAO.log:	3	H	28.1942
Nitromethane_GIAO.log:	4	H	28.1709
Nitromethane_GIAO.log:	5	N	–198.7746
Nitromethane_GIAO.log:	6	O	–574.4917
Nitromethane_GIAO.log:	7	O	–574.4041

TMS_GIAO.log:	1	Si	9.1226
TMS_GIAO.log:	2	C	193.1862
TMS_GIAO.log:	6	H	32.77



1 Mo –310.892
2 O –162.3539
3 O –124.5024
4 N –40.4161
5 N –6.3602
6 N –47.0793
7 N –6.1354
8 B 120.6772
9 H 33.8813
10 H 29.5183
11 C 44.2177
12 C 83.9517
13 H 26.5562
14 C 31.9432
15 C 41.8199
16 C 84.6684
17 H 26.5681
18 C 36.1805
19 C –75.3211
20 C –60.9744
21 C 112.7834
22 H 30.3575
23 H 28.6384
24 C 86.7389

25 C 132.6762
26 H 29.5995
27 H 31.1315
28 C 164.4957
29 H 30.6252
30 H 31.132
31 H 31.5583
32 C 173.409
33 H 30.6465
34 H 29.8556
35 H 29.4688
36 C 175.6598
37 H 30.5076
38 H 30.9617
39 H 30.8475
40 C 175.1556
41 H 30.9257
42 H 30.7927
43 H 30.6284
44 C 172.7874
45 H 30.6521
46 H 30.539
47 H 29.9157

Presence/absence matrix

Comp.	Barrier	Me(allyl)	Me(pyrazole)	tris/bis
1	67.9	1	1	0
2	61.8	0	1	0
3	150.4	1	1	1
4	111.5	0	1	1
5	29.0	1	0	0
6	29.4	0	0	0
7	124.3	1	0	1
8	81.9	0	0	1

Regression Summary
Barrier+ZPE vs. 3 Independents

Count	8
Num. Missing	0
R	.973
R Squared	.947
Adjusted R Squared	.908
RMS Residual	13.206

Regression Coefficients
Barrier+ZPE vs. 3 Independents

	Coefficient	Std. Error	Std. Coeff.	t-Value	P-Value
Intercept	20.475	9.338	20.475	2.193	.0934
allyl	21.200	9.338	.261	2.270	.0857
pz	31.700	9.338	.390	3.395	.0274
bis	69.250	9.338	.852	7.416	.0018

Regression Summary
Barrier+ZPE vs. 5 Independents

Count	8
Num. Missing	0
R	.999
R Squared	.999
Adjusted R Squared	.996
RMS Residual	2.599

Regression Coefficients
Barrier+ZPE vs. 5 Independents

	Coefficient	Std. Error	Std. Coeff.	t-Value	P-Value
Intercept	27.775	2.250	27.775	12.342	.0065
pz	35.250	2.599	.434	13.565	.0054
bis	54.650	3.183	.673	17.172	.0034
ally*bis	36.300	3.675	.387	9.878	.0101
pz*bis	-7.100	3.675	-.076	-1.932	.1931
allyl	3.050	2.599	.038	1.174	.3614