N,N′,N″-Triphenylguanidinate(1−) complexes of ruthenium and palladium: syntheses and crystal structures †

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N,N′,N″-Triphenylguanidine (HTpg) reacted with [Ru(O₂CCF₃)₂(CO)(PPh₃)₂] in boiling toluene to yield [Ru(Tpg)₂(CO)(PPh₃)], the first example of a mononuclear complex containing two chelate guanidinate(1−) ligands. Palladium(II) acetate reacted with HTpg in warm benzene to form an adduct [Pd(O₂CMe)₂(HTpg)₂] which, under more forcing conditions, converts into the novel binuclear guanidinate(1−) bridged complex [{Pd(μ-Tpg)(Tpg)}₂]. Crystal structures have been determined for both guanidinate(1−) complexes.

Guanidines RHNC(=NR)NHR (R = H, alkyl or aryl) are compounds of considerable biological and chemical importance.[2] They are also very strong organic bases which readily undergo protonation to generate resonance-stabilised guanidinium cations (guanidinium, pK_a 13.65).[3] Guanidines are encountered in co-ordination chemistry as guanidinium counter cations and somewhat less frequently as neutral monodentate ligands co-ordinated through the imine nitrogen.[4] However, complexes containing co-ordinated guanidinate(1−) anions are of recent origin and to date are restricted to a relatively small number of examples,[5,6] several of which were first synthesized in our laboratory.[1] We now report the synthesis and crystal structures of two *N,N′,N″*-triphenylguanidinate (Tpg) complexes, the first bis(chelate) guanidinate(1−) derivative [Ru(Tpg)₂(CO)(PPh₃)] and the novel binuclear palladium(II) species [{Pd(μ-Tpg)-(Tpg)}₂].

Results and discussion

Treatment of [Ru(O₂CCF₃)₂(CO)(PPh₃)₂] with *N,N′,N″*-triphenylguanidine (HTpg) in boiling toluene afforded lemon yellow crystals of the bis(guanidinato) complex [Ru(Tpg)₂(CO)(PPh₃)] **1**. In order to establish the stereochemistry of **1** and gain information concerning the co-ordination and structure of the chelate guanidinate(1−) ligands an X-ray crystal structure determination was undertaken using a crystal grown from CH₂Cl₂–MeOH solution. The molecular structure of **1** is shown in Fig. 1; selected bond length and angle data are collated in Table 1. The carbonyl and triphenylphosphine ligands are located at adjacent sites in the distorted octahedral co-ordination sphere. The remaining four sites are occupied by the nitrogen donor atoms of the two chelate guanidinate ligands. The co-ordination sphere is highly distorted due to the presence of the two small 'bite' guanidinate ligands [N–Ru–N 61.47(8) and 62.00(8)°]. The angles around the central carbon atom total 360 ± 1° for each of the guanidinate ligands and thus establish the planarity of the N₂CN skeletons. The values of the dihedral angles between these N₂CN planes and the corresponding N–Ru–N planes [1.20(15) and 3.96(16)°] are even smaller than the value of 4.2(2)° reported by Bailey *et al.*[5] for the ruthenium complex [RuCl(Tpg)(η-MeC₆H₄Prⁱ-*p*)]. The stereochemistry about the non-co-ordinated nitrogens is less unambiguous; in each case the N-bound hydrogen atom has been located but errors associated with their positions are such that, of the angles subtended at these nitrogens, the only ones that can be determined with precision are those involving the attached
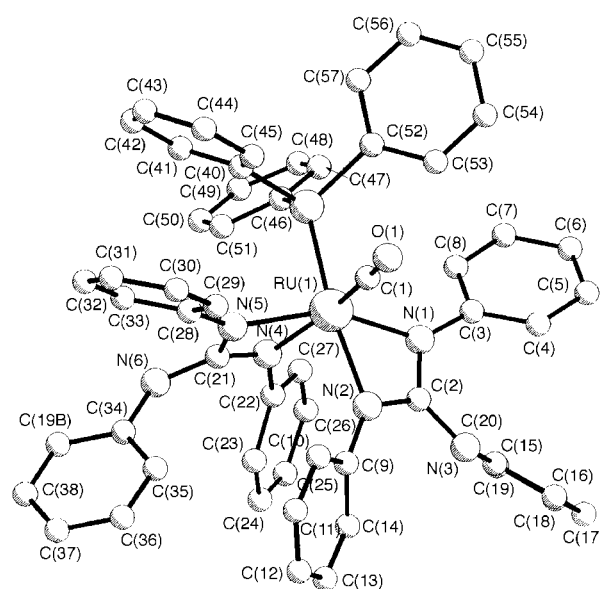
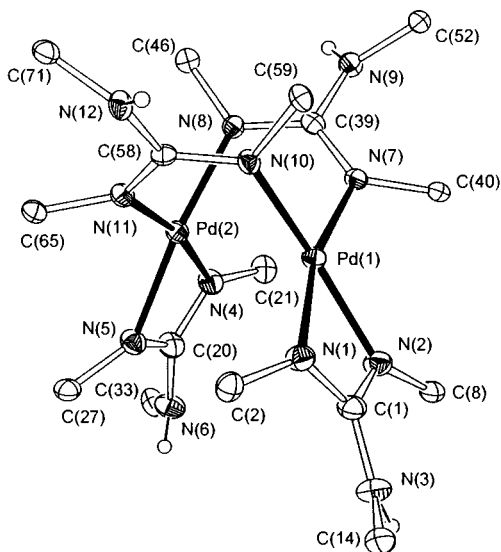**Fig. 1** Molecular structure of [Ru(Tpg)₂(CO)(PPh₃)] **1**.

carbon atoms [C–N–C 126.5(2) and 123.9(2)°]. However, when combined with the somewhat less accurate values available for angles involving the N–H bonds (see Table 1), they give totals of 345.6 and 337.9° for the angles subtended at N(3) and N(6) respectively. These totals, almost equidistant between the theoretical summations for sp² (360°) and sp³ (327°) hybridisation, would appear to imply a stereochemistry midway between the two ideal arrangements. The observation that the corresponding values for the palladium complex **2** (see below) are all very close to the ideal value of 360° (sp²) suggests that complexes **1** and **2** display real differences in stereochemistry at the non-co-ordinated nitrogen atoms.

The phenyl groups attached to the co-ordinated nitrogen atoms and the planar NHPh moiety are all rotated out of the plane of the guanidinate skeleton (torsion angles *ca.* 30 to 60°). The N–C bond lengths within the chelate rings [average 1.330(3) Å] are very similar to those reported for related amidinate [PhN–C(R)–NPh] ligands, and are consistent with the presence of a delocalised N–C–N ligand backbone.[7] The small degree of asymmetry found within the chelate rings can be attributed to the differing *trans* influences of the opposing ligands. In each guanidinate ligand the length of the bonds between the central carbon and the non-co-ordinated nitrogen [C–N average 1.391(3) Å] and in particular the lengths of the

Table 1 Selected bond lengths (Å) and angles and torsion angles (°) for [Ru(Tpg)$_2$(CO)(PPh$_3$)] **1**

Ru–C(1)	1.827(3)	N(3)–C(2)	1.384(3)
Ru–N(5)	2.114(2)	N(3)–C(15)	1.416(3)
Ru–N(1)	2.128(2)	N(3)–H(N3)	0.93
Ru–N(2)	2.138(2)	N(4)–C(21)	1.332(3)
Ru–N(4)	2.150(2)	N(4)–C(22)	1.409(3)
Ru–P	2.3152(7)	N(5)–C(21)	1.331(3)
O(1)–C(1)	1.161(3)	N(5)–C(28)	1.409(3)
N(1)–C(2)	1.332(3)	N(6)–C(21)	1.399(3)
N(1)–C(3)	1.406(3)	N(6)–C(34)	1.425(4)
N(2)–C(2)	1.325(3)	N(6)–H(N6)	1.16
N(2)–C(9)	1.399(3)		
C(1)–Ru–N(5)	103.04(11)	C(2)–N(3)–H(N3)	108.4
C(1)–Ru–N(1)	98.30(11)	C(15)–N(3)–H(N3)	110.7
N(5)–Ru–N(1)	151.24(9)	C(21)–N(4)–C(22)	123.5(2)
C(1)–Ru–N(2)	94.43(11)	C(21)–N(4)–Ru	92.40(16)
N(5)–Ru–N(2)	97.55(8)	C(22)–N(4)–Ru	137.59(17)
N(1)–Ru–N(2)	61.47(8)	C(21)–N(5)–C(28)	127.5(2)
C(1)–Ru–N(4)	164.80(11)	C(21)–N(5)–Ru	94.01(16)
N(5)–Ru–N(4)	62.00(8)	C(28)–N(5)–Ru	138.37(19)
N(1)–Ru–N(4)	95.00(8)	C(21)–N(6)–C(34)	123.9(2)
N(2)–Ru–N(4)	85.47(9)	C(21)–N(6)–H(N6)	104.2
C(1)–Ru–P	89.57(9)	C(34)–N(6)–H(N6)	109.8
N(5)–Ru–P	91.55(6)	O(1)–C(1)–Ru	176.2(3)
N(1)–Ru–P	107.79(6)	N(2)–C(2)–N(1)	110.3(2)
N(2)–Ru–P	168.96(6)	N(2)–C(2)–N(3)	123.8(2)
N(4)–Ru–P	93.36(6)	N(1)–C(2)–N(3)	125.8(2)
C(2)–N(1)–C(3)	126.3(2)	N(2)–C(2)–Ru	55.37(13)
C(2)–N(1)–Ru	94.24(15)	N(1)–C(2)–Ru	54.94(13)
C(3)–N(1)–Ru	138.62(17)	N(3)–C(2)–Ru	178.64(19)
C(2)–N(2)–C(9)	127.7(2)	N(5)–C(21)–N(4)	111.2(2)
C(2)–N(2)–Ru	93.97(16)	N(5)–C(21)–N(6)	126.1(2)
C(9)–N(2)–Ru	137.89(17)	N(4)–C(21)–N(6)	122.5(2)
C(2)–N(3)–C(15)	126.5(2)		
N(1)–Ru–N(2)–C(2)	1.20(15)		
N(4)–Ru–N(5)–C(21)	3.96(16)		

Table 2 Selected bond lengths (Å) and angles and torsion angles (°) for [{Pd(μ-Tpg)(Tpg)}$_2$] **2**

Pd(1)–N(10)	2.037(3)	N(5)–C(20)	1.341(5)
Pd(1)–N(2)	2.045(3)	N(5)–C(27)	1.413(5)
Pd(1)–N(7)	2.055(3)	N(6)–C(20)	1.388(5)
Pd(1)–N(1)	2.057(3)	N(6)–C(33)	1.405(5)
Pd(1)–C(1)	2.505(4)	N(6)–H(N6)	0.827
Pd(1)···Pd(2)	2.9678(4)	N(7)–C(39)	1.331(4)
Pd(2)–N(8)	2.029(3)	N(7)–C(40)	1.438(4)
Pd(2)–N(5)	2.050(3)	N(8)–C(39)	1.344(4)
Pd(2)–N(11)	2.051(3)	N(8)–C(46)	1.413(4)
Pd(2)–N(4)	2.071(3)	N(9)–C(39)	1.382(5)
Pd(2)–C(20)	2.503(4)	N(9)–C(52)	1.410(5)
N(1)–C(1)	1.348(5)	N(9)–H(N9)	0.722
N(1)–C(2)	1.404(5)	N(10)–C(58)	1.335(4)
N(2)–C(1)	1.329(5)	N(10)–C(59)	1.425(4)
N(2)–C(8)	1.416(5)	N(11)–C(58)	1.335(4)
N(3)–C(1)	1.367(5)	N(11)–C(65)	1.433(4)
N(3)–H(N3)	1.005	N(12)–C(58)	1.384(5)
N(3)–C(14)	1.413(5)	N(12)–C(71)	1.404(5)
N(4)–C(20)	1.332(5)	N(12)–H(N12)	0.645
N(4)–C(21)	1.405(5)		
N(10)–Pd(1)–N(2)	165.41(22)	C(27)–N(5)–Pd(2)	138.2(3)
N(10)–Pd(1)–N(7)	90.49(11)	C(20)–N(6)–C(33)	125.0(4)
N(2)–Pd(1)–N(7)	102.35(12)	C(20)–N(6)–H(N6)	113
N(10)–Pd(1)–N(1)	101.82(12)	C(33)–N(6)–H(N6)	118
N(2)–Pd(1)–N(1)	64.47(12)	C(39)–N(7)–C(40)	120.6(3)
N(7)–Pd(1)–N(1)	164.92(12)	C(39)–N(7)–Pd(1)	125.4(2)
N(10)–Pd(1)–Pd(2)	77.84(8)	C(40)–N(7)–Pd(1)	113.9(2)
N(2)–Pd(1)–Pd(2)	111.92(9)	C(39)–N(8)–C(46)	122.0(3)
N(7)–Pd(1)–Pd(2)	75.13(8)	C(39)–N(8)–Pd(2)	119.7(2)
N(1)–Pd(1)–Pd(2)	115.71(9)	C(46)–N(8)–Pd(2)	118.3(2)
N(8)–Pd(2)–N(5)	164.73(12)	C(39)–N(9)–C(52)	127.6(3)
N(8)–Pd(2)–N(11)	90.67(11)	C(39)–N(9)–H(N9)	116
N(5)–Pd(2)–N(11)	104.45(12)	C(52)–N(9)–H(N9)	115
N(8)–Pd(2)–N(4)	100.30(12)	C(58)–N(10)–C(59)	121.0(3)
N(5)–Pd(2)–N(4)	64.47(12)	C(58)–N(10)–Pd(1)	123.5(2)
N(11)–Pd(2)–N(4)	168.39(12)	C(59)–N(10)–Pd(1)	115.5(2)
N(8)–Pd(2)–Pd(1)	80.32(8)	C(58)–N(11)–C(65)	120.2(3)
N(5)–Pd(2)–Pd(1)	104.63(9)	C(58)–N(11)–Pd(2)	122.8(2)
N(11)–Pd(2)–Pd(1)	77.81(8)	C(65)–N(11)–Pd(2)	117.1(2)
N(4)–Pd(2)–Pd(1)	107.60(9)	C(58)–N(12)–C(71)	129.1(4)
C(1)–N(1)–C(2)	126.2(3)	C(58)–N(12)–H(N12)	115
C(1)–N(1)–Pd(1)	92.3(2)	C(71)–N(12)–H(N12)	115
C(2)–N(1)–Pd(1)	132.9(2)	N(2)–C(1)–N(1)	109.7(3)
C(1)–N(2)–C(8)	125.7(3)	N(2)–C(1)–N(3)	123.1(4)
C(1)–N(2)–Pd(1)	93.5(2)	N(1)–C(1)–N(3)	127.2(4)
C(8)–N(2)–Pd(1)	140.8(3)	N(4)–C(20)–N(5)	110.6(3)
C(1)–N(3)–C(14)	128.9(4)	N(4)–C(20)–N(6)	125.5(4)
C(1)–N(3)–H(N3)	123	N(5)–C(20)–N(6)	123.8(4)
C(14)–N(3)–H(N3)	108	N(7)–C(39)–N(8)	121.1(3)
C(20)–N(4)–C(21)	128.5(3)	N(7)–C(39)–N(9)	120.0(3)
C(20)–N(4)–Pd(2)	92.1(2)	N(8)–C(39)–N(9)	118.8(3)
C(21)–N(4)–Pd(2)	137.7(3)	N(11)–C(58)–N(10)	120.8(3)
C(20)–N(5)–C(27)	125.7(3)	N(11)–C(58)–N(12)	121.6(3)
C(20)–N(5)–Pd(2)	92.8(2)	N(10)–C(58)–N(12)	117.5(3)
N(1)–Pd(1)–N(2)–C(1)	0.3(2)		
N(4)–Pd(2)–N(5)–C(20)	0.8(2)		

Fig. 2 Molecular structure of [{Pd(μ-Tpg)(Tpg)}$_2$] **2**. Phenyl rings are represented by the *ipso*-C atoms for clarity.

bonds between the three nitrogen atoms and their attached phenyl groups [C–N average 1.411(3) Å] show little evidence of carbon–nitrogen double bond character. Taken together the bond length and bond angle data suggest that there is a little delocalisation of the lone pair on the non-co-ordinated nitrogen over the guanidine skeleton, and that there appears to be no significant delocalisation of the lone pair electron density from any of the nitrogen atoms out on to the attached phenyl groups.

Treatment of palladium acetate with N,N',N''-triphenylguanidine in benzene at 60 °C leads to formation of a stable insoluble yellow powder which deposits from solution in essentially quantitative yield. On the basis of infrared spectra and elemental analysis data this product is formulated as the adduct [Pd(O$_2$CMe)$_2$(HTpg)$_2$]. On heating with an excess of N,N',N''-triphenylguanidine in boiling toluene the adduct eliminates acetic acid to form the bis(guanidinato)palladium(II) complex **2** which deposited from solution as dark red crystals. The binuclear nature of **2** was confirmed by X-ray diffraction methods which revealed the novel bridged structure [{Pd-(μ-Tpg)(Tpg)}$_2$] and thereby established the first example of a complex containing chelate and bridging guanidinate(1−) ligands. The molecular structure of **2** is shown in Fig. 2; selected bond length and angle data are collated in Table 2. The geometry and dimensions of the N,N',N''-triphenylguanidinato complex **2** are very similar to those previously reported for the corresponding N,N'-diphenylbenzamidinato complex.[8] In both complexes the angles subtended at the palladium by the N-

donor atoms of the chelate ligands are *ca.* 64° and in each case the Pd–N bond lengths for the chelate and bridging ligands are very similar. Evidence for a significant degree of steric interaction between the two halves of the guanidinato complex is provided by values for the non-bridging Pd⋯Pd distance [2.9678(4) Å], the dihedral angle between the two PdN$_4$ planes (39.4°) and the N–Pd⋯Pd–N torsion angle (29°) all of which are significantly larger than those reported for the corresponding *N,N'*-diphenylbenzamidinato complex [2.900(1) Å, 35 and 19° respectively]. The angles subtended at palladium by the N-donor atoms of the chelating guanidinate(1−) ligands [both 64.47(12)°] reflect the small 'bite' of this ligand. In contrast the corresponding angles for the nitrogen atoms of the bridging guanidinate ligands are almost exactly 90° as required for rigorous square planar co-ordination. The Pd–N bond lengths averaging 2.055(3) and 2.043(3) Å for chelate and bridging guanidinato ligands respectively, are very similar to those previously reported for the corresponding *N,N'*-diphenylbenz-amidinate complex.[8] For each of these chelate and bridging guanidinato ligands the sum of the angles subtended at the central carbon equals 360° thereby establishing the planarity of the N$_2$CN skeletons. For each of the chelate guanidinate ligands the dihedral angle between the N$_2$CN plane and the corresponding N–Pd–N plane is less than 1°. Therefore in contrast to the ruthenium complex **1** discussed above, and the ruthenium and rhodium complexes reported by Bailey *et al.*,[5] the palladium complex has essentially planar chelate rings. For the two bridging guanidinate ligands the sum of the angles subtended at each of the co-ordinated nitrogen atoms is exactly 360°. However in the case of the chelate guanidinate ligands there are small deviations from planarity at two of the co-ordinated nitrogens, N(4) and N(5) (sum of angles = 358.3 and 356.7°), and a somewhat larger deviation at a third, N(1) (sum of angles = 351.4°), which we attribute to steric interactions between adjacent phenyl rings. As in the case of the ruthenium complex, the hydrogen atoms attached to the non-co-ordinated nitrogens have been located (average N–H 0.8 Å) but once again errors associated with their positions are such that bond angles incorporating the N–H bonds cannot be determined with a high degree of accuracy. However, the totals obtained for the angles subtended at the non-co-ordinated nitrogen atoms, N(3) 359.9, N(6) 356.0, N(9) 358.6 and N(12) 359.1°, are very close to 360° in three cases and not far removed in the fourth, N(6). Even allowing for the errors associated with the involvement of the N–H groups referred to above, these data suggest the adoption of trigonal planar (sp^2) stereochemistry in each instance, and are in marked contrast to those found for the ruthenium complex **1** (see above). Finally the phenyl groups attached to the co-ordinated nitrogen atoms and the non-co-ordinated NHPh moieties are rotated out of the plane of the guanidinate skeleton.

The C–N bond lengths observed for the chelate and bridging guanidinate ligands in complex **2** are very similar, and agree well with those found for the chelate guanidinate ligands in [Ru(Tpg)$_2$(CO)(PPh$_3$)] **1**. Taken together the bond length and bond angle data for **2** suggest that, as in the case of complex **1**, the lone pair on the non-co-ordinated nitrogen is not extensively delocalised over the guanidinate skeleton, and that delocalisation of the nitrogen lone pairs out into the attached phenyl groups is minimal.

Experimental

Preparations

[Ru{PhNC(NHPh)NPh}$_2$(CO)(PPh$_3$)] 1. Carbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.5 g, 0.57 mmol) and *N,N',N''*-triphenylguanidine (0.8 g, 2.79 mmol) were heated together under reflux in toluene (40 cm^3) for *ca.* 5.5 h to give a greenish yellow solution. Concentration under reduced pressure left an oil which on crystallisation from CH$_2$Cl$_2$–MeOH afforded lemon yellow crystals (0.31 g, 56%), mp 212–214 °C (Found: C, 70.25; H, 4.75; N, 8.6. Calc. for C$_{57}$H$_{47}$N$_6$OPRu: C, 71.0; H, 4.9; N, 8.7%). IR: *ν*(CO) 1930 cm^{-1}, *ν*(NH) 3389, 3400 cm^{-1}. ^{31}P NMR (CDCl$_3$), (145.785 MHz): δ 52.59 (s).

[Pd(O$_2$CMe)$_2${PhNC(NHPh)NHPh}$_2$]. Palladium acetate (0.3 g, 1.34 mmol) was dissolved in benzene (50 cm^3) to give an orange solution. *N,N',N''*-Triphenylguanidine (0.8 g, 2.78 mmol) was then added and the mixture maintained at 60 °C for *ca.* 2.5 h. The product which deposited was filtered off, washed repeatedly with methanol and dried *in vacuo* as yellow microcrystals (0.86 g, 80%), mp 176–178 °C (decomp.) (Found: C, 63.15; H, 5.0; N, 10.4. Calc. for C$_{42}$H$_{40}$N$_6$O$_4$Pd: C, 63.1; H, 5.05; N, 10.5%). IR *ν*(N–H) 3177, *ν*(O$_2$C)$_{asym}$ 1613, 1631 cm^{-1}.

[Pd$_2${μ-PhNC(NHPh)NPh}$_2${PhNC(NHPh)NPh}$_2$]·CH$_2$Cl$_2$. Bis(acetato)bis(*N,N',N''*-triphenylguanidine)palladium (0.4 g, 0.5 mmol) and *N,N',N''*-triphenylguanidine (0.35 g, 1.2 mmol) were stirred and heated together under reflux in toluene (50 cm^3) for *ca.* 2 h. The dark red solution was filtered to remove a small amount of greenish yellow solid residue and then concentrated under reduced pressure to form an oil which was redissolved in the minimum volume of CH$_2$Cl$_2$. Careful addition of MeOH led to slow crystallisation of the product which was filtered off, washed with methanol and dried *in vacuo* as dark maroon crystals (0.18 g, 53%), mp 194–196 °C (decomp.) (Found: C, 62.15; H, 4.3; N, 10.85. Calc. for C$_{38}$H$_{32}$N$_6$Pd·0.5CH$_2$Cl$_2$: C, 61.3; H, 4.35; N, 11.0%). IR: *ν*(N–H) 3396 cm^{-1}.

X-Ray crystallography

Crystals were mounted on thin glass fibres using fast setting epoxy resin and cooled on the diffractometer to the temperature stated using an Oxford Cryostream low temperature attachment. A total of either 90 or 180 oscillation frames each of width either 2 or 1° in φ respectively and of 10–160 s exposure time (depending upon crystal quality) were recorded on a Nonius Kappa CCD diffractometer, using Mo-Kα radiation (λ = 0.71070 Å), with a detector to crystal distance of 25–30 mm. Crystals were indexed from the first ten frames using the DENZO package[10] and positional data were refined along with diffractometer constants to give the final cell parameters. Integration and scaling (DENZO, Scalepack[10]) resulted in unique data sets corrected for Lorentz-polarisation effects and for the effects of crystal decay and absorption by a combination of averaging of equivalent reflections and an overall volume and scaling correction. Crystallographic data are recorded in Table 3. The structures were solved using SHELXS 97[11] and developed *via* alternating least squares cycles and Fourier difference synthesis (SHELXL 97[11]) with the aid of the program RES2INS.[12] In general all non-hydrogen atoms were modelled anisotropically, while hydrogen atoms were assigned an isotropic thermal parameter 1.2 times that of the parent atom (1.5 for terminal atoms) and allowed to ride. Hydrogens bound to nitrogen were located by Fourier difference syntheses and allowed to ride on the atoms to which they are attached. All calculations were carried out with either a Silicon Graphics Indy R5000 work station or an IBM compatible PC.

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Table 3 Crystallographic data for complexes **1** and **2**

	1	2
Molecular formula	$C_{57}H_{47}N_6OPRu$	$C_{76}H_{64}N_{12}Pd_2$
M	964.05	1358.19
T/K	173(2)	123(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
$a/Å$	10.0246(3)	11.5530(3)
$b/Å$	22.7693(7)	25.9674(8)
$c/Å$	20.7373(4)	21.8712(8)
$\beta/°$	94.553(1)	103.190(2)
$U/Å^3$	4718.4(2)	6388.2(3)
Z	4	4
$D_c/g\ cm^{-3}$	1.357	1.412
μ/mm^{-1}	0.414	0.618
$F(000)$	1992	2784
Crystal size/mm	$0.25 \times 0.20 \times 0.20$	$0.10 \times 0.10 \times 0.10$
θ Range for data collection/°	3.37 to 26.00	3.24 to 25.00
Index ranges	0 to 12, 0 to 28, -25 to 25	-13 to 13, -30 to 30, -25 to 26
Reflections collected/unique	36696/8994	51426/11206
R_{int}	0.0520	0.0472
Absorption correction	Scalepack	Scalepack
Refinement method	Full matrix least squares on F^2	Full matrix least squares on F^2
Data/restraints/parameters	8994/0/595	11206/0/827
Goodness of fit on F^2	1.074	1.064
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0387, 0.0898	0.0433, 0.0863
(all data)	0.0507, 0.0983	0.0631, 0.0927
Largest difference peak and hole/e $Å^{-3}$	0.464 and -0.622	0.855 and -0.925

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