Co-ordination chemistry of the organometallic tridentate ligand *trans*-[Ru(2-Ph$_2$PC$_5$H$_4$N-*P*)$_2$(CO)$_3$] and crystal structures of metal complex derivatives

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The complex *trans*-[Ru(2-Ph$_2$PC$_5$H$_4$N-*P*)$_2$(CO)$_3$] **1** reacted with Lewis acids such as ZnCl$_2$, CdCl$_2$, Cd(ClO$_4$)$_2$ and HgCl$_2$ to give a series of heterometallic [RuM(μ-2-Ph$_2$PC$_5$H$_4$N)$_2$X(X′)] (M = Zn, Cd or Hg; X = Cl; X′ = Cl, ClO$_4$ or HgCl$_3$). Crystal structures of [RuZn(μ-2-Ph$_2$PC$_5$H$_4$N)$_2$(CO)$_3$Cl$_2$] **2**, [RuCd(μ-2-Ph$_2$PC$_5$H$_4$N)$_2$(CO)$_3$Cl$_2$]·MeOH **3**·MeOH, [RuCd(μ-2-Ph$_2$PC$_5$H$_4$N)$_2$(CO)$_3$(ClO$_4$)$_2$]·CHCl$_3$ **4**·CHCl$_3$ and [RuHg(μ-2-Ph$_2$PC$_5$H$_4$N)$_2$(CO)$_3$Cl][HgCl$_3$] **5** were determined with Ru–Zn (**2**), Ru–Cd (**3**), Ru–Cd (**4**) and Ru–Hg (**5**) distances being 2.659(1), 2.771(1), 2.705(1) and 2.622(1) Å, respectively. Different co-ordination modes are present in these heterometallic complexes and their spectroscopic properties were studied. The donor–acceptor bonding interactions of complexes **2**–**5** are discussed.

Heterometallic compounds containing metal–metal bonds have been subjected to extensive investigation in recent decades owing to their unique structures, reactivities and spectroscopic properties. Much interest is focused on the study of polydentate ligands with main-group donors, such as 2,6-bis(diphenylphosphino)pyridine, bis(diphenylphosphinomethyl)phenylphosphine or bis(dimethylphosphinomethyl)methylphosphine, as they are able to form various polynuclear complexes.[1] However, examples of polydentate ligands containing both main-group and metal donors are scarce. Balch and co-workers[2] had demonstrated the usefulness of bis(diphenylphosphino)phenylarsine as a tridentate ligand to form polynuclear or heterometallic complexes with Rh^I, Ir^I, Pt^{II} or Au^I. Our particular attention is focused on the study of tridentate ligands containing both main-group donors and an electron-rich metal centre, M. It is expected that such ligand systems would chelate with metal ions (M′) *via* donor–acceptor metal–metal bonding interaction[3] (M→M′) as shown in Scheme 1. This would provide a means to perturb the electron density on M′ and change the spectroscopic and redox properties of the resultant complex.[3–5] The strength of the donor–acceptor bond between two metal centres is dependent on the nature of the Lewis acids as hard acids prefer hard bases whereas soft acids prefer soft bases.

In this work we employ an organometallic tridentate ligand *trans*-[Ru(2-Ph$_2$PC$_5$H$_4$N)$_2$(CO)$_3$] **1** to react with several Lewis acids [ZnCl$_2$, CdCl$_2$, Cd(ClO$_4$)$_2$ and HgCl$_2$] and examine the donor–acceptor bonding interaction in the resultant heterometallic complexes *via* X-ray structural and spectroscopic studies. Complex **1** and the heterometallic complexes are fully characterized by elemental analyses, NMR and IR spectroscopies.

Results and Discussion

Synthesis and spectroscopic characterization

The synthesis of complex **1** has been reported by Balch and co-workers.[6] In this work it was prepared by treating [Ru(CO)$_3$(cod)] (cod = cycloocta-1,5-diene) with 2-Ph$_2$PC$_5$H$_4$N ligand under reflux. This method is advantageous over the previous one in that (i) the absence of side reactions leads to a high product yield, and (ii) the mild conditions required avoid extensive decomposition of the complex formed. However, [Ru(CO)$_3$(cod)] is unstable even at −20 °C under a nitrogen atmosphere but it can be kept in a frozen benzene solution for a few weeks without decomposition.
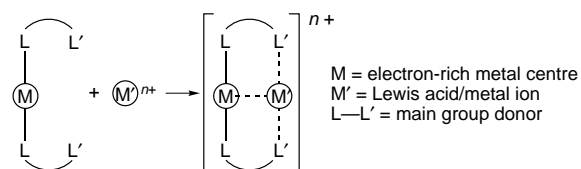
Scheme 1 Chelation of M(L–L′)$_2$ to M′$^{n+}$ *via* donor–acceptor metal–metal bonding interaction
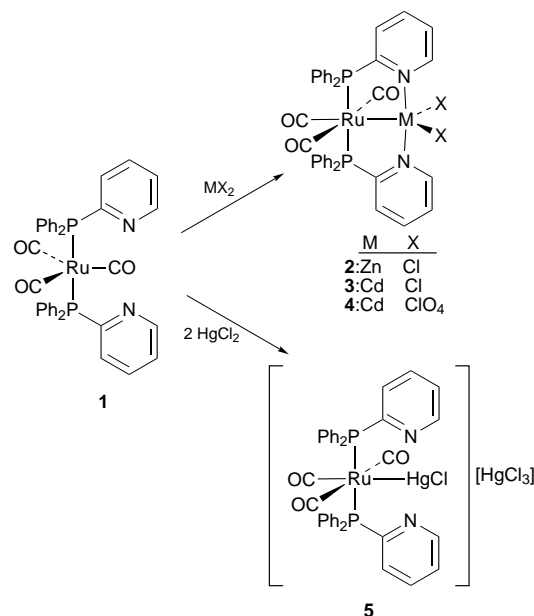
Scheme 2 Preparation of complexes **2**–**5**

The preparation of complexes **2**–**5** is outlined in Scheme 2. Treatment of **1** with anhydrous ZnCl$_2$, CdCl$_2$ or Cd(ClO$_4$)$_2$·4H$_2$O gave the corresponding heterometallic complexes. Our attempts to prepare a Ru–Hg complex by treating **1** with Hg(SCN)$_2$ were unsuccessful. In each case a black Hg$_2$O precipitate was produced together with *cis*,*trans*-[Ru(Ph$_2$PC$_5$H$_4$N)$_2$(CO)$_2$(SCN)$_2$] **6**, which was obtained as pale yellow prisms after recrystallization. It is believed that Ru^0 and Hg^{II} had undergone a redox reaction to give Hg$_2$O and complex **6**. The reaction of **1** with HgCl$_2$ readily afforded complex **5**.
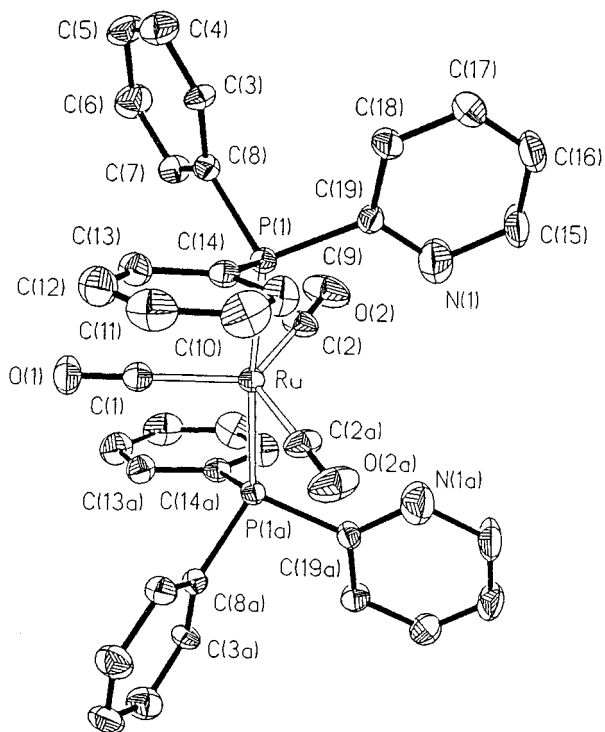
Fig. 1 Perspective view of complex **1**

Fig. 2 Perspective view of complex **2**

Fig. 3 Perspective view of complex **3**

Complex **1** exhibits one $\nu(C\equiv O)$ band at 1897 cm^{-1} which is comparable to that observed for the *trans*-[Ru(CO)$_3$(PPh$_3$)$_2$] analogue,[7] indicating that the three CO groups are equivalent. The $\nu(C\equiv O)$ of **2–5** are 68.5–209.4 cm^{-1} higher in energy than that observed for **1**. Besides, more than one $\nu(C\equiv O)$ stretch is found. These reveal both a decrease in electron density and a change in stereochemistry at the Ru atom. In these complexes the ruthenium–Lewis acid bonding interaction causes a decrease in electron density at the Ru atom and hence decreases the d$_\pi$(Ru) $\longrightarrow$ π*(CO) π-back bonding. This results in an increase of $\nu(C\equiv O)$ for the bimetallic complexes. The extent of change of $\nu(C\equiv O)$ with respect to complex **1** [*i.e.* $\Delta\nu(C\equiv O)$] reflects the strength of Ru$\rightarrow$M bonding interaction. It is found that the $\Delta\nu(C\equiv O)$ follows the order **5 > 4 > 3 $\approx$ 2**, suggesting that the donor–acceptor interactions decrease in the same trend. The increase in the number of C$\equiv$O stretches of complexes **2–5** is attributed to the corresponding change in local symmetry from D_{3h} to C_{2v}. Comparing the IR spectra of Ru–M complexes with the iron analogues, reported by Zhang *et al.*,[8] it is found that $\Delta\nu(C\equiv O)$ for the Ru–M series is larger than that of the related Fe–M complexes. This can be explained by the higher basicity of Ru than that of Fe.

The ^{31}P NMR spectra of complexes **1–6** in CDCl$_3$ exhibit single sets of resonance, indicating that the two phosphine moieties are chemically equivalent. Comparing the spectra of **3** and **4**, it is noted that **4** exhibits a triplet while a singlet is found for **3**. The triplet with ^2J(CdP) 23.0 Hz is indicative of the coupling between the Cd and P atoms, and hence is suggestive of a Ru$\rightarrow$Cd bonding interaction in **4**. The ^{31}P NMR spectrum of **5** shows a singlet with two low-intensity satellite peaks [^2J(HgP) 109.9 Hz], which is due to the two-bond coupling between the Hg and P atoms. The overall +1 charge on complex **5** is the reason for the upfield shift of the signal compared with those of the other neutral complexes. The ^{31}P NMR signal of **6** is much more upfield with respect to those observed for **1–5**, which can be explained by the more electron-withdrawing effect of the ruthenium(II) centre.

Crystal structures

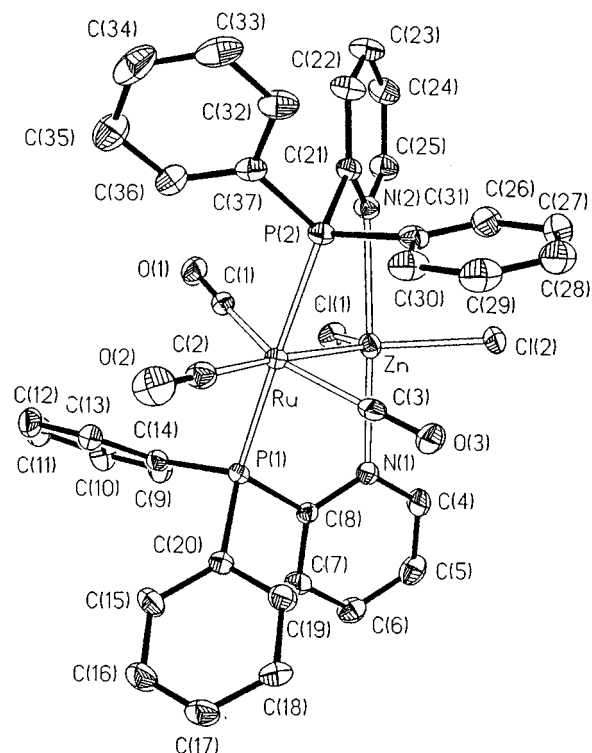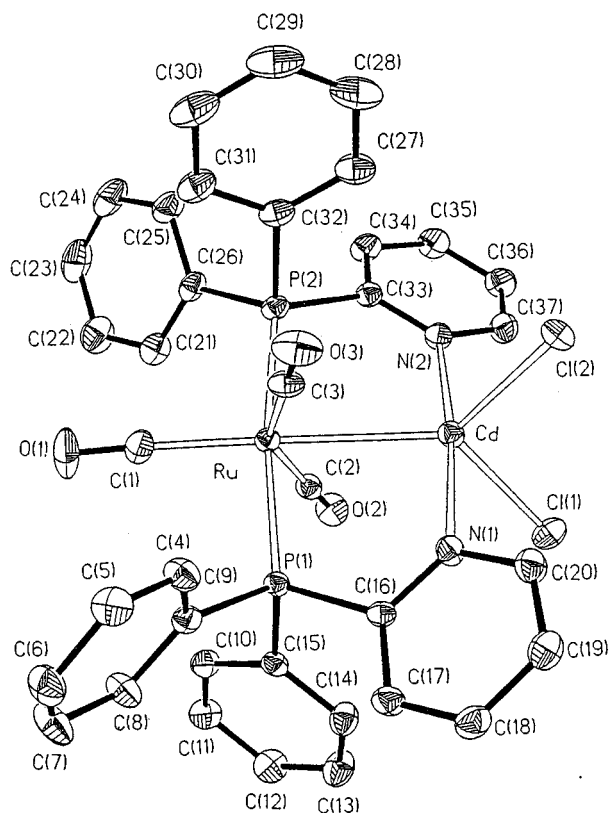Perspective views of complexes **1–6** are depicted in Figs. 1–6.

Selected bond lengths and angles are listed in Tables 1–6. Complex **1** adopts a trigonal-bipyrimidal configuration with two Ph$_2$PC$_5$H$_4$N ligands occupying the axial positions and three CO groups lying on the equatorial plane. The Ru–P distances of 2.350(2) Å are typical of those in some reported ruthenium–phosphine complexes.[6,7]

Complexes **2–4** display a distorted octahedral geometry about the Ru atom, while that for M is a trigonal bipyramid (M = Zn or Cd). The RuP$_2$ unit is nearly linear with
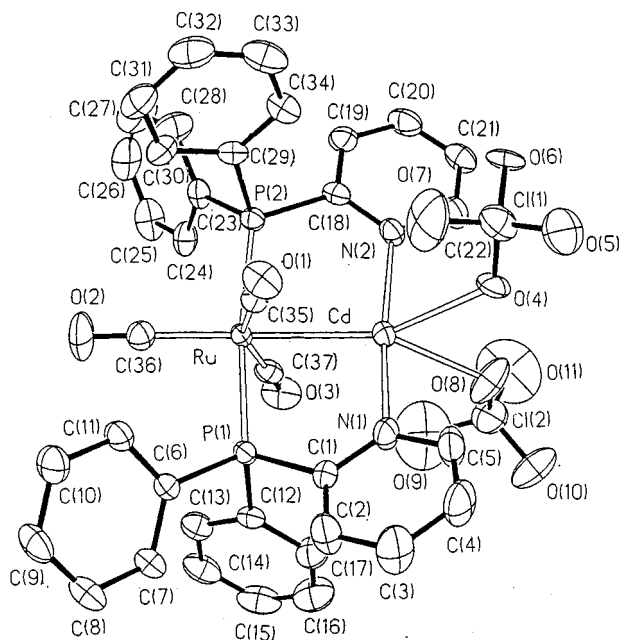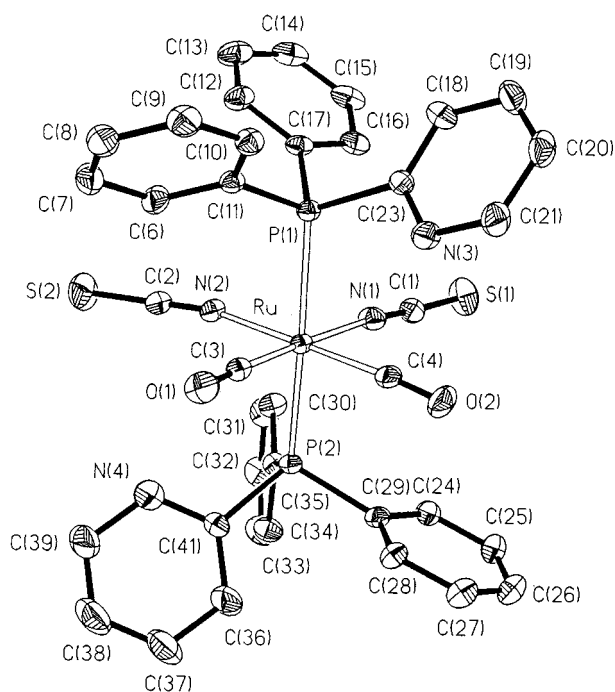
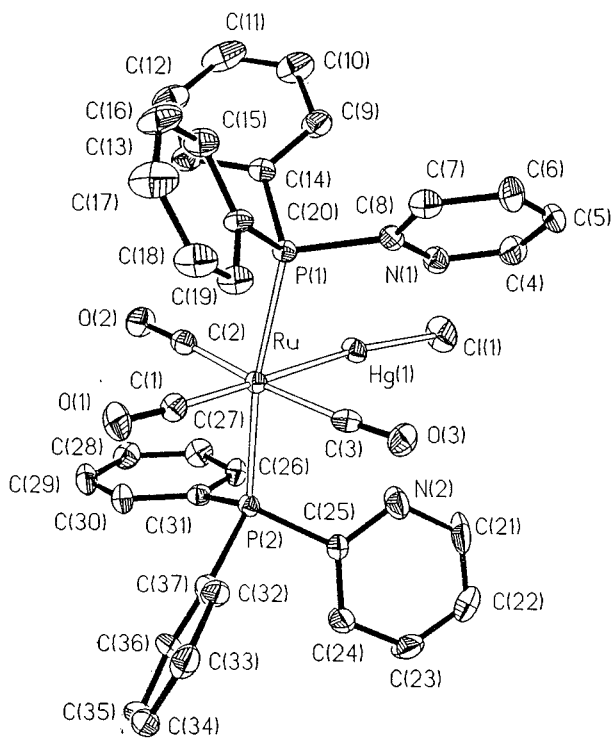**Fig. 4** Perspective view of complex **4**

Fig. 5 Perspective view of complex **5**

Fig. 6 Perspective view of complex **6**

Fig. 7 Top view of Ru–M complexes along the RuP$_2$ axis

P(1)–Ru–P(2) angle close to 180°. Three CO moieties and M lie on a plane perpendicular to the RuP$_2$ axis. Elongation of the Ru–P and Ru–C bonds is a consequence of the Ru→M interaction which reduces the electron density on the Ru. As in many carbonyl complexes with donor–acceptor metal–metal bonds, inwards leaning of the radial CO on the donor metal towards the acceptor metal are observed (ranging from *ca.* 75 to 79°).[5] Thus complex **1** functions as a tridentate ligand with the Ru^0 being one of the donor atoms. The M–N distances fall in the order **4 > 2 > 3**, consistent with the increase in hardness of the Lewis-acid metal ions. In complex **2** the Ru–Zn distance of 2.659(1) Å is greater than the sum of atomic radii of Ru and Zn (2.50 Å), which implies that there is only a weak interaction between Ru and Zn. Comparing complexes **3** and **4**, it is apparent that **4** has a shorter Ru–Cd distance (<sum of atomic radii of Ru and Cd, 2.73 Å) than that of **3**. This is suggestive of a
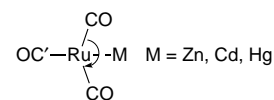
stronger donor–acceptor bond in **4**. To our knowledge, **2**–**4** are the first binuclear Ru–Cd and Ru–Zn complexes to be structurally characterized by single-crystal X-ray analysis.

Complex **5** comprises an organometallic cation [Ru(μ-2-Ph$_2$PC$_5$H$_4$N)$_2$(CO)$_3$(HgCl)]$^+$ and anion [Hg$_2$Cl$_6$]$^{2-}$. An analogous complex with triphenylphosphine as ligand had been reported by Collman and Roper.[9] The Ru atom adopts a distorted octahedral geometry. However, unlike complexes **2**–**4**, the Hg atom is only two-co-ordinated and the complex cation bears a formal +1 charge. It is expected that the soft Hg^{II} would favor the formation of a covalent Ru–Hg bond. This is indeed the case evidenced by the Ru–Hg distance of 2.622(1) Å, which is comparable to those in some covalent Ru–Hg clusters.[10] Thus the Ru–Hg interaction in **5** is best described as covalent rather than an electrostatic donor–acceptor bonding. The relatively long Hg···N(1) and Hg···N(2) distances of 2.832(1) Å and 2.800(1) Å, respectively, imply weak interaction between Hg and the pyridine nitrogen atoms. Hence, the linkage between Ru^0 and Hg^{II} can be considered as unsupported by the bridging phosphine ligands. Inwards leaning of radial carbonyl is also observed, although the extent is much less pronounced compared with those of complexes **2**–**4**. The C–Ru–C angles (Fig. 7) seem to indicate a significant alteration in the nature of the Ru–M bonding (M = Zn, Cd or Hg). This angle is opened widest in complex **5** [169.9(4)°] where there is a clear Ru–Hg bond but it is only 156.2(2)° in **4**, 151.8(1)° in **3** and 150.7(3)° in **2**. Thus, it is anticipated that stronger metal–metal interaction tends to force the radial carbonyl more apart in order to minimize the repulsion between the C≡O and Ru–M bonds. The anionic part consists of a mercury dimer with the two Hg^{II} bridged by two Cl$^-$. Each [Hg$_2$Cl$_6$]$^{2-}$ unit is shared by two cationic parts, thus the anion is formulated as [HgCl$_3$]$^-$.

Complex **6** displays a distorted octahedral configuration about the Ru^{II} with the two Ph$_2$PC$_5$H$_4$N ligands occupying the axial positions. The two SCN and carbonyl groups are *cis* to each other.

Table 1 Selected bond lengths (Å) and angles (°) for complex 1

Ru–P(1)	2.350(2)	Ru–C(1)	1.898(8)
Ru–P(1a)	2.350(2)	Ru–C(2)	1.900(7)
C(1)–O(1)	1.146(10)	Ru–C(2a)	1.900(7)
C(2)–O(2)	1.150(8)		
P(1)–Ru–C(1)	92.7(1)	P(1)–Ru–C(2a)	86.8(2)
P(1)–Ru–C(2)	90.8(2)	P(1a)–Ru–C(2a)	90.8(2)
P(1)–Ru–P(1a)	174.7(1)	C(1)–Ru–P(1a)	92.7(1)
C(1)–Ru–C(2)	115.8(2)	C(2)–Ru–P(1a)	86.8(2)
C(1)–Ru–C(2a)	115.8(2)	Ru–C(1)–O(1)	180.0(1)
C(2)–Ru–C(2a)	128.4(4)	Ru–C(2)–O(2)	178.0(6)

Table 2 Selected bond lengths (Å) and angles (°) for complex 2

Ru–Zn	2.659(1)	Zn–Cl(2)	2.268(2)
Ru–P(1)	2.344(1)	Zn–N(1)	2.320(4)
Ru–P(2)	2.353(2)	Zn–N(2)	2.460(4)
Ru–C(1)	1.912(5)	C(1)–O(1)	1.124(7)
Ru–C(2)	1.955(7)	C(1)–O(1)	1.132(9)
Ru–C(3)	1.951(6)	C(3)–O(3)	1.138(8)
Zn–Cl(1)	2.328(2)		
Zn–Ru–P(1)	85.8(1)	C(2)–Ru–C(3)	103.3(3)
Zn–Ru–P(2)	88.4(1)	Ru–Zn–Cl(1)	124.3(1)
Zn–Ru–C(1)	75.1(2)	Ru–Zn–Cl(2)	127.5(1)
Zn–Ru–C(2)	176.9(2)	Ru–Zn–N(1)	91.0(1)
Zn–Ru–C(3)	75.6(2)	Ru–Zn–N(2)	88.0(1)
P(1)–Ru–P(2)	173.9(1)	Cl(1)–Zn–Cl(2)	108.1(1)
P(1)–Ru–C(1)	87.7(2)	Cl(1)–Zn–N(1)	86.8(1)
P(1)–Ru–C(2)	91.3(2)	Cl(2)–Zn–N(1)	93.5(1)
P(1)–Ru–C(3)	90.7(2)	Cl(1)–Zn–N(2)	91.9(1)
P(2)–Ru–C(1)	88.9(2)	Cl(2)–Zn–N(2)	89.0(1)
P(2)–Ru–C(2)	94.5(2)	N(1)–Zn–N(2)	177.5(1)
P(2)–Ru–C(3)	89.9(2)	Ru–C(1)–O(1)	178.0(5)
C(1)–Ru–C(2)	106.0(3)	Ru–C(2)–O(2)	179.2(6)
C(1)–Ru–C(3)	150.7(3)	Ru–C(3)–O(3)	178.4(5)

Table 3 Selected bond lengths (Å) and angles (°) for complex 3

Ru–Cd	2.771(1)	Cd–Cl(2)	2.454(1)
Ru–P(1)	2.355(1)	Cd–N(1)	2.472(3)
Ru–P(2)	2.360(1)	Cd–N(2)	2.530(3)
Ru–C(1)	1.958(4)	C(1)–O(1)	1.117(6)
Ru–C(2)	1.932(3)	C(2)–O(2)	1.135(4)
Ru–C(3)	1.942(4)	C(3)–O(3)	1.137(5)
Cd–Cl(1)	2.528(1)		
Cd–Ru–P(1)	86.3(1)	C(2)–Ru–C(3)	151.8(2)
Cd–Ru–P(2)	87.5(1)	Ru–Cd–Cl(1)	125.0(1)
Cd–Ru–C(1)	177.4(1)	Ru–Cd–Cl(2)	129.8(1)
Cd–Ru–C(2)	75.4(1)	Ru–Cd–N(1)	88.3(1)
Cd–Ru–C(3)	76.4(1)	Ru–Cd–N(2)	86.7(1)
P(1)–Ru–P(2)	173.5(1)	Cl(1)–Cd–Cl(2)	105.0(1)
P(1)–Ru–C(1)	92.0(1)	Cl(1)–Cd–N(1)	87.4(1)
P(1)–Ru–C(2)	89.0(1)	Cl(2)–Cd–N(1)	91.8(1)
P(1)–Ru–C(3)	90.4(1)	Cl(1)–Cd–N(2)	93.4(1)
P(2)–Ru–C(1)	94.3(1)	Cl(2)–Cd–N(2)	93.3(1)
P(2)–Ru–C(2)	87.8(1)	N(1)–Cd–N(2)	174.4(1)
P(2)–Ru–C(3)	89.8(1)	Ru–C(1)–O(1)	177.8(4)
C(1)–Ru–C(2)	106.5(2)	Ru–C(2)–O(2)	177.9(3)
C(1)–Ru–C(3)	101.7(2)	Ru–C(3)–O(3)	179.2(3)

Table 4 Selected bond lengths (Å) and angles (°) for complex 4

Ru–Cd	2.705(1)	Cd–O(8)	2.365(4)
Ru–P(1)	2.367(1)	Cd–O(8′)	2.197(4)
Ru–P(2)	2.367(1)	Cd–N(1)	2.380(4)
Ru–C(35)	1.938(5)	Cd–N(2)	2.353(4)
Ru–C(36)	1.944(4)	C(35)–O(1)	1.140(6)
Ru–C(37)	1.937(4)	C(36)–O(2)	1.128(5)
Cd–O(4)	2.401(5)	C(37)–O(3)	1.135(6)
Cd–O(4′)	2.274(6)		
Cd–Ru–P(1)	86.8(1)	C(36)–Ru–C(37)	100.0(2)
Cd–Ru–P(2)	85.6(1)	C(35)–Ru–C(37)	156.2(2)
Cd–Ru–C(35)	77.8(1)	Ru–Cd–N(2)	93.9(1)
Cd–Ru–C(36)	177.9(1)	Ru–C(35)–O(1)	177.3(4)
Cd–Ru–C(37)	78.6(1)	Ru–C(36)–O(2)	179.1(4)
P(1)–Ru–P(2)	171.5(1)	Ru–C(37)–O(3)	177.0(4)
P(1)–Ru–C(35)	86.5(1)	O(8)–Cd–N(1)	86.1(2)
P(1)–Ru–C(36)	94.6(1)	O(8)–Cd–N(2)	94.5(2)
P(1)–Ru–C(37)	89.4(1)	O(4)–Cd–N(1)	88.0(2)
P(2)–Ru–C(35)	88.2(1)	O(4)–Cd–N(2)	83.0(2)
P(2)–Ru–C(36)	93.0(1)	O(4)–Cd–O(8)	67.3(2)
P(2)–Ru–C(37)	92.9(1)	Ru–Cd–O(8)	146.6(1)
C(35)–Ru–C(36)	103.7(2)	Ru–Cd–O(4)	145.9(1)

Table 5 Selected bond lengths (Å) and angles (°) for complex 5

Ru–Hg(1)	2.622(1)	Hg(1)–Cl(1)	2.368(3)
Ru–C(1)	1.936(9)	C(1)–O(1)	1.126(1)
Ru–C(2)	1.967(8)	C(2)–O(2)	1.118(1)
Ru–C(3)	1.968(8)	C(3)–O(3)	1.109(9)
Ru–P(1)	2.392(2)	Hg(1)···N(1)	2.832
Ru–P(2)	2.396(2)	Hg(1)···N(2)	2.800
Hg(1)–Ru–C(1)	177.1(2)	C(2)–Ru–P(1)	92.6(2)
Hg(1)–Ru–C(2)	85.4(3)	C(3)–Ru–P(1)	87.0(2)
Hg(1)–Ru–C(3)	84.5(3)	C(1)–Ru–P(2)	93.8(2)
Hg(1)–Ru–P(1)	84.7(1)	C(2)–Ru–P(2)	89.3(2)
Hg(1)–Ru–P(2)	85.3(1)	C(3)–Ru–P(2)	89.4(2)
C(1)–Ru–C(2)	91.8(3)	Ru–Hg(1)–Cl(1)	174.9(1)
C(1)–Ru–C(3)	98.2(3)	Ru–C(1)–O(1)	173.7(7)
C(2)–Ru–C(3)	169.9(4)	Ru–C(2)–O(2)	176.2(8)
P(1)–Ru–P(2)	169.6(1)	Ru–C(3)–O(3)	176.5(6)
C(1)–Ru–P(1)	96.3(2)		

Table 6 Selected bond lengths (Å) and angles (°) for complex 6

Ru–N(1)	2.087(3)	S(1)–C(1)	1.608(4)
Ru–N(2)	2.087(2)	S(2)–C(2)	1.616(3)
Ru–C(3)	1.869(4)	C(3)–O(1)	1.142(5)
Ru–C(4)	1.887(3)	C(4)–O(2)	1.135(4)
Ru–P(1)	2.427(1)	C(1)–N(1)	1.150(5)
Ru–P(2)	2.417(1)	C(2)–N(2)	1.146(4)
N(1)–Ru–N(2)	91.3(1)	C(4)–Ru–P(1)	94.5(1)
N(1)–Ru–C(3)	176.8(1)	C(3)–Ru–P(2)	93.3(1)
N(1)–Ru–C(4)	88.3(1)	C(4)–Ru–P(2)	90.5(1)
N(2)–Ru–C(3)	91.9(1)	P(1)–Ru–P(2)	173.8(1)
N(2)–Ru–C(4)	179.0(1)	Ru–N(1)–C(1)	174.3(3)
C(3)–Ru–C(4)	88.5(1)	Ru–N(2)–C(2)	167.4(3)
N(1)–Ru–P(1)	89.7(1)	Ru–C(3)–O(1)	176.1(2)
N(2)–Ru–P(1)	86.5(1)	Ru–C(4)–O(2)	175.8(3)
N(1)–Ru–P(2)	86.8(1)	S(1)–C(1)–N(1)	177.7(3)
N(2)–Ru–P(2)	88.5(1)	S(2)–C(2)–N(2)	179.3(3)
C(3)–Ru–P(1)	90.5(1)		

Conclusion

The complex *trans*-[Ru(Ph$_2$PC$_5$H$_4$N)$_2$(CO)$_3$] **1** acts as a neutral tridentate ligand and reacts with Lewis acids such as ZnCl$_2$, CdCl$_2$, Cd(ClO$_4$)$_2$ and HgCl$_2$ to form a series of heterobimetallic RuM(μ-Ph$_2$PC$_5$H$_4$N)$_2$X(X′) complexes (M = Zn, Cd or Hg; X = Cl; X′ = Cl, ClO$_4$, or HgCl$_3$). Reactions between **1** and the Lewis acids result in formation of donor–acceptor bonds.[10,11] Complexes **2**–**4** can be considered as simple Ru→M adducts whereas **5** possesses an unsupported Ru–Hg bond. It is found that the Ru–M donor–acceptor bonding interaction decreases with the hardness of the Lewis acids. The Ru–Hg distance in **5** is comparable to some of the covalent Ru–Hg bonds reported previously and hence the interaction is best regarded as covalent rather then donor–acceptor bonding. Comparison between Ru–M complexes with the corresponding iron analogues reveals that the former form stronger donor–acceptor bonds, which is attributed to the increase in basicity from Fe to Ru.

Table 7 X-Ray crystallographic data for complexes **1**–**6**

Complex	**1**	**2**	**3·MeOH**	**4·CHCl₃**	**5**	**6**
Formula	$C_{37}H_{28}N_2O_3P_2Ru$	$C_{37}H_{28}Cl_2N_2O_3P_2RuZn$	$C_{38}H_{32}CdCl_2N_2O_4P_2Ru$	$C_{38}H_{29}CdCl_5N_2O_{11}P_2Ru$	$C_{37}H_{28}Cl_4Hg_2N_2O_3P_2Ru$	$C_{38}H_{28}N_4O_2P_2RuS_2$
M	711.6	828.1	927.0	1142.3	1254.6	799.8
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$	$P\bar{1}$	$P\bar{1}$ (no. 2)
Crystal size/mm	$0.10 \times 0.12 \times 0.10$	$0.26 \times 0.34 \times 0.36$	$0.14 \times 0.18 \times 0.28$	$0.20 \times 0.20 \times 0.20$	$0.10 \times 0.32 \times 0.34$	$0.10 \times 0.12 \times 0.28$
$a/\text{Å}$	24.291(5)	12.235(2)	12.304(2)	13.313(1)	10.172(2)	9.860(1)
$b/\text{Å}$	9.258(2)	24.024(5)	24.165(4)	17.365(1)	13.863(3)	11.204(1)
$c/\text{Å}$	17.845(3)	13.260(3)	13.331(3)	19.942(1)	15.312(3)	17.288(1)
$\alpha/°$					70.77(3)	93.83(1)
$\beta/°$	122.6(3)	100.07(2)	99.85(3)	107.55(3)	83.81(3)	94.46(1)
$\gamma/°$					81.79(3)	105.30(1)
$U/\text{Å}^3$	3378(2)	3838(2)	3905(2)	4396(2)	2013.6(10)	1821.2(9)
Z	4	4	4	4	2	2
$D_c/\text{g cm}^{-3}$	1.399	1.433	1.577	1.726	2.069	1.458
$F(000)$	1448	1676	1848	2264	1180	812
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	0.60	1.141	1.19	1.263	8.358	0.672
No. unique reflections	2973	6763	7443	8627	7565	6611
No. observed reflections	1971 [$I > 4\sigma(I)$]	4703 [$I > 4\sigma(I)$]	7183 [$I > 4\sigma(I)$]	7017 [$I > 6\sigma(I)$]	6386 [$I > 6\sigma(I)$]	5875 [$I > 6\sigma(I)$]
No. variables	206	451	452	645	461	461
Weighting scheme, w	$[\sigma^2(F) + 0.0001F^2]^{-1}$	$[\sigma^2(F) + 0.0005F^2]^{-1}$	$[\sigma^2(F) + 0.0010F^2]^{-1}$	$[\sigma^2(F) + 0.0000F^2]^{-1}$	$[\sigma^2(F) + 0.0005F^2]^{-1}$	$[\sigma^2(F) + 0.0005F^2]^{-1}$
R	0.041	0.043	0.036	0.049	0.042	0.041
wR	0.045	0.063	0.065	0.040	0.059	0.071
S	1.37	1.44	1.68	2.31	1.72	1.92
Residual electron density/e Å^{-3}	+0.40, −0.31	+0.56, −0.65	+0.64, −0.62	+0.75, −0.71	+0.92, −0.69	+0.49, −0.62

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, $S = [\Sigma w(|F_o| - |F_c|)^2/(n - p)]^{\frac{1}{2}}$.

Experimental

Unless otherwise stated, all reactions were performed under a nitrogen atmosphere with the use of standard Schlenk techniques. The solvents were purified by standard methods. The compound $[Ru_3(CO)_{12}]$ (Aldrich) was used as received, as were anhydrous $ZnCl_2$, $CdCl_2$, $HgCl_2$, $Cd(ClO_4)_2\cdot4H_2O$ and $Hg(SCN)_2$. The compounds $2\text{-}Ph_2PC_5H_4N$ and $[Ru(CO)_3(cod)]$ were prepared by the published methods.[12,13]

Physical measurements

Infrared spectra were recorded on a Shimadzu IR-470 or a Nicolet 20SXC FT-IR spectrometer as Nujol mulls, $^{31}P\text{-}\{H\}$ NMR spectra on a JEOL GSX-270 spectrometer with $CDCl_3$ as solvent. Elemental analyses of C, H, and N were carried out by Butterworth Laboratories Ltd.

Preparation of compounds

trans-[Ru(2-Ph$_2$PC$_5$H$_4$N)$_2$(CO)$_3$] 1. To a solution of $[Ru(CO)_3(cod)]$ (0.68 g, 2.30 mmol) in benzene (80 cm^3) was added $2\text{-}Ph_2PC_5H_4N$ (1.23 g, 1.70 mmol) and the mixture heated under reflux for 30 min. The solution was cooled and the solvent removed *in vacuo*. The residue was dissolved in dichloromethane and diethyl ether was added to obtain a yellow precipitate. This was filtered off and washed with MeOH. Complex **1** was obtained as yellow microcrystals (1.1 g, 79%) by recrystallization from CH_2Cl_2–MeOH solution (Found: C, 62.21; H, 3.91; N, 3.92. Calc. for $C_{37}H_{28}N_2O_3P_2Ru$: C, 62.48; H, 3.94; N, 3.94%); $\tilde{v}_{max}/cm^{-1}$ (Nujol) 1897vs (CO); $\delta_P(CDCl_3)$ 50.09.

[RuZn(μ-2-Ph$_2$PC$_5$H$_4$N)$_2$(CO)$_3$Cl$_2$] 2. Anhydrous $ZnCl_2$ (0.20 g, 1.40 mmol) was added to a solution of complex **1** (0.2 g, 1.40 mmol) in dichloromethane (30 cm^3). The mixture was stirred for 2 h at room temperature then filtered and the filtrate concentrated. Methanol was added, giving pale yellow crystals of **2** (0.5 g, 43%) (Found: C, 52.33; H, 3.31; N, 3.29. $C_{37}H_{28}Cl_2N_2O_3P_2RuZn$ requires C, 52.40; H, 3.30; N, 3.30%); $\tilde{v}_{max}/cm^{-1}$ (Nujol) 2040.8vs, 1981.3vs and 1965.6s (CO); $\delta_P(CDCl_3)$ 61.20.

[RuCd(μ-2-Ph$_2$PC$_5$H$_4$N)$_2$(CO)$_3$Cl$_2$]·MeOH 3·MeOH. Anhydrous $CdCl_2$ (0.26 g, 1.40 mmol) was added to a solution of complex **1** (1.00 g, 1.40 mmol) in dichloromethane (30 cm^3). The mixture was stirred for 2 h at room temperature. The solution was filtered and the filtrate concentrated. Methanol was added to give pale yellow crystals of **3·MeOH** (0.78 g, 60%) (Found: C, 49.19; H, 3.25; N, 3.02. $C_{38}H_{32}CdCl_2N_2O_4P_2Ru$ requires C, 49.19; H, 3.45; N, 3.02%); $\tilde{v}_{max}/cm^{-1}$ (Nujol) 2035.6vs, 1984.4vs and 1965.5s (CO); $\delta_P(CDCl_3)$ 59.40.

[RuCd(μ-2-Ph$_2$PC$_5$H$_4$N)$_2$(CO)$_3$(ClO$_4$)$_2$]·CHCl$_3$ 4·CHCl$_3$. The compound $Cd(ClO_4)_2\cdot4H_2O$ (0.54 g, 1.40 mmol) was added to a solution of complex **1** (1.00 g, 1.40 mmol) in dichloromethane (50 cm^3) then stirred for 2 h at room temperature. The solvent was removed *in vacuo* and pale yellow crystals of **4·CHCl$_3$** (1.04 g, 65%) were obtained by slow evaporation of the CHCl$_3$ solution (Found: C, 39.50; H, 2.49; N, 2.41. $C_{38}H_{29}CdCl_5N_2O_{11}P_2Ru$ requires C, 39.92; H, 2.54; N, 2.45%); $\tilde{v}_{max}/cm^{-1}$ (Nujol) 2068.2vs, 2021.4vs and 1973.0s (CO); $\delta_P(CDCl_3)$ 61.70 [$^2J(CdP)$ 23.0 Hz.]

[RuHg(μ-2-Ph$_2$PC$_5$H$_4$N)$_2$(CO)$_3$Cl][HgCl$_3$] 5. Anhydrous $HgCl_2$ (0.38 g, 1.40 mmol) reacted readily with complex **1** (1.00 g, 1.40 mmol) in dichloromethane (50 cm^3) to afford a pale yellow solution. The solvent was removed *in vacuo* after stirring for 2 h. Methanol was added to give pale yellow crystals of **5** (1.04 g, 65%) (Found: C, 34.97; H, 2.12; N, 2.14. $C_{37}H_{28}Cl_4Hg_2N_2O_3P_2Ru$ requires C, 35.40; H, 2.23; N, 2.23%); $\tilde{v}_{max}/cm^{-1}$ (Nujol) 2106.42vs, 2049.6vs and 2036.1s (CO); $\delta_P(CDCl_3)$ 48.70 [$^2J(HgP)$ 109.9 Hz].

cis,trans-[Ru(2-Ph$_2$PC$_5$H$_4$N)$_2$(CO)$_3$(SCN)$_2$] 6. Anhydrous $Hg(SCN)_2$ (0.44 g, 1.40 mmol) was added to a solution of complex **1** (1.00 g, 1.40 mmol) in dichloromethane (50 cm^3). Immediately a black precipitate was formed. The mixture was stirred at room temperature for 15 min, the black precipitate was then filtered off and the filtrate concentrated. Methanol was added to give yellow crystals (0.67 g, 60%) (Found: C, 58.48; H, 3.49; N, 7.02. $C_{38}H_{28}N_4O_2P_2RuS_2$ requires C, 58.51; H, 3.49; N, 7.00%); $\tilde{v}_{max}/cm^{-1}$ (Nujol) 2075.2vs and 2031.5vs (CO); $\delta_P(CDCl_3)$ 22.9.

X-Ray crystallography

Information concerning the X-ray data collection and structure refinement is summarized in Table 7. The intensities of complexes **1**–**4** and **6** were collected on a Rigaku RAXIS IIC imaging-plate diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å).[14] Crystals of suitable size were mounted on the top of glass fibres. Intensity data were collected using the ω–2θ scan technique with collection ranges: **1**, $0 \leq h \leq 28$, $0 \leq k \leq 11$, $-21 \leq l \leq 17$, $2\theta_{max} = 50°$; **2**, $0 \leq h \leq 14$, $0 \leq k \leq 28$, $-15 \leq l \leq 15$, $2\theta_{max} = 50°$; **3**, $0 \leq h \leq 15$, $-30 \leq k \leq 30$, $-10 \leq l \leq 16$, $2\theta_{max} = 55°$; **4**, $0 \leq h \leq 16$, $-21 \leq k \leq 21$, $-25 \leq l \leq 24$, $2\theta_{max} = 55°$ and **6**, $-12 \leq h \leq 11$, $0 \leq k \leq 14$, $-21 \leq l \leq 21$, $2\theta_{max} = 55°$. The absorption correction was based on ABSOR.[15] Diffraction data for complex **5** were collected on a Siemens R3m/V diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Intensity data were collected using the ω–2θ scan technique: $-12 \leq h \leq 11$, $0 \leq k \leq 14$, $-21 \leq l \leq 21$, 2θ 7–55°. The structures of all complexes were solved by direct methods using the SHELXTL PLUS system[16] and refinement (based on F) by full-matrix least squares. Hydrogen atoms were generated using idealized geometry and allowed to ride on their parent C atoms with assigned isotropic thermal parameters.

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References

1 A. L. Balch, *Prog. Inorg. Chem.*, 1993, **41**, 239.
2 A. L. Balch, C. T. Hunt, C. L. Lee, M. M. Olmstead and J. P. Farr, *J. Am. Chem. Soc.*, 1981, **103**, 3764; A. L. Balch, L. A. Fossett, R. R. Guimerans, M. M. Olmstead and P. E. Reedy, jun., *Inorg. Chem.*, 1986, **25**, 1397; A. L. Balch, L. A. Fossett, M. M. Olmstead and P. E. Reedy, jun., *Organometallics*, 1986, **5**, 1929; A. L. Balch, M. Ghendini, D. E. Oram and P. E. Reedy, jun., *Inorg. Chem.*, 1987, **26**, 1223; A. L. Balch, D. E. Oram and P. E. Reedy, jun., *Inorg. Chem.*, 1987, **26**, 1836; D. A. Bailey, A. L. Balch, L. A. Fossett, M. M. Olmstead and P. E. Reedy, jun., *Inorg. Chem.*, 1987, **26**, 2413; A. L. Balch, B. J. Davis, F. Neve and M. M. Olmstead, *Organometallics*, 1989, **8**, 1000.
3 Z. Z. Zhang and H. Cheng, *Coord. Chem. Rev.*, 1996, **147**, 1; I. W. Howell and D. P. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1972, 2393, 2396.
4 D. A. Roberts, W. C. Mercer, G. L. Geoffroy and C. G. Pierpont, *Inorg. Chem.*, 1986, **25**, 1439; H. Nakatsuji, M. Hada and A. Kawashima, *Inorg. Chem.*, 1992, **31**, 1740.
5 F. W. B. Einstein, R. K. Pomeroy, P. Rushman and A. C. Willis, *J. Chem. Soc., Chem. Commun.*, 1983, 854; F. W. B. Einstein, M. C. Jennings, R. Krentz, R. K. Pomeroy, P. Rushman and A. C. Willis, *Inorg. Chem.*, 1987, **26**, 1341; R. J. Batchelor, H. B. Davis, F. W. B. Einstein and R. K. Pomeroy, *J. Am. Chem. Soc.*, 1990, **112**, 2036.
6 A. Maisonnet, J. P. Farr, M. M. Olmstead, C. T. Hunt and A. L. Balch, *Inorg. Chem.*, 1982, **21**, 3961.
7 F. Piacenti, M. Bianchi, E. Benedetti and G. Braca, *Inorg. Chem.*, 1968, **7**, 1815.

8 Z. Z. Zhang, H. Cheng, S. M. Kuang, Y. Q. Zhou, Z. X, Liu, J. K. Zhang and H. G. Wang, *J. Organomet. Chem.*, 1996, **516**, 1.
9 J. P. Collman and W. R. Roper, *Chem. Commun.*, 1966, 244.
10 J. M. Burlitch, *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, ch. 42.
11 D. F. Shriver, *Acc. Chem. Res.*, 1970, **3**, 231.
12 G. R. Newkome and D. C. Hager, *J. Org. Chem.*, 1978, **43**, 947.
13 A. J. P. Domingos, J. A. S. Howell, B. F. G. Johnson and J. Lewis, *Inorg. Synth.*, 1976, **16**, 103.
14 J. Tanner and K. Krause, *Rigaku J.*, 1994, **11**, 4; 1990, **7**, 28; K. L. Krause and G. N. Phillips, jun., *J. Appl. Crystallogr.*, 1992, **25**, 146; M. Sato, M. Yamamoto, K. Imada, Y. Katsube, N. Tanaka and T. Higashi, *J. Appl. Crystallogr.*, 1992, **25**, 348.
15 T. Higashi, *An Empirical Absorption Correction Based on Fourier Coefficient Fitting*, Rigaku Corporation, Tokyo, 1995, p. 1.
16 G. M. Sheldrick, SHELXTL PLUS, Siemens Analytical X-Ray Instruments, Madison, WI, 1990.