Reactions of $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(PPh_3)_3]$ with Group 6 Metal Carbonyls. Crystal Structure and Reactivity with Diphosphines of the Linear Heterotrinuclear Complex $[Ru_2Mo\{\mu\text{-}C_6H_4(NH)_2\text{-}1,2\}_2(CO)_6(PPh_3)_2]$†

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The compound $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(PPh_3)_3]$ **1** reacts with the Group 6 metal carbonyls, $[M(CO)_6]$, in hot aromatic solvents giving different reaction products according to the stability of the metal carbonyl: $[Ru_2\{\mu\text{-}C_6H_4(NH)_2\text{-}1,2\}(CO)_4(PPh_3)_2]$ **2** (M = Cr); $[W(CO)_5(PPh_3)]$ and *trans*-$[W(CO)_4(PPh_3)_2]$ (M = W) and the dark brown $[Ru_2Mo\{\mu\text{-}C_6H_4(NH)_2\text{-}1,2\}_2(CO)_6(PPh_3)_2]$ **3** (M = Mo). The structure of **3** has been established from X-ray diffraction analysis. This compound reacts, in boiling toluene, with diphosphines $(Ph_2P)_2X$ [X = CH_2 (dppm) or C_4H_8 (dppb)] to form $[Ru_2Mo\{\mu\text{-}C_6H_4(NH)_2\text{-}1,2\}_2(CO)_4\text{-}(diphosphine)_2]$ (diphosphine = dppm **4** or dppb **5**) and for X = C_2H_4 (dppe) or C_3H_6 (dppp) a mixture of $[Mo(CO)_4(diphosphine)]$ and $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(CO)(diphosphine)]$ was obtained. The new trinuclear complexes have been characterised by elemental analysis and by spectroscopic (IR and NMR) methods.

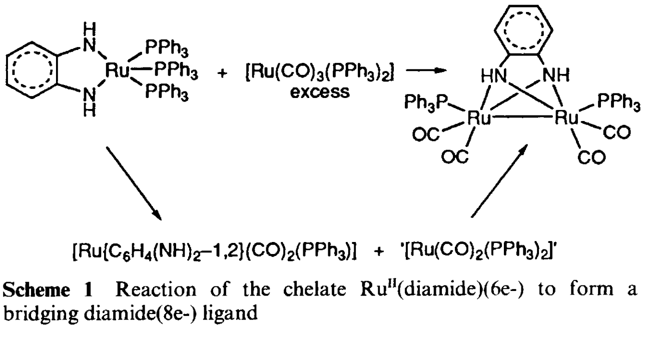
Complexes of the transition metals containing the bidentate dianionic ligand $C_6H_4(NH)_2\text{-}1,2$ were recently reported.[1,2] The more oxidised forms of this and other related ligands (charge 0 or 1 −) also occur in complexes as well as products from oxidation of the dianionic ligand complexes.[3] The catecholate (2 −) form is usually found to be the most stable,[1,2a,4] and it can be assumed to be a six-electron donor through the formation of two σ and one π bond when chelating a transition metal.[1b] The dianion $C_6H_4(NH)_2\text{-}1,2$ is also able to co-ordinate metal centres in binuclear complexes in a bridging mode, stabilising a tetrahedrane framework, thus behaving as an eight-electron donor and leading to the formation of metal–metal bonds, as in $[Ru_2\{\mu\text{-}C_6H_4(NH)_2\text{-}1,2\}(CO)_4(PPh_3)_2]$ and its derivatives.[5] These compounds were occasionally obtained from reactions between $[Ru(CO)_3(PPh_3)_2]$ and $[Ru\{C_6H_4(NH)_2\text{-}1,2\}L_3]$ (L = a phosphine), and suggested a way to prepare new heterobinuclear ruthenium complexes by treating the above ruthenium complexes with other low-oxidation-state metal compounds. Thus we attempted the syntheses of binuclear Ru–M (M = Cr, Mo or W) complexes by reaction of $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(PPh_3)_3]$ **1** with $[M(CO)_6]$. Heteronuclear compounds with Ru–M bonds are known, although only partially characterised,[6] and also cyclic polynuclear clusters[7] with Ru–Mo bonds which are the result of adding molybdenum moieties to the cluster $[Ru_3(CO)_{12}]$. They are of some interest because of their catalytic properties.[8]

We now report the synthesis and structure of the new trinuclear complex $[Ru_2Mo\{\mu\text{-}C_6H_4(NH)_2\text{-}1,2\}_2(CO)_6(PPh_3)_2]$ and its reactivity with some diphosphines.

Results and Discussion

Reactions of Complex **1** *with* $[Mo(CO)_6]$ (M = Cr, Mo *or* W).—Complex **1** reacts with the carbonyl complex $[Ru(CO)_3(PPh_3)_2]$ (> 120 °C) to form $[Ru_2\{\mu\text{-}C_6H_4(NH)_2\text{-}1,2\}(CO)_4(PPh_3)_2]$ **2**, which can be represented as the addition of the known complex[1a] $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(CO)_2(PPh_3)]$, in an $\eta^3\text{-}RuN_2$ mode, to the unsaturated moiety '$[Ru(CO)_2(PPh_3)_2]$' with the subsequent elimination of one PPh_3 ligand. This reaction implies that the six-electron $C_6H_4(NH)_2\text{-}1,2$ group is transformed into an eight-electron donor bridging ligand, with the simultaneous reduction of ruthenium(II) by the ruthenium(0) complex, resulting in the formation of a binuclear Ru^I complex (Scheme 1).

Different reaction products were obtained when compound **1** reacted with the Group 6 metal hexacarbonyls in boiling aromatic solvents, as the result of the variable stability of $[M(CO)_6]$. With excess of $[Cr(CO)_6]$ the known binuclear compound **2**[5] and *trans*-$[Cr(CO)_4(PPh_3)_2]$[9] were obtained; thus the chromium(0) complex has reduced the ruthenium(II) to give a ruthenium(I) binuclear complex (oxidised chromium species were not detected), and also transferred CO to the ruthenium centres, but a Ru–Cr bond was not stable enough to be formed under the reaction conditions. The most stable $[W(CO)_6]$ did not reduce the ruthenium(II) diamido complex under prolonged reaction times or UV radiation, and only a mixture of the substituted tungsten derivatives $[W(CO)_5\text{-}(PPh_3)]$[9] and *trans*-$[W(CO)_4(PPh_3)_2]$[10] was obtained and $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(CO)(PPh_3)_2]$[1a] was also detected. The most labile $[Mo(CO)_6]$, when allowed to react with **1** in boiling



Scheme 1 Reaction of the chelate Ru^{II}(diamide)(6e-) to form a bridging diamide(8e-) ligand

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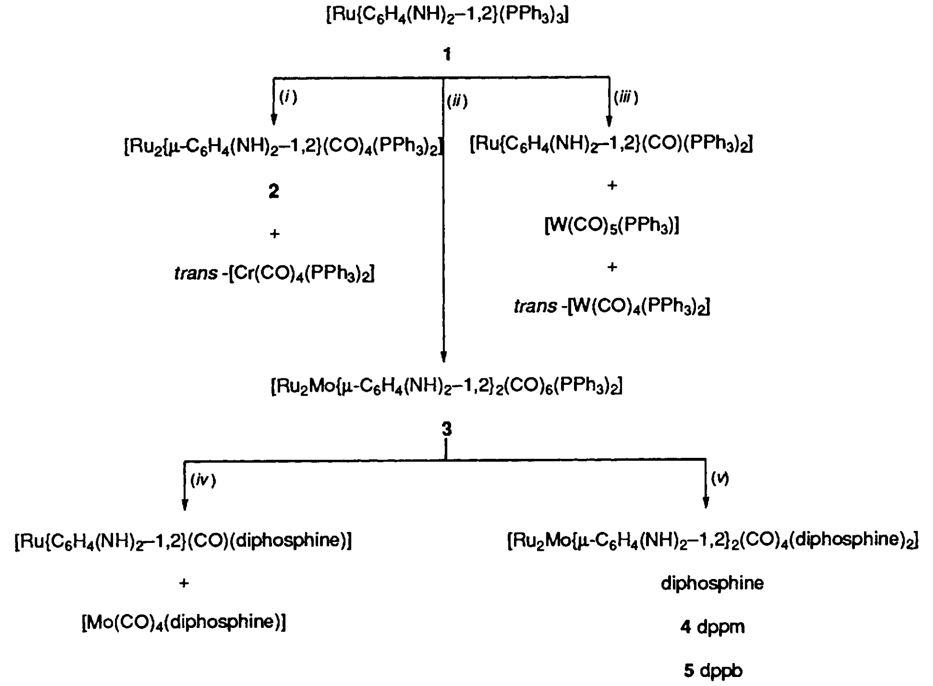
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

toluene, led to the formation of the trinuclear complex $[Ru_2Mo\{\mu\text{-}C_6H_4(NH)_2\text{-}1,2\}_2(CO)_6(PPh_3)_2]$ **3** in high yield as a red-brown crystalline solid.

The reactions of compound **1** with the Group 6 metal carbonyls and of compound **3** with diphosphines (see below) are summarised in Scheme 2.

Crystal Structure of Compound **3**.—A crystal of compound **3**, obtained from a toluene solution, was used for X-ray analysis (Fig. 1). The molecular structure consists of a quasi-linear Ru–Mo–Ru arrangement, the Ru–Mo distances [2.700(2) and 2.708(2) Å] (Table 1) being consistent with single intermetallic bonds, 0.2–0.3 Å shorter than Ru–Mo single bonds in carbonyl clusters with a sulfur bridging the metals[7c] and 0.35 Å shorter than in $[RuMo(CO)_6(\mu\text{-dppm})_2]$ (dppm = $Ph_2PCH_2PPh_2$) where there is ambiguity about the presence of a Ru–Mo bond.[11] The Ru–Mo bonds in compound **3** are 0.14 Å longer than Ru–Ru bonds in **2**, where also a bridging diamide tends to shorten the intermetallic distance, which could be explained by the formation of two *trans* Ru–Mo bonds. Assuming for each ruthenium an oxidation number of +1 and for the molybdenum of +2, there should be a lower electronic contribution from the Mo^{II} (d^4) than from the Ru^I (d^7), leading to both Mo-bonded CO groups adopting an incipient bridging mode, thus balancing the electron-density requirements on the rutheniums. The average distance Ru–C(Mo) of 2.69(1) Å also suggests this possibility, the Mo–C–O angles being 169(1) and 170(1)°. The molybdenum atom is in the centre of a distorted square antiprism, co-ordinated by four amidic N, two CO and two Ru, and each ruthenium is in the centre of an irregular trigonal antiprism as observed in compound **2**.[5a]



Scheme 2 (*i*) $[Cr(CO)_6]$ (excess)–mesitylene, heat; (*ii*) $[Mo(CO)_6]$–toluene, heat; (*iii*) $[W(CO)_6]$–mesitylene, heat; (*iv*) dppe– or dppp–toluene, heat; (*v*) dppm– or dppb–toluene, heat

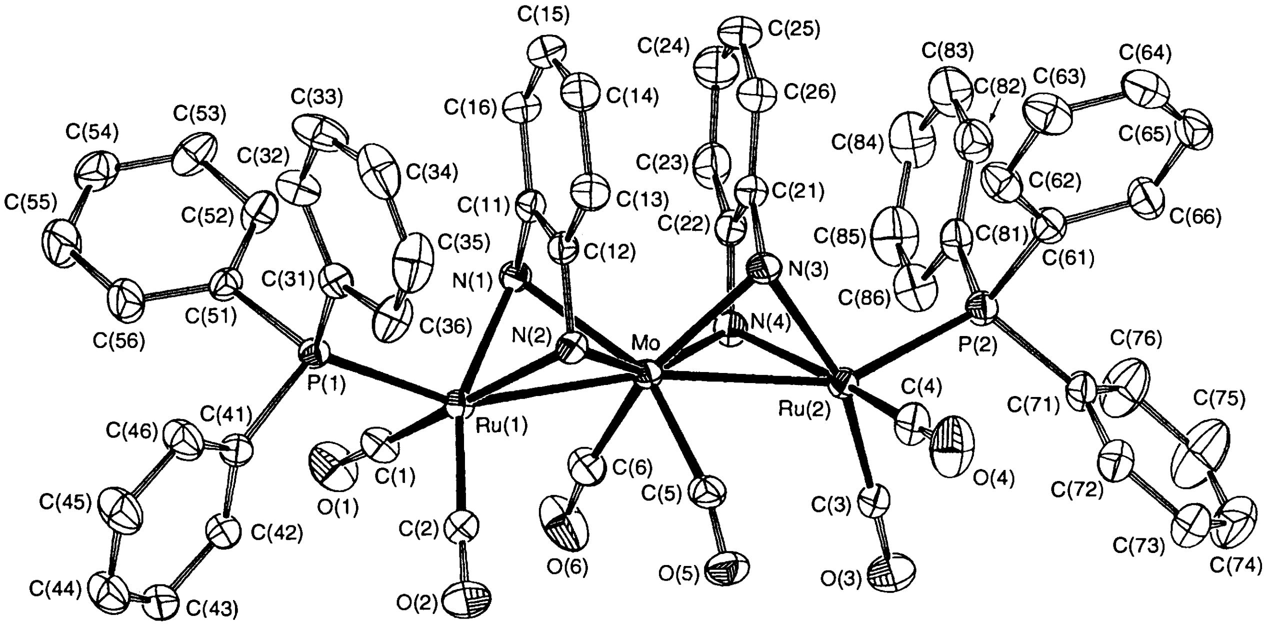


Fig. 1 Molecular structure of the complex $[Ru_2Mo\{\mu\text{-}C_6H_4(NH)_2\text{-}1,2\}_2(CO)_6(PPh_3)_2]$ **3** with the atomic numbering scheme

Table 1 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for compound **3**

Mo–Ru(1)	2.700(2)	Ru(1)–C(2)	1.88(1)
Mo–Ru(2)	2.708(2)	Ru(1)–P(1)	2.38(1)
Mo–N(1)	2.26(1)	Ru(1)–C(6)	2.70(1)
Mo–N(2)	2.19(1)	Ru(1) ··· O(6)	3.44(1)
Mo–N(3)	2.24(1)	C(1)–O(1)	1.14(1)
Mo–N(4)	2.20(1)	C(2)–O(2)	1.14(1)
Mo–C(5)	1.96(1)	C(5)–O(5)	1.18(1)
Mo–C(6)	1.94(1)	C(6)–O(6)	1.16(1)
Ru(1)–N(1)	2.15(1)	N(1)–C(11)	1.41(1)
Ru(1)–N(2)	2.12(1)	N(2)–C(12)	1.42(1)
Ru(1)–C(1)	1.89(1)		
Ru(1)–Mo–Ru(2)	167.1(2)	Ru(1)–Mo–N(3)	137.3(2)
N(1)–Mo–N(2)	65.8(3)	Ru(1)–Mo–N(4)	138.7(3)
N(1)–Mo–N(3)	99.7(3)	N(1)–Ru(1)–N(2)	68.9(4)
N(1)–Mo–N(4)	100.2(3)	N(1)–Ru(1)–C(1)	98.7(5)
N(1)–Mo–C(5)	148.5(4)	N(1)–Ru(1)–C(2)	158.2(5)
N(1)–Mo–C(6)	91.1(4)	N(1)–Ru(1)–P(1)	103.9(3)
N(2)–Mo–N(4)	152.9(4)	N(1)–Ru(1)–Mo	54.1(3)
N(2)–Mo–C(5)	90.1(4)	N(2)–Ru(1)–C(1)	164.6(5)
N(2)–Mo–C(6)	116.2(5)	N(2)–Ru(1)–C(2)	95.4(5)
C(5)–Mo–C(6)	81.5(5)	N(2)–Ru(1)–Mo	52.5(3)
Ru(1)–Mo–N(1)	50.5(3)	P(1)–Ru(1)–Mo	149.0(2)
Ru(1)–Mo–N(2)	50.1(3)	Mo–C(5)–O(5)	169(1)
Ru(1)–Mo–C(5)	98.7(4)	Mo–C(6)–O(6)	170(1)
Ru(1)–Mo–C(6)	68.8(4)	Ru(1)–C(1)–O(1)	178(1)
Ru(1)–C(2)–O(2)	177(1)		

Spectroscopic Properties of Compound **3**.—From the IR spectrum of compound **3** two groups of CO ligands are detected: three bands (toluene solution) at 2022, 2008 and 1955 cm^{-1} are assigned to the four terminal CO bonded to the ruthenium atoms (they are close to the bands found for complex **2**), and two weak–medium intensity bands at 1853 and 1795 cm^{-1} can be assigned to the other two *cis*-CO bonded to molybdenum. Only one signal for ν(NH) is observed at 3345 cm^{-1} which probably accounts for the equivalence of the four NH groups. The low wavenumbers for the Mo-bonded CO groups are consistent with a semibridging co-ordination as already shown in the solid state, but also with an important electron density on molybdenum afforded by basic ligands like the diamides. In the ^{13}C NMR spectrum (CD_2Cl_2 solution) two singlets at δ 242.15 and 156.20, intensity ratio 1:2, are assigned to the Mo- and Ru-bonded CO groups respectively [*J*(CP) not resolved], supporting a semibridging co-ordination of the former; however, values as high as δ 250 have been found for some terminal carbonyls in molybdenum complexes.[12] According to the presence of the two resonances, any fluxional process involving exchange of CO between Mo and Ru is excluded under the experimental conditions. Two broad singlets at δ 117.90 and 113.85 can be assigned to the benzenediamide ligand; a third signal could be observed as a shoulder at δ 128.70.

Other NMR data (^{1}H, ^{31}P) confirm that in solution the molecule has a two-fold symmetry axis; only one signal (^{31}P NMR) is observed for the two PPh_3 ligands, and the eight aromatic protons from the diamido rings exhibit two doublets of doublets (^{1}H NMR) at δ 5.66 and 5.24. These and the above ^{13}C NMR data suggest equivalence, in solution, between both diamides and, for each diamide, between opposite carbons (and hydrogens), namely: C(11) and C(12), C(13) and C(16), C(14) and C(15). The multiplet at δ 5.66, with the largest coupling constants, is assigned to the 4,5-protons in the benzenediamide. The ^{1}H NMR spectrum of a trinuclear complex prepared with the 4,5-dimethyl derivative of $C_6H_4(NH)_2$-1,2 as the bridging ligand (**3a**) showed only one singlet at δ 5.15 from the 3,6-aromatic protons in the diamide. No signals at low field were detected for **3a** and a broad singlet at δ 8.00 for **3** could be related to the NH protons.

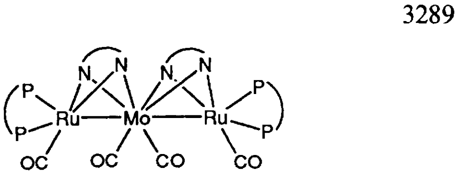


Fig. 2 Structure assigned (*syn*- or *anti*-) to the complex [$Ru_2Mo\{\mu$-$C_6H_4(NH)_2$-1,2$\}_2(CO)_4(dppb)_2$] **5**

Reactions of [$Ru_2Mo\{\mu$-$C_6H_4(NH)_2$-1,2$\}_2(CO)_6(PPh_3)_2$] **3** *with Diphosphines*.—Different types of reaction products were formed when complex **3** was treated with excesses of the diphosphines $Ph_2P(CH_2)_nPPh_2$ [$n = 1$ (dppm), 2 (dppe), 3 (dppp) or 4 (dppb)], in boiling aromatic solvents. With dppe and dppp purple solutions were obtained; their IR spectra showed the presence of the known [$Mo(CO)_4$(diphosphine)][13] and [$Ru\{C_6H_4(NH)_2$-1,2$\}$(CO)(diphosphine)][1a] (purple) as the only carbonyl complexes. Lower diphosphine:**3** ratios led to the same reaction products, leaving some unreacted compound **3**. With dppm or dppb the trinuclear structure is maintained and the substitution derivatives [$Ru_2Mo\{\mu$-$C_6H_4(NH)_2$-1,2$\}_2(CO)_4$(diphosphine)$_2$] (diphosphine = dppm **4** or dppb **5**) were obtained. These are the only observed products even if a ratio diphosphine:**3** $\leqslant$ 1:1 is used.

The different behaviour of these diphosphines towards complex **3** can be explained based on their different abilities to form the chelate Mo(diphosphine). These chelates are easily formed with dppe or dppp, even with a deficiency of diphosphine, the complexes [$Mo(CO)_4$(diphosphine)] always being detected as the first reaction products, which also implies a two-CO transfer, one from each ruthenium, to the molybdenum, and cleavage of the Ru–Mo bonds. The less-stable chelates formed by dppm and dppb with molybdenum are not detected, under the reaction conditions, and intermetallic bond cleavage did not occur, only substitution products being obtained.

The trinuclear derivatives were characterised by spectroscopic methods. Complexes **4** and **5** show analogous IR spectra in the carbonyl region: two two-band groups, those at higher frequencies being related to the Ru-bonded CO, and two less-intense bands at lower frequencies assigned to the Mo-bonded CO. It must be pointed out that for complex **5** one of the bands from the CO co-ordinated to the ruthenium atoms is very weak, suggesting the presence of an almost linear arrangement for OC–Ru–Mo–Ru–CO. The introduction of these diphosphine ligands produces in **4** and **5**, as expected, a shift to lower values of all the ν(CO). However, this shift is considerably larger for the Mo- than for the Ru-bonded CO. This could be attributed to some additional bridging interaction between CO (Mo) and Ru. Both complexes exhibit two bands in their solid-state IR spectra around 3350 cm^{-1} assignable to ν(NH).

The substitution of one PPh_3 and one ruthenium-bonded CO by one diphosphine leads to products with ^{31}P-{^{1}H} NMR spectra containing two resonances, according to the non-equivalence of the two phosphorus, as already observed for substitution derivatives of the binuclear complex **2**.[5b] Thus, a structure like that in Fig. 2 is proposed for complexes **4** and **5**, with the possibility of *syn* or *anti* isomers, which in the case of **5** could both be present as deduced from their ^{31}P and ^{1}H NMR spectra. The ^{31}P NMR spectrum at room temperature (C_6D_6) shows four resonances which can be grouped into two pairs according to their intensity ratios, 1:8:1:8, the first and third sharp signals (δ 49.13 and 33.65) being assignable to one of the isomers and the second and fourth signals (δ 45.79 and 31.00) to the other, but one resonance for the latter isomer (δ 45.79) is broad. When the spectrum is run at 223 K the four resonances are observed as sharp singlets, suggesting a fluxional behaviour for one of the isomers, the probable mechanism involving cleavage of one of the Ru–P bonds (dppb is a weak chelating ligand) in a dissociative–associative process without a *syn–anti* isomerisation, as the isomer in lower yield is not affected by a

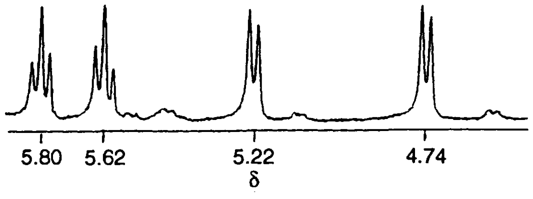


Fig. 3 Proton NMR spectrum, in C_6D_6, of complex **5**

fluxional process at room temperature. The ^1H NMR spectrum (Fig. 3) also shows the presence of two complexes detected between δ 4.00 and 5.90, where the resonances from the aromatic $C_6H_4(NH)_2$ protons are observed as a group of four signals (two 'triplets' and two doublets) at δ 5.80 (t), 5.62 (t), 5.22 (d) and 4.74 (d) for the isomer in higher yield and at δ 5.45 (m), 5.10 (m), 4.57 (d) and 4.10 (d) for the other (this last group of the four less-intense signals is not included in Experimental section). The possible fluxionality of one of the isomers is not detected in the ^1H NMR spectrum.

Experimental

All reactions were carried out under nitrogen with Schlenk techniques. Toluene, hexane and tetrahydrofuran were freshly distilled under nitrogen after drying by refluxing over sodium. Mesitylene was degassed by nitrogen bubbling. Microanalytical data (C, H and N) were obtained from a Perkin Elmer 240-B elemental analyser. Infrared spectra were recorded from Nujol mulls (KBr discs) or solutions (CaF_2 discs) with a Perkin Elmer 1720-XFT spectrometer, ^1H, ^{31}P and ^{13}C NMR spectra on a Bruker AC-300 spectrometer (data referenced to $SiMe_4$ and 85% external H_3PO_4). Alumina (activity IV) was used in chromatographic separations. The compound $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(PPh_3)_3]$ was prepared by a published procedure;[14] $[M(CO)_6]$ (M = Cr, Mo or W) and diphosphines were used as supplied without further purification.

Reactions of Complex **1** *with* $[Cr(CO)_6]$.—A solution of compound **1** (0.100 g, 0.100 mmol) and $[Cr(CO)_6]$ (0.022 g, 0.100 mmol) in toluene (5 cm^3) was refluxed for 2 h to obtain a pale brown solution. IR (solution): 2001s, 1969m and 1933s (compound **2**), 1900s $\{trans\text{-}[Cr(CO)_4(PPh_3)_2]\}$ and 1980 cm^{-1} $\{$excess of $[Cr(CO)_6]\}$. The same reaction products are detected when the reaction is carried out in boiling mesitylene for 30 min.

With $[W(CO)_6]$. A solution of complex **1** (0.070 g, 0.070 mmol) and $[W(CO)_6]$ (0.013 g, 0.037 mmol) in mesitylene (4 cm^3) was refluxed for 90 min. The brown solution was chromatographed (eluting with toluene): the first fraction contained (IR) $[W(CO)_5(PPh_3)]$ and the second *trans*-$[W(CO)_4(PPh_3)_2]$; a third purple fraction, eluted with tetrahydrofuran (thf), contained $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(CO)(PPh_3)_2]$.

Synthesis of $[Ru_2Mo\{\mu\text{-}C_6H_4(NH)_2\text{-}1,2\}_2(CO)_6(PPh_3)_2]$ **3**.—A solution of complex **1** (0.500 g, 0.503 mmol) and $[Mo(CO)_6]$ (0.066 g, 0.250 mmol) in toluene (5 cm^3) was refluxed for 2 h. After 1 d at room temperature the brown reaction solution was filtered, the dark brown crystalline solid washed three times with hexane and dried under vacuum. Yield 0.270 g (79%) (Found: C, 54.3; H, 3.7; N, 4.5. $C_{54}H_{42}MoN_4O_6P_2Ru_2$ requires C, 53.9; H, 3.5; N, 4.6%). IR: ν(NH) 3345w; ν(CO) 2022s, 2008m, 1955s, 1853m and 1795m cm^{-1} (toluene). NMR: ^1H (C_6D_6), δ 5.66 [dd, J(HH) 5.2 and 2, 4 H, C_6H_4] and 5.24 [dd, J(HH) 4.6 and 1.1 Hz, 4 H, C_6H_4]; $^{31}P\text{-}\{^1H\}$ (C_6D_6), δ 36.2 (s, 2 P, PPh_3); ^{13}C (CD_2Cl_2), δ 242.15 (s, 2 C, MoCO), 156.20 (s, 4 C, RuCO), 128.70 (s, sh, 4 C, C_6H_4), 117.90 (s, 4 C, C_6H_4) and 113.85 (s, 4 C, C_6H_4).

The same procedure was applied to prepare $[Ru_2Mo\{\mu\text{-}C_6H_2Me_2\text{-}4,5\text{-}(NH)_2\text{-}1,2\}_2(CO)_6(PPh_3)_2]$ **3a**, but using $[Ru\{C_6H_2Me_2\text{-}4,5\text{-}(NH)_2\text{-}1,2\}(PPh_3)_3]$. ^1H NMR (C_6D_6): δ 5.15 [s, 2 H, $C_6H_2(CH_3)_2$].

Table 2 Crystal data for complex **3**

Formula	$C_{54}H_{42}MoN_4O_6P_2Ru_2$
M	1202.98
Crystal system	Triclinic
Space group	$P\bar{1}$
Crystal colour	Dark brown
Crystal size/mm	0.40 × 0.17 × 0.13
a/Å	17.085(6)
b/Å	13.510(4)
c/Å	12.465(8)
α/°	92.841(7)
β/°	92.00(8)
γ/°	106.49(2)
U/Å^3	2751(2)
Z	2
D_c/Mg m^{-3}	1.45
μ(Mo-Kα)/cm^{-1}	8.55
F(000)	1204
Drift correction range	0.99–1.03
h, k, l range	−22, −16, 0 to 20, 16, 14
Number of measured reflections	10 571
Number of unique reflections	9628
R_{int} (for some double measured)	0.021
Observed reflections [$I > 3\sigma(I)$]	7730
Number of refined parameters	623
R	0.054
Maximum shift/e.s.d.	0.006
Final peaks in Fourier difference synthesis (maximum, minimum)/e Å^{-3}	0.46, −0.94

Reactions of Complex **3** *with* dppe *or* dppp.—A mixture of compound **3** (0.050 g, 0.041 mmol) and the diphosphine (0.124 mmol) was boiled in toluene (3 cm^3) for 1 h. The purple solution was chromatographed and a first yellow fraction was eluted with toluene in which [Mo(CO)$_4$(diphosphine)] was identified [IR 2022m, 1914vs and 1895s for dppe and 2018m and 1900vs(br) cm^{-1} for dppp]. A second purple solution was recovered after elution with thf in which the complexes $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(CO)(\text{diphosphine})]$ were detected (IR 1926s for dppe and 1924s cm^{-1} for dppp).

$[Ru_2Mo(\mu\text{-}C_6H_4(NH)_2\text{-}1,2\}_2(CO)_4(dppm)_2]$ **4**.—The compound **3** (0.064 g, 0.053 mmol) and $(Ph_2P)_2CH_2$ (0.042 g, 0.109 mmol) were refluxed in toluene (3 cm^3) for 1 h. The brown solution was chromatographed and a first brown fraction eluted with toluene. The volume was reduced to 3 cm^3 and hexane (3 cm^3) added. After 2 d at room temperature a brown crystalline solid was collected, washed twice with hexane and dried (vacuum). Yield *ca*. 60% (Found: C, 56.1; H, 4.2; N, 3.9. $C_{66}H_{56}MoN_4O_4P_4Ru_2$ requires C, 57.0; H, 4.0; N, 4.0%). IR: ν(NH) 3348w; ν(CO) 2008m, 1944vs, 1826w and 1751w cm^{-1} (toluene). $^{31}P\text{-}\{^1H\}$ NMR (C_6D_6): δ 22.98 (s, 1 P, dppm) and −0.55 (s, 1 P, dppm).

$[Ru_2Mo\{\mu\text{-}C_6H_4(NH)_2\text{-}1,2\}_2(CO)_4(dppb)_2]$ **5**.—A mixture of complex **3** (0.057 g, 0.047 mmol) and $(Ph_2P)_2C_4H_8$ (0.040 g, 0.094 mmol) was boiled in toluene (3 cm^3) for 2 h. The brown solution was filtered through an alumina column and eluted with toluene to get first a red-brown fraction, the volume of which was lowered to 3 cm^3 and hexane (6 cm^3) added. After 1 d at room temperature red-brown crystals were collected, washed with hexane and dried. Yield 60% (Found: C, 59.2; H, 4.8; N, 3.7. $C_{72}H_{68}MoN_4O_4P_4Ru_2$ requires C, 58.6; H, 4.6; N, 3.8%). IR: ν(NH) 3345w; ν(CO) 2010vw, 1920vs, 1817w and 1757m cm^{-1} (toluene). NMR: ^1H (C_6D_6), δ 5.80 [t, J(HH) 7.3, 2 H, C_6H_4], 5.62 [t, J(HH) 7.3, 2 H, C_6H_4], 5.22 [d, J(HH) 7.1, 2 H, C_6H_4] and 4.74 [d, J(HH) 7.1 Hz, 2 H, C_6H_4]; $^{31}P\text{-}\{^1H\}$ (C_6D_6–toluene, 223 K), δ 51.28 (s, 2 P, dppb), 45.43 (s, 2 P, dppb), 34.00

Table 3 Fractional positional parameters for complex **3** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Mo	0.271 36(5)	0.022 62(6)	−0.022 08(6)
Ru(1)	0.396 90(5)	0.155 99(6)	0.094 55(6)
Ru(2)	0.145 67(5)	−0.073 17(6)	−0.163 66(6)
P(1)	0.456 1(2)	0.232 7(2)	0.265 3(2)
P(2)	0.050 0(2)	−0.232 7(2)	−0.227 9(2)
C(1)	0.500 4(7)	0.147 4(8)	0.053 4(9)
O(1)	0.561 9(5)	0.139 1(7)	0.028 6(8)
C(2)	0.408 3(6)	0.283 5(8)	0.034 0(8)
O(2)	0.411 5(6)	0.359 7(7)	−0.003 3(8)
C(3)	0.176 6(6)	−0.040 2(8)	−0.303 3(8)
O(3)	0.195 0(6)	−0.018 3(8)	−0.387 1(7)
C(4)	0.069 4(7)	0.001 5(9)	−0.173 9(9)
O(4)	0.022 7(6)	0.049 9(8)	−0.174 8(9)
C(5)	0.242 7(7)	0.120 4(8)	−0.115 7(8)
O(5)	0.238 1(5)	0.189 0(6)	−0.168 0(6)
C(6)	0.369 7(7)	0.057 9(9)	−0.102 9(9)
O(6)	0.421 1(6)	0.070 9(9)	−0.163 8(8)
N(1)	0.342 7(5)	−0.004 1(6)	0.124 4(6)
N(2)	0.270 2(5)	0.125 8(6)	0.119 0(6)
N(3)	0.147 6(5)	−0.082 2(6)	0.008 0(6)
N(4)	0.243 3(5)	−0.130 3(6)	−0.107 9(7)
C(11)	0.288 0(6)	−0.014 2(8)	0.208 5(8)
C(12)	0.246 1(6)	0.060 9(8)	0.205 1(8)
C(13)	0.184 8(7)	0.060 5(9)	0.274 1(8)
C(14)	0.167 4(7)	−0.014(1)	0.350 8(9)
C(15)	0.208 6(8)	−0.086(1)	0.355 3(9)
C(16)	0.269 6(7)	−0.087 7(9)	0.283 6(9)
C(21)	0.159 8(7)	−0.178 4(8)	0.035 2(9)
C(22)	0.215 4(7)	−0.204 9(8)	−0.030 5(9)
C(23)	0.238 3(8)	−0.293 2(9)	−0.015(1)
C(24)	0.203(1)	−0.357(1)	0.065(2)
C(25)	0.145(1)	−0.333(1)	0.128(1)
C(26)	0.123 8(8)	−0.242(1)	0.133(1)
C(31)	0.383 9(6)	0.241 6(8)	0.367 3(8)
C(32)	0.382 7(7)	0.194 4(8)	0.463 9(9)
C(33)	0.323 8(9)	0.199(1)	0.537(1)
C(34)	0.267 7(8)	0.253(1)	0.515(1)
C(35)	0.270 7(8)	0.301(1)	0.422(1)
C(36)	0.328 5(8)	0.297(1)	0.347(1)
C(41)	0.523 0(6)	0.366 2(7)	0.264 2(8)
C(42)	0.573 1(6)	0.395 0(8)	0.180 0(9)
C(43)	0.627 5(7)	0.493 2(9)	0.180(1)
C(44)	0.632 5(8)	0.564(1)	0.265(1)
C(45)	0.583 1(9)	0.535(1)	0.351(1)
C(46)	0.528 5(8)	0.437 5(9)	0.351(1)
C(51)	0.525 2(6)	0.169 0(8)	0.329 7(8)
C(52)	0.501 5(8)	0.063 2(9)	0.332 4(9)
C(53)	0.550 6(9)	0.012(1)	0.384 5(9)
C(54)	0.624 7(8)	0.065(1)	0.430(1)
C(55)	0.649 7(9)	0.170(1)	0.428(2)
C(56)	0.600 9(8)	0.223(1)	0.377(1)
C(61)	−0.046 2(6)	−0.270 8(8)	−0.162 0(9)
C(62)	−0.051 0(7)	−0.230 7(9)	−0.059(1)
C(63)	−0.121 6(8)	−0.263(1)	−0.004(1)
C(64)	−0.190 7(8)	−0.336(1)	−0.055(1)
C(65)	−0.187 7(7)	−0.376(1)	−0.157(1)
C(66)	−0.115 7(7)	−0.344 0(9)	−0.211(1)
C(71)	0.015 5(7)	−0.236 7(9)	−0.370 3(9)
C(72)	−0.012 4(7)	−0.157(1)	−0.407(1)
C(73)	−0.040 7(8)	−0.156(1)	−0.513(1)
C(74)	−0.041(1)	−0.236(1)	−0.585(1)
C(75)	−0.013(1)	−0.315(2)	−0.550(1)
C(76)	0.015(1)	−0.318(1)	−0.444(1)
C(81)	0.087 3(7)	−0.346 6(8)	−0.221 3(9)
C(82)	0.050 9(8)	−0.430 2(9)	−0.162(1)
C(83)	0.082 9(9)	−0.515(1)	−0.158(1)
C(84)	0.151(1)	−0.516(1)	−0.216(1)
C(85)	0.187 3(9)	−0.434(1)	−0.274(1)
C(86)	0.156 7(8)	−0.347(1)	−0.278(1)

(s, 2 P, dppb) and 29.34 (s, 2 P, dppb); (273 K) 49.13 (s, 2 P, dppb), 45.79 (br s, 2 P, dppb), 33.65 (s, 2 P, dppb) and 31.00 (s, 2 P, dppb).

Crystallographic Data Collection, Resolution and Refinement of the Structure of Complex **3**.—Experimental data are collected in Table 2. The data were collected at 293 K on an Enraf-Nonius-CAD4 single-crystal diffractometer using Mo-Kα radiation (λ = 0.710 73 Å) and a graphite-crystal monochromator. Unit-cell dimensions were determined from the angular settings of 25 reflections, $0 \leqslant \theta \leqslant 25°$. The space group was determined from systematic absences. The ω–2θ scan technique was used, with a variable scan rate and a maximum scan time of 60 s per reflection. The intensity of the primary beam was checked by monitoring three standard reflections every 60 min. A drift correction was applied. Profile analysis[15] was performed on all reflections. A semiempirical absorption correction was applied, using ψ scans[16] (correction factors from 0.72 to 1.00). Lorentz and polarisation corrections were applied and the data were reduced to $|F_o|$ values. The positions of the Mo and Ru atoms were obtained from a Patterson map, those of the remaining non-hydrogen atoms by DIRDIF.[17] An absorption correction was applied by use of DIFABS[18] (maximum and minimum values 0.78 and 1.16). Full-matrix least-squares refinement was made with a local version of SHELX 76.[19] All non-hydrogen atoms in the molecule were refined anisotropically. The hydrogen atoms were placed in calculated positions and their overall isotropic thermal parameters refined. Final R = 0.054. No weights applied. During the final stages of refinement the positional parameters and the anisotropic thermal parameters of the non-hydrogen atoms were refined. The atomic scattering factors were taken from ref. 20. The structure was drawn with the EUCLID[21] program and the geometrical calculations were made with PARST.[22] All calculations were made on a DEC MicroVax 3400 computer of the Scientific Computer Centre of the Universidad de Oviedo.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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