The Synthesis of some Bi- and Tri-metallic Clusters containing Rhodium; *X*-Ray Crystal Structures of $[MoRh_3(\mu_3\text{-}CO)_3(CO)_3(PPh_3)_3\text{-}(\eta\text{-}C_5H_5)]\cdot CH_2Cl_2$ and $[MoRhPt(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu\text{-}1\text{-}\sigma{:}1\text{—}2\text{-}\eta\text{-}C_6H_5)\text{-}(PPh_3)_2(\eta\text{-}C_5H_5)]$ *

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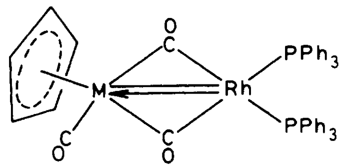
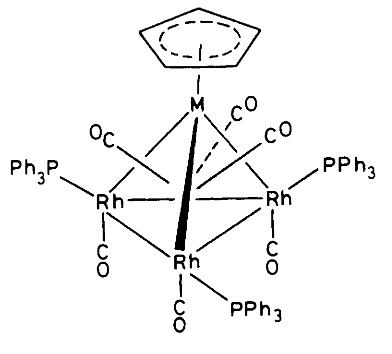
Treatment of the complexes $[MRh(\mu\text{-}CO)_2(CO)(PPh_3)_2(\eta\text{-}C_5H_5)]$ (M = Mo or W) with $[Fe_2(CO)_9]$ in tetrahydrofuran at room temperature affords the tetranuclear 56 valence-electron cluster compounds $[MRh_3(\mu_3\text{-}CO)_3(CO)_3(PPh_3)_3(\eta\text{-}C_5H_5)]$. The structure of the molybdenumtrirhodium species, which crystallises with a molecule of CH_2Cl_2, has been established by a single-crystal *X*-ray diffraction study. The metal-atom core approximates to a regular tetrahedron, with Rh–Rh separations 2.710(1)—2.729(1) Å, and Mo–Rh distances 2.764(1)—2.778(1) Å. The molybdenum atom carries the $\eta\text{-}C_5H_5$ ligand, and a CO and a PPh_3 group are attached to each rhodium atom. These terminal carbonyl ligands are directed below the Rh_3 triangle, and the three ligated phosphorus atoms lie above. In addition, a CO group triply bridges each of the $MoRh_2$ faces of the cluster. The reaction between $[MoRh(\mu\text{-}CO)_2(CO)(PPh_3)_2(\eta\text{-}C_5H_5)]$ and $[Pt(C_2H_4)(PPh_3)_2]$ in tetrahydrofuran at 50 °C yields the complexes $[MoPt(\mu\text{-}PPh_2)(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)]$ and $[MoRhPt(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu\text{-}1\text{-}\sigma{:}1\text{—}2\text{-}\eta\text{-}C_6H_5)\text{-}(PPh_3)_2(\eta\text{-}C_5H_5)]$. The structure of the 44 valence-electron trimetal compound has been determined by *X*-ray diffraction. The three metal atoms form a triangle [Mo–Pt 2.958(1), Mo–Rh 2.619(1), and Pt–Rh 2.662(1) Å], the molybdenum atom carries the $\eta\text{-}C_5H_5$ ligand, and the platinum and rhodium atoms are co-ordinated by PPh_3 groups. The three edges of the metal triangle are bridged; the Mo–Rh edge by two CO ligands, the Mo–Pt by PPh_2, and the Rh–Pt by a C_6H_5 group. One carbon of the phenyl group is σ bonded to platinum and together with an adjacent carbon is η^2-co-ordinated to the rhodium. The n.m.r. data (^1H, $^{13}C\text{-}\{^1H\}$, and $^{31}P\text{-}\{^1H\}$) for the new compounds are reported and discussed.



(1a); M = Mo
(1b); M = W



(2a); M = Mo
(2b); M = W

Various organometallic complexes containing two or more different transition elements have been prepared by adding co-ordinatively unsaturated metal–ligand fragments to di- or tri-metal compounds possessing multiple metal–metal bonds.[1,2] Among unsaturated species, the compounds $[Os_3(\mu\text{-}H)_2(CO)_{10}]$,[3,4] $[M_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (M = Co [5] or Rh [6]), $[MM'(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (M = Co, M′ = Rh [7]; M = Co, M′ = Ir [8]), $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$,[9,10] and $[Re_2(\mu\text{-}H)_2(CO)_8]$ [11] have been successfully employed in combination with 'carbene-like' metal–ligand fragments [2] such as $Pt(CO)(PPh_3)$, $Pt(\eta\text{-}C_8H_{12})$, $Co(CO)(\eta\text{-}C_5H_5)$, $Fe(CO)_4$, $Mn(CO)_2(\eta\text{-}C_5H_5)$, or $Mo(CO)_5$. Recently the interesting bimetal compounds (1) have been reported.[12] The structure of $[MoRh(\mu\text{-}CO)_2\text{-}(CO)(PPh_3)_2(\eta\text{-}C_5H_5)]$ (1a) has been established by *X*-ray diffraction and the metal–metal distance [2.588(1) Å] corresponds to that expected for a double bond. To account for this structural feature, it is proposed that a Mo–Rh σ bond is supplemented by a donor link from rhodium to molybdenum. Irrespective of the details of the metal–metal interaction, the compounds (1) are electronically unsaturated, since they have only 30 valence electrons, rather than the 34 required to give 18 electron configurations at both metal centres. They are thus prime candidates for studies with co-ordinatively unsaturated metal–ligand fragments, and in this paper we describe reactions with $[Fe_2(CO)_9]$ and with $[Pt(C_2H_4)(PPh_3)_2]$, sources of $Fe(CO)_4$ and $Pt(PPh_3)_2$, respectively. It was anticipated that the products would contain molybdenum and rhodium with iron or platinum. However, although reactions readily occurred, the products were unexpected in nature.

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* 1,2,4;2,3,4;1,3,4-Tri-μ_3-carbonyl-1,2,3-tricarbonyl-4-η^5-cyclopentadienyl-1,2,3-tris(triphenylphosphine)-*tetrahedro*-trirhodiummolybdenum(3 *Mo–Rh*)(3 *Rh–Rh*) and 2,3;2,3-di-μ-carbonyl-3-η^5-cyclopentadienyl-1,3-μ-diphenylphosphido-[μ-σ:η^2-phenyl-$C^1(Pt^1)$: $C^{1,2}(Rh^2)$]-1,2-bis(triphenylphosphine)-*triangulo*-platinumrhodiummolybdenum(*Pt–Rh*)(*Pt–Mo*)(*Rh=Mo*) respectively.

Supplementary data available (No. SUP 56024, 13 pp.): full bond distances and angles, thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

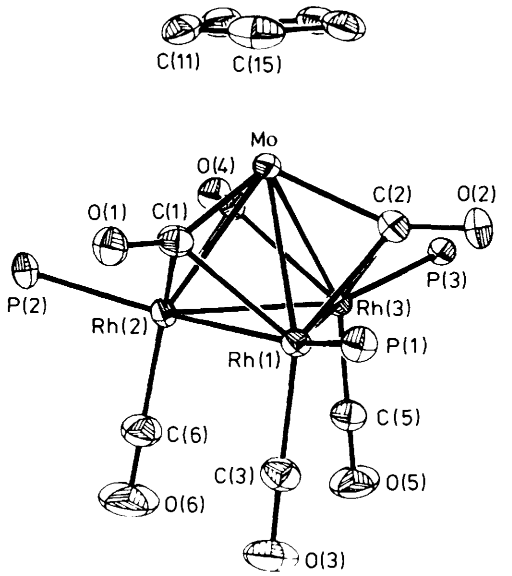


Figure 1. The molecular structure of $[MoRh_3(\mu_3\text{-}CO)_3(CO)_3(PPh_3)_3(\eta\text{-}C_5H_5)]\cdot CH_2Cl_2$ (2a), showing the crystallographic numbering. Phenyl groups have been omitted for clarity

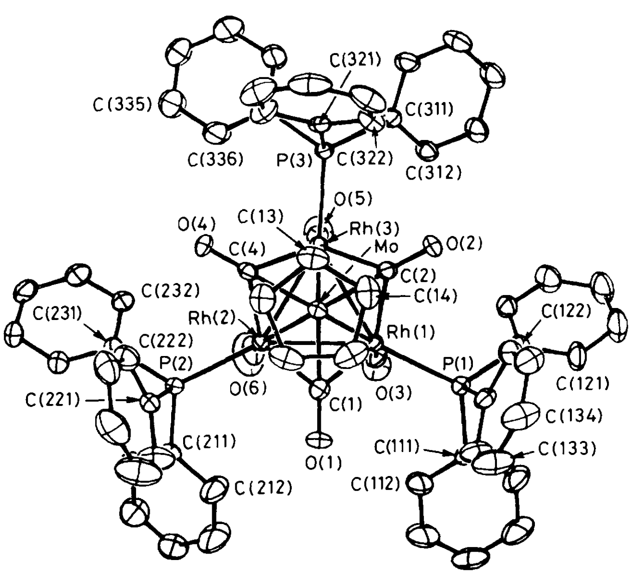


Figure 2. Complex (2a) viewed down the pseudo-three-fold axis perpendicular to the Rh_3 mean plane

Results and Discussion

Treatment of compound (1a) with excess of $[Fe_2(CO)_9]$ in tetrahydrofuran (thf) at room temperature gave a dark solution. Three products were separated by column chromatography on alumina. Two of these products were identified as the known compounds $[Fe(CO)_4(PPh_3)]$ and $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$, while the third was a dark green complex (2a). Reaction between (1b) and $[Fe_2(CO)_9]$ proceeded similarly, yielding $[Fe(CO)_4(PPh_3)]$, $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$, and (2b). The compounds (2) had very similar spectroscopic properties (i.r. and n.m.r.) and were regarded as isostructural. Discussion of the spectra is deferred, however, until the results of an *X*-ray diffraction study on (2a) are described. It was evident from the microanalytical data that both (2a) and (2b) were not simple trimetal species containing iron.

Table 1. Selected internuclear distances (Å) and bond angles (°) for $[MoRh_3(\mu_3\text{-}CO)_3(CO)_3(PPh_3)_3(\eta\text{-}C_5H_5)]\cdot CH_2Cl_2$ (2a)

Rh(1)–Rh(2)	2.710(1)	Mo–Rh(1)	2.778(1)
Rh(1)–Rh(3)	2.719(1)	Mo–Rh(2)	2.772(1)
Rh(2)–Rh(3)	2.729(1)	Mo–Rh(3)	2.764(1)
Rh(1)–C(1)	2.195(5)	Mo–C(1)	2.036(4)
Rh(1)–C(2)	2.279(4)	Mo–C(2)	2.016(5)
Rh(2)–C(1)	2.242(7)	Mo–C(4)	2.031(6)
Rh(2)–C(4)	2.210(4)	C(1)–O(1)	1.188(6)
Rh(3)–C(4)	2.243(5)	C(2)–O(2)	1.179(6)
Rh(3)–C(2)	2.250(7)	C(3)–O(3)	1.145(7)
Rh(1)–C(3)	1.857(5)	C(4)–O(4)	1.182(6)
Rh(2)–C(6)	1.880(7)	C(5)–O(5)	1.127(8)
Rh(3)–C(5)	1.868(6)	C(6)–O(6)	1.121(9)
Mean Rh–P	2.298(1)	Mean Mo–C(cp) *	2.332(2)
Mo–C(1)–O(1)	150.8(5)	Rh(1)–C(3)–O(3)	179.6(6)
Mo–C(2)–O(2)	155.2(5)	Rh(2)–C(6)–O(6)	179.0(6)
Mo–C(4)–O(4)	154.2(4)	Rh(3)–C(5)–O(5)	177.3(5)
Rh(1)–C(1)–O(1)	121.1(3)	Rh(2)–Rh(1)–P(1)	151.4(1)
Rh(2)–C(1)–O(1)	120.3(5)	Rh(3)–Rh(1)–P(1)	143.7(1)
Rh(2)–C(4)–O(4)	119.1(4)	Rh(1)–Rh(2)–P(2)	150.2(1)
Rh(3)–C(4)–O(4)	118.0(4)	Rh(3)–Rh(2)–P(2)	144.7(1)
Rh(3)–C(2)–O(2)	119.2(4)	Rh(1)–Rh(3)–P(3)	144.9(1)
Rh(1)–C(2)–O(2)	118.0(3)	Rh(2)–Rh(3)–P(3)	150.6(1)

* cp = $\eta\text{-}C_5H_5$.

The structure of (2a) is shown in Figures 1 and 2, with the atom-numbering scheme; some selected bond distances and angles are given in Table 1. The molecule contains an essentially regular $MoRh_3$ metal-atom core, with Rh–Rh separations of 2.710(1)—2.729(1) Å, and Mo–Rh distances of 2.764(1)—2.778(1) Å. The Rh–Rh separations appear normal for tetranuclear species, and may be compared with $[Rh_4(CO)_{12}]$ [2.701(8)—2.734(7) Å (non-bridged) and 2.716(6)—2.796(8) Å (bridged)],[13] $[FeRh_3(\mu\text{-}PPh_2)_2(CO)_8]$ [2.71(1)—2.86(1) Å],[14] and $[Rh_4(\mu\text{-}H)_4(\eta\text{-}C_5Me_5)_4][BF_4]_2$ [2.610(5) and 2.829(5) Å].[15] The last cluster, with 58 valence electrons, is unsaturated, as is (2a) with 56. In accord with this feature, the Mo–Rh distances in (2a) appear to be somewhat short. Thus in $[MoRh(\mu\text{-}PMe_2)_2(CO)_4(\eta\text{-}C_5Me_5)]$ the Mo–Rh separation is 2.912(7) Å,[16] while in $[MoRh_2(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5Me_5)_2]$ [7b] the unsupported single Mo–Rh bonds are 3.001(1) and 3.017(1) Å. These distances fall within the range (2.8—3.0 Å) expected for Mo–Rh linkages.[12]

Ignoring the $\eta\text{-}C_5H_5$ ring, the molecule has near perfect C_{3v} symmetry, as may be best seen from Figure 2. The triply-bridging CO ligands asymmetrically bridge the three $MoRh_2$ faces [Mo–CO, 2.016(5)—2.036(4); Rh–CO, 2.195(5)—2.279(4) Å]. Moreover, these C–O vectors, although mutually coplanar, are not perpendicular to their respective $MoRh_2$ faces but are tilted away from the molybdenum at angles of 15.4, 18.0, and 18.5° for C(1)–O(1), C(2)–O(2), and C(4)–O(4), respectively. From Figure 2 it can be seen that the Mo–C(2) and Mo–C(4) vectors are partially eclipsed by the cyclopentadienyl ring carbon atoms C(14) and C(12), respectively, whilst Mo–C(1) is staggered relative to C(11) and C(15). This factor presumably accounts for the *ca.* 3° difference in the tilt angle for C(1)–O(1). The shorter $Mo\text{-}\mu_3\text{-}CO$ distances compared with those for $Rh\text{-}\mu_3\text{-}CO$ are accompanied by larger Mo–C–O angles [150.8(5)—155.2(5)° *versus* 118.0(4)—121.1(3)° for Rh–C–O], indicating a greater interaction between the bridging CO ligands and molybdenum, compared with the rhodium centres. Hence the μ-CO ligands

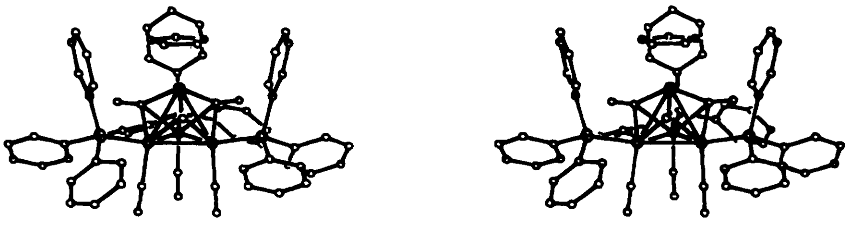


Figure 3. Stereoscopic view of (2a), illustrating the conformation of the phenyl groups, and the steric protection afforded the metal atoms

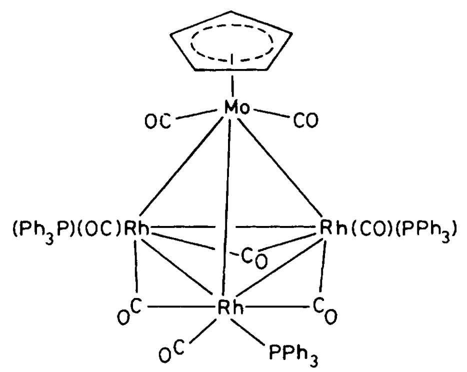
are best described as 'semi-triply bridging'. Formally a symmetric μ_3-CO ligand donates two-thirds of an electron to each metal atom and with this proviso there is a 16 electron configuration at molybdenum. Clearly in (2a) all the metal atoms are electron deficient in terms of the 18 electron formalism, and it is likely that the unsaturation is delocalised over the whole $MoRh_3$ framework. However, the greater Mo–μ_3-CO interactions would tend to reduce electron deficiency at the molybdenum centre. Clusters such as (2a) with 56 valence electrons are rare, but another example is the compound $[Re_4(\mu\text{-}H)_4(CO)_{12}]$.[17]

The PPh_3 and terminal CO ligands in (2a) display the usual geometry, and the cyclopentadienyl group lies almost parallel with the plane of the rhodium atoms. From the stereoview (Figure 3) it can be seen that the disposition of the phenyl rings accounts for the relatively high shielding observed (see below) for the C_5H_5 protons in the ^1H n.m.r. spectrum. Close non-bonded contacts between phenyl group carbon atoms and the cyclopentadienyl hydrogen atoms range from 2.74 to 3.83 Å, the nearest contact being H(13) $\cdots$ C(323). The ring currents of the phenyl groups are presumably responsible for the anomalous shielding, an effect also observed by previous workers [18] for the protons on the third and fourth carbon atoms from the metal in the complexes $[IrCl_2\{(CH_2)_nMe\}(CO)(PPh_3)_2]$ ($n > 3$). Figure 3 also illustrates the severe steric restraints involved in accessibility of the metal atoms to ligand attack. The relative chemical inertness of this highly unsaturated cluster may be in part attributed to steric factors.

In solution, the spectroscopic data for the compounds (2) are consistent with the solid-state structure established for (2a). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed that the environments of the ligated phosphorus nuclei are equivalent. The spectrum consisted of a symmetric 24 line pattern which was analysed by iterative procedures in terms of an $(AX)_3$ spin system yielding the following parameters: J(RhP) -173, J(RhRh) $+3$, and J(PP) $+51$ Hz. The value of J(RhP) is in accord with previous observations,[19] whilst that found for J(RhRh) may be compared with the values of 8.2 and 10.3 Hz recorded from the spectra of the compounds $[Rh_4(\mu_3\text{-}H)_4(\eta\text{-}C_5Me_5)_4][BF_4]_2$ and $[Rh_3(\mu\text{-}H)_3(\mu_3\text{-}O)(\eta\text{-}C_5Me_5)_3][PF_6]$,[15,20] respectively.

The ^1H n.m.r. spectra of the complexes (2) show resonances for the η-C_5H_5 protons [(2a), δ 3.80; (2b), δ 3.87] *ca.* 1 p.p.m. upfield from the usual shift for such signals.[21] As mentioned above, this shielding is attributed to the proximity of the phenyl rings.

The local symmetry of the bridging CO ligands in (2a) is D_{3h}, since they are coplanar and the inter-vector angles are close to 120°. Hence one band (E' mode) is expected in the CO stretching region of the i.r. spectrum. However, in addition to a medium band at 1 689 cm^{-1}, there is a weak absorption at 1 724 cm^{-1}, tentatively assigned to the A_1 symmetric stretching mode. This observation is in accord with the overall C_{3v} symmetry of the molecule. The i.r. spectrum of (2b) shows CO stretching bands at 1 717w and 1 680m cm^{-1}, as expected for a species with similar structure.

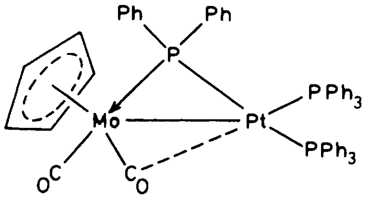


(3)

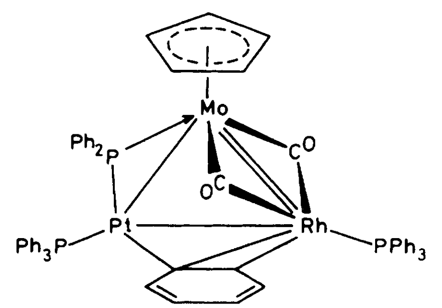
The very unsaturated nature of (2a) suggested that it might react readily with donor ligands, but the steric restrictions revealed by the X-ray diffraction study implied limited reactivity. In order to investigate this matter, the reaction between (2a) and CO, a ligand with low steric requirements, was studied. On saturating a thf solution of (2a) with CO the colour changed from dark green to orange, and new bands appeared in the i.r. spectrum at 2 028m, 1 995m, 1 971s, 1 928m, 1 895w, and 1 833w cm^{-1}. Moreover, the ^1H n.m.r. spectrum of the orange solution showed a characteristic resonance for an η-C_5H_5 ligand at δ 5.24 and the signal in the spectrum of (2a) at δ 3.80 had disappeared. On purging the orange solution with nitrogen, it reverted to the green colour of (2a) and the peak in the ^1H n.m.r. spectrum at δ 3.80 reappeared. It thus became evident that (2a) reacts reversibly with carbon monoxide. Instability of the orange product has prevented characterisation, but it is tentatively proposed that it is the 60 electron complex $[MoRh_3(\mu\text{-}CO)_3(CO)_5(PPh_3)_3(\eta\text{-}C_5H_5)]$ (3). A similar $MoCo_3$ compound, $[Co_3Mo(\mu\text{-}CO)_3(CO)_8(\eta\text{-}C_5H_5)]$, has been structurally characterised,[22] having three $Co(CO)_2$ groups instead of the three Rh(CO)(PPh_3) fragments present in (2a). Steric crowding around the basal plane may be responsible for the instability of (3), and its ready reversion to (2a).

Formation of the compounds (2) by treating the species (1) with $[Fe_2(CO)_9]$ is obviously a complicated process. The $[Fe_2(CO)_9]$ evidently functions as a source of CO, which replaces co-ordinated PPh_3 at rhodium, and leads to the isolation of $[Fe(CO)_4(PPh_3)]$. No evidence was obtained for any iron containing cluster resulting from addition of 'carbene-like' $Fe(CO)_4$ to the multiple bond of (1). However, such an addition process might be the first step in a sequence of reactions leading to the final products. The formation of the species $[M_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (M = Mo or W) shows that M–Rh bond fission also occurs in the reactions leading to (2). In view of these results, the reaction between (1a) and $[Pt(C_2H_4)(PPh_3)_2]$ was investigated, since the latter is a source of the inorganic 'carbene' $Pt(PPh_3)_2$.

Treatment of (1a) with $[Pt(C_2H_4)(PPh_3)_2]$ in thf at 50 °C afforded a dark solution from which an orange complex (4),



(4)



(5)

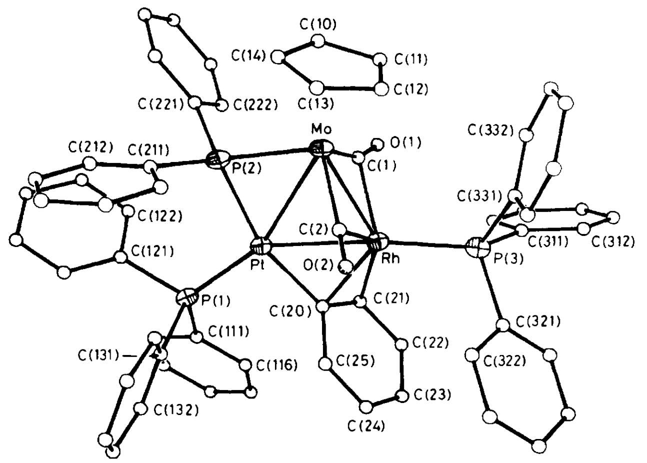


Figure 4. The molecular structure of [MoRhPt(μ-CO)$_2$(μ-PPh$_2$)(μ-1-σ:1—2-η-C$_6$H$_5$)(PPh$_3$)$_2$(η-C$_5$H$_5$)] (5), showing the crystallographic numbering

Table 2. Selected internuclear distances (Å) and bond angles (°) for [MoRhPt(μ-CO)$_2$(μ-PPh$_2$)(μ-1-σ:1—2-η-C$_6$H$_5$)(PPh$_3$)$_2$(η-C$_5$H$_5$)] (5)

Mo–Rh	2.619(1)	Pt–C(20)	2.070(8)
Mo–Pt	2.958(1)	Rh–C(20)	2.163(7)
Pt–Rh	2.662(1)	Rh–C(21)	2.412(8)
Pt–P(1)	2.246(2)	C(20)–C(21)	1.411(11)
Rh–P(3)	2.250(2)	C(21)–C(22)	1.398(13)
Mo–P(2)	2.381(2)	C(22)–C(23)	1.341(15)
Pt–P(2)	2.296(2)	C(23)–C(24)	1.393(14)
Mo–C(1)	2.029(8)	C(24)–C(25)	1.380(13)
Mo–C(2)	2.014(8)	C(25)–C(20)	1.418(11)
Rh–C(1)	2.141(9)		
Rh–C(2)	2.189(8)		
Mean Mo–C(cp) *	2.334(7)		
Mo–Pt–Rh	55.3(11)	Pt–C(20)–Rh	77.9(2)
Mo–Rh–Pt	68.1(1)	C(20)–Rh–C(21)	35.4(3)
Pt–Mo–Rh	56.6(1)	Pt–Rh–P(3)	174.2(1)
Pt–P(2)–Mo	78.4(1)	Rh–Pt–P(1)	147.4(1)
Mo–C(1)–O(1)	160.1(7)	P(2)–Pt–C(20)	159.1(2)
Rh–C(1)–O(1)	121.4(6)		
Mo–C(2)–O(2)	160.2(6)		
Rh–C(2)–O(2)	121.5(6)		

* cp = η-C$_5$H$_5$.

and a green compound (5) could be isolated. Microanalytical and spectroscopic data for [MoPt(μ-PPh$_2$)(CO)$_2$(PPh$_3$)$_2$(η-C$_5$H$_5$)] (4) established the bimetal structure shown. The ^{31}P-{^{1}H} n.m.r. spectrum was especially informative, showing three resonances, each a doublet of doublets with ^{195}Pt satellite peaks. The signal at lowest field (δ 186.8 p.p.m.) is characteristic [23] for a μ-PPh$_2$ group bridging a metal–metal bond, the large ^{195}Pt–^{31}P coupling (2 599 Hz) confirming that the phosphido-ligand was attached to a platinum atom. The other signals at δ 29.1 and 27.1 can be ascribed to a *cis*-Pt(PPh$_3$)$_2$ group [*J*(PP) 4 Hz] in which the phosphorus nuclei are non-equivalent. Strong ^{31}P–^{31}P coupling (218 Hz) between the phosphido-nucleus and the phosphorus resonating at δ 29.1 suggests that these two nuclei are mutually *transoid*, with a *cisoid* coupling (11 Hz) of μ-PPh$_2$ to the third phosphorus resonating at δ 27.1. In agreement with this assignment, the latter signal shows the stronger ^{195}Pt–^{31}P coupling (3 372 Hz), in accord with this PPh$_3$ group being *transoid* to the Mo–Pt bond.[24] The ^{1}H n.m.r. spectrum has a characteristic signal for the η-C$_5$H$_5$ group at δ 4.46.

The i.r. spectrum of (4) has CO stretching bands at 1 906 and 1 816 cm^{-1}. However, the ^{13}C-{^{1}H} n.m.r. spectrum, when measured at room temperature, showed no resonances for these ligands, indicating rapid site-exchange on the n.m.r. time-scale at *ca.* 25 °C. Measurement of the spectrum at −40 °C resulted in the appearance of two broad CO bands at δ 241.3 and 236.1 p.p.m., with unresolved coupling. The signal at δ 236.1, however, had ^{195}Pt satellite peaks [*J*(PtC) 50 Hz], consistent with incipient semi-bridging, a feature further indicated by the low-frequency i.r. stretching band at 1 816 cm^{-1}.

The analytical and spectroscopic data for [MoRhPt(μ-CO)$_2$(μ-PPh$_2$)(μ-1-σ:1—2-η-C$_6$H$_5$)(PPh$_3$)$_2$(η-C$_5$H$_5$)] (5) did not establish the molecular structure, and so a single-crystal *X*-ray diffraction study was carried out. The molecular structure is shown in Figure 4, and the important internuclear distances and bond angles are given in Table 2. The core of the molecule consists of a triangle of metal atoms MoRhPt with metal atom separations: Mo–Rh 2.619(1), Mo–Pt 2.958(1), and Pt–Rh 2.662(1) Å. Each edge of the triangle has bridging ligands, the Mo–Pt vector being asymmetrically bridged by a PPh$_2$ group [Mo–P(2), 2.381(2) and Pt–P(2), 2.296(2) Å]. Diphenylphosphido-ligands also asymmetrically bridge the metal-metal bonds in the heteronuclear complexes [FeIr(μ-PPh$_2$)(CO)$_5$(PPh$_3$)$_2$] [Fe–P, 2.239(2) and Ir–P, 2.292(2)] [25] and [Mn$_2$Pt(μ-PPh$_2$)$_2$(CO)$_9$] [Mn–P, 2.239(3) and Pt–P, 2.312(3) Å].[26]

Interestingly, the $\overline{\text{Mo}(\mu\text{-CO})_2\text{Rh}}$ fragment present in (1a) also occurs in (5), with the Mo–Rh separation in the former being slightly shorter (*ca.* 0.03 Å). Corresponding bond lengths and angles in each $\overline{\text{Mo}(\mu\text{-CO})\text{Rh}}$ unit within (5) are identical within experimental error (Table 2), whereas in (1a) there is greater asymmetry.[12] The $\overline{\text{Mo}(\mu\text{-CO})_2\text{Rh}}$ fragment in (5) is nearly planar, with a dihedral angle of 7° between the mean planes defined by Mo,Rh,C(1),O(1) and Mo,Rh,C(2),O(2).

The Rh–Pt edge of the cluster is bridged by a phenyl group, evidently produced by cleavage from a PPh_3 ligand in (1a). This phenyl group is σ bonded to the platinum [C(20)–Pt, 2.070(8) Å] and η^2-co-ordinated to the rhodium [C(20)–Rh, 2.163(7) and C(21)–Rh, 2.412(8) Å]. Indeed C(20)–C(21) can be viewed as part of a μ-vinyl system. The longer C(21)–Rh distance (*ca.* 0.25 Å), compared with C(20)–Rh, is as expected in comparison with other bridged vinyl systems.[27] In the compound $[Os_4(\mu\text{-}H)_3(\mu\text{-}C_6H_9)(CO)_{11}]$, containing a bridging cyclohexene ring, σ bonded to one osmium and π bonded to the other,[28] the η^2-C_2–Os distances differ by *ca.* 0.12 Å, the longer separation being associated, as in (5), with the carbon which is not bridging the metal–metal bond. Inspection of the C–C angles and distances within the phenyl ring in (5) reveal no marked deviation from aromaticity. Although the two shortest bonds [C(22)–C(23) and C(24)–C(25)] are positioned as expected for double-bond fixation, the variations observed are not statistically significant. Moreover, the C_6 ring shows no significant loss of planarity; the greatest deviation from the ring plane being for C(23) (0.017 Å). Thus the aromatic system appears to be only slightly perturbed by interacting with the cluster as a three-electron donor. The Pt atom is 0.106 Å out of the C_6 plane and the hydrogen atom H(21) on C(21) shows no significant displacement towards the rhodium [Rh $\cdots$ H(2) 2.64 Å]. Compound (5) appears to be the first example of a trimetal cluster with a phenyl group attached in a σ:η^2-bonding mode.

The rhodium and platinum atoms each carry a PPh_3 ligand, while the η-C_5H_5 group, as expected, is attached to the molybdenum atom. The co-ordination around the platinum is essentially co-planar, taking into account the atoms P(1), P(2), C(20), and the midpoint of the Mo–Rh vector, the greatest deviation from the mean plane being for the Pt atom itself (0.092 Å). This plane is almost perpendicular (92.1°) to the $\overline{Mo(\mu\text{-}CO)_2Rh}$ plane. Overall (5) has 44 valence electrons, four short of the number required to give each metal centre an 18 electron configuration. The Mo–Rh separation is consistent with a double bond,[12] and the platinum is in a 16 electron distorted square-planar environment; thus the 44 valence-electron situation is understandable.

The spectroscopic data for (5) indicate that the compound retains the structure found in the solid state in solution. Thus the ^{31}P-$\{^1H\}$ n.m.r. spectrum shows three distinct phosphorus environments, with signals at δ 155.8, 30.9, and 19.1 p.p.m. The resonance at δ 155.8 is characteristic[23] for the μ-PPh_2 group, and the remaining two signals at 30.9 and 19.1 p.p.m. are as expected for the $Rh(PPh_3)$ [*J*(RhP) 201, *J*(PP) 17 and 3, *J*(PtP) 32 Hz] and $Pt(PPh_3)$ [*J*(RhP) 6, *J*(PP) 17 and 14, *J*(PtP) 4 263 Hz] groups, respectively. A signal at δ 178.0 in the ^{13}C-$\{^1H\}$ n.m.r. spectrum is tentatively assigned to the bridging carbon atom C(20) (Figure 4), in view of the large ^{195}Pt and ^{103}Rh couplings of 716 and 64 Hz, respectively. The chemical shift is in the region normally associated with μ-σ:η^2-*C*=C nuclei.[27] A resonance at δ 260.3 [*J*(RhC) 31 and *J*(PtC) 61 Hz] is assigned to the μ-CO ligands.[6] In the i.r. spectrum a single band at 1 748 cm^{-1} has an unresolved shoulder to high frequency.

Formation of (4) and (5) from (1a) and $[Pt(C_2H_4)(PPh_3)_2]$ is evidently a complex process. Degradation of PPh_3 ligands attached to rhodium to give μ-PPh_2 groups has been observed previously in several reactions.[29] Isolation of compound (4) requires that the Mo–Rh bond in (1a) is cleaved, just as this bond must also be broken in the synthesis of (2a). The reactions described in this paper show that the bimetal compound (1a) is very reactive towards metal–ligand fragments, but that the nature of the products is unpredictable.

Experimental

Light petroleum refers to that fraction of b.p. range 40—60 °C. Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. The n.m.r. measurements were made with JNM-FX 90Q and FX 200 instruments, and i.r. spectra were recorded in thf with a Nicolet 10-MX FT spectrophotometer. The compounds $[MRh(\mu\text{-}CO)_2(CO)(PPh_3)_2(\eta\text{-}C_5H_5)]$ (M = Mo or W)[12] and $[Pt(\eta\text{-}C_8H_{12})_2]$[30] were prepared as discussed elsewhere. The latter complex was used for the *in situ* preparation of $[Pt(C_2H_4)(PPh_3)_2]$.[31]

Reactions between the Compounds $[MRh(\mu\text{-}CO)_2(CO)(PPh_3)_2(\eta\text{-}C_5H_5)]$ (1) *and* $[Fe_2(CO)_9]$.—(*a*) A thf (140 cm^3) solution of (1a; M = Mo) (1.0 g, 1.14 mmol) was stirred (12 h) with $[Fe_2(CO)_9]$ (0.82 g, 2.28 mmol) at ambient temperature. Removal of solvent *in vacuo* afforded a dark green residue. The latter was transferred to the top of an alumina column (15 × 2 cm). Initial elution with toluene–light petroleum (1 : 1) afforded yellow $[Fe(CO)_4(PPh_3)]$ and pink $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ both identified by their i.r. spectra. Further elution with toluene–light petroleum (3 : 1) afforded a green band. Removal of solvent *in vacuo*, and crystallisation of the residue from dichloromethane–light petroleum (1 : 1) gave dark green *crystals* of $[MoRh_3(\mu_3\text{-}CO)_3(CO)_3(PPh_3)_3(\eta\text{-}C_5H_5)]\cdot CH_2Cl_2$ (2a) (0.15 g, 27%) (Found: C, 52.3; H, 3.4. $C_{65}H_{50}MoO_6P_3Rh_3\cdot CH_2Cl_2$ requires C, 52.5; H, 3.5%), m.p. 278 °C (decomp.); $\nu_{max.}$(CO) at 2 000s, 1 955w, 1 724w, and 1 689m cm^{-1}. N.m.r.: ^1H ([$^2H_1$]chloroform), δ 3.80 (s, 5 H, C_5H_5), and 7.2—7.8 p.p.m. (m, 45 H, C_6H_5); ^{13}C-$\{^1H\}$ ([$^2H_1$]chloroform), δ 251.7 [t, μ_3-CO, *J*(RhC) 41], 192.1 [d, CO, *J*(RhC) 66 Hz], 137.8—125.3 (C_6H_5), and 96.3 p.p.m. (C_5H_5); ^{31}P-$\{^1H\}$ {[$^2H_6$]benzene, relative to 85% H_3PO_4 (external), positive values representing shifts to high frequency of the reference}, δ 29.8 p.p.m. [$(AX)_3$ system, *J*(RhP) −173, *J*(RhRh) +3, *J*(PP) +51 Hz, as determined from spectral simulation].

(*b*) In a similar reaction, compound (1b; M = W) (0.8 g, 0.83 mmol) with $[Fe_2(CO)_9]$ (0.61 g, 1.6 mmol) gave $[Fe(CO)_4(PPh_3)]$, $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$, and dark green *crystals* of $[WRh_3(\mu_3\text{-}CO)_3(CO)_3(PPh_3)_3(\eta\text{-}C_5H_5)]$ (2b) (0.05 g, 12%) (Found: C, 51.4; H, 3.2. $C_{65}H_{50}O_6P_3Rh_3W$ requires C, 51.6; H, 3.3%), m.p. 280 °C (decomp.); $\nu_{max.}$(CO) at 1 999s, 1 953w, 1 717w, and 1 680m cm^{-1}. N.m.r.: ^1H ([$^2H_1$]chloroform), δ 3.87 (s, 5 H, C_5H_5) and 7.2—8.0 p.p.m. (m, 45 H, C_6H_5); ^{13}C-$\{^1H\}$ ([$^2H_2$]dichloromethane), δ 243.4 (μ_3-CO), 192.5 (CO), 137.3—128.0 (C_6H_5), and 95.1 p.p.m. (C_5H_5); ^{31}P-$\{^1H\}$, ([$^2H_2$]dichloromethane), δ 26.5 p.p.m. [$(AX)_3$ pattern, *J*(RhP) −176, *J*(RhRh) 3, and *J*(PP) 49 Hz].

Reaction between $[MoRh(\mu\text{-}CO)_2(CO)(PPh_3)_2(\eta\text{-}C_5H_5)]$ (1a) *and* $[Pt(C_2H_4)(PPh_3)_2]$.—Compound (1a) (0.44 g, 0.5 mmol) was treated with a solution of $[Pt(C_2H_4)(PPh_3)_2]$, prepared *in situ* by dissolving $[Pt(\eta\text{-}C_8H_{12})_2]$ (0.28 g, 0.7 mmol) in thf (70 cm^3) at 0 °C, saturating the solution with ethylene, and adding PPh_3 (0.37 g, 1.4 mmol). Ethylene was displaced with nitrogen, and the mixture warmed to *ca.* 50 °C for *ca.* 36 h. The dark solution obtained was evaporated *in vacuo* and the residue transferred to the top of an alumina column (4 × 30 cm) maintained at *ca.* 10 °C. Gradient elution with dichloromethane–light petroleum mixtures (1 : 4—2 : 3) gave trace quantities of yellow and red bands followed by a dark green solution. Removal of solvent *in vacuo* and crystallisation from dichloromethane—diethyl ether by vapour diffusion afforded dark green *crystals* of $[MoRhPt(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu\text{-}1\text{-}\sigma\text{:}1\text{—}2\text{-}\eta\text{-}$

Table 3. Atomic positional (fractional co-ordinates) parameters ($\times 10^4$), with estimated standard deviations in parentheses for [$MoRh_3(\mu_3$-$CO)_3(CO)_3(PPh_3)_3(\eta$-$C_5H_5)]\cdot CH_2Cl_2$ (2a)

Atom	*x*	*y*	*z*
Rh(1)	5 663(1)	7 812(1)	3 018(1)
Rh(2)	4 099(1)	8 650(1)	2 422(1)
Rh(3)	3 562(1)	6 603(1)	2 752(1)
Mo	4 023(1)	7 039(1)	1 479(1)
P(1)	7 292(1)	7 724(1)	3 177(1)
P(2)	3 424(1)	9 819(1)	1 684(1)
P(3)	2 294(1)	4 884(1)	2 529(1)
C(1)	5 234(4)	8 534(4)	1 939(3)
C(2)	4 572(4)	6 140(4)	2 288(3)
C(3)	6 275(4)	8 571(4)	4 024(3)
C(4)	2 758(4)	7 173(4)	1 621(3)
C(5)	3 722(4)	6 944(4)	3 761(3)
C(6)	4 421(5)	9 419(5)	3 373(3)
C(11)	3 851(5)	7 392(5)	230(3)
C(12)	2 841(5)	6 667(4)	124(3)
C(13)	2 957(5)	5 721(4)	364(3)
C(14)	4 053(5)	5 863(5)	610(3)
C(15)	4 609(5)	6 904(5)	524(3)
C(111)	8 474(4)	9 018(4)	3 544(3)
C(112)	8 296(5)	9 942(5)	3 440(4)
C(113)	9 174(6)	10 936(6)	3 685(5)
C(114)	10 203(6)	11 008(6)	4 018(4)
C(115)	10 412(5)	10 103(6)	4 142(5)
C(116)	9 547(5)	9 109(6)	3 900(4)
C(121)	7 728(4)	6 828(4)	3 863(3)
C(122)	8 497(5)	6 423(5)	3 878(4)
C(123)	8 797(6)	5 762(6)	4 400(5)
C(124)	8 340(7)	5 476(6)	4 909(5)
C(125)	7 576(6)	5 843(6)	4 899(4)
C(126)	7 261(5)	6 509(4)	4 370(3)
C(131)	7 330(4)	7 248(4)	2 294(3)
C(132)	7 715(5)	7 938(5)	1 856(3)
C(133)	7 672(6)	7 557(5)	1 161(4)
C(134)	7 255(5)	6 486(5)	912(4)
C(135)	6 852(5)	5 786(5)	1 325(4)
C(136)	6 874(5)	6 149(4)	2 007(3)
C(211)	4 406(4)	11 220(4)	2 063(4)
C(212)	4 166(6)	12 015(5)	2 257(5)
C(213)	4 984(7)	13 048(5)	2 588(6)
C(214)	5 989(7)	13 280(5)	2 716(5)
C(215)	6 271(7)	12 503(6)	2 528(7)
C(216)	5 482(6)	11 472(5)	2 215(7)
C(221)	3 047(4)	9 667(4)	634(3)
C(222)	2 063(5)	8 872(5)	124(3)
C(223)	1 767(6)	8 698(5)	−669(4)
C(224)	2 463(7)	9 311(6)	−972(4)
C(225)	3 432(8)	10 087(7)	−463(5)
C(226)	3 728(6)	10 274(6)	317(4)
C(231)	2 150(4)	9 824(4)	1 664(3)
C(232)	1 767(4)	9 276(4)	2 183(4)
C(233)	824(5)	9 308(5)	2 192(4)
C(234)	287(5)	9 870(5)	1 719(4)
C(235)	628(5)	10 378(5)	1 187(4)
C(236)	1 559(4)	10 346(5)	1 167(4)
C(311)	2 835(4)	3 972(4)	3 146(3)
C(312)	3 887(4)	4 394(4)	3 753(3)
C(313)	4 354(5)	3 739(5)	4 215(4)
C(314)	3 751(5)	2 642(5)	4 067(4)
C(315)	2 695(5)	2 210(5)	3 449(4)
C(316)	2 243(5)	2 868(4)	2 992(3)
C(321)	1 668(4)	4 126(4)	1 539(3)
C(322)	2 171(5)	3 539(4)	1 358(3)
C(323)	1 686(6)	2 986(4)	594(4)
C(324)	748(5)	3 040(5)	12(3)
C(325)	292(5)	3 651(6)	200(4)
C(326)	726(4)	4 189(5)	948(3)
C(331)	1 074(4)	4 808(4)	2 646(3)
C(332)	484(6)	3 964(6)	2 885(5)
C(333)	−475(7)	3 929(7)	2 898(6)
C(334)	−857(6)	4 706(6)	2 673(5)
C(335)	−269(6)	5 552(6)	2 460(6)
C(336)	715(6)	5 607(5)	2 470(5)
O(1)	5 883(3)	9 327(3)	1 878(2)
O(2)	4 842(3)	5 421(3)	2 512(2)
O(3)	6 647(4)	9 040(4)	4 643(2)
O(4)	1 834(2)	7 075(3)	1 405(2)
O(5)	3 861(4)	7 161(4)	4 381(2)
O(6)	4 598(5)	9 867(5)	3 940(3)
Cl(1)	8 360(4)	2 197(6)	5 985(3)
Cl(2)	7 996(9)	2 264(9)	4 560(5)
C(7)	7 403(9)	1 698(10)	5 074(11)

$C_6H_5)(PPh_3)_2(\eta$-$C_5H_5)]$ (5) (0.25 g, 38%) (Found: C, 56.5; H, 3.7. $C_{61}H_{50}MoO_2P_3PtRh$ requires C, 56.3; H, 3.8%), m.p. 228 °C (decomp.); $\nu_{max.}$(CO) at 1 748br cm^{-1}. N.m.r.: ^1H ([$^2H_2$]dichloromethane), δ 4.29 (s, 5 H, C_5H_5) and 6.33—7.31 p.p.m. (m, 45 H, C_6H_5); ^{13}C-{^1H} ([$^2H_1$]chloroform), δ 260.3 [d, μ-CO, *J*(RhC) 31, *J*(PtC) 61], 178.0 [d, μ-CPtRh, *J*(RhC) 64, *J*(PtC) 716 Hz], 143.0—121.8 (C_6H_5), and 89.6 p.p.m. (C_5H_5); ^{31}P-{^1H} ([$^2H_2$]dichloromethane), δ 155.8 [d of d of d, μ-PPh_2, *J*(PP) 14 and 3, *J*(RhP) 1, *J*(PtP) 1 830], 30.9 [d of d of d, $RhPPh_3$, *J*(PP) 17 and 3, *J*(RhP) 201, *J*(PtP) 32], and 19.1 p.p.m. [d of d of d, $PtPPh_3$, *J*(PP) 17 and 14, *J*(RhP) 6, *J*(PtP) 4 263 Hz].

Further elution of the column gave an orange solution which after treatment as above gave orange *microcrystals* of [MoPt-(μ-$PPh_2)(CO)_2(PPh_3)_2(\eta$-$C_5H_5)$] (4) (0.16 g, 28% based on Pt used) (Found: C, 57.9; H, 4.0. $C_{55}H_{45}MoO_2P_3Pt$ requires C, 58.8; H, 4.0%), m.p. 234 °C (decomp.); $\nu_{max.}$(CO) at 1 906s and 1 816s cm^{-1}. N.m.r.: ^1H ([$^2H_1$]chloroform), δ 4.46 (s, 5 H, C_5H_5) and 6.76—7.61 p.p.m. (m, 40 H, C_6H_5); ^{13}C-{^1H} ([$^2H_2$]dichloromethane), δ 136.7—127.1 (C_6H_5) and 88.9 p.p.m. (η-C_5H_5); at −40 °C ([$^2H_8$]toluene), δ 241.3 [d, CO, *J*(PC) 20], 236.1 [d, CO, *J*(PC) 7, *J*(PtC) 50 Hz], 137.6—124.3 (C_6H_5), and 88.8 p.p.m. (C_5H_5); ^{31}P-{^1H} ([$^2H_2$]dichloromethane), δ 186.8 [d of d, μ-PPh_2, *J*(PP) 218 and 11, *J*(PtP) 2 599], 29.1 [d of d, PPh_3 *trans* to μ-PPh_2, *J*(PP) 218 and 4, *J*(PtP) 3 271], and 27.1 p.p.m. [d of d, PPh_3 *cis* to μ-PPh_2, *J*(PP) 11 and 4, *J*(PtP) 3 372 Hz].

Crystal Structure Determination of [$MoRh_3(\mu_3$-$CO)_3(CO)_3(PPh_3)_3(\eta$-$C_5H_5)]\cdot CH_2Cl_2$ (2a).—Liquid–liquid diffusion of light petroleum into a solution of (2a) in dichloromethane afforded dark green prisms. A small section (*ca.* 0.15 × 0.24 × 0.36 mm) was cut and mounted on a glass fibre. Intensities were collected at 298 K in the range $2.9 \leqslant 2\theta \leqslant 50°$ using the θ—2θ scan mode, on a Nicolet *P*3*m* diffractometer. Three reflections ($8\,2\,\bar{4}$, $5\,\bar{2}\,\bar{7}$, and $\bar{3}\,4\,\bar{5}$) were remeasured every 50 recorded, and the data showed no significant decay. Of the total 6 913 independent reflections measured, 6 254 satisfied the criterion $I \geqslant 2.5\sigma(I)$, and only these were used in the solution and refinement of the structure. The intensities were corrected for Lorentz and polarisation effects, and an empirical correction was applied for *X*-ray absorption.[32]

Crystal data. $C_{65}H_{50}MoO_6P_3Rh_3\cdot CH_2Cl_2$, $M = 1\,509$, triclinic, $a = 14.510(4)$, $b = 13.486(3)$, $c = 18.935(4)$ Å, $\alpha = 89.22(2)$, $\beta = 114.88(2)$, $\gamma = 110.91(2)°$, $U = 3\,099$ Å^3, $Z = 2$, $D_c = 1.62$ g cm^{-3}, $F(000) = 1\,488$, space group $P\bar{1}$, Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 11.8 cm^{-1}.

Table 4. Atomic positional (fractional co-ordinates) parameters (× 10^4), with estimated standard deviations in parentheses for [MoRhPt(μ-CO)$_2$(μ-PPh$_2$)(μ-1-σ:1—2-η-C$_6$H$_5$)(PPh$_3$)$_2$(η-C$_5$H$_5$)] (5)

Atom	*x*	*y*	*z*
Pt	5 650(1)	1 745(1)	1 765(1)
Mo	6 140(1)	3 208(1)	2 328(1)
Rh	5 044(1)	1 975(1)	2 665(1)
P(1)	5 467(2)	990(1)	1 099(1)
P(2)	6 720(2)	2 837(1)	1 550(1)
P(3)	4 394(2)	2 070(1)	3 412(1)
O(1)	7 631(5)	1 927(4)	2 941(2)
O(2)	3 314(5)	3 150(3)	2 225(2)
C(1)	6 911(8)	2 295(5)	2 709(3)
C(2)	4 347(7)	3 022(4)	2 276(3)
C(112)	6 136(4)	−532(3)	792(2)
C(113)	6 175	−1 356	818
C(114)	5 625	−1 749	1 186
C(115)	5 036	−1 318	1 529
C(116)	4 997	−494	1 503
C(111)	5 547	−101	1 134
C(122)	7 761(4)	1 186(3)	792(2)
C(123)	8 623	1 338	461
C(124)	8 262	1 503	−19
C(125)	7 039	1 515	−168
C(126)	6 177	1 363	162
C(121)	6 538	1 198	642
C(132)	3 332(5)	577(2)	531(2)
C(133)	2 268	766	261
C(134)	1 873	1 549	233
C(135)	2 542	2 143	474
C(136)	3 606	1 955	745
C(131)	4 001	1 172	773
C(212)	6 618(5)	3 210(4)	557(2)
C(213)	6 050	3 513	133
C(214)	4 987	3 948	151
C(215)	4 492	4 080	592
C(216)	5 060	3 778	1 016
C(211)	6 123	3 342	998
C(222)	8 994(7)	2 212(4)	1 745(2)
C(223)	10 249	2 190	1 749
C(224)	10 866	2 772	1 508
C(225)	10 227	3 376	1 263
C(226)	8 972	3 398	1 259
C(221)	8 356	2 816	1 500
C(312)	4 912(5)	1 640(4)	4 382(2)
C(313)	5 531	1 223	4 754
C(314)	6 460	707	4 653
C(315)	6 771	609	4 178
C(316)	6 152	1 026	3 806
C(311)	5 222	1 541	3 908
C(322)	1 994(5)	2 000(3)	3 062(2)
C(323)	786	1 775	3 056
C(324)	398	1 270	3 411
C(325)	1 219	991	3 773
C(326)	2 427	1 216	3 780
C(321)	2 815	1 720	3 425
C(332)	5 447(4)	3 387(3)	3 865(2)
C(333)	5 500	4 178	4 008
C(334)	4 479	4 656	3 944
C(335)	3 406	4 344	3 735
C(336)	3 353	3 553	3 591
C(331)	4 374	3 075	3 656
C(10)	7 739(5)	4 095(4)	2 465(3)
C(11)	7 069	4 049	2 882
C(12)	5 897	4 354	2 760
C(13)	5 843	4 588	2 268
C(14)	6 982	4 428	2 086
C(20)	4 553(7)	1 039(4)	2 158(3)
C(21)	5 045(9)	563(5)	2 540(3)
C(22)	4 344(9)	54(5)	2 801(3)
C(23)	3 157(10)	1(5)	2 684(4)
C(24)	2 607(8)	472(5)	2 321(4)
C(25)	3 288(7)	981(5)	2 061(3)

The metal atoms were located from a Patterson synthesis, and all other non-hydrogen atoms by successive electron-density difference syntheses, including a molecule of dichloromethane as solvent of crystallisation. Hydrogen atoms were incorporated at calculated positions, except for the solvent molecule, with C–H 0.96 Å and $U_H = 1.2 \times U_{iso.}$ of the parent carbon atom. All non-hydrogen atoms were refined with anisotropic thermal parameters. The structure was refined by a blocked-cascade least-squares process, with a weighting scheme of the form $w = [\sigma^2(F_o) + 0.000\ 3|F_o|^2]^{-1}$, where $\sigma(F_o)$ is the estimated error in $|F_o|$ based on counting statistics only, and this gave a satisfactory weight analysis. Convergence was obtained at *R* 0.030 (*R'* 0.032), and a final electron-density difference map showed no peaks >0.85 or < -0.76 e Å^{-3}. Scattering factors and corrections for anomalous dispersion were from ref. 33. All calculations were performed on an 'Eclipse' Data General computer with the SHELXTL system of programs.[32] Atom co-ordinates for compound (2a) are given in Table 3.

Crystal Structure Determination of [MoRhPt(μ-CO)$_2$(μ-PPh$_2$)(μ-1-σ:1—2-η-C$_6$H$_5$)(PPh$_3$)$_2$(η-C$_5$H$_5$)] (5).—Compound (5) was crystallised by vapour diffusion from dichloromethane–diethyl ether. Diffracted intensities were collected at room temperature from a crystal of dimensions *ca.* 0.50 × 0.35 × 0.10 mm, using the ω scan mode. Of the total 6 842 unique reflections for $2.9 \leqslant 2\theta \leqslant 45°$, 4 988 satisfied the criterion $I \geqslant 2.5\sigma(I)$, and only these were used in the solution and refinement of the structure. Three check reflections (0 8 0, 0 3 $\overline{11}$, and $\bar{1}$ 7 $\bar{1}$) were used as standards, with no significant decay being observed. The intensities were corrected for Lorentz and polarisation effects, and numerically for *X*-ray absorption.[32]

Crystal data. $C_{61}H_{50}MoO_2P_3PtRh$, $M = 1\ 301$, monoclinic, $a = 11.116(2)$, $b = 16.902(3)$, $c = 27.792(5)$ Å, $\beta = 93.84(1)°$, $U = 5\ 210(2)$ Å^3, $Z = 4$, $D_c = 1.66$ g cm^{-3}, $F(000) = 2\ 568$, space group $P2_1/n$, $\mu(\text{Mo-}K_\alpha) = 33.8$ cm^{-1}.

The structure was solved as for (2a). The positional parameters of the hydrogen atoms H(22)—H(25) were refined with fixed isotropic thermal parameters (0.06 Å^2), and all remaining hydrogen atoms were included at calculated positions (C–H 0.960 Å, and $U_{iso.} = 1.2$ times that of the parent carbon atom). The phenyl and cyclopentadienyl rings were also refined with fixed geometries (C–C 1.395 and 1.420 Å, respectively). All non-hydrogen atoms were allowed anisotropic thermal parameters. Weights were ascribed according to the scheme $w = [\sigma^2(F_o) + 0.000\ 08|F_o|^2]^{-1}$. Refinement,[32] as for (2a), converged to *R* 0.036 (*R'* 0.034), and a final electron-density synthesis revealed no peaks >1.10 or < -0.69 e Å^{-3}. Scattering factors and corrections for anomalous dispersion were taken from ref. 33. Atom co-ordinates for (5) are listed in Table 4.

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