Cleavage of Phosphorus–Phenyl and Phosphorus-2-Pyridyl Bonds in the Reactions of Mixed Phenyl(2-pyridyl)phosphines with $[Ru_3(CO)_{12}]$†

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The compound $[Ru_3(CO)_{12}]$ reacts at room temperature in tetrahydrofuran with tri(2-pyridyl)phosphine, $P(2\text{-}C_5H_4N)_3$, when catalysed by $[N(PPh_3)_2]Cl$, to give a product derived by cleavage of a phosphorus–2-pyridyl bond, $[Ru_3(\mu\text{-}2\text{-}C_5H_4N)\{\mu_3\text{-}P(2\text{-}C_5H_4N)_2\}(CO)_9]$ **1**. No simple substitution compounds could be isolated. The likely intermediates $[Ru_3(CO)_n\{P(2\text{-}C_5H_4N)_3\}]$ ($n = 10$ and/or 11) spontaneously decarbonylate while a 2-pyridyl group migrates from phosphorus to ruthenium atoms. A similar reaction using phenyldi(2-pyridyl)phosphine, $PPh(2\text{-}C_5H_4N)_2$, leads to the competitive transfer of 2-pyridyl and phenyl groups to give almost equal quantities of two products, $[Ru_3(\mu\text{-}2\text{-}C_5H_4N)\{\mu_3\text{-}PPh(2\text{-}C_5H_4N)\}(CO)_9]$ and $[Ru_3(\mu\text{-}PhCO)\{\mu_3\text{-}P(2\text{-}C_5H_4N)_2\}(CO)_9]$. The crystal structure of **1** shows that the 2-pyridyl group that has migrated bridges two ruthenium atoms with no Ru–Ru bond between them and that the di(2-pyridyl)phosphido ligand is triply bridging with one nitrogen co-ordinated and one free. As in the reported reaction of $[Ru_3(CO)_{12}]$ with $PPh_2(2\text{-}C_5H_4N)$ to give $[Ru_3(\mu\text{-}PhCO)\{\mu_3\text{-}PPh(2\text{-}C_5H_4N)\}(CO)_9]$, the reason why P–C bond cleavage occurs under remarkably mild conditions and the mechanism of the processes have still to be determined.

Ligand cleavages in triruthenium and triosmium carbonyl clusters are a major feature of their chemistry and the rate-determining steps often appear to be the loss of CO ligands to create unsaturation.[1] For this reason elevated temperatures are often used. Triphenylphosphine and mixed alkylarylphosphines normally undergo orthometallation (C–H bond cleavage) as the first step in what may be a series of subsequent steps. For example, $[Os_3(CO)_{11}(PMePh_2)]$ thermally converts to $[Os_3(\mu_3\text{-}C_6H_4)(\mu_3\text{-}PMe)(CO)_9]$.[2] An early intermediate in the process is $[Os_3(\mu\text{-}H)(\mu\text{-}C_6H_4PMePh)(CO)_{10}]$ which decarbonylates to afford $[Os_3(\mu\text{-}H)(\mu_3\text{-}C_6H_4PMePh)(CO)_9]$ (crystal structure determined). This cluster loses benzene and picks up CO to give $[Os_3(\mu_3\text{-}C_6H_4PMe)(CO)_{10}]$ (crystal structure determined).[3] Finally decarbonylation and P–C bond cleavage gives the ultimate product. In contrast, Lugan *et al.*[4] have shown that, by using catalysts for CO displacement such as $[N(PPh_3)_2]CN$ or sodium diphenylketyl, $[Ru_3(CO)_{12}]$ reacts with diphenyl(2-pyridyl)phosphine, $PPh_2(2\text{-}C_5H_4N)$, at room temperature in tetrahydrofuran (thf) to give $[Ru_3(CO)_{11}\{PPh_2(2\text{-}C_5H_4N)\}]$ rapidly, and that this converts at 25 °C over 48 h or within 2 h at 40 °C to the μ-benzoyl cluster $[Ru_3(\mu\text{-}PhCO)\{\mu_3\text{-}PPh(2\text{-}C_5H_4N)\}(CO)_9]$ **4** in 85% yield. In this example orthometallation was not observed. They reason that the phenyl group migrates from phosphorus to ruthenium atoms to give the unobserved cluster $[Ru_3(Ph)\{\mu_3\text{-}PPh(2\text{-}C_5H_4N)\}(CO)_{10}]$ and that the phenyl group then migrates from ruthenium to CO to give cluster **4**. The direct thermal reaction of the ligand with $[Ru_3(CO)_{12}]$ in methanol gives simply the trisubstituted product $[Ru_3(CO)_9\{PPh_2(2\text{-}C_5H_4N)\}_3]$ without any P–C bond cleavage.[5] The ligand $PPh_2(2\text{-}C_5H_4N)$ is well known for its ability to bridge and stabilize compounds with more than one metal atom[6] and there appears to be just the one reported example of a cleavage reaction of this kind.[4] In this work we have treated tertiary phosphines with two or three 2-pyridyl substituents to explore these migration reactions. When there is only one 2-pyridyl substituent, this does not migrate but remains part of the phosphorus-containing ligand. When there are three 2-pyridyl substituents, one of these migrates but, when there are two 2-pyridyl substituents, there is a competitive migration of 2-pyridyl and phenyl substituents.

Results and Discussion

Using a method related to that developed by Lugan *et al.*[4] for diphenyl(2-pyridyl)phosphine, $[Ru_3(CO)_{12}]$ was treated with tri(2-pyridyl)phosphine, $P(2\text{-}C_5H_4N)_3$, in thf with $[N(PPh_3)_2]Cl$ as a catalyst. The initial rapid colour change from orange to deep red on addition of the salt probably indicates that CO substitution has occurred to give either $[Ru_3(CO)_{11}\{P(2\text{-}C_5H_4N)_3\}]$ or $[Ru_3(CO)_{10}\{\mu\text{-}P(2\text{-}C_5H_4N)_3\}]$ or both. No attempt was made to isolate clusters at this stage and after 4 d at room temperature the IR spectrum of the reaction solution showed that further reaction had occurred. Work-up of the solution using thin-layer chromatographic separation on silica gave product **1** (58%), which had the apparent stoichiometry $[Ru_3(CO)_9\{P(2\text{-}C_5H_4N)_3\}]$. Osmium clusters corresponding to the proposed ruthenium intermediates, $[Ru_3(CO)_{11}\{P(2\text{-}C_5H_4N)_3\}]$ and $[Ru_3(CO)_{10}\{\mu\text{-}P(2\text{-}C_5H_4N)_3\}]$, and other related mixed phenyl(2-pyridyl)phosphine complexes have been isolated but these are very much more stable in solution at room temperature.[7] However, we have shown that the cluster $[Os_3(CO)_{10}\{\mu\text{-}PPh_2(2\text{-}C_5H_4N)\}]$ does undergo ligand cleavage but only at elevated temperatures, for example in refluxing *n*-heptane.[8]

The cluster **1** was characterised by ^1H NMR (Table 1), by IR and $^{31}P\text{-}\{^1H\}$ NMR (Table 2), by $^{13}C\text{-}\{^1H\}$ NMR spectroscopy (Table 3), and by single-crystal X-ray diffraction (see later). Since $P(2\text{-}C_5H_4N)_3$ contains four potential donor atoms, the stoichiometry of **1** may be achieved without P–C bond cleavage. However, it was shown to contain three different 2-pyridyl rings. Fig. 1 shows the ^1H NMR spectrum of cluster **1** together with those of clusters **2**–**4**, also described in this paper. One 2-pyridyl ring of **1** gave ^1H NMR signals showing a lack of any ^{31}P coupling which strongly indicated that it was no longer part of the original ligand and that P–C bond cleavage had occurred. The chemical shift for the H^6 proton of this ring

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

Table 1 Proton NMR spectroscopic data[a] for compounds **1–3** and for the previously reported compound [Ru_3(μ-PhCO){μ_3-PPh(2-C_5H_4N)}-$(CO)_9$] **4**[b]

Compound	2-Pyridyl rings[c]				Phenyl rings	
	Proton	A	B	C	Ph	μ-PhCO
1	H^6	8.43	8.30	8.83		
	H^5	6.52	6.95	7.33		
	H^4	6.87	7.30	7.82		
	H^3	7.52	6.57	7.97		
2	H^6	8.43	8.29		7.91 (*o*)	
	H^5	6.52	6.90		7.56 (*m*)	
	H^4	6.88	7.22		7.49 (*p*)	
	H^3	7.52	6.14			
3	H^6		8.34	8.82		7.62 (*o*)
	H^5		7.02	7.35		7.34 (*m*)
	H^4		7.35	7.83		7.41 (*p*)
	H^3		6.70	7.90		
4	H^6		8.31		7.82 (*o*)	7.62 (*o*)
	H^5		6.99		7.56 (*m*)	7.34 (*m*)
	H^4		7.30		7.50 (*p*)	7.41 (*p*)
	H^3		6.26			

[a] Recorded at 400 MHz in CD_2Cl_2 at 20 °C. [b] No ^1H NMR data were reported previously.[4] [c] 2-Pyridyl ring assignments: ring A, μ-2-pyridyl; ring B, co-ordinated 2-pyridyl of phosphido ligand; ring C, non-co-ordinated 2-pyridyl of phosphido ligand.

Table 2 IR and ^{31}P-{^1H} NMR spectroscopic data for compounds **1–3** and for the previously reported compound [Ru_3(μ-PhCO){μ_3-PPh(2-C_5H_4N)}$(CO)_9$] **4**[4]

Compound	ν(CO)[a]/cm^{-1}	^{31}P-{^1H} NMR[b]
1	2069m, 2045vs, 2021vs, 1992s, 1975m, 1967m, 1955m	43.9
2	2068m, 2044vs, 2020s, 1992s, 1977s, 1968m, 1956m	37.1
3	2075m, 2050vs, 2025vs, 2001 (sh), 1997s, 1985m, 1978s, 1971m, 1959m	57.2
4[c]	2074m, 2049vs, 2024vs, 2005 (sh), 1997s, 1983 (sh), 1978s, 1972 (sh), 1960m	51.2

[a] Recorded in cyclohexane. [b] Recorded at 162 MHz in CD_2Cl_2 at 20 °C, singlets observed in each case. [c] Previously reported[4] IR data for **4**: 2060w, 2045vs, 2020s, 1992m, 1973m, 1955m cm^{-1} (hexane).

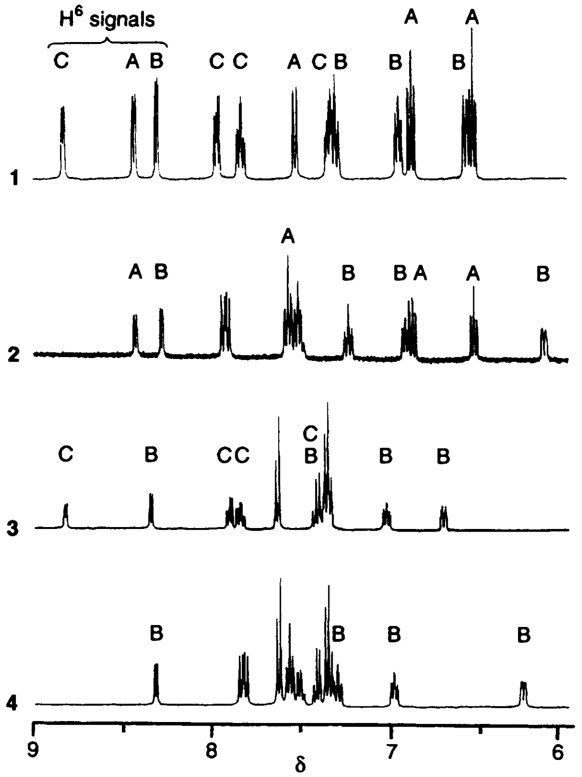
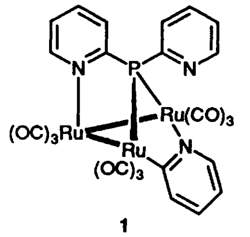


Fig. 1 400 MHz ^1H NMR spectra of compounds **1–4**. The pyridyl ring signals are labelled as in Tables 1 and 3; ring A = μ-2-pyridyl, ring B = co-ordinated 2-pyridyl of a phosphido ligand, ring C = non-co-ordinated ring of a phosphido ligand



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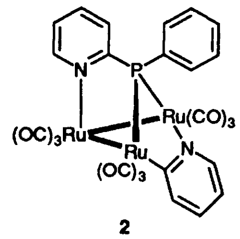

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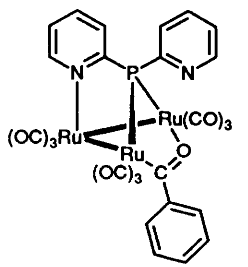

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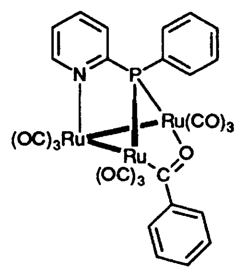

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(δ 8.43), the most easily assigned signal, is consistent with co-ordinated rather than non-co-ordinated pyridine, so we considered that the cleaved 2-pyridyl was bridging two ruthenium atoms. The ^1H NMR signals of the two remaining pyridyl rings showed that one was co-ordinated (δ 8.30 for H^6) and the other not (δ 8.83 for H^6) and that both were still bound to phosphorus. The H^6 signal in the free ligand is observed at δ 8.69 (recorded in $CDCl_3$). These data are consistent with the formulation [Ru_3(μ-2-C_5H_4N){μ_3-P(2-$C_5H_4N)_2$}$(CO)_9$] for **1**. This would require the μ-2-pyridyl to be a three-electron donor and the μ_3-di(2-pyridyl)phosphido ligand a five-electron donor making the compound a 50-electron cluster. The lack of NMR evidence for a hydride ligand showed that C–H cleavage had not occurred as seen with triphenylphosphine and with mixed alkylarylphosphines.

The crystal structure of cluster **1** is shown in Fig. 2 and selected bond lengths and angles are in Table 4. The unit cell contains two independent molecules, molecule A containing Ru(1)–Ru(3) and molecule B containing Ru(4)–Ru(6) and the former is illustrated. The structure is closely related to the known structure of [Ru_3(μ-PhCO){μ_3-PPh(2-C_5H_4N)}$(CO)_9$] **4**[4] with the μ-PhCO ligand replaced by μ-2-pyridyl and with di(2-pyridyl)phosphido instead of the phenyl(2-pyridyl)phosphido ligand. The metal atoms in the two compounds have closely similar co-ordination geometries. The Ru(1) ··· Ru(3) distance for the 2-pyridyl bridged pair is 3.708(1) Å [Ru(4) ··· Ru(6) 3.701(1) Å], consistent with the cluster having 50 electrons and there being no metal–metal bond across this edge. The non-bonded Ru ··· Ru distances in closely related compounds are 3.639(1) Å in the cluster [Ru_3(μ-PhCO){μ_3-PPh(2-C_5H_4N)}$(CO)_9$] **4**[4] and 3.498(1) Å in [Ru_3(μ-I){μ_3-PPh-(2-C_5H_4N)}$(CO)_9$].[9] The other Ru–Ru distances in cluster **1** are in the range 2.855(1)–2.868(1) Å and are normal bonding distances for Ru–Ru single bonds. The μ_3 ligand leads to a very stable arrangement and various substitution reactions have

Table 3 $^{13}C-\{^1H\}$ NMR spectroscopic data[a] for compounds **1**–**3** and for the previously reported compound $[Ru_3(\mu\text{-}PhCO)\{\mu_3\text{-}PPh(2\text{-}C_5H_4N)\}(CO)_9]$ **4**

	2-Pyridyl rings[b]			Phenyl rings	
Compound	A	B	C	Ph	PhCO
1[c]	211.9 (8.6)	185.8 (51.2)	163.3 (21.1)		
	153.8 (2.5)	154.8 (12.3)	149.9 (13)		
	141.9 (2.9)	134.9 (4)	136.1 (7.4)		
	129.7	124.7 (7.4)	127.3 (27)		
	117.9	123.2 or 123.1	123.2 or 123.1		
2[c]	211.8 (8.3)	187.7 (49.6)		138.1 (4)	
	153.7 (3)	154.7 (12.1)		133.8 (12.6)	
	141.9 (2.7)	135.0 (6)		129.9 or 129.8	
	129.9 or 129.8	124.2 (8.4)		128.9 (8.7)	
	117.9	123.0			
3[c]		185.1 (53.9)	163.0 (23.3)		151.1
		155.0 (12.7)	150.0 (13.2)		131.5
		135.2 (4.3)	136.3 (7.4)		128.0
		125.6 (7.6)	127.2 (27.2)		127.8
		123.5 or 123.4	123.5 or 123.4		
4[c]		186.9 (52.4)		137.8 (5.9)	151.0
		154.8 (12.2)		133.6 (12.3)	131.5
		135.3 (5.6)		130.0 (2.1)	128.0
		125.0 (8.9)		129.0 (8.8)	127.7
		123.4			

[a] Recorded at 100.6 MHz in $CDCl_3$ at 20 °C; doublets with $J(^{31}PC)$/Hz given in parentheses or singlets (no ^{31}P coupling detected). [b] 2-Pyridyl ring assignments: ring A, μ-2-pyridyl; ring B, co-ordinated 2-pyridyl of phosphido ligand; ring C, non-co-ordinated 2-pyridyl of phosphido ligand. [c] Sharp sets of unassigned CO singlets or doublets were observed: **1**, δ 189.6–204.2; **2**, δ 189.6–203.9; **3**, δ 188.0–203.5; **4**, δ 187.8–203.6.

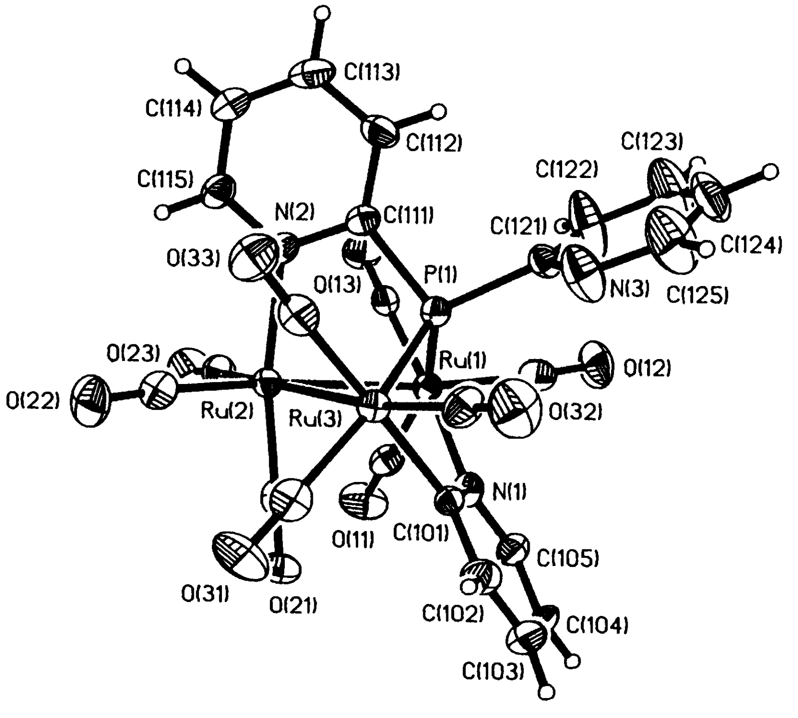


Fig. 2 Molecular structure of molecule A of the cluster $[Ru_3(\mu\text{-}2\text{-}C_5H_4N)\{\mu_3\text{-}P(2\text{-}C_5H_4N)_2\}(CO)_9]$ **1**

been described for $[Ru_3(\mu\text{-}PhCO)\{\mu_3\text{-}PPh(2\text{-}C_5H_4N)\}(CO)_9]$ **4** in which the $Ru_3\{\mu_3\text{-}PPh(2\text{-}C_5H_4N)\}$ arrangement is maintained.[4,10]

One crystallographic problem is that of correctly positioning the nitrogen and carbon atoms in the 2-pyridyl rings. We assumed that the μ_3 ligands are bonded through phosphorus and nitrogen atoms and that the ligand has not been C-metallated. The ^1H NMR spectrum is totally consistent with this. Although the positions given for N(1) and N(3) in molecule A and for N(4) and N(6) in B led to somewhat more satisfactory thermal parameters, we could not rule out some indeterminate degree of disorder of the rings containing these atoms. Indeed, a likely situation is of disorder between enantiomers with the μ-2-pyridyl ligands in opposite orientations, but we have made no attempt to model this as it would not fundamentally modify our chemical interpretation of the structure.

By using phenyldi(2-pyridyl)phosphine with $[Ru_3(CO)_{12}]$ under the same reaction conditions, two clusters were obtained: $[Ru_3(\mu\text{-}2\text{-}C_5H_4N)\{\mu_3\text{-}PPh(2\text{-}C_5H_4N)\}(CO)_9]$ **2** and $[Ru_3(\mu\text{-}PhCO)\{\mu_3\text{-}P(2\text{-}C_5H_4N)_2\}(CO)_9]$ **3** in similar yields but lower than from the other pyridylphosphines, diphenyl(2-pyridyl)-phosphine and tri(2-pyridyl)phosphine. Cluster **2** is directly analogous to cluster **1** and cluster **3** to $[Ru_3(\mu\text{-}PhCO)\{\mu_3\text{-}PPh(2\text{-}C_5H_4N)\}(CO)_9]$ **4** obtained by Lugan *et al.*[4] Fig. 1

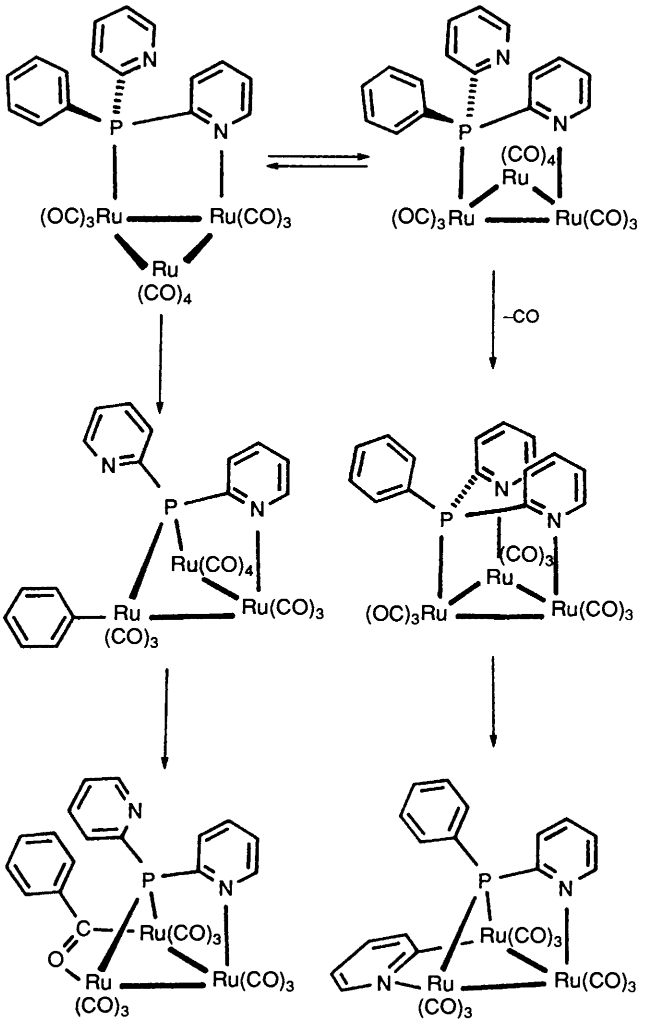
Table 4 Selected bond lengths (Å) and angles (°) for the two independent molecules in the unit cell of [Ru_3(μ-2-C_5H_4N){μ_3-P(2-C_5H_4N)$_2$}$(CO)_9$] **1** *

	Molecule A	Molecule B
Ru(1)–Ru(2)	2.856(1)	2.855(1)
Ru(2)–Ru(3)	2.858(1)	2.868(1)
Ru(1) · · · Ru(3)	3.708(1)	3.701(1)
Ru(1)–P(1)	2.362(2)	2.358(2)
Ru(3)–P(1)	2.363(2)	2.347(2)
Ru(1)–N(1)	2.155(7)	2.183(8)
Ru(2)–N(2)	2.186(7)	2.192(7)
Ru(3)–C(101)	2.147(7)	2.145(7)
N(1)–C(101)	1.37(1)	1.33(1)
N(1)–C(105)	1.38(1)	1.39(1)
C(101)–C(102)	1.41(1)	1.39(1)
C(102)–C(103)	1.36(1)	1.38(1)
C(103)–C(104)	1.39(1)	1.35(1)
C(104)–C(105)	1.38(1)	1.36(1)
N(2)–C(111)	1.35(1)	1.33(1)
N(2)–C(115)	1.34(1)	1.35(1)
C(111)–C(112)	1.40(1)	1.39(1)
C(112)–C(113)	1.39(1)	1.36(2)
C(113)–C(114)	1.37(1)	1.36(2)
C(114)–C(115)	1.37(1)	1.37(2)
N(3)–C(121)	1.34(1)	1.33(1)
N(3)–C(125)	1.39(2)	1.37(1)
C(121)–C(122)	1.32(1)	1.39(1)
C(122)–C(123)	1.39(2)	1.36(2)
C(123)–C(124)	1.29(2)	1.34(2)
C(124)–C(125)	1.34(2)	1.37(2)
Ru(1)–Ru(2)–Ru(3)	80.9(1)	80.6(1)
Ru(1)–Ru(2)–N(2)	89.4(2)	87.8(2)
Ru(3)–Ru(2)–N(2)	86.4(2)	88.4(2)
Ru(2)–Ru(1)–P(1)	68.2(1)	67.8(1)
Ru(2)–Ru(1)–N(1)	90.8(2)	90.2(2)
Ru(2)–Ru(3)–P(1)	68.2(1)	67.8(1)
Ru(2)–Ru(3)–C(101)	90.6(2)	90.6(2)
Ru(1)–P(1)–Ru(3)	103.4(1)	103.7(1)
Ru(1)–P(1)–C(111)	108.7(3)	109.0(3)
Ru(3)–P(1)–C(111)	106.7(3)	107.1(3)
P(1)–C(111)–N(2)	109.9(6)	109.8(6)
Ru(2)–N(2)–C(111)	116.3(5)	116.3(5)
C(111)–P(1)–C(121)	103.6(4)	101.9(4)

* Atom labels refer to those in molecule A. Data given for molecule B correspond to those for molecule A.

shows the ^1H NMR spectra of compounds **1–4** which may be correlated with these structures. We have assigned the signals with some confidence (Table 1) and believe that the structures shown are firmly established. Note that the ν(CO) IR spectrum of cluster **1** (Table 2) is very similar to that of **2** and likewise that of **3** is very similar to that of cluster **4**.

The course of the reaction steps leading to clusters **1–4** may be discussed in the light of secondary evidence. We presume that each reaction occurs *via* the bridging ligand systems, [Ru_3(μ-L)$(CO)_{10}$], where L is a mixed phenyl(2-pyridyl)phosphine, in which the phosphorus atom and one of the 2-pyridyl groups are co-ordinated. It is unlikely that loss of CO from [Ru_3L$(CO)_{11}$] would not lead to such a cluster. We have isolated and structurally characterised the related cluster [Os_3{μ-PPh_2(2-C_5H_4N)}$(CO)_{10}$], which is thermally stable in solution at room temperature unlike its ruthenium analogue.[7] Intermediates of this type with bridging ligands such as at the left of Scheme 1 would account for the total lack of 2-pyridyl transfer when using PPh_2(2-C_5H_4N), while 2-pyridyl transfer occurs competitively with phenyl transfer using PPh(2-C_5H_4N)$_2$. 2-Pyridyl transfer occurs readily when using P(2-C_5H_4N)$_3$. Thus we can deduce that only terminal substituents migrate and, when the 2-pyridyl ring forms part of the bridge, it is not cleaved from the phosphine. Scheme 1 shows a possible route to the products from PPh(2-C_5H_4N)$_2$. The two isomers of the supposed intermediate, [Ru_3{μ-PPh(2-C_5H_4N)$_2$}$(CO)_{10}$], would be in rapid equilibrium; we have established this is the case for the isolable osmium analogue[7] and the ruthenium cluster is not likely to be less dynamic. We propose that each isomer gives a different product by transfer of the nearest group to the non-bridged ruthenium atom. The formation of the μ_3-PPh(2-C_5H_4N)$_2$ cluster prior to 2-pyridyl transfer is a possibility. We do not know whether migration occurs before or after CO loss. If CO loss occurs before P–Ph cleavage then the CO must re-co-ordinate to give the PhCO product. However, if P–C cleavage occurs before CO loss, we would conclude that the subsequent phenyl migration to CO occurs readily, while the 2-pyridyl ligand rapidly displaces CO to form the μ-2-pyridyl product. Interestingly the cluster [Os_3{μ-PPh_2(2-C_5H_4N)}$(CO)_{10}$] is stable in solution at room temperature but on heating gives [Os_3(Ph){μ_3-PPh(2-C_5H_4N)}$(CO)_9$] as the dominant product;[8] phenyl migration from osmium to CO is expected to be much less favourable than phenyl migration from ruthenium to CO.



Scheme 1

Experimental

The 2-pyridyl ligands, PPh_2(2-C_5H_4N)[5] and P(2-C_5H_4N)$_3$,[11] were synthesised essentially as reported previously, while PPh(2-C_5H_4N)$_2$ was prepared in a similar way to P(2-C_5H_4N)$_3$,[11] using $PPhCl_2$ instead of PCl_3 as the starting material. The compounds $PPhCl_2$, [N$(PPh_3)_2$]Cl and [$Ru_3(CO)_{12}$] were used as supplied by Aldrich. Phosphorus trichloride was used as supplied by BDH.

Table 5 Fractional atomic coordinates (× 10^4) for $[Ru_3(\mu\text{-}2\text{-}C_5H_4)\{\mu_3\text{-}P(2\text{-}C_5H_4)_2\}(CO)_9]$ **1**

	Molecule A				Molecule B		
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	3 459(1)	8 445(1)	1 387(1)	Ru(4)	8 315(1)	6 643(1)	2 208(1)
Ru(2)	2 164(1)	8 457(1)	378(1)	Ru(5)	7 222(1)	7 857(1)	2 025(1)
Ru(3)	3 069(1)	7 380(1)	−354(1)	Ru(6)	8 330(1)	8 466(1)	1 130(1)
P(1)	3 176(1)	7 185(1)	920(1)	P(2)	8 182(1)	7 110(1)	1 001(1)
N(1)	4 184(4)	8 507(4)	506(4)	N(4)	9 209(4)	7 513(5)	2 328(4)
N(2)	1 733(3)	7 439(4)	928(3)	N(5)	6 730(4)	7 221(4)	1 072(4)
N(3)	4 087(6)	5 914(6)	807(5)	N(6)	9 234(4)	6 998(4)	21(4)
C(101)	4 033(4)	8 116(4)	−139(4)	C(131)	9 206(4)	8 169(4)	1 944(4)
C(102)	4 544(5)	8 206(6)	−678(5)	C(132)	9 817(5)	8 666(5)	2 053(5)
C(103)	5 162(5)	8 667(6)	−595(6)	C(133)	10 434(5)	8 490(6)	2 525(5)
C(104)	5 311(5)	9 067(6)	56(6)	C(134)	10 433(5)	7 819(6)	2 906(5)
C(105)	4 817(4)	8 968(5)	590(5)	C(135)	9 828(5)	7 338(6)	2 803(5)
C(111)	2 246(4)	6 903(5)	1 176(4)	C(141)	7 211(5)	6 936(5)	622(4)
C(112)	2 023(5)	6 229(5)	1 530(5)	C(142)	6 965(6)	6 596(6)	−39(5)
C(113)	1 267(6)	6 110(6)	1 622(5)	C(143)	6 214(7)	6 542(7)	−217(7)
C(114)	759(5)	6 660(5)	1 365(5)	C(144)	5 729(6)	6 814(7)	257(8)
C(115)	1 008(5)	7 313(5)	1 021(5)	C(145)	5 988(5)	7 163(6)	896(6)
C(121)	3 796(5)	6 383(5)	1 298(5)	C(151)	8 731(5)	6 579(5)	350(4)
C(122)	4 013(8)	6 338(7)	1 999(7)	C(152)	8 661(6)	5 779(5)	247(5)
C(123)	4 506(9)	5 763(9)	2 262(8)	C(153)	9 076(7)	5 417(6)	−244(6)
C(124)	4 774(7)	5 286(8)	1 807(8)	C(154)	9 585(7)	5 827(8)	−583(6)
C(125)	4 601(9)	5 361(8)	1 091(9)	C(155)	9 664(6)	6 609(8)	−442(6)
C(11)	3 475(5)	9 594(6)	1 432(5)	C(41)	8 254(6)	6 668(7)	3 259(6)
O(11)	3 475(5)	10 248(4)	1 449(4)	O(41)	8 207(5)	6 704(6)	3 868(4)
C(12)	4 325(6)	8 232(5)	2 071(5)	C(42)	9 043(5)	5 829(5)	2 114(5)
O(12)	4 782(4)	8 122(5)	2 506(4)	O(42)	9 454(5)	5 339(4)	2 047(5)
C(13)	2 747(5)	8 385(5)	2 108(5)	C(43)	7 481(6)	5 954(6)	2 045(5)
O(13)	2 336(4)	8 363(4)	2 552(3)	O(43)	7 000(5)	5 519(5)	1 935(5)
C(21)	2 716(5)	9 200(5)	−109(5)	C(51)	7 789(6)	8 362(6)	2 780(5)
O(21)	3 041(4)	9 655(4)	−412(4)	O(51)	8 103(5)	8 690(5)	3 253(4)
C(22)	1 387(5)	8 439(5)	−398(5)	C(52)	6 631(5)	8 788(6)	1 820(5)
O(22)	943(4)	8 498(5)	−862(4)	O(52)	6 301(4)	9 348(5)	1 749(4)
C(23)	1 699(5)	9 203(6)	970(5)	C(53)	6 591(6)	7 339(7)	2 679(5)
O(23)	1 430(5)	9 692(4)	1 286(4)	O(53)	6 231(5)	7 067(6)	3 090(5)
C(31)	2 829(5)	7 936(6)	−1 252(6)	C(61)	8 251(5)	9 487(5)	1 561(5)
O(31)	2 684(5)	8 283(5)	−1 767(4)	O(61)	8 200(5)	10 071(4)	1 832(5)
C(32)	3 691(5)	6 567(6)	−703(5)	C(62)	9 081(5)	8 717(5)	468(5)
O(32)	4 022(5)	6 082(5)	−957(4)	O(62)	9 525(4)	8 892(5)	86(4)
C(33)	2 173(6)	6 754(5)	−491(5)	C(63)	7 519(5)	8 628(4)	404(5)
O(33)	1 652(4)	6 381(4)	−569(4)	O(63)	7 049(3)	8 688(4)	−46(3)

Reaction of $[Ru_3(CO)_{12}]$ *with Tri(2-pyridyl)phosphine.*—A solution of $[Ru_3(CO)_{12}]$ (0.327 g, 0.512 mmol) and the tertiary phosphine (0.138 g, 0.520 mmol) in freshly distilled thf (80 cm^3) was stirred under nitrogen at room temperature. Addition of $[N(PPh_3)_2]Cl$ (*ca.* 0.010 g) resulted in the orange solution turning deep red over *ca.* 2 min, indicating the formation of $[Ru_3(CO)_{11}\{P(2\text{-}C_5H_4N)_3\}]$. Stirring at room temperature was continued for 4 d. Removal of the solvent and work-up by thin-layer chromatography (TLC) [SiO_2; eluent, dichloromethane–light petroleum (b.p. 30–40 °C) (v/v, 1 : 1)] gave some impure $[Ru_3(CO)_{12}]$ (0.014 g) and a yellow band which yielded $[Ru_3(\mu\text{-}2\text{-}C_5H_4N)\{\mu_3\text{-}P(2\text{-}C_5H_4N)_2\}(CO)_9]$ **1** as yellow crystals (0.244 g, 58%) (Found: C, 35.0; H, 1.35; N, 5.05. $C_{24}H_{12}N_3O_9PRu_3$ requires C, 35.15; H, 1.5; N, 5.1%).

Reaction of $[Ru_3(CO)_{12}]$ *with Phenyldi(2-pyridyl)phosphine.*—*A solution of* $[Ru_3(CO)_{12}]$ (0.298 g, 0.466 mmol) and the tertiary phosphine (0.126 g, 0.477 mmol) in freshly distilled thf (70 cm^3), using $[N(PPh_3)_2]Cl$ (0.007 g) as a catalyst was treated under essentially the same conditions. Work-up by TLC [SiO_2; eluent, dichloromethane–light petroleum (b.p. 30–40 °C) (v/v, 1 : 3)] gave some impure $[Ru_3(CO)_{12}]$ (0.008 g) and two distinct bands which yielded $[Ru_3(\mu\text{-}2\text{-}C_5H_4N)\{\mu_3\text{-}PPh(2\text{-}C_5H_4N)\}(CO)_9]$ **2** as yellow crystals (0.080 g, 21%) (Found: C, 36.4; H, 1.85; N, 3.15. $C_{25}H_{13}N_2O_9PRu_3$ requires C, 36.65; H, 1.6; N, 3.4%) and $[Ru_3(\mu\text{-}PhCO)\{\mu_3\text{-}P(2\text{-}C_5H_4N)_2\}(CO)_9]$ **3** as yellow crystals (0.066 g, 17%) (Found: C, 37.35; H, 1.65; N, 3.3. $C_{26}H_{13}N_2O_{10}Ru_3$ requires C, 36.85; H, 1.55; N, 3.3%).

Structure Determination of $[Ru_3(\mu\text{-}2\text{-}C_5H_4N)\{\mu_3\text{-}P(2\text{-}C_5H_4N)_2\}(CO)_9]$ **1**.—A suitable bright yellow crystal was obtained from dichloromethane–*n*-heptane at −20 °C.

Crystal data. $C_{24}H_{12}N_3O_9PRu_3$, $M = 820.57$, monoclinic, $a = 17.873(4)$, $b = 17.124(5)$, $c = 18.421(6)$ Å, $\beta = 94.40(2)°$, $U = 5621(2)$ Å^3 (from 31 orientation reflections in the range $12 \leqslant 2\theta \leqslant 26°$), space group $P2_1/c$, $Z = 8$, $D_c = 1.95$ g cm^{-3}, $F(000) = 3168$. Crystal dimensions 0.40 × 0.33 × 0.18 mm, $\mu(Mo\text{-}K\alpha) = 16.7$ cm^{-1}.

Data collection and processing. Nicolet R3v/m diffractometer, 10 539 intensity data, 9832 unique, *hkl* range 0,0,−22 to 22,21,22 ($5 \leqslant 2\theta \leqslant 50°$) collected at 20 °C (Mo-Kα radiation; $\lambda = 0.710\,73$ Å) in ω–2θ scan mode; corrections for Lorentz and polarisation effects and based on small variations in intensity of three standard reflections, empirical absorption correction based on psi-scans.

Structure solution and refinement. Direct methods, 721 parameters in model, 7429 data with $I_o > 1.5\sigma(I_o)$, $R = 0.0530$ and $R' = 0.0503$ where $R = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o) + 0.000\,51F_o^2]$. All non-H atoms were refined anisotropically. The unit cell contains two independent but very similar clusters containing the groups of atoms Ru(1), Ru(2), Ru(3) and Ru(4), Ru(5), Ru(6) respectively. The H atoms were included in the model in idealised positions (C–H 0.96 Å, U_{iso} = 0.08 Å^2). Alternative positions for N(1), N(3), N(4) and N(6) atoms were tested but gave less suitable thermal parameters. The largest shift-to-error in the final refinement was 0.023 and the largest peak in the final Fourier difference map was 0.67 e Å^{-3}. All calculations were carried out using a MicroVax II computer with SHELXTL-PLUS.[12] Table 5 lists the fractional atomic coordinates for molecules A and B.

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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