The Analogy Between Alkenes and the Dinuclear Species $[MRh(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (M = Co or Rh); Dynamic Nuclear Magnetic Resonance, *X*-Ray Crystallographic, and Extended-Hückel Molecular-orbital Studies of the Bonding between Unsaturated CoRh and Rh_2 Fragments and the Pentacarbonylmolybdenum Group *

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Treatment of $[Mo(CO)_5(thf)]$ (thf = tetrahydrofuran) with $[CoRh(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ affords the heterotrimetallic complex $[MoCoRh(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5Me_5)_2]$. Variable-temperature $^{13}C\text{-}\{^1H\}$ n.m.r. studies on this species revealed that in solution rotation of the $CoRh(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$ fragment occurs about an axis through the Mo and the midpoint of the Co–Rh vector, and that the preferred orientation of the Co–Rh vector with respect to the four equatorial carbonyl ligands of the square-pyramidal $Mo(CO)_5$ moiety is staggered. The estimated barrier to rotation ($\Delta G^{\ddagger}_{258} = 52.3 \pm 1.3$ kJ mol^{-1}) is in the range observed and calculated for the hindered rotation of alkenes in related d^6 ML_5 alkene complexes where, however, the orientational preference of the alkene is to lie so as to eclipse an LML vector. The structure of the analogous trinuclear compound $[MoRh_2(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5Me_5)_2]$ has been determined by a single-crystal *X*-ray diffraction study. The core of the molecule consists of an $MoRh_2$ isosceles triangle [Mo–Rh (mean) 3.009(1), Rh–Rh 2.623(1) Å]. The molybdenum atom carries five carbonyl groups, the rhodium atoms are each ligated by an $\eta\text{-}C_5Me_5$ group, and the Rh–Rh vector, staggered with respect to the four equatorial carbonyl groups of the $Mo(CO)_5$ fragment, is symmetrically bridged by two CO ligands. Relatively short non-bonded contacts between the oxygen atoms of the equatorial CO ligands and the hydrogen atoms of the $\eta\text{-}C_5Me_5$ groups suggest a significant steric barrier to the 'alkene-like' rotation of the $Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$ fragment. Extended-Hückel molecular-orbital calculations on the model species $[MoRh_2(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5H_5)_2]$ indicate that the dirhodium fragment and an alkene bond to an $Mo(CO)_5$ moiety in a similar fashion. However, whereas the barrier to alkene rotation in d^6 ML_5 alkene complexes derives from electronic effects, no significant electronic contribution to the barrier of rotation of the trinuclear metal complex is indicated.

We have described [1–4] the synthesis, structures, and dynamic properties of a series of trinuclear mixed-metal clusters, which may be considered to be inorganic analogues of cyclopropane or as ML_n π complexes of an 'inorganic alkene.' These clusters contain metal–ligand fragments isolobal [5] with CH_2, *e.g.* d^{10} PtL_2, d^8 $Fe(CO)_4$, or d^6 $M(CO)_5$ (M = Cr, Mo, or W), bonded to a dimetal fragment $MRh(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$ (M = Co [4] or Rh [6]) isolobal with ethylene.[7] Hoffmann and co-workers [7] have discussed the nature of the bonding in the structurally characterised [8] anion $[Rh_3(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]^-$, and in several related complexes, including the parent methylene-bridged compound [9] $[Rh_2(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5H_5)_2]$ and the trirhodium clusters of formula $[Rh_3(CO)_3(\eta\text{-}C_5H_5)_3]$.[10] The trinuclear anion can be considered to be a complex of the d^{10} fragment $Rh(CO)_2^-$ and 'alkene-like' $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$, and the neutral trirhodium species as d^8 $Rh(CO)(\eta\text{-}C_5H_5)$ adducts.

The bonding, rotational barrier, and conformational preferences of a series of η^2-alkene complexes of d^6 ML_5 fragments of the Group 6 metals have also been examined from a theoretical standpoint.[11] Since we have recently synthesised [3] a series of d^6 $M(CO)_5$ (M = Cr, Mo, or W) adducts of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$, it was of interest to investigate in detail, by physical and theoretical means, the barrier to rotation of $MRh(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$ (M = Co or Rh) groups relative to an $M(CO)_5$ fragment, and thus obtain a quantitative comparison of the bonding between alkenes and metals, and between CoRh or Rh_2 dimers and metals. A preliminary account of some aspects of this work has appeared.[12]

Results and Discussion

We have previously described [3] the synthesis of the compounds (1)—(3) by treating photochemically generated $[M'(CO)_5L]$ species [M' = Cr, Mo, or W; L = tetrahydrofuran (thf) or MeCN] with the unsaturated $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ dimer. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectra, at room temperature or below, display resonances due to the two equivalent $\eta\text{-}C_5Me_5$ ligands, the μ-CO groups, and on the Group 6 metal the unique axial CO and the four equivalent equatorial CO ligands. For compound (2), at −50 °C in $CD_2Cl_2\text{-}CH_2Cl_2$, the μ-CO groups give rise to a triplet resonance [δ 246.2 p.p.m., *J*(RhC) 44 Hz], the axial CO appears as a singlet (δ 215.0), and the four equatorial CO ligands as a singlet at δ 206.8. The tungsten analogue (3) has a similar $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum, however, ^{183}W satellite peaks are observed for the terminal CO resonances but not for the μ-CO signal. The absence of ^{183}W coupling to the μ-CO groups confirms that there is no interaction of these ligands with the $W(CO)_5$ centre. The 1 : 4 intensity ratio for the resonances due to the terminal CO groups in the spectra of compounds (2) and (3) is consistent with either a static structure in which the $M'(CO)_5$ moiety is rigidly co-ordinated to the Rh_2 system, the Rh–Rh vector being staggered with respect to the four equatorial CO ligands, or a dynamic system in which rapid rotation of the Rh_2 moiety occurs about an axis through M', the *trans*-CO group, and the midpoint of the Rh–Rh vector.

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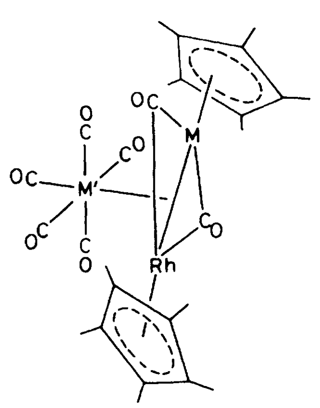
* *Supplementary data available* (No. SUP 56043, 7 pp.): H-atom co-ordinates, thermal parameters, complete bond distances and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. unit employed: eV ≈ 1.60×10^{-19} J.



	M	M'
(1)	Rh	Cr
(2)	Rh	Mo
(3)	Rh	W
(4)	Co	Mo

$$\begin{tikzcd}[Mo(CO)_6] \arrow[r, "(i)"] & [Mo(CO)_5(thf)] \arrow[d, "(ii)"] \\ [Mo(CO)_4(^{13}CO)(thf)] & [Mo(CO)_5(^{13}CO)] \arrow[l, "(i)"']\end{tikzcd}$$

Scheme. (*i*) U.v. irradiation at 0 °C in thf; (*ii*) ^{13}CO (90%^{13}C) in thf

In order to distinguish between the static and the dynamic possibilities, it was necessary to employ an asymmetric 'metal–alkene,' and such a compound $[CoRh(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ has recently been synthesised and structurally characterised in our laboratory.[4] This species was treated in thf with $[Mo(CO)_5(thf)]$ to form the heterotrimetallic complex (4), which was characterised by elemental analysis, i.r., and n.m.r. spectroscopy. In order to facilitate the projected $^{13}C\text{-}\{^1H\}$ n.m.r. study, the ^{13}C-enriched complex $[MoCoRh(\mu\text{-}CO)_2(CO)_4(^{13}CO)(\eta\text{-}C_5Me_5)_2]$ was also synthesised *via* the procedure outlined in the Scheme. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum was recorded as a function of temperature in CH_2Cl_2–CD_2Cl_2 as solvent. At −60 °C three resonances for the $Mo(CO)_5$ moiety were observed of relative intensity 1 : 2 : 2 (Figure 1), corresponding to a staggered conformation.

Peaks occurred at δ 213.7 for the CO ligand on the Mo which is *trans* to the Co–Rh vector, and at 211.0 and 209.8 p.p.m. for the four equatorial CO ligands of the $Mo(CO)_5$ group. The μ-CO ligands on the CoRh fragment gave rise to a doublet signal [257.4 p.p.m., *J*(RhC) 44 Hz]. Upon warming to −15 °C, coalescence of the signals due to the equatorial $Mo(CO)_4$ carbonyl groups occurs, with no change observed for the *trans*-Mo(CO) or μ-CO groups. Warming to room temperature produces a spectrum displaying two sharp signals of relative intensity 1 : 4 due to the $Mo(CO)_5$ group. The signal for the equatorial CO ligands appears at 210.4 p.p.m., centred between the two resonances for these four ligands observed at −60 °C.

These spectra are in accord with hindered rotation of the $CoRh(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$ group with respect to the $Mo(CO)_5$ moiety, analogous to the well known rotation of metal-co-ordinated alkenes. For the apparent two-site exchange process, the rate constant at the coalescence temperature[13] $k_c = \pi|\nu_a - \nu_b|/\sqrt{2}$ is $k_{258} = 140\ s^{-1}$, where $|\nu_a - \nu_b|$ (the inter-peak separation at the low temperature limit) is 63 Hz, and thus $\Delta G^{\ddagger}_{258} = 52.3 \pm 1.3$ kJ mol^{-1}.

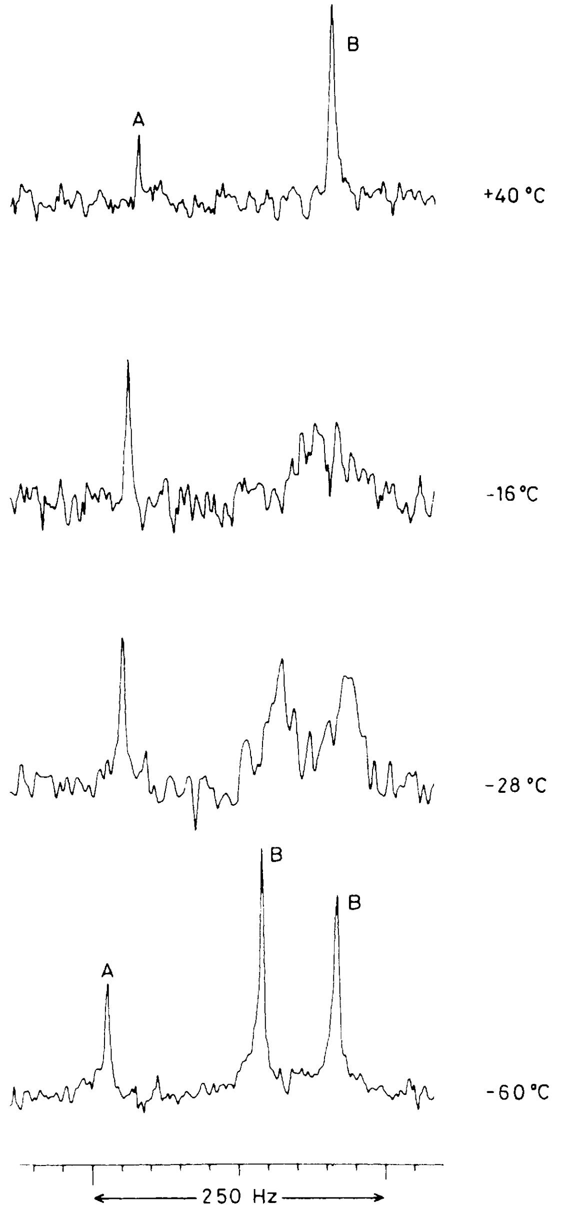
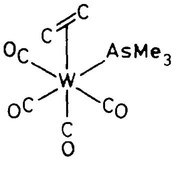
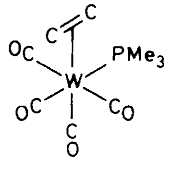


Figure 1. The variable-temperature $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of $[MoCoRh(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5Me_5)_2]$ (4) in the terminal CO region, measured in CH_2Cl_2–CD_2Cl_2: A = *trans*-Mo(CO), B = *cis*-$Mo(CO)_4$. For chemical shifts see text



(5)



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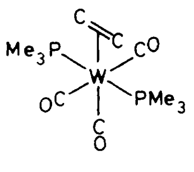


(7)

It is interesting to compare these observations with those reported for Group 6 metal (d^6 ML_5)-alkene complexes. A barrier to rotation of 65 kJ mol^{-1} at 98 °C has been observed for ethylene rotation in the compound *trans*-$[Mo(dppe)_2(C_2H_4)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$), and it is suggested[14] that the preferred conformation is one in which the ethylene

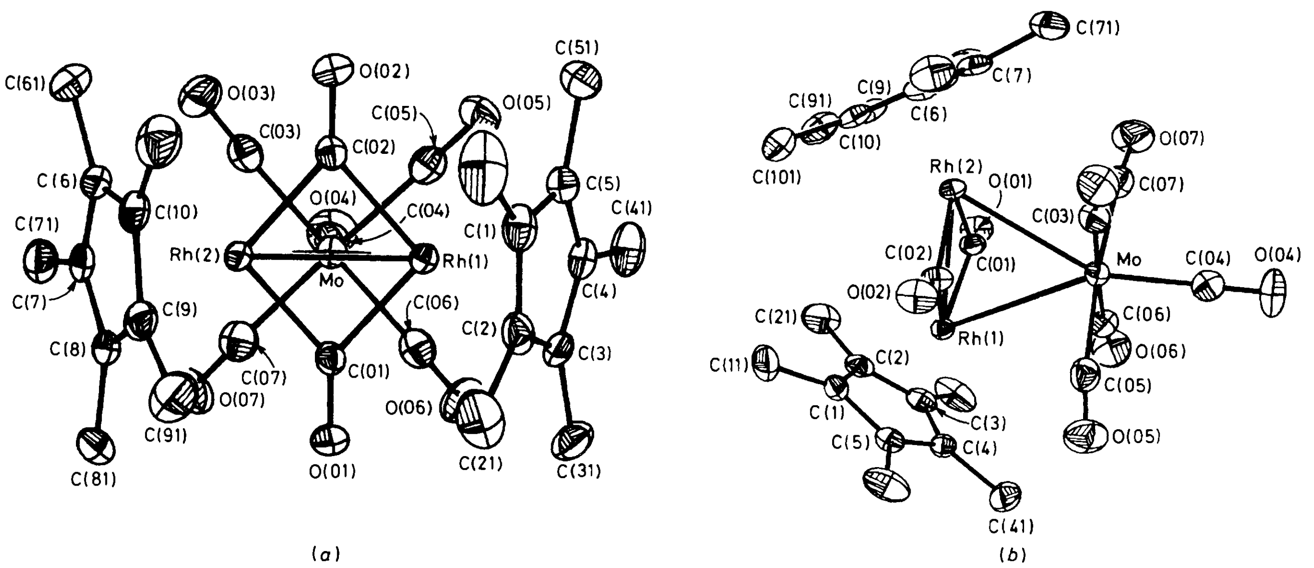


Figure 2. (*a*) The molecular structure of $[\mathrm{MoRh_2(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5Me_5)_2}]$ (2), showing the crystallographic numbering. (*b*) The molecule viewed perpendicular to the metal-atom triangle

ligands are mutually staggered, but eclipse the P–Mo–P vectors. This latter geometry is opposite to that found in solution for complex (4) containing an ' inorganic alkene.' The alkene also prefers to eclipse a major axis of the equatorial plane of the ligands in the tungsten complexes (5)—(7), where the alkene is dimethyl maleate or dimethyl fumarate.[15,16] In these systems, the barrier to rotation varies from 33.5 kJ mol^{-1} for (6; alkene = dimethyl maleate) to 80.0 kJ mol^{-1} for (7; alkene = dimethyl fumarate).

Extended-Hückel molecular-orbital (EHMO) calculations have led to an estimated[11] barrier of *ca.* 42 kJ mol^{-1} for rotation of an ethylene ligand (hydrogens bent back by 20°) attached to a $\mathrm{Cr(CO)_5}$ fragment, with the preferred geometry that in which the $\mathrm{C_2H_4}$ group eclipses an equatorial OC–Cr–CO vector. In addition, *ab initio* LCAO-MO-SCF calculations[17] for the two model *trans*-bis(ethylene) complexes $[\mathrm{Mo(PH_3)_4(C_2H_4)_2}]$ and $[\mathrm{Mo(CO)_4(C_2H_4)_2}]$ show that the electronically preferred geometry is one in which the ethylenes are mutually staggered, but eclipse P–Mo–P or OC–Mo–CO vectors, respectively. The computed barrier to ethylene rotation in *trans*-$[\mathrm{Mo(PH_3)_4(C_2H_4)_2}]$ is 67 kJ mol^{-1}. Thus, although the observed activation energy for CoRh rotation in complex (4) is in the range observed, and predicted for alkene rotation on d^6 $\mathrm{ML_5}$ moieties, the preferred orientation for the ' inorganic alkene ' appears from solution n.m.r. measurements to be different from that of ' organic alkenes.'

In order to examine the orientation of the Co–Rh vector in complex (4) in the solid state a single-crystal *X*-ray diffraction study was attempted. However, disorder problems precluded a satisfactory refinement.[12] Attention was, therefore, focused on the $\mathrm{MoRh_2}$ complex (2).

The molecular geometry is illustrated in Figure 2, and selected bond distances and angles are given in Table 1. The Rh–Rh vector is staggered with respect to the equatorial CO ligands of the $\mathrm{Mo(CO)_4}$ group. The Rh–Rh separation [2.623(1) Å] is longer than that in $[\mathrm{Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2}]$ [2.564(1) Å],[4] but shorter than in $[\mathrm{PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2}]$ [2.647(2) Å][1] or in the anion $[\mathrm{Rh_3(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2}]^-$ (2.66 Å).[8] The carbonyl groups C(1)O(1) and C(2)O(2) symmetrically bridge the two rhodium atoms [mean Rh–C(O) 1.995(3) Å], and are inclined toward the Mo atom at the carbon atoms, although O(1) and O(2) bend ' back ' over the Rh–Rh vector; these oxygen atoms are 0.27 and 0.17 Å, respectively, from their μ-$\mathrm{CRh_2}$ planes. The Mo–C(01) (2.842 Å) and Mo–C(02) (3.087 Å) distances are significantly longer than the corresponding Pt–μ-CO distances of 2.56(2) and 2.476(13) Å in $[\mathrm{PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2}]$,[1] and the $\mathrm{(OC)_2Rh}$–μ-CO distance of 2.40 Å in the anion $[\mathrm{Rh_3(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2}]^-$.[8] This indicates a substantially weaker interaction of the μ-CO ligands with the third metal centre in (2), compared with those in the $\mathrm{PtRh_2}$ and trirhodium clusters.

Table 1. Selected bond distances (Å) and angles (°) for the compound $[\mathrm{MoRh_2(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5Me_5)_2}]$ (2)

Rh(1)–Rh(2)	2.623(1)	Rh(1)–C(η-$\mathrm{C_5Me_5}$) [a]	2.247(3)
Rh(1)–Mo	3.017(1)	Rh(2)–C(η-$\mathrm{C_5Me_5}$) [a]	2.249(3)
Rh(2)–Mo	3.001(1)	Mo–CO [a,b]	2.061(4)
Rh(1)–C(01)	1.993(3)	Mo–C(04)	1.988(4)
Rh(1)–C(02)	2.003(3)	Mo–C(01)	2.842
Rh(2)–C(01)	1.994(3)	Mo–C(02)	3.087
Rh(2)–C(02)	1.991(3)	C(01)–O(01)	1.191(4)
		C(02)–O(02)	1.184(4)
Mo–Rh(1)–Rh(2)	63.8(1)	Mo–Rh(2)–Rh(1)	64.5(1)
Rh(1)–Mo–Rh(2)	51.7(1)	Mo–C(04)–O(04)	179.3(3)
Mo–C–O [a,b]	174.7(3)		
Rh(1)–C(01)–Rh(2)	82.3(1)	Rh(1)–C(02)–Rh(2)	82.1(1)
Rh(1)–C(01)–O(01)	137.0(3)	Rh(2)–C(01)–O(01)	137.3(2)
Rh(1)–C(02)–O(02)	137.3(3)	Rh(2)–C(02)–O(02)	139.2(3)
Rh(1)–Rh(2)–C(01)	48.8(1)	Rh(1)–Rh(2)–C(02)	49.2(1)
Rh(2)–Rh(1)–C(01)	48.9(1)	Rh(2)–Rh(1)–C(02)	48.8(1)
C(01)–Rh(1)–C(02)	97.0(1)	C(01)–Rh(2)–C(02)	97.4(1)

[a] Mean distance. [b] Equatorial carbonyl groups C(03)O(03), C(05)-O(05), C(06)O(06), and C(07)O(07).

Table 2 compares the geometry of compound (2) with those of $[\mathrm{PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2}]$ and $[\mathrm{Rh_3(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2}]^-$, using the nomenclature of ref. 7 to describe the distortion of the $\mathrm{Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2}$ moiety upon co-ordination. The value of ξ is somewhat smaller for (2) than for the above mentioned $\mathrm{PtRh_2}$ and $\mathrm{Rh_3}^-$ clusters, presumably in order to minimise non-bonded interactions between the Me

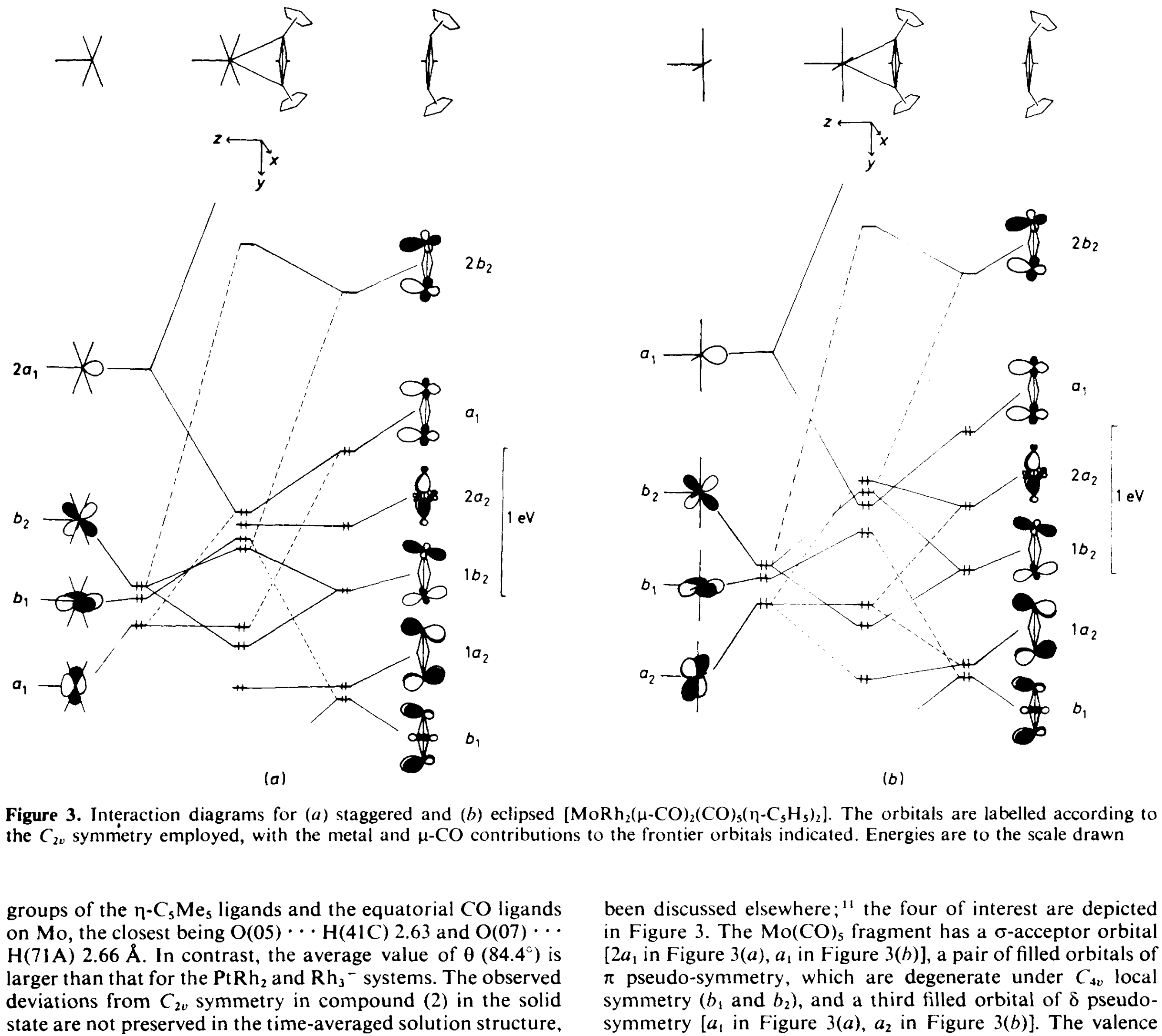


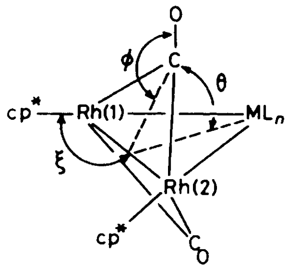
Figure 3. Interaction diagrams for (*a*) staggered and (*b*) eclipsed [$MoRh_2(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5H_5)_2$]. The orbitals are labelled according to the C_{2v} symmetry employed, with the metal and μ-CO contributions to the frontier orbitals indicated. Energies are to the scale drawn

groups of the η-C_5Me_5 ligands and the equatorial CO ligands on Mo, the closest being O(05) ··· H(41C) 2.63 and O(07) ··· H(71A) 2.66 Å. In contrast, the average value of θ (84.4°) is larger than that for the $PtRh_2$ and Rh_3^- systems. The observed deviations from C_{2v} symmetry in compound (2) in the solid state are not preserved in the time-averaged solution structure, and are thus presumably due to crystal-packing forces. Finally, the equatorial CO ligands of the $Mo(CO)_5$ moiety all show significant non-linearity [mean Mo−C−O 174.7(3)°], bending away from the Rh_2 unit, and with Mo−CO distances [mean 2.061(4) Å] which are longer than the Mo−C(4)O(4) axial bond [1.988(4) Å]. Thus, in summary the shorter Rh−Rh distance, the smaller value of ξ, and larger value of θ in (2) compared with the other trimetal complexes indicate less ' rehybridisation ' of the ' inorganic alkene ' on co-ordination to a d^6 ML_5 fragment than to a d^{10} ML_2 moiety [$Pt(CO)(PPh_3)$ or $Rh(CO)_2^-$].

In order to explore further the relationship between inorganic alkenes and the unsaturated molecule [$Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$], EHMO calculations were carried out on the model compound [$MoRh_2(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5H_5)_2$] ($C_{2v}$ symmetry) with $\xi = 150°$, $\phi = 180°$, and $\theta = 90°$ (see Table 2 for definition of ξ, φ, and θ). The results of these calculations are illustrated in Figure 3 where the interactions between the $Mo(CO)_5$ and the $Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$ fragment frontier orbitals are shown with the Rh−Rh vector either staggered [Figure 3(*a*)] or eclipsed [Figure 3(*b*)] with respect to the equatorial OC−Mo−CO vectors. The valence orbitals of the C_{4v} square-pyramidal d^6 ML_5 fragment [here $Mo(CO)_5$] are well known, and have been discussed elsewhere;[11] the four of interest are depicted in Figure 3. The $Mo(CO)_5$ fragment has a σ-acceptor orbital [$2a_1$ in Figure 3(*a*), a_1 in Figure 3(*b*)], a pair of filled orbitals of π pseudo-symmetry, which are degenerate under C_{4v} local symmetry (b_1 and b_2), and a third filled orbital of δ pseudo-symmetry [a_1 in Figure 3(*a*), a_2 in Figure 3(*b*)]. The valence orbitals of [$Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$] have also been previously[7] described, the six of importance in the present discussion being also illustrated (Figure 3). These include an acceptor orbital of π pseudo-symmetry ($2b_2$), and filled orbitals of σ (a_1), π ($1b_2$ and b_1), and δ ($1a_2$ and $2a_2$) pseudo-symmetry. Binding of the two fragments then occurs by orbital interactions of the type that are responsible for alkene bonding to d^6 ML_5 moieties. Thus, there is donation of electron density to the $Mo(CO)_5$ fragment *via* the orbitals of a_1 symmetry, and back donation from the $Mo(CO)_5$ group *via* orbitals of b_2 symmetry.

These calculations allow an examination of the electronic nature of the alkene $\xleftrightarrow[o]{}$ [$Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$] relationship in some detail. According to the octet and effective atomic number rules, respectively, both ethylene and [$Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$] have formal double bonds. In molecular-orbital terms they have filled a_1 (σ-donor) and empty b_2 (π-acceptor) orbitals under C_{2v} local symmetry. The familiar bending back of substituents on a co-ordinated alkene[18] is exactly paralleled by the bending back of the cyclopentadienyl ligands in $Mo(CO)_5$-complexed [$Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$] ($\xi = 150°$). This bending back causes rehybridisation such that the a_1 donor orbital (Rh−Rh, π) is raised in energy by *ca.* 0.54 eV, and becomes the highest occupied molecular orbital (h.o.m.o.), and the

Table 2. Comparison of molecular parameters (°) of ML_n adducts of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5R_5)_2]$ (R = Me or H)



ML_n	$Mo(CO)_5$ [a]	$Pt(CO)(PPh_3)$ [b]	$Rh(CO)_2^-$ [c]
θ	84.4 [d]	79.8 [e]	77.5 (74 [f])
ξ	150.1 [C(1)—C(5)]	155.0 [Rh(1)]	159.4 (157 [f])
	151.5 [C(6)—C(10)]	149.2 [Rh(2)]	
ϕ	169.2 [g]	169.6 [h]	170.0 (176 [f])

[a] This work. [b] Ref. 1. [c] Ref. 8, cp* is $\eta\text{-}C_5H_5$ in this complex. [d] Average of 89.5 and 79.3°. [e] Average of 81.5 and 78.0°. [f] Calculated, see ref. 7. [g] Average of 171.7 and 166.7°. [h] Average of 169.9 and 169.3°.

$2b_2$ (Rh–Rh, π^*) acceptor orbital is reduced in energy by *ca.* 0.33 eV, both becoming better hybridised for overlap with the $Mo(CO)_5$ fragment. One principal difference between the valence orbitals of C_2H_4 and $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ is the absence of a high-lying filled orbital of a_2 symmetry in ethylene. The eclipsed orientation of alkenes in d^6 ML_5 alkene complexes is preferred since it is this conformation which minimises the unfavourable four-electron interaction between the δ-pseudo-symmetry orbital of the d^6 ML_5 moiety and the alkene π orbital, the a_1 and b_2 interactions being insensitive to alkene rotation.[11] For the ' inorganic alkene,' such four-electron interactions persist in both eclipsed and staggered orientations, since in either conformation the δ-type orbital of the d^6 ML_5 moiety finds a symmetry match in $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$. Thus in Figure 3(*a*) the h.o.m.o. of the staggered conformer is calculated to be of a_1 symmetry, whereas in Figure 3(*b*) for the eclipsed conformer the h.o.m.o. is of a_2 symmetry; in each case there is a contribution from the $Mo(CO)_5$ orbital of δ pseudo-symmetry.

The total energy, *i.e.* the sum of the one-electron energies, for staggered $[MoRh_2(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5H_5)_2]$ is 0.24 eV below that of eclipsed $[MoRh_2(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5H_5)_2]$. These calculations yield a barrier to rotation of *ca.* 23 kJ mol^{-1}, only about half the value observed for compound (4). However, the calculations correctly predict the preferred orientation of the Rh_2-based fragment. Although it is tempting to ascribe the calculated conformational preference to frontier-orbital effects, in fact the sum of the energies of the seven occupied orbitals shown in Figure 3 differ by only 0.03 eV. These calculations are, therefore, in accord with the conclusion drawn from the structural evidence that the barrier to rotation is largely steric in origin, *i.e.* in molecular-orbital terms the result of repulsive four-electron interactions between low-lying filled orbitals. On a cautionary note, it is clear that this is a greatly simplified view, since we have ignored the effects of asymmetry in substituting Rh for Co, the coupling of methyl rotation, cyclopentadienyl rotation, and ' alkene ' rotation, *etc.*

As noted in the introduction, other metal complexes containing the $Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$ moiety show barriers to rotation, which parallel those for the corresponding alkene complex. Thus, the d^{10} ML_2 $[PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$ complex has a high barrier, the d^8 ML_4 complexes $[FeMRh(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ (M = Co[4] or Rh[2]) a much lower one, and the cation $[PtRh_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]^+$ (ref. 1) an intermediate one. The latter species may be considered to contain a $PtH(CO)(PPh_3)^+$ (d^8 ML_3) T-shaped fragment co-ordinated to the dirhodium unit. The observed barriers to alkene rotation, and the preferred conformations in d^{10} ML_2, d^8 ML_4, and d^8 ML_3 (T-shaped) alkene-metal complexes have been considered to be determined primarily by metal-based frontier-orbital characteristics, Berry pseudo-rotation effects, and ligand–alkene steric interactions, respectively.[11] Broadly similar factors are likely to hold for the ' inorganic alkene ' considered here.

Finally, others[7] have discussed the interaction of the μ-CO ligands in the $Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$ group with the $Rh(CO)_2^-$ moiety in the trinuclear anionic cluster $[Rh_3(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]^-$. It has been pointed out that the leaning back of the cyclopentadienyl rings permits the μ-CO ligands to bend towards the third metal atom and accept electron density from the d^{10} ML_2 fragment *via* an interaction of vacant μ-CO π^* orbitals with filled *d* orbitals of $Rh(CO)_2^-$. In the case of the d^6 ML_5 complexes (1)—(4), the corresponding $\mu\text{-}CO\text{-}M(CO)_5$ interaction is very much weaker, as indicated by the $^{13}C\text{-}\{^1H\}$ n.m.r. measurements, and the *X*-ray structural data for (2). This is because the *d* orbitals in question are substantially stabilised by the terminal CO ligands on the Group 6 metal. The calculations show a net transfer of *ca.* 0.5 electron from the $Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$ fragment to the $Mo(CO)_5$ group in our model species $[MoRh_2(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5H_5)_2]$. This observation is in accord with the relatively low values of the stretching frequencies observed for the terminal CO ligands in compound (2).

Experimental

Reactions were performed under an atmosphere of dry oxygen-free nitrogen or argon, using Schlenk-tube techniques. High-vacuum apparatus was used for ^{13}CO enrichment. Solvents were rigorously dried prior to use. Light petroleum is that fraction of b.p. 40—60 °C. Photochemical reactions were carried out in an ice-cooled quartz Schlenk tube under an argon purge, with magnetic stirring, using a 450-W medium-pressure mercury lamp. The compounds $[MRh(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (M = Co[4] or Rh[6]) were prepared as described previously.

Synthesis of $[MoCoRh(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5Me_5)_2]$ (4).—Molybdenum hexacarbonyl (0.11 g, 0.4 mmol) in thf (100 cm^3) was irradiated for 0.5 h and the resulting solution of $[Mo(CO)_5(thf)]$ was treated with $[CoRh(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (0.15 g, 0.31 mmol). After stirring for 24 h, solvent was removed *in vacuo* and the resulting residue was dissolved in diethyl ether–light petroleum (1 : 5) and chromatographed on alumina affording, after removal of solvent, green *crystals* of $[MoCoRh(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5Me_5)_2]$ (4) (0.20 g, 90%) (Found: C, 44.1; H, 4.4. $C_{27}H_{30}CoMoO_7Rh$ requires C, 44.8; H, 4.2%), $\nu_{max.}$(CO) at 2 050m, 1 950s, 1 947 (sh), 1 937m, and 1 748w cm^{-1} (hexane); ^1H n.m.r. ($CDCl_3$), δ 1.60 [d, 15 H, RhC_5Me_5, *J*(RhH) 1.0 Hz] and 1.69 (s, 15 H, CoC_5Me_5).

Preparation of $[MoCoRh(\mu\text{-}CO)_2(CO)_4(^{13}CO)(\eta\text{-}C_5Me_5)_2]$.—Molybdenum hexacarbonyl (0.066 g, 0.25 mmol) in thf (50 cm^3) was irradiated for 10 min. The resulting solution was transferred to a Schlenk flask (250 cm^3) which was then attached to a high-vacuum line, cooled to −196 °C, and evacuated. Carbon monoxide (*ca.* 90% ^{13}CO, 10 cm^3, 0.42 mmol) was introduced *via* a Toepler pump and the reaction vessel was isolated, removed from the vacuum line, and warmed to 0 °C. After 3 h, argon was introduced, and the pale

Table 3. Atomic positional parameters (fractional co-ordinates) ($\times 10^4$) for complex (2), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Rh(1)	1 747(1)	3 115(1)	4 852(1)
Rh(2)	2 965(1)	2 144(1)	3 974(1)
Mo	2 182(1)	1 520(1)	5 525(1)
O(01)	− 160(2)	2 129(1)	3 745(1)
C(01)	954(3)	2 289(2)	4 107(2)
C(02)	3 772(3)	2 853(2)	4 847(2)
O(02)	4 875(2)	3 105(1)	5 121(2)
C(03)	4 269(4)	1 299(2)	5 465(2)
O(03)	5 434(3)	1 160(2)	5 498(2)
C(04)	2 204(4)	730(2)	6 381(2)
O(04)	2 225(3)	281(2)	6 878(2)
C(05)	2 807(4)	2 295(2)	6 418(2)
O(05)	3 180(3)	2 673(2)	6 970(2)
C(06)	97(4)	1 710(2)	5 626(2)
O(06)	− 1 047(3)	1 772(2)	5 699(2)
C(07)	1 486(4)	672(2)	4 701(2)
O(07)	1 047(3)	187(2)	4 295(2)
C(1)	1 815(3)	4 361(2)	4 652(2)
C(2)	462(4)	4 083(2)	4 312(2)
C(3)	− 234(3)	3 799(2)	4 940(2)
C(4)	703(3)	3 887(2)	5 683(2)
C(5)	1 956(3)	4 248(2)	5 513(2)
C(11)	2 891(5)	4 735(2)	4 209(3)
C(21)	− 162(5)	4 118(2)	3 425(2)
C(31)	− 1 691(4)	3 485(2)	4 846(3)
C(41)	337(4)	3 712(2)	6 508(2)
C(51)	3 205(4)	4 486(2)	6 105(2)
C(6)	4 890(3)	1 801(2)	3 408(2)
C(7)	3 874(3)	1 199(2)	3 278(2)
C(8)	2 635(3)	1 497(2)	2 791(2)
C(9)	2 882(3)	2 283(2)	2 648(2)
C(10)	4 284(3)	2 476(2)	3 032(2)
C(61)	6 373(3)	1 719(2)	3 819(2)
C(71)	4 129(4)	383(2)	3 515(2)
C(81)	1 333(4)	1 063(2)	2 452(2)
C(91)	1 886(4)	2 796(3)	2 131(2)
C(101)	5 026(4)	3 226(2)	2 990(2)

yellow solution was transferred back into the photolysis vessel. Following further irradiation (10 min), $[CoRh(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (0.10 g 0.21 mmol) was added, and the solution stirred for 24 h. The solvent was removed *in vacuo*, and the residue dissolved in diethyl ether–light petroleum (1 : 5) and chromatographed, affording green crystals of labelled (4), $\nu_{max.}$(CO) at 2 050m, 2 043w, 1 949vs, 1 936m, 1 915m, 1 895w, and 1 748w cm^{-1} (hexane).

Crystal Structure Determination for Complex (2).—Diffracted intensities were recorded from a single crystal (approximate dimensions 0.25 × 0.3 × 0.4 mm) mounted under nitrogen gas in a Lindemann glass capillary on a Nicolet *P*3/*m* automated four-circle diffractometer. Of the total 4 814 reflections measured at 200 K, 4 347 were deemed independent, and satisfied the criteria $I \geqslant 1\sigma(I)$. The data were corrected for Lorentz, polarisation, and *X*-ray absorption effects, the latter by an empirical method [19] using azimuthal scan data ($\mu R = 0.275$).

Crystal data. $C_{27}H_{30}MoO_7Rh_2$, $M = 767.3$, monoclinic, $a = 9.625(4)$, $b = 17.500(8)$, $c = 16.714(9)$ Å, $\beta = 97.72(2)°$, $U = 2\,790(2)$ Å^3, $Z = 4$, $D_c = 1.83$ g cm^{-3}, $F(000) = 1\,520$, space group $P2_1/n$ (no. 14, non-standard setting), Mo-K_α *X*-radiation, graphite monochromator, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 16.2 cm^{-1}; θ—2θ scans, $2\theta \leqslant 50°$.

The structure was solved by Patterson methods, and all the non-hydrogen atoms located by successive electron-density difference syntheses. Refinement, by blocked-cascade least squares, was carried out using anisotropic thermal parameters for all non-hydrogen atoms. The methyl group H atoms were incorporated at calculated positions (C–H 0.96 Å), and refined as members of rigid methyl groups. Refinement converged at *R* 0.026 (*R′* 0.025) with weights applied according to the scheme $w = [\sigma^2(F_o) + 0.000\,13|F_o|^2]^{-1}$. All computations were carried out within the laboratory on an Eclipse (Data General) computer with the SHELXTL system of programs.[19] Scattering factors, with corrections for anomalous dispersion, were from ref. 20. Atom co-ordinates for complex (2) are given in Table 3.

EHMO Calculations.—Hückel parameters for all calculations were from ref. 21. A series of EHMO calculations [22] were carried out to establish the validity of the approximations made. Thus calculations were performed on $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_4H)_2]$ with C–H distances set to 1.08 Å using the geometry derived from the structural analysis of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$,[4] and on $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ using an identical atomic arrangement, merely replacing the eight methyl groups by hydrogen atoms. In addition, four geometries for the model species $[MoRh_2(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5H_5)_2]$ were investigated: (*i*) as in the structure of compound (2), replacing Me groups by H atoms; (*ii*) as for (*i*), but rotating the $Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$ fragment by 45° about the Mo–Rh$_2$ centroid axis, and the C_5H_5 ligands by 36° about their Rh–C_5H_5 centroid axes; (*iii*) using the relative fragment orientations as in (1), but with full C_{2v} symmetry and Rh–Rh 2.62, C–C 1.42, C–O(bridge) 1.19, C–O(terminal) 1.15, μ-C–Rh 2.00, Rh–C(H) 2.25, Mo–C 2.03, and Mo–Rh 3.01 Å, Mo–C–O 180, $\xi = 150$, $\phi = 180$, and $\theta = 90°$; (*iv*) as for (*iii*), but with the fragments rotated as in (*ii*). For each situation the molecular orbitals for the full molecule and its constituent $Mo(CO)_5$ and $Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$ fragments were calculated. These calculations showed: (*a*) the replacement of Me groups by H did not alter the characteristics of the frontier orbitals of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ markedly, the a_1 being lowered in energy by *ca.* 0.16 eV, the energies of the other orbitals by 0.04—0.09 eV; (*b*) constraining the molecular geometry of $[MoRh_2(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5H_5)_2]$ to C_{2v} with $\xi = 150$, $\phi = 180$, and $\theta = 90°$ raises the calculated total energy of this species by *ca.* 0.3 eV, but does not significantly affect the nature and symmetry of the frontier orbitals, or the magnitude and direction of the conformational preference discussed above. Figure 3 illustrates the results of calculations using geometries (*iii*) and (*iv*).

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