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The identification of all five isomers of [(η^5-C_5H_5)$_2$$Mo_2(CO)_5$-(CNMe)] and the mechanisms of fluxionality†

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Received 7th April 2000, Accepted 15th May 2000

[(η^5-C_5H_5)$_2$$Mo_2(CO)_5$(CNMe)] has been re-examined by ^{1}H and ^{13}C NMR spectroscopy in $(CD_3)_2NCDO$ and all five isomers have been identified. Activation energies have been determined for their interconversion and ligand scrambling. The lowest energy dynamic process is intramolecular ligand exchange *via* [(η^5-C_5H_5)$_2$$Mo_2$($\mu$-CO)($\mu$-CNMe)(CO)$_4$] which is more facile in the *gauche*-isomer with $\Delta G^\ddagger = 11.7 \pm 0.2$ kcal mol^{-1} than in the *trans*-isomer with $\Delta G^\ddagger = 12.2 \pm 0.2$ kcal mol^{-1}. The next lowest energy dynamic process is intramolecular ligand exchange *via* [(η^5-C_5H_5)$_2$$Mo_2$($\mu$-CO)$_2(CO)_3$(CNMe)] which is more facile in the *gauche*-isomer with $\Delta G^\ddagger = 12.4 \pm 0.2$ and 12.6 ± 0.2 kcal mol^{-1} than in the *trans*-isomer with $\Delta G^\ddagger = 14.5 \pm 0.2$ kcal mol^{-1}. The highest energy dynamic process is rotation about the Mo–Mo bond which was only detected in the isomers with CNMe *cis* to the Mo–Mo bond where $\Delta G^\ddagger = 14.4 \pm 0.2$ and 14.7 ± 0.2 kcal mol^{-1}.

When in 1973, Cotton and co-workers examined the fluxionality of [(η^5-C_5H_5)$_2$$Mo_2(CO)_5$(CNMe)],[1] they showed that although there are five possible isomers, (**1**) to (**5**), see Fig. 1, only two or possibly three isomers are present in acetone solution in significant concentrations. They showed that it exists in solution as a mixture of non-bridged isomers which interconvert at room temperature. The isocyanide ligand passes between the molybdenum atoms. They showed that, in acetone, the major isomer present is the *trans,trans*-isomer, (**1**). Support for this came from the determination of the crystal structure.[1] They suggested that a second most abundant isomer has the isocyanide *cis* to the Mo–Mo bond, and although unable to decide between (**2**), (**4**), and (**5**), favoured (**4**) or (**5**).

There have subsequently been several developments which have made the problem more amenable to study. The increase in magnetic field strength has markedly increased the resolution of NMR spectrometers. Also, in 1989, Lindsell and Tomb showed that d_6-DMSO increases the concentration of the *gauche*-isomer of [(η^5-C_5H_5)$_2$$W_2(CO)_6$] making the investigation of the fluxionality of [(η^5-C_5H_5)$_2$$W_2(CO)_6$] feasible by ^{13}C NMR spectroscopy.[2] This led to the investigation of the fluxionality of [(η^5-C_5H_5)$_2$$Mo_2(CO)_6$] in d_7-DMF.[3] This work showed that the most facile dynamic process in [(η^5-C_5H_5)$_2$$Mo_2(CO)_6$] is intramolecular carbonyl exchange between the molybdenum atoms with $\Delta G^\ddagger = 13.9 \pm 0.2$ kcal mol^{-1} for the *gauche*-isomer of [(η^5-C_5H_5)$_2$$Mo_2(CO)_6$] and 14.9 ± 0.2 kcal mol^{-1} for the *trans*-isomer. The well established rotation about the Mo–Mo bond is a higher energy process with $\Delta G^\ddagger_{278} = 15.3 \pm 0.2$ and 15.5 ± 0.2 kcal mol^{-1} for *trans→gauche* isomerisation and *gauche→trans* isomerisation respectively. As for [(η^5-C_5H_5)$_2$$W_2(CO)_6$], *gauche→gauche* isomerism was not detected.[2,3]

Experimental

Solution NMR spectra were measured using a Bruker WH400 spectrometer. The signals were referenced to the central CD_2H (^{1}H) or CD_3 (^{13}C) low frequency signal of $(CD_3)_2NCHO$ at δ 2.91 (^{1}H) or δ 30.1 (^{13}C). This will result in an error in the absolute shifts of ±0.05 ppm (^{1}H) or ±0.5 ppm (^{13}C). The chemical shifts are quoted to two decimal places to permit their *relative* positions to be compared. The temperature was measured using a Comark electronic thermometer by replacing the sample with an NMR tube containing a thermocouple in Me_2NCHO. Rates of exchange were either determined below coalescence using the equation $k = \pi\Delta\nu$ s^{-1}, where $\Delta\nu$ is the contribution to the line width due to exchange or by magnetisation transfer.[4] $\Delta G^\ddagger$ values were obtained using the Eyring equation:-

$$\Delta G^\ddagger = RT\left(23.759 - \ln\frac{k}{T}\right)$$

Magnetisation transfer measurements were performed as previously described.[4] The COSY-90 NMR spectra were recorded using a spectral width of 4 KHz and a 1024 × 256 data set. The EXSY NMR spectrum was recorded using a spectral width of 4000 Hz, a 1024 × 256 data set and a mixing time of 0.05 s.

^{13}CO-Enriched [$Cp_2Mo_2(CO)_6$][5]

A red solution of [$Cp_2Mo_2(CO)_6$] (1.50 g, 3.06 mmol) in *m*-xylene (60 ml) was refluxed for 2 h and then *m*-xylene was evaporated by using a fast nitrogen gas stream at high temperature. The resulting brown solid [$Cp_2Mo_2(CO)_4$] was dissolved in CH_2Cl_2 (50 ml) and then treated with 99% ^{13}CO gas for 30 min at which point the absorption of gas ceased. The red solution was purified by chromatography on an alumina column using CH_2Cl_2 as the eluent. 33% ^{13}CO-Enriched [$Cp_2Mo_2(CO)_6$] (1.1 g, 73%) was obtained.

^{13}CO-Enriched [$Cp_2Mo_2(CO)_5$(CNMe)]

A brown solution of [$Cp_2Mo_2(CO)_4$] in CH_2Cl_2 (50 ml) derived from ^{13}CO-enriched [$Cp_2Mo_2(CO)_6$] (0.90 g, 1.84 mmol), prepared by the method described above, was reacted with CNMe (0.23 ml, 4.40 mmol) for 24 h. The red reaction mixture was concentrated and chromatographed on a column filled with alumina, eluted firstly with hexane to remove the unreacted [$Cp_2Mo_2(CO)_6$] and then with hexane–CH_2Cl_2 (1 : 1) to give a red sample of [$Cp_2Mo_2(CO)_5$(CNMe)][1] (0.10 g, 10.8%).

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† Electronic Supplementary information (ESI) available: magnetisation transfer data. See http://www.rsc.org/suppdata/dt/b0/b002849p/

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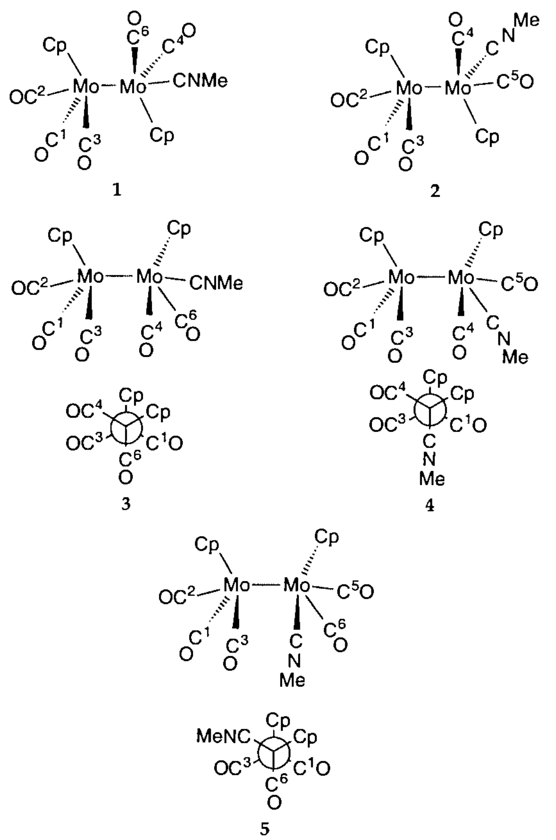


Fig. 1 The five possible isomers of [$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(CNMe)$], ignoring enantiomers, and the Newman projections of isomers (**3**), (**4**), and (**5**).

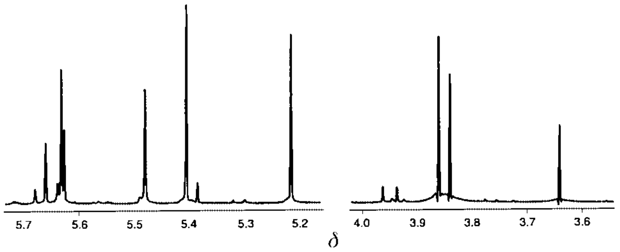


Fig. 2 The 400.13 MHz ^1H NMR spectrum of [$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(CNMe)$] in $(CD_3)_2NCDO$ at −78 °C. The resolution of the signals has been enhanced using a Gaussian transformation.

Results

The compound [$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(CNMe)$] can exist in solution as five isomers, (**1**) to (**5**), disregarding enantiomers, see Fig. 1. The cyclopentadienyl ligands can be *trans* or *gauche* about the Mo–Mo bond. For the *trans*-isomers, there are two possible positions for the CNMe group, either *trans* or *cis* to the Mo–Mo bond, as in (**1**) and (**2**). For the *gauche*-isomers, there are three possible positions for the CNMe group, *trans* to the Mo–Mo bond in (**3**), and *cis* to the Mo–Mo bond as in (**4**) and (**5**). The difference between (**4**) and (**5**) is best seen in the form of Newman projections, see Fig. 1. The torsion angle between the MeNC and cyclopentadienyl ligand is 180° in (**4**) and 60° in (**5**).

A solution of [$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(CNMe)$] in $(CD_3)_2$-NCDO at −78 °C,[6] shows ^1H NMR signals for five isomers in the intensity ratio 1:0.89:0.38:0.15:0.13, see Fig. 2. This is most clearly seen in the MeNC region of the spectrum, where five separate signals are seen at δ 3.63, 3.84, 3.87, 3.94, and 3.97. Examination of Fig. 2 also shows nine of the ten expected cyclopentadienyl signals between δ 5.2 and 5.7. There must be the corresponding five pairs of cyclopentadienyl signals in the same intensity ratio and one signal must be obscured under another. On the basis of intensity, the signals due to the three major isomers can be identified, see Table 1. Due to the similarity in intensities, this does not differentiate between the two minor isomers.[7]

Table 1 The assignment of the ^1H chemical shifts of the isomers of [$Mo_2(\eta\text{-}C_5H_5)_2(CO)_5(CNMe)$] to individual isomers. The shifts are given for a solution in $(CD_3)_2NCDO$ at −78 °C

	MeNC	$\eta^5\text{-}C_5H_5$
Isomer a	3.87	5.21, 5.41
Isomer b	3.84	5.48, 5.63
Isomer c	3.64	5.63, 5.67
Isomers d and e	3.94	5.38, 5.41 (obscured)
	3.97	5.65, 5.68

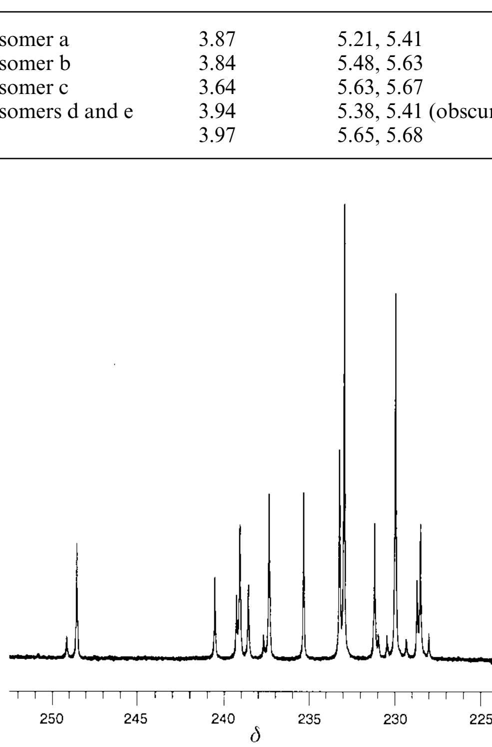


Fig. 3 The 100.62 MHz ^{13}C NMR spectrum of ^{13}CO-enriched [$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(CNMe)$] in $(CD_3)_2NCDO$ at −62 °C.

Examination of the five possible structures in Fig. 1 shows that in (**1**), there are three types of carbonyls in the intensity ratio 1:2:2. In the other four isomers all five carbonyls are inequivalent. The ^{13}C NMR spectrum in $(CD_3)_2NCDO$ at −62 °C of a sample of [$Mo_2(\eta\text{-}C_5H_5)_2(CO)_5(CNMe)$], partially enriched in ^{13}CO, shows all of the possible 23 carbonyl signals, see Fig. 3. The signal at δ 248.5 consists of partially overlapped signals at δ 248.50 (weak) and δ 248.55 (moderately strong).[7] The signal at δ 239.2 consists of three weak signals at δ 239.26, 239.20, and 239.17. The signal at δ 233.1 consists of overlapped signals at δ 233.15 and 233.06.

Previous work on [$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$][3] has provided information which can be used to assist in making carbonyl assignments: (i) The carbonyl *trans* to the Mo–Mo bond is at high frequency compared with the *cis*-carbonyls. (ii) $^2J(^{13}C^{13}C)$ is significant between the ^{13}CO *trans* to the Mo–Mo bond with both ^{13}COs *cis* to the Mo–Mo bond. Coupling is not detected between the ^{13}COs *cis* to the Mo–Mo bond nor across the Mo–Mo bond. (iii) Carbonyl exchange is *via* the merry-go-round mechanism, *via* an intermediate/transition state analogous to the structure of [$(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu\text{-}CNCF_3)_2(CO)_4$].[8] (iv) Carbonyl exchange is more facile in the *gauche*-isomer than in the *trans*-isomer. (v) Carbonyl exchange is more facile than rotation of the Mo–Mo bond. (vi) The activation energies for carbonyl exchange and Mo–Mo bond rotation are expected to be similar in [$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$] and [$Mo_2(\eta\text{-}C_5H_5)_2(CO)_5$-(CNMe)].

Assignment of the ^{13}CO signals due to (1)

In Fig. 3, two strong signals at δ 229.87 and 232.82 stand clear

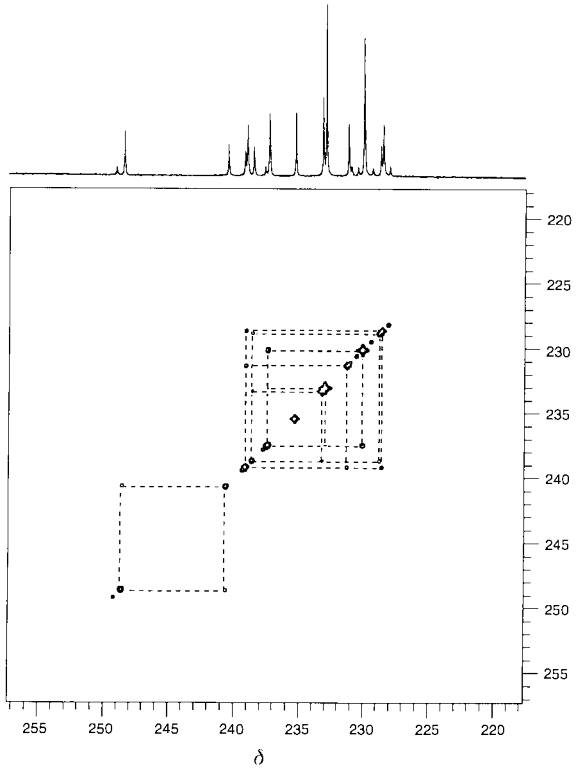


Fig. 4 The COSY-90 100.62 MHz ^{13}C NMR spectrum of ^{13}CO-enriched [(η^5-C_5H_5)$_2$$Mo_2(CO)_5$(CNMe)] in $(CD_3)_2NCDO$ at −62 °C.

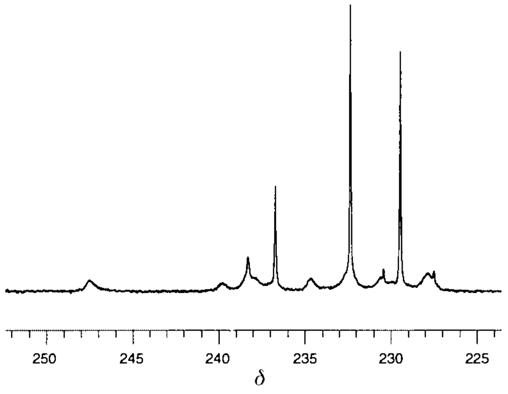


Fig. 5 The 100.62 MHz ^{13}C NMR spectrum of ^{13}CO-enriched [(η^5-C_5H_5)$_2$$Mo_2(CO)_5$(CNMe)] in $(CD_3)_2NCDO$ at −13 °C.

of the pack. As (**1**) has carbonyl intensities 2 : 2 : 1, and all the other isomers have intensities 1 : 1 : 1 : 1 : 1, this is consistent with (**1**) being the major isomer, a. Confirmation of this comes in several ways. A COSY-90 ^{13}C NMR spectrum shows coupling between the signals at δ 237.25, relative intensity 1, and 229.87, relative intensity 2, see Fig. 4.[9] Hence these are the carbonyls on the unsubstituted molybdenum atom with C^{1}O and C^{3}O at δ 229.87 and C^{2}O at δ 237.25. These chemical shifts are in reasonably good agreement with those observed for the parent compound *trans*-[Mo_2(η-C_5H_5)$_2$(CO)$_6$] where C^{1}O and C^{3}O are at δ 227.5 and C^{2}O is at δ 235.8 in *d*$_7$-DMF–DMF.[3] The signal at δ 233.0 is due to the carbonyls on the substituted molybdenum atom, C^{4}O and C^{5}O. It therefore appears that substitution of CO by CNMe produces a high frequency shift, and this information is used to help with assignments. On warming, these signals remain relatively sharp up to −13 °C, consistent with them coming from the same species, see Fig. 5. When the sample is dissolved in $(CD_3)_2CO$, see Fig. 6, then the signals at δ 235.3, 230.9, and 227.9 are due to the major species, which is (**1**) both on the basis of the intensities being 1 : 2 : 2 and in agreement with Cotton's work.[1]

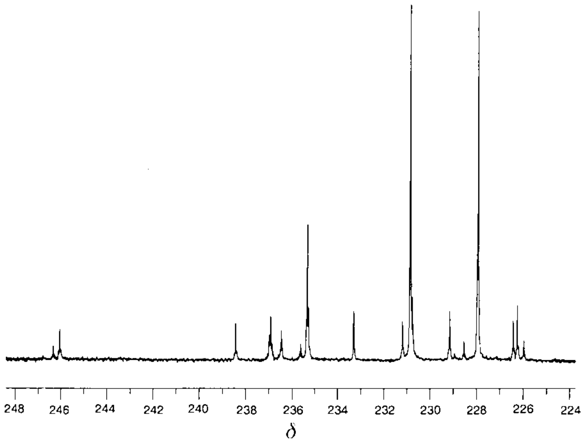


Fig. 6 The 100.62 MHz ^{13}C NMR spectrum of ^{13}CO-enriched [(η^5-C_5H_5)$_2$$Mo_2(CO)_5$(CNMe)] in $(CD_3)_2CO$ at −70 °C.

Assignment of the ^{13}CO signals due to (3) and (4)

The assignment of the medium intensity ^{13}CO NMR signals is assisted considerably by a ^{13}C COSY-90 NMR spectrum of ^{13}CO-enriched [(η^5-C_5H_5)$_2$$Mo_2(CO)_5$(CNMe)] in $(CD_3)_2NCDO$ at −62 °C, see Fig. 4. Cross-peaks are only detected for the major and two intermediate intensity isomers, a, b, and c. Following from the previous work on [(η^5-C_5H_5)$_2$$Mo_2(CO)_6$],[3] connectivities are observed between ^{13}CO *trans* to the Mo–Mo bond with the ^{13}COs *cis* to the Mo–Mo bond but NOT between inequivalent ^{13}COs *cis* to the Mo–Mo bond. Four coupled groups of carbonyls are identified:- δ 248.55 and 240.47; δ 238.48 and 233.06, 228.75; δ 238.97 and 233.15, 228.44; δ 237.25 and 229.87. The signals at δ 237.25 and 229.87 have already been assigned to (**1**) and can be disregarded. It is possible to make the following deductions:- (i) by analogy with previous work, in each case the high frequency signal is due to ^{13}CO *trans* to the Mo–Mo bond. (ii) The two sets of three carbonyls at δ 238.48 and 233.06, 228.75 and at δ 238.97 and 233.15, 228.44 must arise from Mo(CO)$_3$ groups. The signals at δ 238.48 and 238.97 are assigned to ^{13}COs *trans* to the Mo–Mo bond both on the basis of chemical shift and the COSY cross peaks. There is a cross peak from the ^{13}CO *trans* to the Mo–Mo bond to both ^{13}CO groups *cis* to the Mo–Mo bond but not between the two *cis*-^{13}CO groups here and in *gauche*-[(η^5-C_5H_5)$_2$$Mo_2(CO)_6$].[3] (iii) The remaining pair of signals at δ 248.55 and 240.47 must be due to a Mo(CO)$_2$-(CNMe) group as it only contains two carbonyls of equal intensity. On the basis of the observation of coupling which is not observed between carbonyls *cis* to the Mo–Mo bond and the relative chemical shifts, the signal at δ 248.55 is due to the ^{13}CO *trans* to the Mo–Mo bond and that at δ 240.47 is due to the ^{13}CO *cis* to the Mo–Mo bond. The missing third ligand on the molybdenum must be a CNMe group. The high frequency shift of both signals compared with *ca.* δ 238 and 230 found in Mo(CO)$_3$ groups is attributed to the presence of CNMe on the same molybdenum atom.

Support for these assignments comes from examination of the structures in Fig. 1. The ^{13}CO chemical shift of *ca.* δ 249 is unusual for this group of compounds. The highest frequency CO group in [Cp_2Mo_2(CO)$_6$] is at δ 235.8 (*trans*-isomer) and δ 237.3 (*gauche*-isomer) for the carbonyl *trans* to the Mo–Mo bond. In the assignment of the ^{13}CO NMR signals of (**1**), it has been noted that substitution of CO by CNMe produces a high frequency shift. Hence these shifts of *ca.* δ 249 arise from the carbonyl being *trans* to a Mo–Mo bond and *cis* to a CNMe group. Support for this conclusion comes from the fact that there are three structures containing this grouping, namely (**2**), (**4**), and (**5**), and three signals are observed at *ca.* δ 249 for the ^{13}CO *trans* to the Mo–Mo bond.

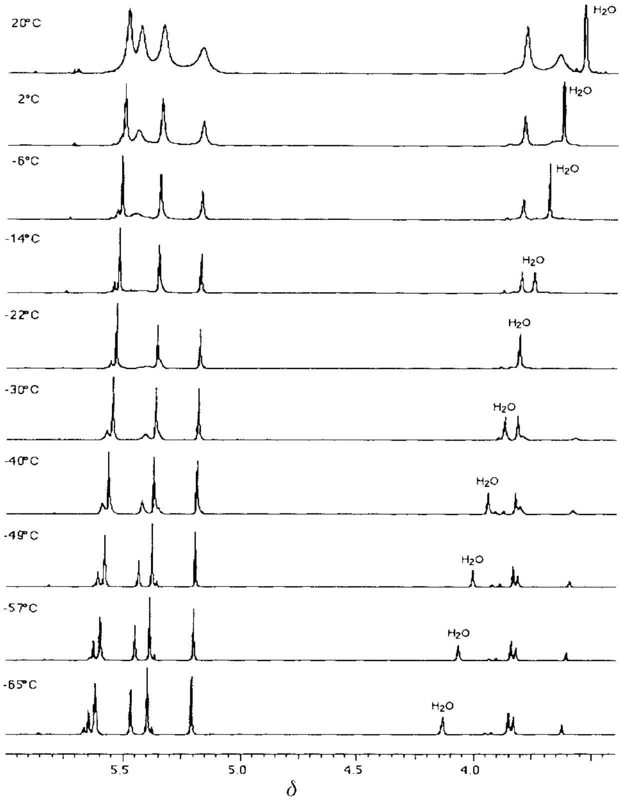


Fig. 7 The variable temperature 400.13 MHz ^1H NMR spectrum of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(CNMe)]$ in $(CD_3)_2NDO$.

Intensities can now be used to assign the signals to species b and c.[9] Compound b has carbonyls at δ 238.97 (*trans* to the Mo–Mo bond) and 233.15, 228.44 $[Mo(CO)_3]$ and δ 235.21 and 231.09 $[Mo(CO)_2(CNMe)$ with CNMe *trans* to the Mo–Mo bond]. Compound c has carbonyls at δ 238.48 (*trans* to the Mo–Mo bond) and 233.06, 228.75 $[Mo(CO)_3]$ and δ 248.55 (*trans* to the Mo–Mo bond) and 240.47 $[Mo(CO)_2(CNMe)$ group with the CNMe *cis* to the Mo–Mo bond].

The assignment of the structure of b is now straightforward. The lack of coupling in Fig. 4 between the $Mo(CO)_2(CNMe)$ carbonyls at δ 235.21 and 231.09 and the chemical shifts show that the CNMe group has to be *trans* to the Mo–Mo bond. The only possible structure with five inequivalent carbonyls is (**3**).

On the basis of the deductions so far, c has the MeNC ligand *cis* to the Mo–Mo bond. The structure of c could therefore be (**2**), (**4**), and (**5**). The assignment of isomers (**2**), (**4**), and (**5**) and the remaining signals becomes possible when the dynamic processes are considered. When the solution is warmed from −60 °C, exchange becomes significant on the NMR time scale, see Fig. 7 and 8.

^1H NMR magnetisation transfer measurements at −50 °C, show exchange involving the signals of isomers b and c. The exchange is between the cyclopentadienyl signals at δ 5.48 and 5.67, and between the methyl signals at δ 3.59 and 3.81, with the rate of leaving isomer b being 3.4 s^{-1} and the rate of leaving isomer c being 2.1 s^{-1}, corresponding to $\Delta G^{\ddagger}_{223} = 12.4 \pm 0.2$ and 12.6 ± 0.2 kcal mol^{-1} respectively. Previously Cotton *et al.* reported that $\Delta G^{\ddagger}_{223} = 13.0 \pm 0.5$ kcal mol^{-1} for this exchange.[1] Exchange was not proven between the two cyclopentadienyl signals at δ 5.63 due to their proximity. At low temperatures two signals are observed, while above −49 °C only one signal is observed at δ 5.63. This signal persists until above −6 °C, when the signal broadens due to further exchange processes, see Fig. 7. Isomer b has two cyclopentadienyl signals at δ 5.48 and 5.63, and isomer c has them at δ 5.63 and 5.67. The exchange between the signals at δ 5.48 and 5.67 has been proven by magnetisation transfer. There is no way that this could occur without the two signals at δ 5.63 exchanging at the same time.

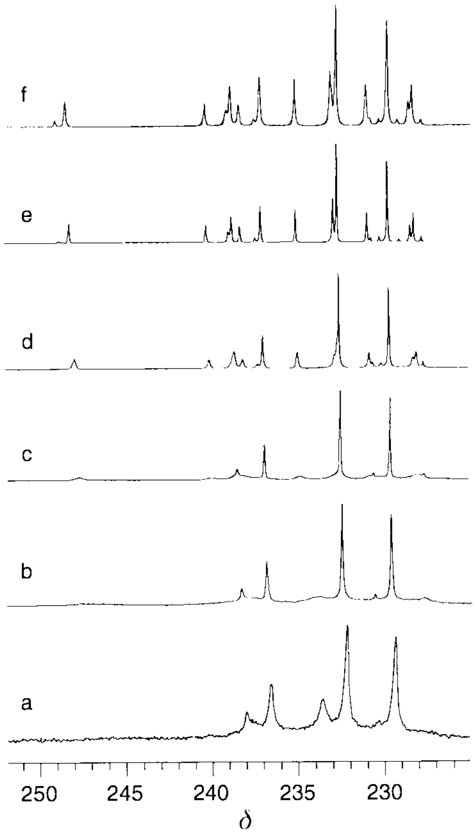


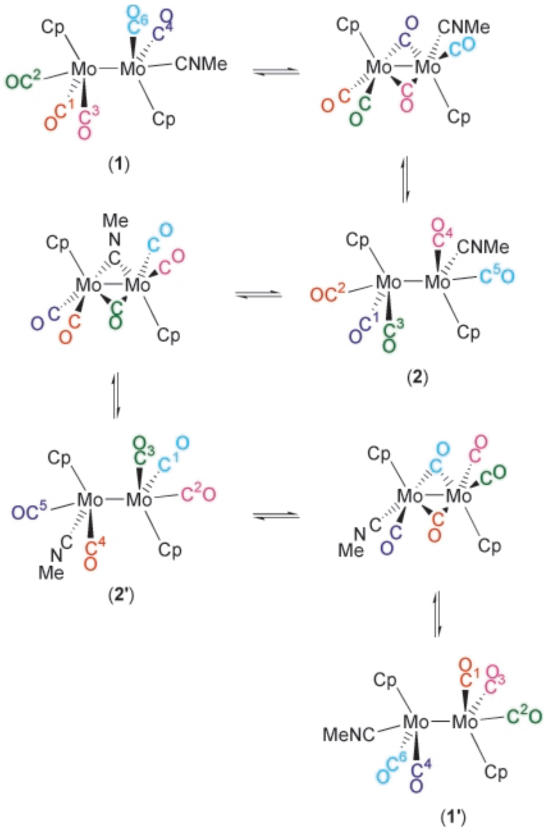
Fig. 8 The 100.62 MHz ^{13}C NMR spectrum of the carbonyl region of ^{13}CO-enriched $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(CNMe)]$ in d_7-DMF at (a) 18 °C; (b) 2 °C; (c) −18 °C; (d) −36 °C; (e) −54 °C; (f) −73 °C.

It has already been deduced from the ^{13}C NMR spectra that isomer b is (**3**). Hence the second intermediate intensity isomer has a facile exchange pathway with (**3**). Only two exchange mechanisms have been identified for $[Cp_2Mo_2(CO)_6]$, the merry-go-round mechanism and rotation about the Mo–Mo bond.[3] It can be anticipated that these two mechanisms will also operate in $[Cp_2Mo_2(CO)_5(CNMe)]$.

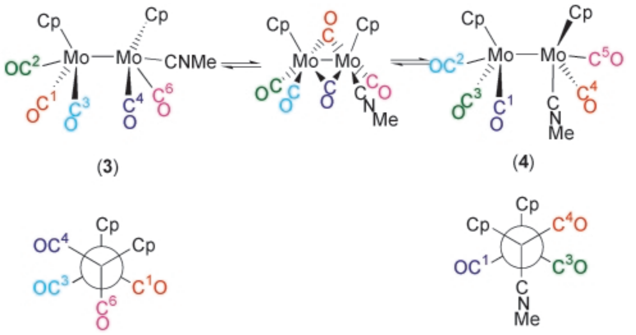
The consequences of applying the merry-go-round mechanism to the isomers of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(CNMe)]$ are summarised in Schemes 1 to 3. Examination of the Schemes 1 to 3 shows that the merry-go-round mechanism results in the exchanges (**1**) $\rightleftharpoons$ (**2**), (**3**) $\rightleftharpoons$ (**4**), and carbonyl exchange within (**5**). Schemes 4 and 5 show the consequences of rotation about the Mo–Mo bond which interconvert (**1**) $\rightleftharpoons$ (**3**) and (**2**) $\rightleftharpoons$ (**4**) $\rightleftharpoons$ (**5**). Hence fluxionality by these two mechanisms only converts (**3**) to (**1**) or (**4**). (**1**) has already been assigned, so c must be (**4**). This is consistent with previous work on $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ which has shown that rotation about the Mo–Mo bond has a higher activation energy than the merry-go-round mechanism.[3]

This assignment (**4**) using the mechanism given in Scheme 2, makes specific predictions about which pairs of carbonyls exchange. This was tested using a ^{13}C EXSY spectrum measured at −38 °C, where there is exchange between (**3**) and (**4**), see Fig. 9. As predicted by Scheme 2, there is pairwise exchange of carbonyls between (**3**) and (**4**). The pairs of ^{13}CO groups in isomers (**3**) and (**4**) which are exchanged are summarised in Table 2.

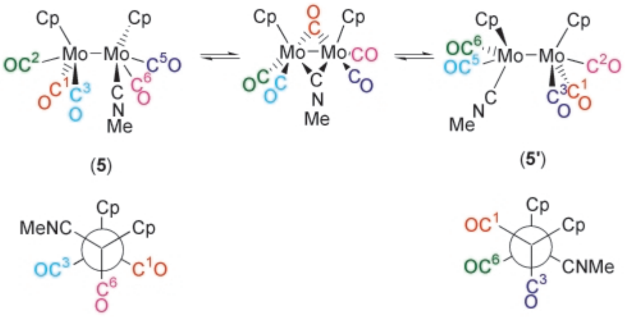
The pairwise exchange in Table 2 permits the complete assignment of the carbonyl signals for (**3**) and (**4**). This is done in conjunction with the exchange pathway in Scheme 2: (i) the signal at δ 238.97 in (**3**) which has been assigned to C^2O exchanges with the signal at δ 228.75 which must be due to C^3O in (**4**). (ii) The signal at δ 248.55 in (**4**) which has been assigned as C^5O exchanges with the signal at δ 233.15 which must be due



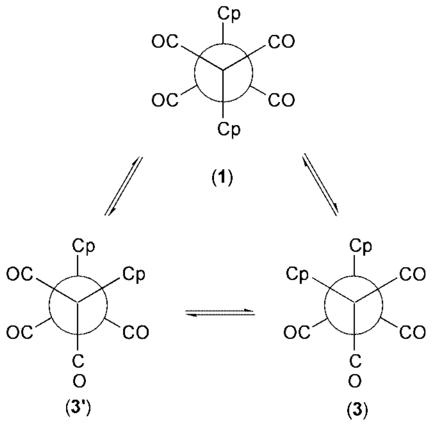
Scheme 1 The mechanism of carbonyl and methyl isocyanide exchange between the molybdenum atoms in *trans*-[(η^5-C_5H_5)$_2$$Mo_2(CO)_5$(CNMe)]. Colours are used to identify the carbonyls during the exchanges. Numbering is related to that in Fig. 1. Hence the exchange path followed by carbonyl, **1**–2(green), can be identified by looking for the green carbonyl in each structure. (Note the **1** refers to structure (**1**) and the 2(green) to C^2O(green).) Comparison with the numbering in Fig. 1 shows that the (**1**) $\rightleftharpoons$ (**2**) interconversion exchanges the carbonyls **1**–1(red), **1**–3(magenta) with **2**–2(red), **2**–4(magenta); **1**–2(green) with **2**–3(green); and **1**–4(purple), **1**–6(blue) with **2**–1(purple), **2**–5(blue). The (**2**) $\rightleftharpoons$ (**2′**) interconversion exchanges the carbonyls **2**–1(purple) with **2′**–5(purple); **2**–2(red) with **2′**–4(red) and **2**–3 is unchanged. The (**2**) $\rightleftharpoons$ (**2′**) interconversion also exchanges the cyclopentadienyl groups.



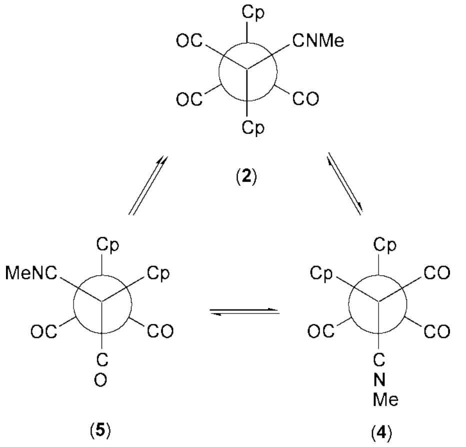
Scheme 2 The mechanism of carbonyl and methyl isocyanide exchange between the molybdenum atoms in *gauche*,*cis*-[(η^5-C_5H_5)$_2$$Mo_2(CO)_5$(CNMe)], (**3**) and (**4**). Colours are used to identify the carbonyls during the exchanges. Hence the exchange path followed by carbonyl, **3**–1(red), can be identified by looking for the red carbonyl in each structure. (Note the bold **3** refers to structure (**3**) and the 1(red) to C^1O(red).) The numbering follows that in Fig. 1. The exchange produces the pairwise carbonyl exchanges **3**–1(red) $\rightleftharpoons$ **4**–4(red); **3**–2(green) $\rightleftharpoons$ **4**–3(green); **3**–3(blue) $\rightleftharpoons$ **4**–2(blue); **3**–4(purple) $\rightleftharpoons$ **4**–1(purple); and **3**–6(magenta) $\rightleftharpoons$ **4**–5(magenta).



Scheme 3 The mechanism of carbonyl and methyl isocyanide exchange between the molybdenum atoms in *cis*-[(η^5-C_5H_5)$_2$$Mo_2(CO)_5$(CNMe)], (**5**). Colours are used to identify the carbonyls during the exchanges. Hence the exchange path followed by carbonyl, **5**–2(green), can be identified by looking for the green carbonyl in each structure. (Note the bold **5** refers to structure (**5**) and the 2(green) to C^2O(green).) Comparison with Fig. 1 shows that this produces the pairwise carbonyl exchanges **5**–2(green) $\rightleftharpoons$ **5′**–6(green)/**5**–6(magenta) $\rightleftharpoons$ **5**–2(magenta); **5**–3(blue) $\rightleftharpoons$ **5′**–5(blue)/**5**–5(purple) $\rightleftharpoons$ **5′**–3(purple); and **5**–1(red) is unaffected. The cyclopentadienyl groups also exchange.



Scheme 4 The rotation of the Mo–Mo bond interconverting *trans*,*trans*- and *gauche*,*trans*-[(η^5-C_5H_5)$_2$$Mo_2(CO)_5$(CNMe)]. Note that (**3**) and (**3′**) are enantiomers.



Scheme 5 The rotation of the Mo–Mo bond interconverting *trans*,*cis*- and *gauche*,*cis*-[(η^5-C_5H_5)$_2$$Mo_2(CO)_5$(CNMe)]. Note that all the compounds are chiral.

to C^6O in (**3**). (iii) The signal at δ 240.47 in (**4**) which has been assigned as C^4O exchanges with the signal at δ 231.09 which must be due to C^1O in (**3**). (iv) The signal at δ 238.48 in (**4**) which has been assigned to C^2O exchanges with the signal at δ 228.44 which must be due to C^3O in (**3**). (v) This leaves the exchanging pair at δ 235.21 and 233.06 which are assigned to C^4O in (**3**) and C^1O in (**4**).

These assignments are consistent with those made above from the ^{13}C COSY spectrum giving further support to the assignments of the signals to (**3**) and (**4**).

Assignment of the ^{13}CO signals due to (2) and (5)

The major isomer, a is (**1**). The intermediate isomers, b and c, are (**3**) and (**4**). Hence, the minor isomers, d and e, are (**2**)

Table 2 The correlations observed in the ^{13}C EXSY spectrum between (**3**) and (**4**) at −38 °C

(**3**)	(**4**)
233.15	248.55
231.09	240.47
228.44	238.48
235.21	233.06
238.97	228.75

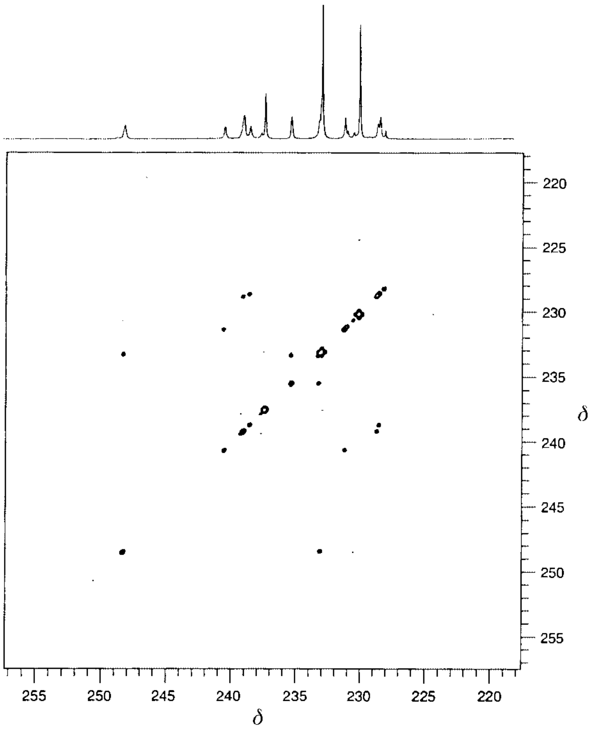


Fig. 9 The EXSY 100.62 MHz ^{13}C NMR spectrum of ^{13}CO-enriched [(η^5-$C_5H_5)_2Mo_2(CO)_5(CNMe)$] in $(CD_3)_2NCDO$ at −38 °C.

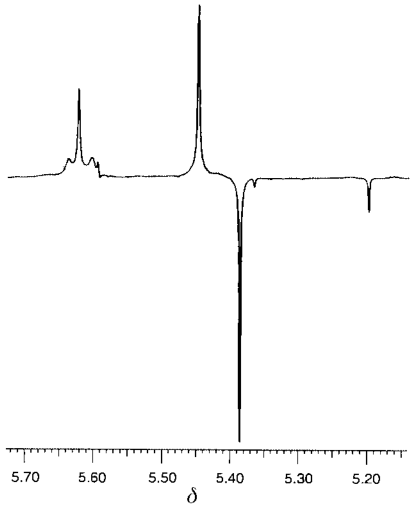


Fig. 10 The partial 400.13 MHz ^{1}H NMR spectrum of [(η^5-$C_5H_5)_2$-$Mo_2(CO)_5(CNMe)$] in $(CD_3)_2NDO$ at −55 °C. The spectrum was obtained by applying a composite (90_x–240_y–90_x) pulse, delay 1.345 s, and a 90° pulse so that the signal at δ 5.59 is approximately nulled.

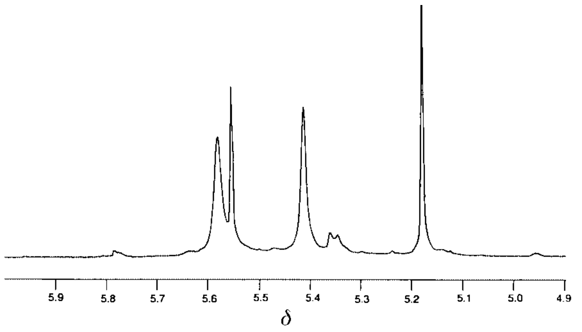


Fig. 11 The partial 400.13 MHz ^{1}H NMR spectrum of the cyclopentadienyl signals of [(η^5-$C_5H_5)_2Mo_2(CO)_5(CNMe)$] at −38 °C in d_7-DMF. The spectrum was obtained by applying a composite (90_x–240_y–90_x) pulse, delay 1.843 s, and a 90° pulse so that the signal at δ 5.36 is approximately nulled.

and (**5**). (**2**) and (**5**) differ considerably in the temperature at which fluxionality starts. One of the minor compounds shows exchange of the cyclopentadienyl groups at −55 °C resulting in considerable signal broadening, with $\Delta G^{\ddagger}_{218}$ = 11.7 ± 0.2 kcal mol^{-1}, see Fig. 10. In the second minor compound, cyclopentadienyl exchange does not occur until −38 °C, with $\Delta G^{\ddagger}_{235}$ = 12.2 ± 0.2 kcal mol^{-1}, see Fig. 11. In both cases, the exchange equilibrates pairwise the cyclopentadienyl groups and does not involve exchange with another isomer. Therefore the exchange must involve CNMe exchange between the molybdenum atoms as is shown in Schemes 1 and 3 for (**2**) and (**5**) respectively.

(**2**) can be assigned from exchange with (**1**). Magnetisation transfer measurements were performed at −22 °C between the cyclopentadienyl signal of (**1**) at δ 5.22 and the other signals and showed that the first destination was the averaged signal at δ 5.36. This signal must be due to (**2**), see Scheme 1. Hence the minor isomer which begins exchange at −55 °C is (**5**) and the one that begins exchange at −38 °C is (**2**). At −22 °C, the rate of exchange from (**2**) to (**1**) is 1.2 s^{-1}, giving $\Delta G^{\ddagger}_{251}$ = 15.1 ± 0.2 kcal mol^{-1} for (**1**)→(**2**) and $\Delta G^{\ddagger}_{251}$ = 14.5 ± 0.2 kcal mol^{-1} for (**2**)→(**1**), see Scheme 1. This can be compared with carbonyl exchange in [(η^5-$C_5H_5)_2Mo_2(CO)_6$] with $\Delta G^{\ddagger}$ = 14.9 ± 0.2 kcal mol^{-1}.[3]

The ^{13}CO signals of (**2**) and (**5**) can now be partially assigned. At −62 °C, the remaining ten weak ^{13}CO NMR signals are observed at δ 249.13, 248.50, 239.26, 239.20, 239.17, 237.58, 230.86, 230.33, 229.27, and 227.91. Further assignment of the ^{13}CO NMR signals to isomers (**2**) and (**5**) is possible when the dynamic processes are considered: (i) At −36 °C, exchange in (**5**) is relatively rapid. This results in C^{2}O, C^{3}O, C^{5}O, and C^{6}O being broadened by exchange, while C^{1}O remains sharp, see Scheme 3. As (**2**) is only just beginning to exchange, its ^{13}CO signals will still be relatively sharp. (ii) At −36 °C, six ^{13}CO signals due to (**2**) and (**5**) at δ 249.13, 237.58, 230.86, 230.33, 239.2‡ and 227.91 are still relatively sharp. These must be all five signals from (**2**) and C^{1}O from (**5**). (iii) Above −36 °C, C^{1}O, C^{2}O, C^{4}O, and C^{5}O of (**5**) are predicted to be broadened by merry-go-round exchange, while C^{3}O remains sharp, see Scheme 1. (iv) On further warming to −13 °C, the signals at δ 230.86 and 227.91 remain sharp. These must be C^{3}O from (**2**) and C^{1}O from (**5**) as neither exchange with another carbonyl during the merry-go-round mechanisms in Schemes 1 and 3. (v) At −38 °C, the EXSY spectrum in Fig. 9 shows weak correlations between the signals δ 249.13 and 230.33 and between δ 239.2 and 237.58.

These results permits a partial assignment of the carbonyl signals for (**2**) and (**5**). (i) By analogy with (**4**), the signal at δ 249.13 must arise from C^{5}O. This signal is still sharp at −36 °C, and as only C^{1}O remains sharp from (**5**), this signal must be C^{5}O from (**2**). (ii) Similarly, the signal at δ 248.50 must arise from C^{5}O from (**5**). This signal is broad at −36 °C. (iii) The EXSY spectrum in Fig. 9 shows a weak correlation

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‡ Due to the weakness and proximity of the signals, the relative assignment of this signal to those at δ 239.26, 239.20 or 239.17 at −62 °C is unknown.

Table 3 The assignment of the ^{13}CO signals for the five isomers of $[Mo_2(\eta\text{-}C_5H_5)_2(CNMe)(CO)_5]$

	Carbonyl group					
Compound	1	2	3	4	5	6
1	229.87	237.25	229.87	232.82	—	232.82
2	230.33	237.58/239.2 [a]	230.86/227.91 [b]	237.58/239.2 [a]	249.13	—
3	231.09	238.97	228.44	235.21	—	233.15
4	233.06	238.48	228.75	240.47	248.55	—
5	230.86/227.91 [b]	239.2	229.27	—	248.50	239.2
trans-$[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ [3]	227.5	235.8	227.5	227.5	235.8	227.5
cis-$[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ [3]	230.0	237.3	227.1	230.0	237.3	227.1

[a,b] The superscripts *a* and *b* pair assignments which may need interchanging.

between the signals δ 249.13 and 230.33. The signal at δ 249.13 has been assigned to C^5O in (**2**). In Scheme 1, C^5O of (**2**) exchanges with C^1O of (**2**). Hence the signal at δ 230.33 must be C^1O of (**2**). (iv) The EXSY spectrum in Fig. 9 shows a weak correlation between the signals δ 237.58 and 239.2. From Scheme 1, the exchanging pairs of carbonyls from (**2**) are C^1O, C^2O, C^4O, and C^5O. C^1O and C^5O have been assigned above at δ 230.33 and 249.13. Hence the signals at δ 237.58 and 239.2 arise from C^2O and C^4O, but due to their proximity in chemical shift a relative assignment cannot be made. (v) At −18 °C, the weak signals at δ 230.86 and 227.91 remain sharp enough to be seen and must arise from C^3O in isomer (**2**) and C^1O in isomer (**5**), but due to their proximity in chemical shift a relative assignment cannot be made. (vi) The remaining carbonyls at δ 239.2, 239.2 and 229.27 must be due to carbonyls C^2O, C^3O, and C^6O of (**5**). The assignments are made on the basis of chemical shifts, see Table 3.

Magnetisation transfer was used at −22 °C to demonstrate that (**2**) exchanges with (**4**) and (**5**) with a rate of transfer to (**4**) of 1.6 s^{-1}, corresponding to $\Delta G^{\ddagger}_{251} = 14.4 \pm 0.2$ kcal mol^{-1} and to (**5**) of 0.8 s^{-1}, corresponding to $\Delta G^{\ddagger}_{251} = 14.7 \pm 0.2$ kcal mol^{-1}. This exchange occurs by rotation about the Mo–Mo bond, see Scheme 5.

No firm evidence was found for rotation about the Mo–Mo bond in (**1**) with the magnetisation transfer going to (**3**), see Scheme 4. The problem arises because a faster pathway exists, (**1**)→(**2**)→(**4**)→(**3**). This is consistent with an activation energy in *trans*-$[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ of $\Delta G^{\ddagger} = 15.3 \pm 0.2$ kcal mol^{-1} [13] which would result in a rate of rotation in (**1**) being too slow to detect in the presence of the other exchange mechanisms.

Discussion

Activation energies

There are three types of dynamic processes observed in this NMR investigation:- inter-metal ligand exchange *via* $[(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}CNMe)(\mu\text{-}CO)(CO)_4]$, inter-metal ligand exchange *via* $[(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}CO)_2(CNMe)(CO)_3]$ and rotation about the Mo–Mo bond. It has been established previously for $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ that carbonyl exchange is more facile than rotation about the Mo–Mo bond and that carbonyl exchange is more facile for the *gauche*-isomer than for the *trans*. The same is true for $[(\eta^5\text{-}C_5H_5)_2Mo_2(CNMe)(CO)_5]$, with the additional mechanism of inter-metal isocyanide exchange being of even lower energy. Inter-metal ligand exchange in the *gauche*-isomers *via* $[(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}CNMe)(\mu\text{-}CO)(CO)_4]$ is the lowest energy process, producing (**5**) $\rightleftharpoons$ (**5′**) exchange with $\Delta G^{\ddagger}_{218} = 11.7 \pm 0.2$ kcal mol^{-1}. Similarly for the *trans*-isomers, inter-metal ligand exchange *via* $[(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}CNMe)(\mu\text{-}CO)(CO)_4]$ is the lowest energy process, producing (**2**) $\rightleftharpoons$ (**2′**) exchange with $\Delta G^{\ddagger}_{235} = 12.2 \pm 0.2$ kcal mol^{-1}.

The other two *gauche*-isomers, (**3**) and (**4**) undergo exchange *via* $[(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}CO)_2(CNMe)(CO)_3]$ with $\Delta G^{\ddagger}_{223} = 12.4 \pm 0.2$ for (**4**)→(**3**) and 12.6 ± 0.2 kcal mol^{-1} for (**3**)→(**4**). The *trans*-isomers, (**1**) and (**2**), undergo exchange *via* $[(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}CO)_2(CNMe)(CO)_3]$ with $\Delta G^{\ddagger}_{251} = 15.1 \pm 0.2$ kcal mol^{-1} for (**1**)→(**2**) and $\Delta G^{\ddagger}_{251} = 14.5 \pm 0.2$ kcal mol^{-1} for (**2**)→(**1**).

These observations are consistent with the previous observation that inter-metal ligand exchange is easier for the *gauche*- than for the *trans*-isomer. Also the movement of the isocyanide ligand into the bridge is easier than for carbonyl. It has been found previously that substitution of carbonyl by isocyanide promotes bridge formation. In $[Mn_2(CO)_{10}]$, $\Delta G^{\ddagger} > 20$ kcal mol^{-1}.[10] While the barrier in $[Mn_2(CO)_8(CNBu^t)_2]$[11] is $\Delta G^{\ddagger}_{345} = 25.5$ kcal mol^{-1} and in $[Mn_2(CO)_7(CNMe)_3]$, $\Delta G^{\ddagger}_{298} = 19.1$ kcal mol^{-1}.[12] The corollary is that an isocyanide ligand stabilises the bridged isomer. An extreme example is the stabilisation of the bridged isomer in $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu\text{-}CNCF_3)_2(CO)_4]$.[8] More commonly, it increases the activation energy for bridge-opening. This is what has been found in the $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_{4-n}(CNR)_n]$ system. Hence in *trans*-$[(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_2(CO)_2]$, the activation energy for bridge-opening is <6.5 kcal mol^{-1},[13] while in *trans*-$[(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CNMe)(\mu\text{-}CO)(CO)_2]$ the activation energy has increased to 9.1 kcal mol^{-1}.[14] An extreme example is the introduction of a $CNCF_3$ group into $[Fe_3(CO)_{12}]$ which increases the activation energy for carbonyl scrambling from <6 kcal mol^{-1} to *ca.* 12.5 kcal mol^{-1}.[15,16] When there is complete substitution of carbonyl by isocyanide in $[(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CNMe)_2(CNMe)_2]$, no fluxionality is observed.[17]

Two barriers for rotation about the Mo–Mo bond were observed in this work. Rotation about the Mo–Mo bond in (**2**) was detected with $\Delta G^{\ddagger}_{251} = 14.4 \pm 0.2$ kcal mol^{-1} to (**4**) and $\Delta G^{\ddagger}_{251} = 14.7 \pm 0.2$ kcal mol^{-1} to (**5**). The higher barrier for (**2**) to (**5**) is consistent with this mechanism requiring the CNMe to pass the cyclopentadienyl group on the unsubstituted molybdenum. The barrier to rotation about the Mo–Mo bond to interconvert (**1**) and (**3**) was measured and is greater than 15 kcal mol^{-1}.

Variable temperature ^{1}H NMR spectra

Examination of the variable temperature ^{1}H NMR spectra in Fig. 7 show a number of features which can be explained in the light of these investigations. For (**5**), the cyclopentadienyl signals at δ 5.65 and 5.68 at −65 °C exchange readily *via* the mechanism in Scheme 3 and produce a singlet which is clearly resolved between −30 and −6 °C. The facile exchange of (**3**) and (**4**) results in pairwise exchange of cyclopentadienyl and methyl isocyanide groups. The two singlets at δ 5.63 coalesce to form one signal at −57 °C and remain reasonably sharp until bond rotation becomes significant above 0 °C. The other pairs of cyclopentadienyl groups at δ 5.67 and 5.48 and methyl groups at δ 3.64 and 3.84 have a larger separation and a broad averaged signal is observed for both pairs of signals until above 0 °C.

^{13}C Chemical shifts

The assignments of isomers and signals present a consistent picture. Comparison of the ^{13}C chemical shifts of the carbonyls in Table 3 shows that carbonyls in equivalent positions for the five isomers fall in similar positions in the spectrum. Hence for the $(\eta^5\text{-}C_5H_5)Mo(CO)_3$ moiety, C^1O and C^3O fall in a narrow band around δ 230. In the cases of *gauche*-isomers C^1O, which is in a position to move into a bridging position is at higher frequency than C^3O. This is consistent with the observation of similar behaviour in $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ and could be due to this carbonyl moving slightly towards a bridging position with the consequent high frequency shift.[3] The substitution of a carbonyl by MeNC in the $(\eta^5\text{-}C_5H_5)Mo(CNMe)(CO)_2$ moiety causes all the carbonyls to move to high frequency. The carbonyls in the C^5O position move to a characteristic position at approximately δ 249.

Conclusions

All five isomers of $[Mo_2(\eta\text{-}C_5H_5)_2(CNMe)(CO)_5]$ have been identified and the activation energies for their interconversion determined. The merry-go-round mechanism is of lower energy when it involves a (μ-CNMe)(μ-CO) intermediate than when it involves a $(\mu\text{-}CO)_2$ intermediate. The merry-go-round mechanism is more facile in the *gauche*- than the *trans*-isomers. Rotation about the Mo–Mo bond is the highest energy dynamic process observed.

Acknowledgements

We wish to thank the EPSRC and the University of Sheffield for financial support.

References

1 R. D. Adams, M. D. Brice and F. A. Cotton, *J. Am. Chem. Soc.*, 1973, **95**, 6594.

2 W. E. Lindsell and P. J. Tomb, *J. Organomet. Chem.*, 1989, **378**, 245.

3 X. Chen and B. E. Mann, *Organometallics*, 1996, **15**, 3703.

4 M. Grassi, B. E. Mann, B. T. Pickup and C. M. Spencer, *J. Magn. Reson.*, 1986, **69**, 92.

5 M. H. Chisholm, F. A. Cotton, M. W. Extine and L. A. Rankel, *J. Am. Chem. Soc.*, 1978, **100**, 807.

6 This is considerably below the freezing point of pure DMF and the lowering of the freezing point is attributed to freezing point depression and possibly also to supercooling.

7 Note that the ^{13}C chemical shifts are temperature dependent. The chemical shifts at −62 °C are used in the text.

8 D. Lentz, I. Brudgam and H. Hartl, *J. Organomet. Chem.*, 1986, **299**, C38.

9 Care is always required in using ^{13}C intensities. ^{13}CO groups do not have significant NOEs. The relaxation at 9.4 T is predominantly chemical shift anisotropy (csa). Terminal carbonyls have similar csa and as the molecules are all of the same molecular mass, correlation times will be similar. The relative intensities of species in the ^{13}C NMR spectra match those in the ^{1}H NMR spectra within experimental error and the relative intensities of assigned signals for a given isomer match the theoretical ones within experimental error.

10 S. P. Schmidt, F. Basolo, C. M. Jensen and W. C. Trogler, *J. Am. Chem. Soc.*, 1986, **108**, 1895.

11 D. J. Robinson, G. W. Harris, J. C. A. Boeyens and N. J. Coville, *J. Chem. Soc., Chem. Commun.*, 1984, 1307.

12 R. D. Adams and D. F. Chodosh, *J. Organomet. Chem.*, 1975, **87**, C48.

13 J. G. Bullitt, F. A. Cotton and T. J. Marks, *J. Am. Chem. Soc.*, 1970, **92**, 3166; *Inorg. Chem.*, 1972, **11**, 671; O. A. Gansow, A. R. Burke and W. D. Vernon, *J. Am. Chem. Soc.*, 1972, **94**, 2550; *J. Am. Chem. Soc.*, 1976, **98**, 5823; L. J. Farrugia and L. Mustoo, *Organometallics*, 1992, **11**, 2941.

14 M. A. Guillevic, E. L. Hancock and B. E. Mann, *J. Chem. Soc., Dalton Trans.*, 1992, 1729.

15 F. A. Cotton, *Inorg. Chem.*, 1966, **5**, 1083.

16 D. Lentz and R. Marschall, *Organometallics*, 1991, **10**, 1487.

17 G. McNally, P. T. Murray and A. R. Manning, *J. Organomet. Chem.*, 1983, **243**, C87.