Organometallics **1996,** *15,* 3703−3707 3703

Observation of Inter-Metal Carbonyl Exchange in $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ and $[(\eta^5\text{-}C_5H_5)_2MoW(CO)_6]$

Xuetai Chen and Brian E. Mann*,†

Department of Chemistry, The University of Sheffield, Sheffield S3 7HF, U.K.

Received April 1, 1996⊗

Inter-metal carbonyl exchange in $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ and $[(\eta^5\text{-}C_5H_5)_2MoW(CO)_6]$, *via* $[(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}CO)_2(CO)_4]$ and $[(\eta^5\text{-}C_5H_5)_2MoW(\mu\text{-}CO)_2(CO)_4]$, has been observed by ^{13}C NMR spectroscopy. The $\Delta G^{\ddagger}$ for the exchange is 13.9 ± 0.2 kcal mol^{-1} for the *gauche* isomer of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ and 14.9 ± 0.2 kcal mol^{-1} for the *trans* isomer.

Inter-metal carbonyl exchange is well established for derivatives of group 8 and 9 metals but is relatively uncommon for derivatives of group 6 and 7 metals.[1] For example, in $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$[2] and $[Fe_3(CO)_{12}]$,[3] carbonyl exchange is extremely facile, with activation energies well below 10 kcal mol^{-1}. However, it has been shown for $[Mn_2(CO)_{10}]$ that even at 130 °C there is no evidence of carbonyl exchange, setting a lower limit of 20 kcal mol^{-1} for the activation energy of inter-metal carbonyl exchange.[4] Inter-metal carbonyl exchange has been demonstrated to occur in $[MnRe(CO)_{10}]$ with $\Delta G^{\ddagger}_{348} = 27$ kcal mol^{-1}.[5] Substitution can reduce the activation energy for inter-metal carbonyl exchange with $\Delta G^{\ddagger}_{345}$ falling to 25.5 kcal mol^{-1} in $[Mn_2(CO)_8(CNBu^t)_2]$,[6] $\Delta G^{\ddagger}_{298} = 19.1$ kcal mol^{-1} in $[Mn_2(CO)_7(CNMe)_3]$,[7] and $\Delta G^{\ddagger}_{297} = 16.3$ kcal mol^{-1} for isomerization of a,e-$[Mn_2(CO)_8(PBu^n{}_3)_2]$ to a,a-$[Mn_2(CO)_8(PBu^n{}_3)_2]$.[8]

Moving to group 6, it might then be expected that inter-metal carbonyl exchange should be even more difficult. However, in 1973, Adams, Brice, and Cotton demonstrated the exchange of MeNC between the molybdenum atoms in $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(CNMe)]$ and, by implication, a corresponding CO transfer.[9] They determined a free energy of activation of 13.0 ± 0.5 kcal mol^{-1}, but the exact nature of this dynamic process is not clear.

One of the clearest demonstrations of carbonyl exchange between molybdenum atoms occurs with $[(\eta^5\text{-}C_5R_5)(OC)_3MoMo(\eta^7\text{-}C_7H_7)(CO)_2]$, R = H and Me, where three separate ^{13}CO signals are observed in the intensity ratio 1:2:2 at −80 °C and average to a broad singlet at 40 °C.[10] Inter-metal carbonyl exchange is also involved in the fluxionality of $[(\eta^5\text{-}C_5H_5)\overline{W(CO)_2(\mu\text{-}PPH_2)Cr}(CO)_5]$[11] and **1**.[12] In contrast, $[(\eta^5{:}\eta^{5\prime}\text{-azulene})Mo_2(CO)_6]$, **2**, and its derivatives do not show inter-metal carbonyl exchange, but localized scrambling is facile.[13]

In addition to ligand exchange, it has been established that $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ undergoes restricted rotation about the Mo−Mo bond.[14] In most solvents, the *trans* isomer is dominant. In 1989, Lindsell and Tomb demonstrated that $[(\eta^5\text{-}C_5H_5)_2W_2(CO)_6]$, in d_6-DMSO/THF, consists of a 55:45 mixture of *gauche* and *trans* isomers, **3** and **4**, M = W, which undergo exchange by rotation of the W−W bond, with *gauche*−*trans* interconversion being facile, but *gauche*−*gauche* being too slow to detect; see Scheme 1.[15] This is completely analogous to the observations by Farrugia on $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$[2] and our observations on $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_{4-n}(CNMe)_n]$, $n = 1$ and 2.[16] Lindsell and Tomb observed a weak EXSY peak between the carbonyl *trans* to the W−W bond and one of the *cis*-carbonyls in the *gauche* isomer and attributed the peak to a $^{13}C-^{13}C$ nOe. The work of Lindsell and Tomb, which showed that, in DMSO/THF, $[(\eta^5\text{-}C_5H_5)_2W_2(CO)_6]$ exists with the *gauche* form in a slight excess,[15] raised the possibility of using DMF as a low-temperature solvent for $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$, where both the *gauche* and *trans* forms would be present in substantial quantities.

Experimental Section

$[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$, enriched by approximately 35% in ^{13}CO, was synthesized by exposing a stirred solution of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4]$ in CH_2Cl_2 to ^{13}CO for 30 min, when the absorption of gas ceased.[17] The resulting ^{13}CO-enriched $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ was purified by chromatography on alumina using CH_2Cl_2 as the eluent.

The NMR spectra were recorded using a Bruker WH400 NMR spectrometer, and the temperatures were measured by

---

† E-mail: b.mann@sheffield.ac.uk.

⊗ Abstract published in *Advance ACS Abstracts*, August 1, 1996.

(1) Mann, B. E. *Spectroscopic properties of inorganic and organometallic compounds*; Specialist Periodical Report; Royal Society of Chemistry: London, 1971−1995; Vols. 5−28, Chapter 1, Section 3. Band, E.; Muetterties, E. L. *Chem. Rev.* **1979**, *78*, 639.

(2) Farrugia L. J.; Mustoo, L. *Organometallics* **1992**, *11*, 2941.

(3) Adams, H.; Bailey, N. A.; Bentley, G. W.; Mann, B. E. *J. Chem. Soc., Dalton Trans.* **1989**, 1831.

(4) Aime, S.; Milone, L.; Osella, D.; Hawkes, G. E.; Randall, E. W. *J. Organomet. Chem.* **1979**, *178*, 171.

(5) Schmidt, S. P.; Basolo, F.; Jensen, C. M.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 1894.

(6) Robinson, D. J.; Harris, G. W.; Boeyens, J. C. A.; Coville, N. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1307.

(7) Adams R. D.; Chodosh, D. F. *J. Organomet. Chem.* **1975**, *87*, C48.

(8) Zhang, H. T.; Brown, T. L. *J. Am. Chem. Soc.* **1993**, *115*, 107.

(9) Adams, R. D.; Brice, M.; Cotton, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 6594.

(10) Ricalton, A.; Whiteley, M. W. *J. Organomet. Chem.* **1989**, *361*, 101.

(11) Shyu, S.-G.; Hsu, J.-Y.; Wen, Y.-S. *J. Organomet. Chem.* **1993**, *453*, 97.

(12) Drage, J. S.; Vollhardt, K. P. C. *Organometallics* **1985**, *4*, 191; **1986**, *5*, 280.

(13) Cotton, F. A.; Hunter, D. L.; Lahuerta, P. *J. Organomet. Chem.* **1973**, *87*, C42. Cotton, F. A.; Lahuerta, P.; Stults, B. R. *Inorg. Chem.* **1976**, *15*, 1866. Cotton, F. A.; Hanson, B. E. *Inorg. Chem.* **1976**, *15*, 2806.

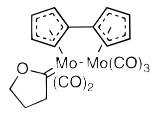
(14) Adams, R. D.; Cotton, F. A. *Inorg. Chim. Acta* **1973**, *7*, 153.

(15) Lindsell, W. E.; Tomb, P. J. *J. Organomet. Chem.*, **1989**, *378*, 245.

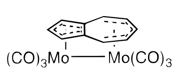
(16) Guillevic, M. A.; Hancox, E. L.; Mann, B. E. *J. Chem. Soc., Dalton Trans.* **1992**, 1729.

(17) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 807.

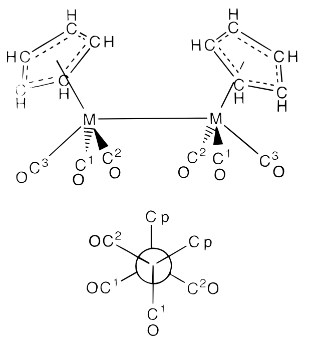
S0276-7333(96)00247-6 CCC: $12.00



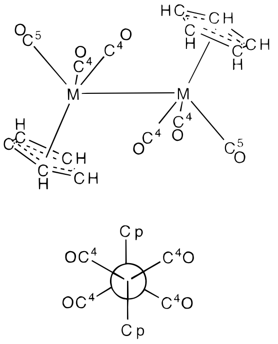
(1)



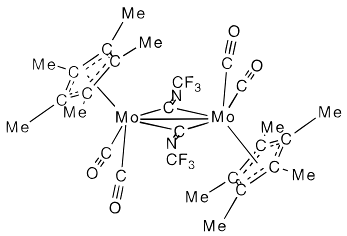
(2)



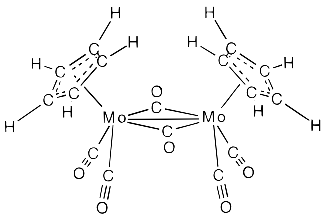
3



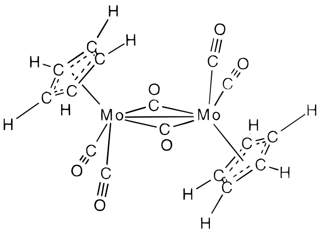
4



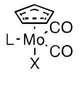
5



6

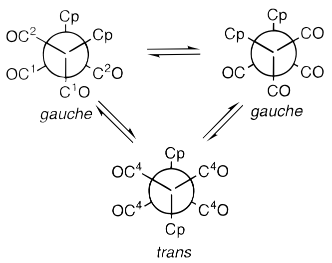


7



(8)

Scheme 1. Rotation of the M−M Bond in $[(\eta^5\text{-}C_5H_5)_2M_2(CO)_6]$, M = Mo and W, Viewed along the M−M Bond with the Carbonyls *trans* to the M−M Bond Omitted for Clarity



replacing the sample with an NMR tube containing CH_2Cl_2 and a thermocouple connected to a Comark electronic thermometer. Carbon-13 chemical shifts were referenced to the central line of the low frequency CD_3 signal of $(CD_3)_2NCDO$ at δ 30.1. Selective π pulses were generated using the DANTE pulse sequence.[18] Magnetization transfer measurements were performed and the data analyzed as previously described.[19]

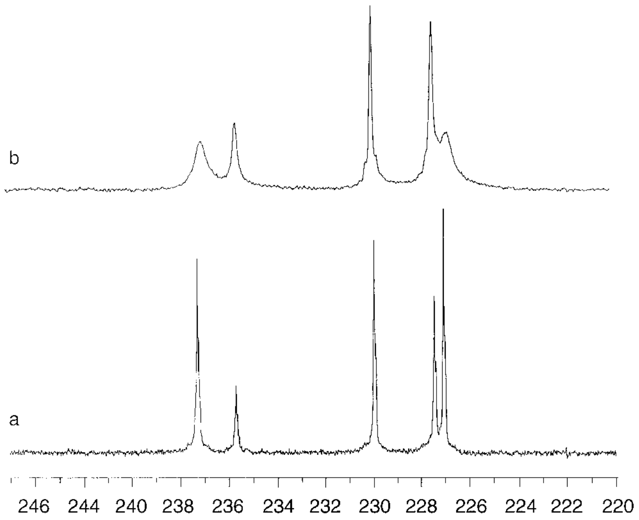


Figure 1. The 100.62 MHz ^{13}C NMR spectrum of the carbonyl region of *ca.* 35% ^{13}CO-enriched $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ in DMF/d_7-DMF, 4:1, (a) at −40 °C and (b) at 10 °C.

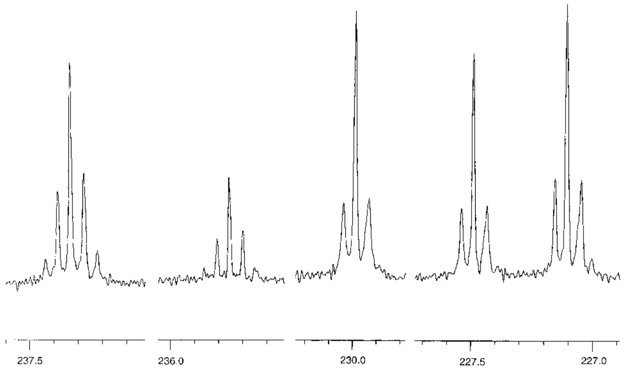


Figure 2. The 100.62 MHz ^{13}C NMR spectrum of the carbonyl region of *ca.* 35% ^{13}CO-enriched $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ in DMF/d_7-DMF, 4:1, at −40 °C. The spectrum has been resolution enhanced using a Gaussian weighting function. Each tick mark represents 0.1 ppm.

Results and Discussion

The ^{13}C NMR spectrum of the carbonyl region of ^{13}C-enriched $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ in DMF/d_7-DMF, 4:1, at −40 °C, is shown in Figure 1a. It has previously been established that $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ exists in solution as a mixture of *gauche* and *trans* isomers.[14] In the *gauche* isomer, **3**, there are three carbonyl environments, in the intensity ratio 1:1:1. This is most clearly observed in the Newman projection. The two carbonyls *cis* to the Mo−Mo bond are inequivalent, with C^1O having a torsion angle of 180° with respect to the cyclopentadienyl on the second molybdenum, while the corresponding angle for C^2O is 60°. The third carbonyl C^3O is *trans* to the Mo−Mo bond. In the *trans* isomer, **4**, M = Mo, there are two carbonyl environments, *trans* and *cis* to the Mo−Mo bond in the intensity ratio 1:2.

In DMF/d_7-DMF, 4:1, at −40 °C, the *gauche* and *trans* isomers are present in an approximate concentration ratio of 1.6:1; see Figure 1. There is fine structure due to $^{13}C-^{13}C$ coupling; see Figure 2. The signals due to C^3 and C^5 show overlapping singlets, doublets, and

---

[18] Morris, G. A.; Freeman, R. *J. Magn. Reson.* **1978**, *29*, 433.

[19] Grassi, M.; Mann, B. E.; Pickup, B. T.; Spencer, C. M. *J. Magn. Reson.* **1986**, *69*, 92.

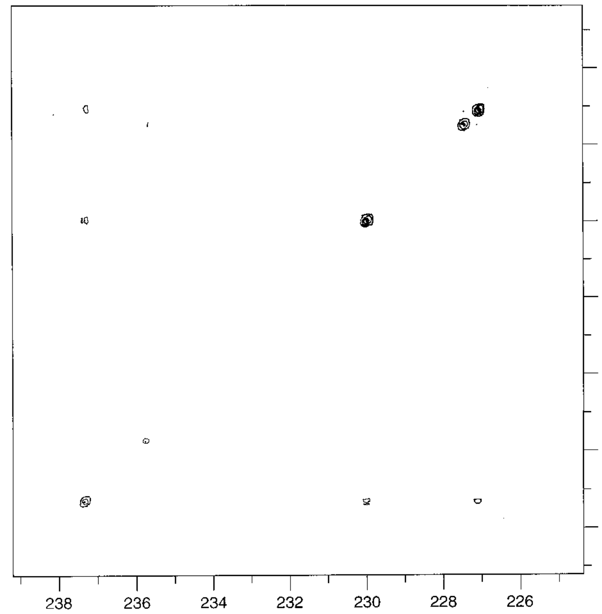


Figure 3. The 100.62 MHz COSY ^{13}C NMR spectrum of the carbonyl region of *ca.* 35% ^{13}CO-enriched $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ in DMF/d_7-DMF, 4:1, at −40 °C.

triplets due to coupling to none, one, and two ^{13}CO groups. C^1, C^2, and C^4 only show overlapping singlets and doublets implying that $^2J(C^1,C^2)$ is negligible. This was confirmed in the COSY-90 spectrum (see Figure 3), which showed coupling between the carbonyl at δ 237.3 and those at 230.0, and 227.1 and between the carbonyls at δ 235.8 and 227.5.[20] This permits the assignment of the carbonyls at δ 237.3, 230.0, and 227.1 being due to the *gauche* isomer and those at δ 235.8 and 227.5 to the *trans* isomer.[21] On the basis of intensity, the signal of the *trans* isomer at δ 235.8 is assigned to C^5O and at 227.5 to C^4O. By analogy, the signal of the *gauche* isomer at δ 237.3 is assigned to C^3O, and those at δ 227.1 and 230.0 are assigned to C^1O and C^2O. It is noteworthy that, in the *trans* isomer, coupling is observed between C^4O and C^5O, and in the *gauche* isomer, coupling is observed between C^1O and C^3O and between C^2O and C^3O but not between C^1O and C^2O. Each of the observed coupling constants is 10.5 Hz. This is consistent with observations of $^2J(^{31}P^{13}CO)$ in $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PR_3)X]$, R = alkyl or aryl group, where $^2J(^{31}P^{13}CO)_{cis}$ is *ca.* 25 Hz, while $^2J(^{31}P^{13}CO)_{trans}$ is *ca.* 5 Hz.[22,23] In this group of compounds, coupling to $^{31}PR_3$ is anticipated to be approximately double that to ^{13}CO. For example, in $[W(CO)_5(PR_3)]$, $^1J(^{183}W^{13}C)$ is *ca.* 125 Hz,[24] while $^1J(^{183}W^{31}P)$ is *ca.* 250 Hz.[25]

At 10 °C, all the carbonyl signals are broadened by exchange, but the signals of the *gauche* isomer at δ 237.3 and 227.1 are broadened the most, and the signal at δ 230.0, also due to the *gauche* isomer, is broadened the least; see Figure 1b. The exchange between the carbonyls at δ 237.3 and 227.1 was investigated quantitatively by applying a selective π DANTE pulse[18] at δ 237.3 and monitoring the magnetization transfer to the signal at δ 227.1. The magnetization transferred exclusively[26] to this site at −19.5 ± 2 °C. The data were fitted as previously described to yield excellent agreement between the experimental and calculated changes in signal height; see Figure 4. The rate of exchange was determined as 5.5 ± 0.1 s^{-1}, corresponding to a $\Delta G^\ddagger$ = 13.9 ± 0.2 kcal mol^{-1}.

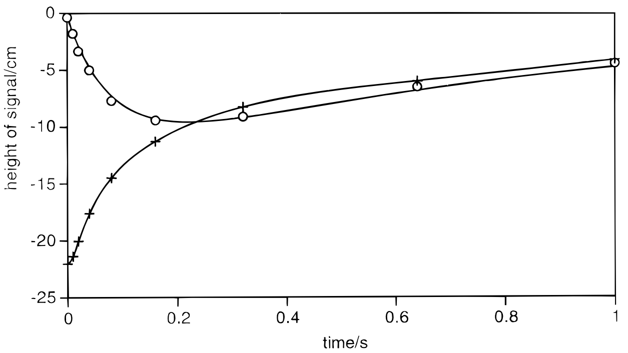


Figure 4. Changes in height of the ^{13}C NMR signals of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ at δ 237.3 and 227.1 at −19.5 ± 2 °C as a function of time after applying a selective DANTE π-pulse at δ 237.3: (+) signal at δ 237.3; (o) signal at δ 227.1.

The mechanism of this exchange has been anticipated by Cotton *et al.*, in the proposed mechanism of CNMe exchange in $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(CNMe)]$ and CO exchange in $[(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_2(CO)_2]$.[27] They postulated intermediates, $[(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}CO)_2(CO)_3(CNMe)]$ and $[(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}CO)(\mu\text{-}CNMe)(CO)_4]$. The proposed bridged structure was subsequently confirmed by Lentz *et al.*, who determined the X-ray structure of $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu\text{-}CNCF_3)_2(CO)_4]$, **5**.[28] Note that in **5** all the terminal carbonyls are equivalent.

For the *gauche*-isomer, **3**, M = Mo, it is probable that the mutually *trans*-carbonyls C^2O in Scheme 1 form a bridge, analogous to the mechanism reported by Cotton for $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$.[9] For the *gauche* isomer, the bridged intermediate, **6**, simply exchanges C^2O between equivalent positions on the two molybdenum atoms, while C^1O and C^3O move into equivalent positions and exchange. This requires C^1O to be assigned to the signal at δ 227.1 and C^2O to δ 230.0. The movement of C^2O into a bridging position is possibly anticipated in the X-ray structure of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$,[29] where the nonbonded $Mo\cdots C^2$ distance is 3.178 Å, which can be compared with the $Mo\cdots C^1$ distance of 3.247 Å, although the difference in distances is only of the order of 2σ or 3σ.

At 1 ± 2 °C, two further dynamic processes become significant, namely the well-documented rotation about the Mo−Mo bond which interconverts the *gauche* and *trans* isomers, see Scheme 1, and carbonyl exchange between the molybdenum atoms in the *trans* isomer.

---

[20] Referenced to the low-frequency $^{13}CH_3$ of the $(CH_3)_2NCHO$ at δ 30.1.

[21] In the *gauche* isomer, the two carbonyls on each molybdenum *cis* to the Mo−Mo bond are inequivalent. In the Newman projection in Scheme 1, it can be seen that one is between two CO groups on the other molybdenum and the other CO group is between a cyclopentadienyl and CO ligand.

[22] Beach, D. L.; Barnett, K. W. *J. Organomet. Chem.* **1975**, *97*, C27.

[23] Todd, L. J.; Wilkinson, J. R.; Hickey, J. P.; Beach, D. L.; Barnett, K. W. *J. Organomet. Chem.* **1978**, *154*, 151.

[24] Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London, 1981.

[25] Verkade, J. G. *Coord. Chem. Rev.* **1972**, *9*, 1.

[26] No magnetization transfer to any other site was detected. This is consistent with other exchange mechanisms being at least 1 order of magnitude slower.

[27] Adams, R. D.; Cotton, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 6589.

[28] Lentz, D.; Brudgam, I.; Hartl, H. *J. Organomet. Chem.* **1986**, *299*, C38.

[29] Gould, R. O.; Barker, J.; Kilner, M. *Acta Crystallogr. C, Cryst. Struct. Commun.* **1988**, *44*, 461.

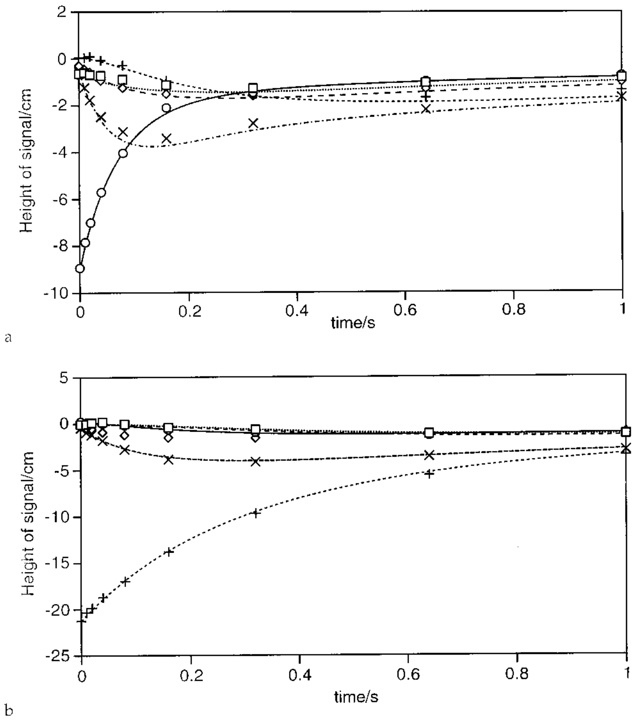


Figure 5. Changes in height of the ^{13}C NMR signals of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ at 1 ± 2 °C as a function of time after applying a selective DANTE π-pulse at (a) δ 235.8 and (b) δ 230.0. The symbols used for the various signals are as follows: (□) signal at δ 237.3; (○) signal at δ 235.8; (+) signal at δ 230.0 (x) signal at δ 227.5; (◇) signal at δ 227.1.

This was investigated quantitatively using magnetization transfer in two interleafed experiments, first by applying a selective π DANTE pulse[18] to the signal at δ 235.8, C^5O, and then, in a separate set of measurements, to the signal at δ 230.0, C^2O. The magnetization transfer was monitored as a function of time between the selective π pulse and the general $F(\pi,2)$ pulse and analyzed as previously described.[19] The data were fitted[19] to yield rates of 4.1 s^{-1} for *trans* → *gauche* isomerization, 2.6 s^{-1} for *gauche* → *trans* isomerization, and 7.4 s^{-1} for $C^5O \rightarrow C^4O$ exchange, corresponding to $\Delta G^{\ddagger}_{278} = 15.3 \pm 0.2$, 15.5 ± 0.2, and 14.9 ± 0.2 kcal mol^{-1}, respectively. The fit is shown in Figure 5. Examination of Figure 5a shows that when C^5O is inverted, the dominant magnetization transfer is to C^4O, which is due to exchange *via* the bridged intermediate **7**. There is also slower exchange to the *cis* isomer due to rotation about the Mo−Mo bond. The barrier is 1 kcal mol^{-1} higher than for the *gauche* isomer, presumably reflecting the fact that all four carbonyls C^4O are equivalent, while, in the *gauche* isomer, only the two carbonyls, C^2O, are suitable for bridging. Examination of Figure 5b shows that when C^2O is inverted, the dominant magnetization transfer is to C^4O, which is due to rotation about the Mo−Mo bond. There was no exchange detected corresponding to rotation interconverting C^1O and C^2O. Hence *gauche*−*gauche* interconversion is a slower process, presumably due to the difficulty of the two cyclopentadienyl groups passing each other. The same conclusion has been reached previously for $[(\eta^5\text{-}C_5H_5)_2W_2(CO)_6]$[15] and $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$.[2,16] It should be noted that the lowest energy carbonyl exchange process *via* the $[(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}CO)_2(CO)_4]$ intermediate, **6**, for the *gauche* isomer does involve the cyclopentadienyl groups passing each other. The $\Delta G^{\ddagger}$ value for rotation is comparable with that previously reported by Adams and Cotton.[14] They gave a rate which yields $\Delta G^{\ddagger}_{303} = 15.4$ kcal mol^{-1}, but they did not specify if the rate given referred to the *trans* → *gauche* or *gauche* → *trans* isomerization.

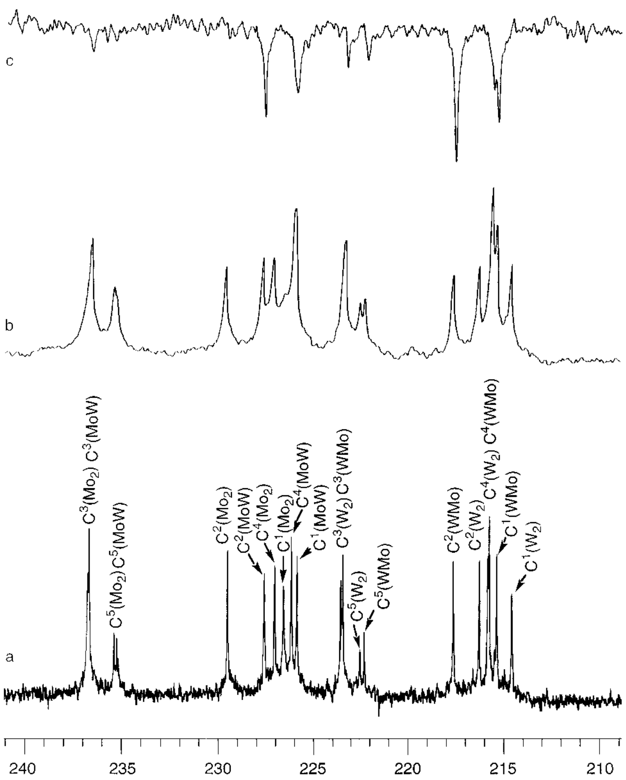


Figure 6. The 100.62 MHz ^{13}C NMR spectrum of the carbonyl region of *ca.* 18% ^{13}CO-enriched $[(\eta^5\text{-}C_5H_5)_2M_2(CO)_6]$, $M_2 = Mo_2$, MoW, and W_2, in DMF/d_7-DMF, 4:1. Part a: At −20 °C. The ^{13}CO signals are tentatively assigned. M_2 is given in parentheses. In the case of the mixed complex, the first symbol refers to the atom attached to the ^{13}CO. Part b: At 10 °C. Part c: Difference spectrum at 10 °C with presaturation at δ 217.8, using a 3 s DANTE pulse sequence.

The exchange of C^1O and C^3O and of C^4O and C^5O could arise from a rearrangement centered on one molybdenum atom. This is unlikely, as the barrier for this process is normally somewhat higher and would be expected to exchange C^1O, C^2O, and C^3O. Faller and Anderson have shown that $[(\eta^5\text{-}C_5H_5)Mo(CO)_2LX]$ undergo *cis* ↔ *cis* and *cis* ↔ *trans* isomerization but with a higher activation energy unless R = H.[30] However, the localized carbonyl scrambling in $[(\eta^5{:}\eta^{5'}\text{-azulene})Mo_2(CO)_6]$, **2**, and its derivatives is facile.[13] It cannot therefore be assumed that the observed carbonyl exchange in $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ involves inter-metal exchange. The mechanism usually proposed for ligand exchange in $[(\eta^5\text{-}C_5H_5)Mo(CO)_2LX]$ complexes is *via* a 3:3:1 structure, **8**. In the case of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$, the second molybdenum could occupy the equatorial, L, or axial, R, position. The pairwise exchange of carbonyls in the low-energy process of *gauche*-$[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ could be explained either by the second molybdenum atom occupying an equatorial position, where there are two equivalent equatorial carbonyls, and one axial carbonyl or the second molybdenum occupying the

---

[30] Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852.

axial position with restricted rotation of the Mo−Mo bond in **8** allowing only two carbonyls to exchange.

Inter-metal carbonyl exchange was unambiguously demonstrated by synthesizing $[(\eta^5\text{-}C_5H_5)_2MoW(CO)_6]$, by taking a solution of ^{13}CO-enriched $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ and an equimolar quantity of $[(\eta^5\text{-}C_5H_5)_2W_2(CO)_6]$ in benzene under N_2 and exposing to sunlight for 15 min. The solution was evaporated and the mixture dissolved in DMF/d_7-DMF, 4:1. The 100.62 MHz ^{13}C NMR spectrum at −20 °C of the carbonyl region is shown in Figure 6a. By comparison with the chemical shifts of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$ and $[(\eta^5\text{-}C_5H_5)_2W_2(CO)_6]$,[15] the signals due to ^{13}CO attached to molybdenum come from δ 226−238 and to tungsten from δ 214−224. In each case the carbonyls *cis* to the metal−metal bond occur in the low-frequency group and the carbonyls *trans* to the metal−metal bond in the high-frequency group. The DANTE pulse sequence was used at 10 °C to provide a 3 s presaturation pulse of the signal at δ 217.4, which is probably $C^2O(WMo)$[31] in $[(\eta^5\text{-}C_5H_5)_2MoW(CO)_6]$. The spectrum at 10 °C without presaturation is shown in Figure 6b. The spectrum in Figure 6c shows the difference spectrum between this one and one recorded with presaturation. In addition to magnetization transfer to carbonyls attached to tungsten at δ 215.2, 215.5, 222.0, and 223.2, magnetization transfer also occurs to the carbonyls attached to molybdenum at δ 225.7/225.9, 227.4, and possibly at 236.4. Without further assignment, this provides unambiguous evidence for carbonyl exchange between tungsten and molybdenum in $[(\eta^5\text{-}C_5H_5)_2MoW(CO)_6]$. Tentative assignments of the signals due to $[(\eta^5\text{-}C_5H_5)_2MoW(CO)_6]$ are given in Figure 6. Irradiation at WC^2O, at δ 217.4, in $[(\eta^5\text{-}C_5H_5)_2MoW(CO)_6]$ is transferred into $C^4O(WMo)$ and $C^1O(WMo)$ at δ 215.2 and 215.5 by rotation about the Mo−W bond. It is transferred to $C^2O(MoW)$ at δ 223.2 by inter-metal exchange. There is transfer to $C^4O(MoW)$ by a combination of rotation and inter-metal exchange.

Examination of the assignments in Figure 6a shows that the saturation transfer of Figure 6c involves all the carbonyls of $[(\eta^5\text{-}C_5H_5)_2MoW(CO)_6]$, apart from $C^5(MoW)$.[32,33] The failure to observe saturation transfer from $C^2(WMo)$ to $C^5(MoW)$ is not surprising as a minimum of three steps are required for the transfer.[34] In view of the exchange demonstrated here for $[(\eta^5\text{-}C_5H_5)_2M_2(CO)_6]$, $M_2 = Mo_2$ and MoW, it is probable that the EXSY peak observed by Lindsell between C^1O and C^2O of $[(\eta^5\text{-}C_5H_5)_2W_2(CO)_6]$ also arises from exchange and not the nOe previously suggested.[15]

In conclusion, the mechanism originally proposed by Cotton to explain the fluxionality of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(CNMe)]$ has been unambiguously demonstrated to occur in $[(\eta^5\text{-}C_5H_5)_2M_2(CO)_6]$, $M_2 = Mo_2$ and MoW. Carbonyl exchange in these compounds is remarkably facile and could be occurring in many other related compounds.

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

OM960247Y

---

[31] The convention is adopted that the numbering for structures **3** and **4** is used, followed by the atom to which the carbonyl is attached. Hence $C^1O(MoW)$ means carbonyl 1 from **3**, which is attached to molybdenum in $[(\eta^5\text{-}C_5H_5)_2MoW(CO)_6]$.

[32] $C^1O(MoW)$ and $C^4O(MoW)$ overlap, and it is not possible to determine whether the saturation transfer is to both sites.

[33] The first symbol refers to the atom attached to the ^{13}CO giving the particular signal.

[34] Two bridging transfers and a rotation of the Mo−W bond are required.