Alkene-like Rotation of Unsaturated Rh_2 and CoRh Fragments when bonded to Molybdenum Pentacarbonyl; *X*-Ray Crystal Structure of $[MoRh_2(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5Me_5)_2]$

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Studies ($^{13}C\{^1H\}$ n.m.r. and *X*-ray diffraction) on the compounds $[MMoRh(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5Me_5)_2]$ (M = Co or Rh) show that the preferred orientation of the MRh groups with respect to the *cis*-CO ligands of the $Mo(CO)_5$ moiety is staggered, but in the CoMoRh species rotation occurs in solution about an axis through the Mo and the mid-point of the Co–Rh vector.

We have recently reported[1] the synthesis of $[MoRh_2(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5Me_5)_2]$ (**1**) an inorganic analogue[2] of a d^6-ML_5-(alkene) complex.[3–5] At room temperature and at −60 °C the molecule (**1**) has a $^{13}C\{^1H\}$ n.m.r. spectrum with three resonances for the CO ligands; a triplet signal at δ 246.2 p.p.m. [J(RhC) 44 Hz] for the μ-CO and two signals for the $Mo(CO)_5$ group at 215.0 and 206.8 p.p.m. with relative intensity 1:4. In (**1**) the fragment $Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$ is isolobal with C_2H_4,[6] and the $^{13}C\{^1H\}$ n.m.r. data could be interpreted in terms of either a static structure in which an $Mo(CO)_5$ moiety is rigidly co-ordinated to the dirhodium system, the Rh–Rh vector being staggered with respect to the four *cis*-CO ligands or that on the n.m.r. time scale rapid rotation of the Rh_2 moiety is occurring about an axis through the Mo, the *trans*-CO group, and the midpoint of the Rh–Rh vector.

An *X*-ray diffraction study on (**1**)[†] established the structure shown in Figure 1 where the molecule is projected onto the mean plane of the $Mo(CO)_4$ fragment. It will be seen immediately that the Rh–Rh vector is staggered with respect to the CO ligands of the $Mo(CO)_4$ group. The rhodium separation is 2.623(1) Å, and compares with 2.564(1) Å in $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$.[7] The carbonyl groups C(01)O(01) and C(02)O(02) are symmetrically bridging [mean Rh–C(O) 1.995(3) Å] and are inclined towards the Mo atom at the carbon atoms, although O(01) and O(02) bend back over the Rh–Rh vector.

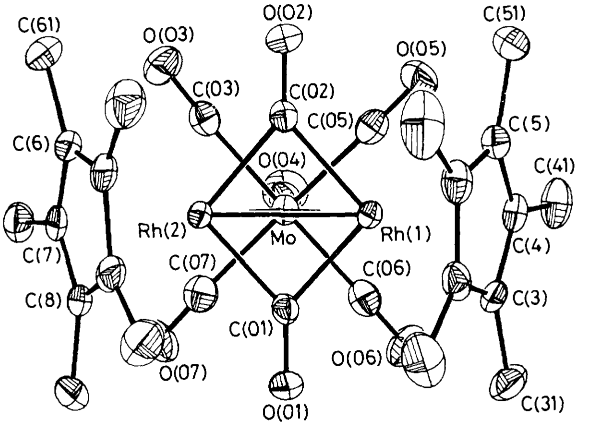


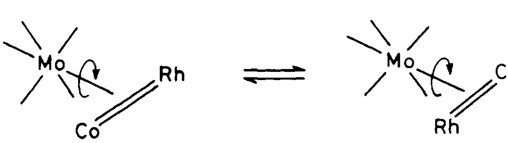
Figure 1. The molecular structure of $[MoRh_2(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5Me_5)_2]$ (**1**). Dimensions: Rh(1)–Rh(2) 2.623(1), Rh(1)–Mo 3.017(1), and Rh(2)–Mo 3.001(1) Å.

$[MoRh_2(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5Me_5)_2]$
(**1**)

$[CoMoRh(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5Me_5)_2]$
(**2**)

The mean planes of the η-C_5Me_5 ligands are inclined at 30° (150°) to the Rh–Rh vector at a mean Rh–C distance of 2.248(3) Å. The equatorial CO ligands of the $Mo(CO)_5$ fragment are all significantly nonlinear [mean Mo–C–O 174.6(3)°] and the Mo–C(O) distances [mean 2.061(4) Å] are longer than the linear Mo–C(04)O(04) axial distance [1.988(4) Å].

The information available from the structural study on (**1**) in the solid state and the $^{13}C\{^1H\}$ n.m.r. data do not resolve the question of possible rotation of the Rh_2 fragment in solution mentioned above. However, the heteronuclear, unsaturated dimetal compound $[CoRh(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ has recently been prepared[7] and treatment of this species with photochemically generated $[Mo(thf)(CO)_5]$ (thf = tetrahydrofuran) in thf at 0 °C afforded the dark green complex $[CoMoRh(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5Me_5)_2]$ (**2**)[‡] (90%). If a staggered conformation is also preferred for (**2**) the limiting low-temperature $^{13}C\{^1H\}$ n.m.r. spectrum should show three resonances for the CO ligands of the $Mo(CO)_5$ group of relative intensity 2:2:1. Such a spectrum is observed at −60 °C. However, on warming coalescence of peaks due to the *cis*-$Mo(CO)_4$ carbonyl groups occurs at *ca.* −15 °C, with no change observed for the *trans*-



Scheme 1

[†] *Crystal data for* (**1**): $C_{27}H_{30}O_7MoRh_2$, M = 767.3, monoclinic, a = 9.625(4), b = 17.500(8), c = 16.714(9) Å, β = 97.72(2)°, U = 2 790(2) Å^3, Z = 4, D_c = 1.83 g cm^{-3}, $F(000)$ = 1 519.7. Space group $P2_1/n$ (No. 14), Mo-K_α *X*-radiation (graphite monochromator), λ = 0.710 69 Å, μ(Mo-K_α) = 16.2 cm^{-1}. Intensities [4 423 with $I \geqslant 1\sigma(I)$] were measured on a Nicolet *P*3*m* four-circle diffractometer at 200 K to $2\theta \leqslant 55°$ and corrected for Lorentz, polarisation, and *X*-ray absorption effects. The structure was refined to R 0.026 (R' 0.025) by blocked cascade least squares using the SHELXTL system of programmes.

The atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[‡] For compound (**2**): ν_{CO} at 2 050m, 1 950s, 1 947(sh), 1 937m, and 1 748w cm^{-1} (pentane); n.m.r. (coupling constants in Hz); ^1H ($CDCl_3$) δ 1.60 [d, 15 H, RhC_5Me_5, J(RhC) 1] and 1.69 (s, 15 H, CoC_5Me_5); $^{13}C\{^1H\}$ (CD_2Cl_2–CH_2Cl_2) at room temperature, δ 256.6 [d, μ-CO, J(RhC) 43], 213.7 (1 × CO, MoCO), 210.4 (4 × CO, MoCO), 105.4 [d, RhC_5Me_5, J(RhC) 5], 97.7 (CoC_5Me_5), 9.2 (Me), and 8.4 p.p.m. (Me); at −60 °C, δ 257.4 [d, μ-CO, J(RhC) 44], 213.7 (1 × CO, MoCO), 211.0 (2 × CO, MoCO), 209.8 (2 × CO, MoCO), 104.7 [d, RhC_5Me_5, J(RhC) 5], 97.1 (CoC_5Me_5), 8.9 (Me), and 8.0 p.p.m. (Me). Low resolution *X*-ray data on (**2**) show the same overall configuration as (**1**) with the Co–Rh vector similarly aligned with respect to the $Mo(CO)_5$ moiety. Disorder in the solid state precluded a satisfactory full refinement of these limited data. $C_{27}H_{30}O_7CoMoRh$, M = 723.3, 293 K, a = 15.462(9), b = 16.035(6), c = 23.57(2) Å, β = 97.22(5)°, U = 5 797(6) Å^3, for space group $I2/m$, Z = 4.

Mo(CO) or μ-CO groups. At room temperature the spectrum shows two signals due to the $Mo(CO)_5$ group of relative intensity 4 : 1.

These spectra are in accord with the hindered rotation of the $CoRh(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$ group with respect to the $Mo(CO)_5$ moiety; the estimated activation energy, $\Delta G^\ddagger$ at -15 °C is 52.3 ± 1.3 kJ mol^{-1} (Scheme 1). This barrier is in the range observed,[3–5] (*ca.* 35—80 kJ mol^{-1}) for hindered rotation of organic alkenes in their d^6–ML_5 complexes. For the model complex $[Cr(CO)_5(C_2H_4)]$, a barrier of *ca.* 42 kJ mol^{-1} has been calculated.[8]

We thank the S.E.R.C. for support and I.C.I. New Science Group for a C.A.S.E. research studentship (R. D. B.).

Received, 28th March 1983; Com. 402

References

1 R. D. Barr, M. Green, K. Marsden, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 507.

2 R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 711.

3 J. W. Byrne, H. V. Blaser, and J. A. Osborn, *J. Am. Chem. Soc.*, 1975, **97**, 3871.

4 U. Koemm, C. G. Kreiter, and H. Strack, *J. Organomet. Chem.*, 1978, **148**, 179.

5 L. D. Brown, C. F. J. Barnard, J. A. Daniels, R. J. Mawby, and J. A. Ibers, *Inorg. Chem.*, 1978, **17**, 2932.

6 A. R. Pinhas, T. A. Albright, P. Hofmann, and R. Hoffmann, *Helv. Chim. Acta*, 1980, **63**, 29.

7 M. Green, D. R. Hankey, J. A. K. Howard, P. Louca, and F. G. A. Stone, preceding communication.

8 T. A. Albright, R. Hoffmann, J. C. Thibeault, and D. L. Thorn, *J. Am. Chem. Soc.*, 1979, **101**, 3801.