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Synthesis and structures of (3-methyl-2-pyridyl)diphenylphosphane derivatives of metal clusters

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Abstract

An unsymmetric bidentate ligand (3-methyl-2-pyridyl)diphenylphosphane (P(Mepy)Ph$_2$) is able to react with various tetranuclear transition metal clusters such as HRuCo$_3$(CO)$_{12}$, HRuRh$_3$(CO)$_{12}$ and Rh$_4$(CO)$_{12}$. The synthesis and crystal structures of HRuCo$_3$(CO)$_{10}$(P(Mepy)Ph$_2$) (**1**), HRuRh$_3$(CO)$_{10}$(P(Mepy)Ph$_2$) (**2**), RuRh$_2$(CO)$_9$(P(Mepy)Ph) (**3**) and Rh$_6$(CO)$_{14}$(P(Mepy)Ph$_2$) (**4**) are described. In **1**, **2** and **4** the phosphane ligand replaces the carbonyls and acts as a bridging bidentate P–N group. The formation of **3** includes degradation of both the metal cluster core and the ligand itself. One of the P–C bonds in the ligand is cleaved and the ligand caps a metal triangle with a bridging phosphido group together with the nitrogen donor. The reaction between dinuclear Rh$_2$(CO)$_4$Cl$_2$ and P(Mepy)Ph$_2$ gives a binuclear Rh$_2$(μ-CO)Cl$_2$(P(Mepy)Ph$_2$)$_2$ (**5**) with bridging ligands in a head-to-tail arrangement. The crystal structure is also given.
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1. Introduction

Diphenyl(2-pyridyl)phosphane (PPh$_2$py) (Scheme 1) is a bidentate heterodonor ligand with a variable coordination capability. The coordination types of the ligand in mono- and dinuclear transition metal complexes have been reviewed by Zhang and Cheng [1] and Newkome [2].

In principle, the simple monodentate coordination of PPh$_2$py is possible via either phosphorus or nitrogen atoms. Nitrogen is stronger σ donor, but it is also a weaker π-acceptor, which explains the preference for coordination through the phosphorus. In fact, several monodentate P-bonded complexes are known, while no monodentate nitrogen-bonded compounds have been reported thus far. In these cases, the reactions and the bonding of the ligand closely resemble those of PPh$_3$.

The monodentate coordination by phosphorus leaves the N-donor available for further reactions. Chelation to the same metal center is one possibility. This type of coordination frequently leads to a strained, rather unstable four-membered ring system. Most typically, the ligand forms binuclear complexes with between one and three bridging ligands. PPh$_2$py is a rigid ligand with a short bite capacity. Because of its rigidity, the ligand does not permit long distances between the bridged metals. This makes PPh$_2$py a convenient building block, especially for binuclear complexes. The synthesis of binuclear homo- and heteronuclear compounds has been studied widely in recent years [3]. The rich reactive features of complexes with heterodonor ligands under moderate conditions have attracted considerable attention because of their possible applications in catalyst design [4].

The heterodonor nature of the ligand also offers alternative coordination modes in multinuclear complexes. PPh$_2$py has previously been found to be reactive towards transition metal clusters. Its reactions with

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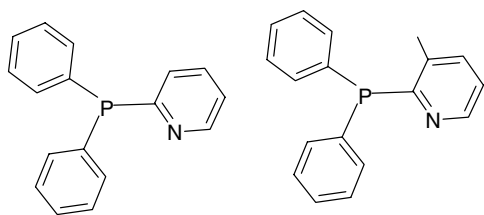
Scheme 1. PPh$_2$py and P(Mepy)Ph$_2$.

$Ru_3(CO)_{12}$ are among the most studied processes [5], and the derivatives of $Os_3(CO)_{12}$ [6,7], $Os_4(CO)_{12}$ [8], $Co_4(CO)_{12}$ [9] and $Ir_4(CO)_{12}$ [10,11] are also reported.

Previously, we have studied several mixed-donor (P/O, P/S, P/N), potentially bidentate triphenylphosphane derivatives. We have studied their synthesis and their coordination modes in mono- and dinuclear rhodium complexes [12]. In addition, the dependence between the electronic and steric properties of the phosphanes used as a cocatalyst in alkene hydroformylation and in the chemo- and regioselectivity of the products has been studied [13,14]. Furthermore, we have systematically studied the reactions of the cluster family $H_xRu_xCo_yRh_z(CO)_{12}$ with various types of ligands, such as phosphanes, thioethers, selenium and tellurium compounds. In these studies, we found clear site selectivities that depend on the metal composition and the ligand [15–18].

In the present study, we investigated the coordination modes of the methyl-substituted derivative of diphenyl(2-pyridyl)phosphane (PPh$_2$py) (3-methyl-2-pyridyl)diphenylphosphane (P(Mepy)Ph$_2$) (Scheme 1), in polynuclear metal clusters. The reactivity of P(Mepy)Ph$_2$ towards the tetranuclear homometallic cluster Rh$_4$(CO)$_{12}$ and, for the sake of comparison, also in the dinuclear complex Rh$_2$(CO)$_4$Cl$_2$ was subjected to examination. In particular, we were interested in reactions involving the mixed metal compounds HRuCo$_3$(CO)$_{12}$ and HRuRh$_3$(CO)$_{12}$.

2. Results and discussion

2.1. Synthesis and structure of HRuCo$_3$(CO)$_{10}$ (P(Mepy)Ph$_2$) (1)

When a tetrahedral mixed metal cluster HRuCo$_3$(CO)$_{12}$ reacts with the P(Mepy)Ph$_2$ ligand in refluxing dichloromethane, HRuCo$_3$(CO)$_{10}$(P(Mepy)-Ph$_2$) (1) is formed as the only stable product. The crystal structure (Fig. 1) shows that the P(Mepy)Ph$_2$ ligand is coordinated in the bridging mode to two adjacent cobalt atoms by replacing two axial carbonyl ligands. Apart from this, the cluster structure remains intact. The apical ruthenium has three terminal carbonyl groups. The cobalt triangle has a bridging carbonyl on each edge, and
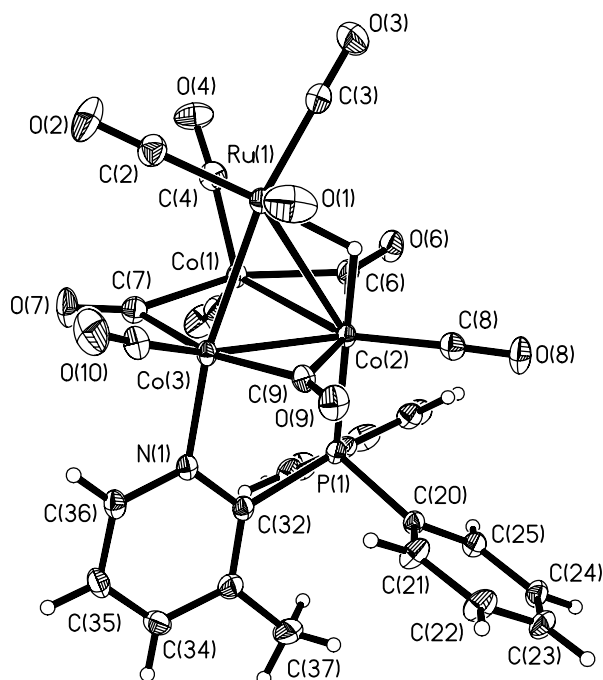

Fig. 1. Molecular structure of HRuCo$_3$(CO)$_{10}$(P(Mepy)Ph$_2$) (1). Selected bond lengths (Å) and angles (°): Co(2)–Ru(1) 2.7708(3), Co(3)–Ru(1) 2.6142(3), Co(2)–Co(3) 2.4217(4), Co(1)–Ru(1) 2.6483(3), Co(1)–Co(3) 2.5135(4), Co(1)–Co(2) 2.5012(4), N(1)–Co(3) 2.007(2), P(1)–Co(2) 2.1832(6), N(1)–C(32)–P(1) 113.84(15), C(32)–P(1)–Co(2) 115.00(7), C(32)–N(1)–Co(3) 122.75(14).

the other carbonyls are terminal. The site selectivity of carbonyl substitution in HRuCo$_3$(CO)$_{12}$ has been reported earlier [18]. In disubstituted derivatives, ligands such as phosphane or sulphur are typically bound to cobalt atoms. If the reactions are conducted using stronger donors such as TeMe$_2$, coordination to apical ruthenium becomes preferable. In addition, the formation of isomeric mixtures or the isomerization of the compounds is also possible, depending on the nature of the ligand.

The hydride ligand can be located on the Ru–Co(2) edge in the crystal structure. Further support for the hydride position is obtained for the Ru–Co bond lengths: the bridged bond is 2.7708(3) Å while the non-bridged bonds are 2.6483(3) and 2.6142(3) Å. The P(Mepy)Ph2 bonded Co–Co bond length is slightly shorter 2.4217(4) than the other two bonds 2.5135(4) and 2.5012(4) Å.

In the ^{1}H NMR of 1, signal at −20.6 ppm (d) with $^2J_{H–P} = 18$ Hz can be seen in the hydride region. The parent cluster HRuCo$_3$(CO)$_{12}$, as well as most of its phosphane or chalcogenide derivatives, has the hydride ligand in the μ_3-Co$_3$ position, which produces a broad signal at −19.6 ppm. The coordination of the bulky donor ligand makes the basal position less favoured in the case of 1. One derivative known earlier, with a Ru–Co edge-bridging hydride, is HRuCo$_3$(CO)$_9$[HC(PPh$_3$)],

which produces a resonance at −20.6 ppm with $^2J_{H-P} = 27.5$ Hz [19].

2.2. Synthesis and structures of $HRuRh_3(CO)_{10}$ $(P(Mepy)Ph_2)$ (2) and $RuRh_2(CO)_9(P(Mepy)Ph)$ (3)

The P(Mepy)Ph$_2$ ligands also readily react with HRuRh$_3$(CO)$_{12}$. With short reaction times (ca. 30 min), the primary product is HRuRh$_3$(CO)$_{10}$(P(Mepy)Ph$_2$) (2) (Fig. 2). As in the case of the RuCo$_3$ cluster, the ligand assumes a bridging coordination mode, and it replaces the carbonyl groups in two adjacent rhodiums, while the rest of the cluster remains intact.

In the parent cluster HRuRh$_3$(CO)$_{12}$, the hydride ligand is fluxional in solution. It can exist in the basal rhodium plane in the μ_3-position, which in ^{1}H NMR yields a quartet at −15.6 ppm ($^1J_{H-Rh} = 11$ Hz) or equally in one of the Ru–Rh bonds, yielding a doublet at −18.5 ppm. ($^1J_{H-Rh} = 16$ Hz) [20].

In the crystal structure of the P(Mepy)Ph$_2$ derivative 2, the hydride can be located in the Ru–Rh(2) bond. Again, the hydride causes lengthening of the metal bond: the bridged Ru–Rh bond is 2.8829(4) Å, while the non-bridged bonds are 2.6791(4) and 2.7383(4) Å. The ^{1}H NMR shows a doublet of doublets at −17.2 ppm ($^1J_{H-Rh} = 60$ Hz, $^2J_{H-P} = 20$ Hz). In the ^{31}P–{^{1}H} NMR

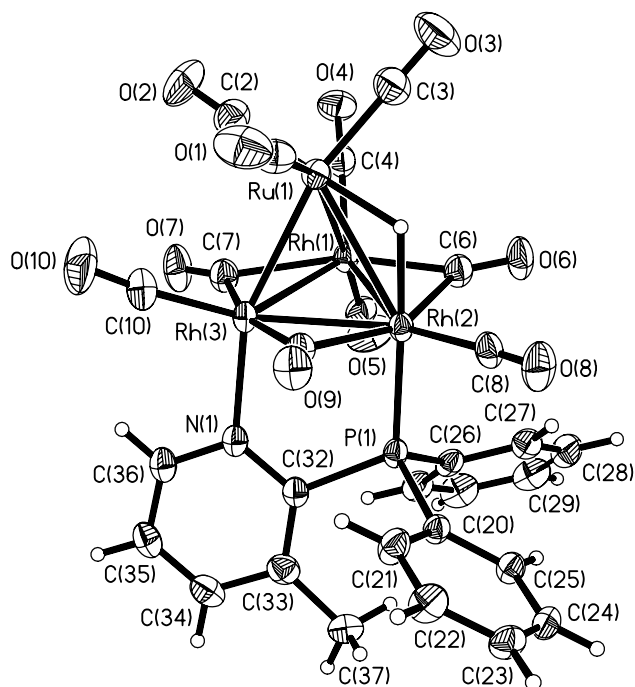Fig. 3. Molecular structure of RuRh$_2$(CO)$_9$(P(Mepy)Ph) (3). Selected bond lengths (Å) and angles (°): Ru(1)–Rh(1) 2.8262(10), Ru(1)–Rh(2) 2.8757(10), Rh(1)–Rh(2) 2.7761(10), P(1)–Rh(1) 2.300(2), P(1)–Ru(1) 2.317(2), N(1)–Rh(2) 2.208(8), N(1)–C(32)–P(1) 109.4(6), C(32)–P(1)–Ru(1) 117.9(3), C(32)–P(1)–Rh(1) 115.8(3), C(32)–N(1)–Rh(2) 121.6(6).

Fig. 2. Molecular structure of HRuRh$_3$(CO)$_{10}$(P(Mepy)Ph$_2$) (2). Selected bond lengths (Å) and angles (°): Ru(1)–Rh(3) 2.6791(4), Ru(1)–Rh(1) 2.7383(4), Ru(1)–Rh(2) 2.8829(4), Rh(1)–Rh(2) 2.7603(3), Rh(1)–Rh(3) 2.7673(3), Rh(2)–Rh(3) 2.6375(3), N(1)–Rh(3) 2.208(3), P(1)–Rh(2) 2.2789(9), N(1)–C(32)–P(1) 115.8(2), C(32)–P(1)–Rh(2) 116.12(10), C(32)–N(1)–Rh(3) 125.0(2).
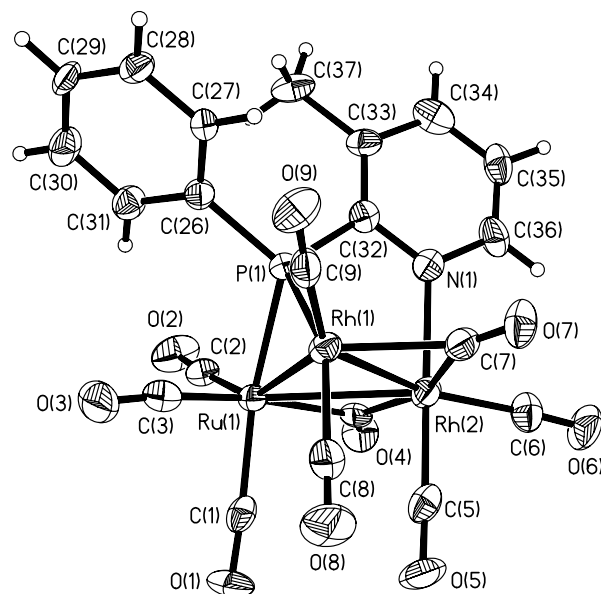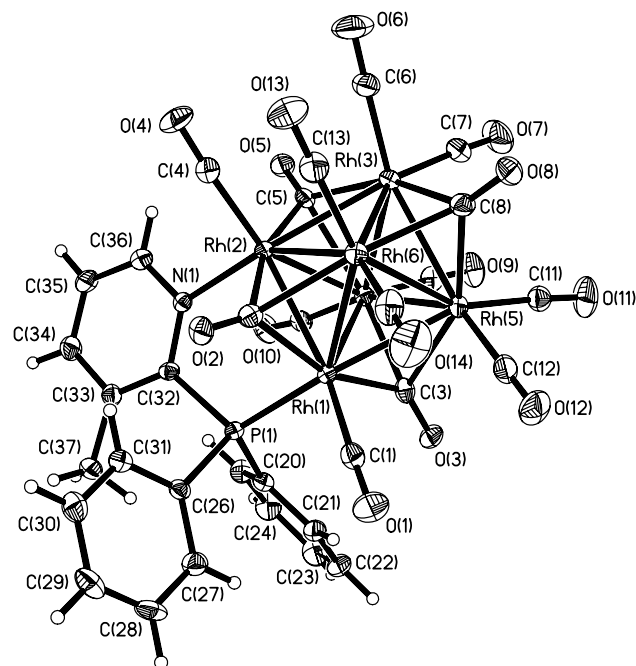

Fig. 4. Molecular structure of Rh$_6$(CO)$_{14}$(P(Mepy)Ph$_2$) (4). Selected bond lengths (Å) and angles (°): Rh(1)–Rh(2) 2.6703(4), Rh(1)–Rh(5) 2.7695(4), Rh(1)–Rh(4) 2.7755(4), Rh(1)–Rh(6) 2.7765(4), Rh(2)–Rh(6) 2.7192(4), Rh(2)–Rh(4) 2.7244(4), Rh(2)–Rh(3) 2.7372(4), Rh(3)–Rh(4) 2.7432(4), Rh(3)–Rh(6) 2.7757(4), Rh(3)–Rh(5) 2.7820(4), Rh(4)–Rh(5) 2.7721(4), Rh(5)–Rh(6) 2.7367(4), N(1)–Rh(2) 2.185(3), P(1)–Rh(1) 2.2894(9), N(1)–C(32)–P(1) 116.5(3), C(32)–P(1)–Rh(1) 113.82(11), C(32)–N(1)–Rh(2) 126.8(2).

spectrum a doublet at 3.7 ppm, with P–Rh coupling constants of 129 Hz is present. The Rh–Rh bond length of the P(Mepy)Ph$_2$ bridged bond is slightly shorter 2.6375(3) than the two other bonds 2.7603(3) and 2.7673(3).

When the reaction time between the HRuRh$_3$(CO)$_{12}$ and the P(Mepy)Ph$_2$ was lengthened (approx. 2 h), a new trinuclear mixed-metal compound, RuRh$_2$(CO)$_9$-(P(Mepy)Ph) (3), was obtained (Fig. 3). It seems likely that 3 is formed when the bridging ligand in 2 stages an attack on the cluster core. As a result, both the metal core and the ligand structure are then ruptured. In 3 the phosphorus atom has created a bond with both the ruthenium and rhodium at the same time, and one of the phenyl rings is removed from the ligand. A similar type of coordination in the Ru$_3$ cluster has been described previously. The oxidative cleavage of a P–C bond in PPh$_2$py provides an organic fragment, PPhpy, which caps the metal triangle through the bridging phosphido group together with the nitrogen of the pyridyl ring. The addition opens one metal bond and leads to the formation of an σ-bonded arylgroup. In many cases, the reductive elimination of benzene is subsequently favored in the presence of the hydride ligand [1,21,22].

No indication of hydride ligands in 3 was obtained using ^{1}H NMR spectroscopy. The ^{31}P NMR spectrum has a doublet at 110.9 ppm, $^1J_{P-Rh} = 96$ Hz.

2.3. Synthesis and structure of Rh$_6$(CO)$_{14}$(P(Mepy)Ph$_2$) (4)

Rh$_6$(CO)$_{14}$(P(Mepy)Ph$_2$) (4) (Fig. 4) was formed in the reaction between tetranuclear Rh$_4$(CO)$_{12}$ and the phosphane ligand as the main product. The formation of Rh$_6$ derivatives from the reactions of Rh$_4$ is a typical cluster rearrangement. Rh$_6$(CO)$_{16}$ cluster has two terminal carbonyls at every metal and four triply bridging carbonyls at opposite sides of the metal octahedron. The structure of 4 is a Rh$_6$(CO)$_{16}$ derivative, where two terminal carbonyls at adjacent metals are replaced by a bridging P(Mepy)Ph$_2$. ^{31} NMR shows a doublet at 24.3 ppm, $^1J_{P-Rh} = 142$ Hz. The ligand bridged metal bond is 2.6703(4), the other bonds lie in the range 2.7192(4)–2.7820(4). In this structure, the effect in metal bond lengths is not so remarkable than in smaller ones.

2.4. Synthesis and structure of Rh$_2$(CO)Cl$_2$ (P(Mepy)-Ph$_2$)$_2$ (5)

Treatment of Rh$_2$(CO)$_4$Cl$_2$ with the ligand in ratio Rh:L = 1:1 leads to the formation of Rh$_2$(CO)Cl$_2$-(P(Mepy)Ph$_2$)$_2$ (5) in good yield. The structure is given in Fig. 5. Two ligands bridge the dimeric Rh skeleton at the *trans* position. The chloride bridges of the original compound have been broken and, in their place, a carbonyl bridged metal–metal bond is formed. The two remaining chlorides are terminal.

The bridging ligands are orientated to produce a head-to-tail conformation. The Rh–Rh distance is 2.5846 Å, which is indicative of a metal–metal bond. Such an arrangement is typical of these dimeric complexed ligands bridged by a bidentate heterodonor. The corresponding structure of Rh$_2$(CO)Cl$_2$(PPh$_2$py) has been published and the geometry discussed in detail [23,24]. The spectroscopic data is consistent with the data supplied for the pyridylphosphane derivative published previously. ^{31}P $\delta = 47.2$ ppm $J = 140$ Hz
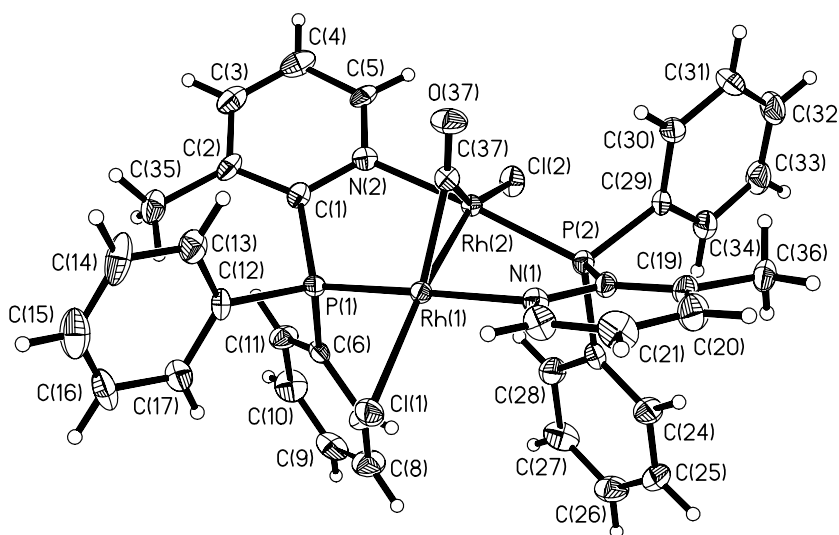

Fig. 5. Molecular structure of Rh$_2$(CO)Cl$_2$(P(Mepy)Ph$_2$)$_2$ (5). Selected bond lengths (Å) and angles (°): Rh(1)–Rh(2) 2.5846(8), Cl(1)–Rh(1) 2.367(2), Cl(2)–Rh(2) 2.354(2), P(1)–Rh(1) 2.223(2), N(2)–Rh(2) 2.125(6), P(2)–Rh(2) 2.226(2), N(1)–Rh(1) 2.125(6), C(37)–Rh(1) 1.946(7), C(37)–Rh(2) 1.940(7), N(1)–C(18)–P(2) 111.9(5), C(18)–P(2)–Rh(2) 115.6(2), C(18)–N(1)–Rh(1) 121.2(5), Rh(2)–C(37)–Rh(1) 83.4(3), O(37)–C(37)–Rh(1) 137.2(6), O(37)–C(37)–Rh(2) 139.4(6).

(44.18 ppm and 144.0 Hz for the pyridylphosphane derivative) and IR CO stretching to 1797 cm^{-1} is the same for both compounds. Thus the methyl substituent at the pyridyl ring has no noticeable effect on its reactions.

3. Experimental

3.1. General considerations

The reactions and chromatographic separations were performed in N_2 using deoxygenated solvents. P(Mepy)Ph$_2$ [25], HRuCo$_3$(CO)$_{12}$ [26], HRuRh$_3$(CO)$_{12}$ [27], Rh$_4$(CO)$_{12}$ [28] and Rh$_2$(CO)$_4$Cl$_2$ [29] were prepared using published methods. The IR spectra were recorded in dichloromethane on a Nicolet 20 SX spectrometer. The NMR spectra were measured in CDCl$_3$ on a Bruker AM-250 spectrometer using SiMe$_4$ (^{1}H) or 85% H$_3$PO$_4$ (^{31}P–{^{1}H}) standard.

3.2. Synthesis of 1

The HRuCo$_3$(CO)$_{12}$ (120 mg, 0.20 mmol) and P(Mepy)Ph$_2$ (55 mg, 0.20 mmol) were refluxed in CH$_2$Cl$_2$ for 1 h:45 min. The solution was evaporated to dryness and separated on a silica column. Elution with hexane and 2:1 hexane–CH$_2$Cl$_2$ produced fractions of byproducts. The hexane–CH$_2$Cl$_2$ 1:1 mixture gave product 1 as a brown band. Yield 57 mg, 35%. Dark cubic crystals of the product were obtained from the CH$_2$Cl$_2$. IR(CH$_2$Cl$_2$): 2075s, 2006vs, 1972w, 1833m, 1811m. NMR: ^{31}P–{^{1}H}: $\delta = 35.7$ ppm. ^{1}H: $\delta = -20.6$ ppm, d, $^2J_{H–P} = 18$ Hz.

3.3. Synthesis of 3 and 2

The HRuRh$_3$(CO)$_{12}$ (130 mg, 0.17 mmol) and P(Mepy)Ph$_2$ (60 mg, 0.23 mmol) were refluxed in H$_2$Cl$_2$ for 2 h. The solution was evaporated to dryness and separated on silica column. The hexane–CH$_2$Cl$_2$ 3:1 mixture gave the trinuclear 3 as an orange band. Yield 20 mg, 15%. Orange crystals of the product were obtained from the CH$_2$Cl$_2$. IR(CH$_2$Cl$_2$): 2076vs, 2038s, 2023 vs, 2006m, 1993w, 1966w, 1886w, 1813w. NMR: ^{31}P–{^{1}H}: $\delta = 110.9$ ppm, d, $J_{P–Rh} = 96$ Hz. The hexane–CH$_2$Cl$_2$ 2:1 mixture gave the tetranuclear 2 as an orange band. Yield 22 mg, 13%. Red crystals of the product were obtained from the CH$_2$Cl$_2$. IR(CH$_2$Cl$_2$): 2087w, 2073s, 2037s, 2024m, 2001vs, 1858m, 1830m. NMR: ^{31}P–{^{1}H}: $\delta = 3.7$ ppm, d, $J_{Rh–P} = 129$ Hz, ^{1}H: $\delta = -17.2$ ppm, d of d, $J_{H–Rh} = 60$ Hz, $^2J_{H–P} = 20$ Hz. In shorter reactions (30 min) 2 was the main product in a 31% yield.

3.4. Synthesis of 4

Rh$_4$(CO)$_{12}$ (120 mg, 0.156 mmol) and P(Mepy)Ph$_2$ (43 mg, 0.156 mmol) were refluxed in CH$_2$Cl$_2$ for 1 h:30 min. The solution was evaporated to dryness and separated on a silica column in N$_2$. Elution with 4:1 and 1:1 hexane–CH$_2$Cl$_2$ mixtures produced small fractions of byproducts. The hexane–CH$_2$Cl$_2$ 1:2 mixture gave the product 4 as a brown band. Yield 76 mg, 57%. Dark crystals of the product were obtained from the CH$_2$Cl$_2$ at −40 °C. IR(CH$_2$Cl$_2$): 2088m, 2056vs, 2026 m, 2002w, 1778w, 1755w. NMR: ^{31}P–{^{1}H}: $\delta = 24.3$ ppm, d, $J_{P–Rh} = 142$ Hz. Further elution with CH$_2$Cl$_2$ gave a brown band of byproducts.

Table 1
Crystal data for compounds 1–5

	1	2	3	4 · 2CH$_2$Cl$_2$	5 · CH$_2$Cl$_2$
Empirical formula	C$_{28}$H$_{17}$Co$_3$NO$_{10}$PRu	C$_{28}$H$_{17}$NO$_{10}$PRh$_3$Ru	C$_{21}$H$_{11}$NO$_9$PRh$_2$Ru	C$_{34}$H$_{20}$Cl$_4$NO$_{14}$PRh$_6$	C$_{38}$H$_{34}$Cl$_4$N$_2$OP$_2$Rh$_2$
Formula weight	836.26	968.20	759.17	1456.74	944.23
Temperature (K)	150(2)	120(2) K	293(2)	150(2) K	293(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	12.1310(2)	12.4864(1)	9.2012(4)	11.4466(1)	14.5912(3)
b (Å)	11.0890(2)	11.1883(1)	15.6249(7)	26.5032(5)	14.0388(3)
c (Å)	22.8930(2)	23.2385(3)	16.6607(7)	15.0688(3)	18.1459(2)
β (°)	104.243(1)	105.004(1)	98.175(2)	111.473(1)	90.341(1)
V (Å^3)	2984.91(8)	3135.78(6)	2370.9(2)	4254.14(12)	3716.99(12)
Z	4	4	4	4	4
ρ_{calc} (Mg/m^3)	1.861	2.051	2.127	2.274	1.687
μ(Mo Kα) (mm^{-1})	2.246	2.130	2.124	2.627	1.296
R_1[a] ($I \geqslant 2\sigma$)	0.0249	0.0244	0.0515	0.0264	0.0630
wR_2[b] ($I \geqslant 2\sigma$)	0.0597	0.0566	0.1133	0.0586	0.1544

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.
[b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/ \sum[w(F_o^2)^2]]^{1/2}$.

3.5. Synthesis of 5

$Rh_2(CO)_4Cl_2$ (50 mg, 0.13 mmol) and $P(Mepy)Ph_2$ (73 mg, 0.26 mmol) were dissolved in methanol in separate flasks. The solutions were combined, and the product **5** was formed as a brown solid. The product was filtered from the solution, washed with methanol and dried in a vacuum. Yield 80 mg, 72%. Orange crystals were formed in the crystallization from the CH_2Cl_2. IR(CH_2Cl_2): 1797 cm^{-1}. NMR: $^{31}P-\{^1H\}$: $\delta = 47.2$ ppm, d, $J_{P-Rh} = 140$ Hz.

3.6. X-ray structure determinations

The X-ray diffraction data were collected by means of a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). The Denzo-Scalepack [30] program package was used for cell refinements and data reduction. All of the structures were solved by direct methods using the SIR-97 (**1**) or SHELXS-97 (**2**–**5**) program and the WinGX graphical user interface [31–33]. A multiscan absorption correction based on equivalent reflections (XPREP in SHELXTL v. 6.12) [34] was applied to **2** and **4** (the T_{min}/T_{max} values were 0.29531/0.32936 and 0.22659/0.30332 for **2** and **4**, respectively). Other data were scaled by Denzo-Scalepack. Structural refinements were performed using SHELXL-97 [35]. In structures **1** and **2**, the hydride hydrogens were located from the difference Fourier map and refined isotropically. All of the other hydrogens were placed in idealized positions and they were constrained to ride on their parent atom. The crystallographic data are summarized in Table 1. Selected bond lengths and angles are shown in Figs. 1–5.

4. Summary

$P(Mepy)Ph_2$ is a ligand that has variable coordination modes. Both phosphorus and nitrogen can be utilized in coordination. In reactions with a metal cluster, a simple substitution of the carbonyl groups is possible, but in some cases both the ligand and the cluster may be ruptured, and the product is an adduct of these fragments. The bridging ligand stabilizes the metal cores. The site selectivity in the Ru–Co cluster favors coordination of the ligand with the cobalt atoms. In the mixed Ru–Rh cluster the coordination first occurs with the rhodium atoms, but in the case of further reactions ruthenium may also be involved. Compared to PPh_2py, the additional methyl group in $P(Mepy)Ph_2$ produces no essential difference in reactivity as a ligand. The rich chemistry P–N ligands open up new opportunities for modifying the catalytic properties of metal clusters.

5. Supplementary material

The crystallographic data for compound **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 219003–219007. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-(0)1223-336033, E-mail: deposit@ccdc.cam.ac.uk].

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