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Olefin ligands

II. Syntheses of 2,6-diallylpyridine (DAP) complexes of iridium(I), ruthenium(II), palladium(II) and platinum(II); crystal structures of [$RuCl_2(PPh_3)$(DAP)] and [$PdCl_2(DAP)_2$]

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Abstract

The tridentate ligand 2,6-diallylpyridine (DAP) has been used to synthesize novel complexes of iridium(I), ruthenium(II), palladium(II) and platinum(II) of formulae [Ir(COD)(DAP)][$IrCl_2$(COD)], [IrCl(CO)(DAP)], [Ir(COD)(DAP)]ClO_4, [$RuCl_2$(PPh_3)(DAP)], [$PdCl_2(DAP)_2$], [$PtCl_2$(DAP)]. All the complexes have been characterized by elemental analysis, IR, and ^1H NMR spectroscopy. The molecular structures of [$RuCl_2(PPh_3)$(DAP)] and [$PdCl_2(DAP)_2$] have been determined by single-crystal X-ray diffraction studies. Crystals of the ruthenium complex are orthorhombic, space group *Pbca*, with $Z = 8$ in a unit cell of dimensions a 11.492(5), b 18.942(3), c 23.083(9) Å. Crystals of the palladium complex are triclinic, space group $P\bar{1}$ with $Z = 1$ in a unit cell of dimensions a 7.950(4), b 8.745(4), c 9.578(4) Å, α 113.02(3), β 90.75(3), γ 116.65(3)°. Both structures were solved by Patterson and Fourier methods and refined by blocked full-matrix least-squares to $R = 0.0528$ for 2742 observed reflections in the first complex and by full-matrix least-squares to $R = 0.0252$ for 1948 observed reflections in the second. In the octahedral ruthenium complex, DAP acts as a tridentate ligand adopting a *mer* configuration and the phosphine ligand is *trans* to the pyridinic nitrogen, while in the *trans* square-planar palladium complex DAP acts as a monodentate *N*-donor ligand.

Introduction

There is considerable interest in complexes of transition metals containing multidentate ligands possessing different types of donor atoms, since their reactivity may be very different from that of complexes with monodentate ligands. We recently reported [1] the preparation, molecular structures, and the spectroscopic properties of several pentacoordinate rhodium(I) complexes containing a tridentate ligand, 2,6-diallylpyridine (DAP), coordinated to the metal through the pyridine nitrogen atom and the double bonds of the allylic groups. In the course of this work it was thought necessary to investigate the reactivity of the DAP ligand towards other platinum group metals, and this paper describes the related iridium(I), ruthenium(II), palladium(II) and platinum(II) complexes, their IR and proton NMR spectra, and the X-ray structure determination of the ruthenium and palladium complexes. The chemistry of the complexes is under investigation.

Results and discussion

The complex $[IrCl(COD)]_2$ (COD = 1,5-cyclooctadiene) reacts with 2,6-diallylpyridine (DAP) in benzene to give a crystalline compound, which on the bases of analytical data (Table 1), IR and ^1H NMR spectra (Table 2) can be formulated as $Ir_2Cl_2(COD)_2(DAP)$. When the reaction is carried out in presence of silver perchlorate, a compound of formula $[Ir(COD)(DAP)]ClO_4$ is obtained. The similarities observed between the molar conductivity, IR and ^1H NMR spectra of these compounds and those of the analogous rhodium species previously described, suggest that in these complexes the DAP ligand behaves as a tridentate ligand and that they can be formulated as ionic compounds of the type $[Ir(COD)(DAP)]$ $[IrCl_2(COD)]$ (I) and $[Ir(COD)(DAP)]ClO_4$ (II).

Treatment of $[IrCl(COE)_2]_2$ (COE = cyclooctene) with DAP in benzene gives a yellow-orange microcrystalline precipitate. This product is not stable, which has

Table 1

Analytical data for the complexes

Compound	M.p. (°C)	Analysis (found (calcd.) (%))			
		C	H	N	Cl
$[Ir(COD)(DAP)][IrCl_2(COD)]$	193–200	39.02 (39.03)	4.60 (4.49)	1.90 (1.69)	7.02 (8.53)
$[Ir(COD)(DAP)]ClO_4$	137–140	42.30 (40.82)	4.67 (4.50)	2.23 (2.51)	6.64 (6.34)
$[RuCl_2(PPh_3)(DAP)]$ [a]	165–170	58.40 (58.69)	4.73 (4.76)	2.45 (2.36)	11.50 (11.95)
$[PdCl_2(DAP)_2]$	164–168	52.27 (53.30)	5.20 (5.29)	5.11 (5.65)	13.90 (14.30)
$[PtCl_2(DAP)$	145–147	32.10 (31.07)	2.98 (3.08)	3.05 (3.29)	17.54 (16.67)
$[IrCl(CO)(DAP)]$	205–209	34.51 (34.74)	3.10 (3.16)	3.08 (3.38)	9.00 (8.54)

[a] Found: P, 5.35; calcd.: 5.22%.

Table 2

IR and ^{1}H NMR data for the complexes

Complexes	IR (cm^{-1})(Nujol)	^{1}H NMR, δ (ppm)(CD_2Cl_2)
[Ir(DAP)(COD)][$IrCl_2$(COD)]	1601(m), 1410(w), 1330(w), 1170(m), 1000(w), 975(m), 810(sh), 795(s), 298(s), 273(s)	7.6(t,1H); 7.2(d,2H); 5.21(m); 4.42(m); 4.1(m); 3.71(m), 3.04(m), 2.96(m), 2.46(m), 2.0(m), 1.23(m)
[Ir(DAP)(COD)](ClO_4)	1605(s), 1570(w), 1335(s), 1240(m), 1175(s), 1168(s), 1100(vs), 900(w), 855(w), 815(m), 795(s), 780(sh), 750(w), 625(vs)	7.51(t,1H); 7.11(d,2H); 6.1(m,2H); 4.52(m,2H); 3.9(m,6H); 3.3(m,4H); 2.98(m,2H); 2.5(m,4H); 2.0(m,2H)
[$RuCl_2$(DAP)(PPh_3)]	3070(w), 3025(w), 1609(m), 1573(m), 1485(m), 1435(s), 1195(m), 1165(m), 1090(s), 900(m), 850(w), 780(s), 753(vs), 742(s), 701(vs), 680(sh)	7.8–7.0(m,18H); 5.9(m,2H); 5.1(m,2H); 4.1(m,6H)
[$PdCl_2(DAP)_2$]	3080(w), 1645(s), 1608(s), 1580(s), 1425(s), 1290(w), 1170(s), 1002(s), 925(vs), 800(s), 780(us), 680(w)	7.6(t,1H); 7.1(d,2H); 6.3(m,2H); 5.3(m,4H); 5.1(m,4H)
[$PtCl_2$(DAP)]	3070(w), 1602(s), 1560(s), 1255(m), 1225(m), 1168(s), 1100(w), 1001(s), 985(s), 927(vs), 900(sh), 810(vs), 770(s)	7.8(t,1H); 7.3(d,2H); 5.78(m,2H); 4.82(m,2H); 4.3(m,4H); 3.68(m,2H)
[IrCl(CO)(DAP)]	2000(vs), 1585(s), 1390(m), 1328(m), 1222(w), 1150(w), 1161(s), 995(w), 818(m), 809(s)	7.5(t,1H); 7.05(d,2H); 4.2(m,2H); 3.9(m,4H); 3.6(m,2H); 2.35(m,2H)

prevented complete characterization, but can be formulated as IrCl(DAP) analogous to the RhCl(DAP) obtained in the same way. A suspension of this precipitate, prepared in situ, reacts readily with CO at atmospheric pressure and room temperature to give the stable compound [IrCl(CO)(DAP)] analogous to the rhodium compound [RhCl(CO)(DAP)] obtained by treating RhCl(DAP) with CO.

The complex [$RuCl_2(PPh_3)_3$] reacts with DAP in a refluxing benzene to give a crystalline red-orange complex whose elemental analysis is consistent with the formula [$RuCl_2$(PPh_3)(DAP)] (III). In order to confirm the formulation and establish the chelating tridentate nature of the DAP ligand an X-ray structural determination was undertaken.

The molecular structure of III is shown in Fig. 1, and selected bond distances and angles are given in Table 3.

In the complex the Ru atom is six-coordinate with a distorted octahedral arrangement, and with the DAP ligand statistically fifty-fifty distributed between two positions. DAP acts as a tridentate ligand, adopting a *mer* configuration through the N pyridinic atom and the two olefinic bonds; the P phosphine atom is *trans* to N, and two Cl atoms complete the coordination. The Ru–C_{olefin} distances seem to differ somewhat, and fall in the range 2.15(2)–2.44(1) Å, while the other coordination distances are normal. In each disordered DAP ligand the olefinic bonds are approximately parallel to the NCl(1)PCl(2) plane (the C=C bonds are tilted by values ranging from 1(2) to 11(1)°), and are arranged in such a manner as to be roughly parallel or perpendicular to the Ru–N bond. These groups are then

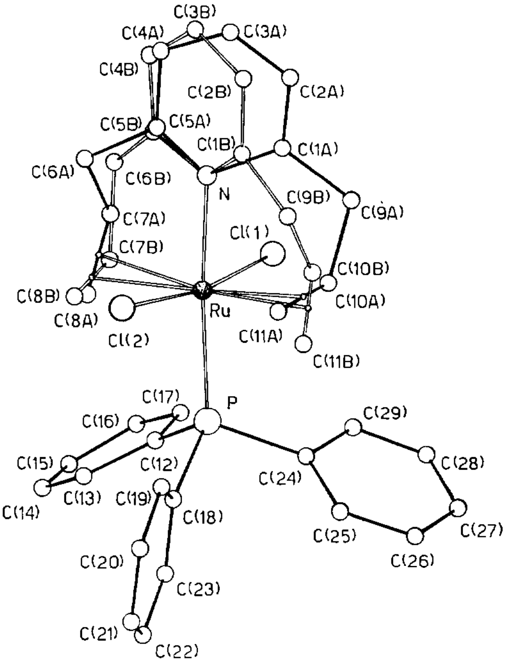

Fig. 1. View of the [$RuCl_2(PPh_3)$(DAP)] complex with the atomic numbering scheme.

related by a pseudo-mirror plane passing through the first plane. The two orientations seem to be equivalent, and this may account for the disorder. The pseudo-symmetry is also preserved in the triphenylphosphine ligand. The non-planarity of Cl(1),Cl(2),M(1A),M(2A) or Cl(1),Cl(2),M(1B),M(2B) (M(1) and M(2) are the midpoints of C(7)=C(8) and C(10)=C(11), respectively, for A and B molecules of DAP) is mainly due to the steric hindrance by the triphenylphosphine ligand. The torsion angle τ[Cl(2)–Ru–P–C(18)] −12.1(3)° reveals an eclipsed conformation and τ[Ru–P–C(18)–C(19)] −15.4(8)° shows that the phenyl ring lies almost in the Cl(2)RuPC(18) plane, so that a phenyl H atom points towards a Cl atom. A C_{phenyl}–H ... Cl interaction is then formed (C(19)–H(19) ... Cl(2) = 3.23(1), H(19) ... Cl(2) = 2.49(7) Å, C(19)–H(19)–Cl(2) = 141(6)°), and at the same time the P–Ru–Cl(2) (99.0(1)°) and Ru–P–C(18) (120.6(3)°) angles are significantly larger than the theoretical values.

A suspension of [$RuCl_2(PPh_3)$(DAP)] in benzene readily reacts with carbon monoxide at room temperature to give the well known carbonyl compound [$RuCl_2(CO)_2(PPh_3)_2$] [2] in which the DAP ligand has been replaced by the carbon monoxide.

$PdCl_2$ reacts with DAP to give a complex of formula [$PdCl_2(DAP)_2$] (IV), whose molecular structure is depicted in Fig. 2, and selected bond distances and angles are listed in Table 3. The Pd coordination is *trans* square-planar; the DAP acts as a *N*-monodentate ligand and the pyridine ring is almost perpendicular to the coordination plane (97.5(1)°). The conformations of the two allylic DAP groups are dissimilar; C(7) is −antiperiplanar whereas C(10) is +synclinal with respect to N (τ[N–C(5)–C(6)–C(7)] −178.0(3)°, τ[N–C(1)–C(9)–C(10)] 83.3(4)°), C(8) is

Table 3

Selected bond distances (Å) and angles (°) (with e.s.d.'s in parentheses)

(A) in complex III

Ru–P	2.408(3)	Ru–C(11A)	2.15(2)	Ru–M(2A)	2.07(2)
Ru–Cl(1)	2.435(3)	Ru–C(7B)	2.19(2)	Ru–M(1B)	2.17(3)
Ru–Cl(2)	2.427(3)	Ru–C(8B)	2.30(3)	Ru–M(2B)	2.24(2)
Ru–N	2.116(6)	Ru–C(10B)	2.26(2)	P–C(12)	1.839(8)
Ru–C(7A)	2.38(2)	Ru–C(11B)	2.40(2)	P–C(18)	1.847(7)
Ru–C(8A)	2.44(1)	Ru–M(1A)	2.29(2)	P–C(24)	1.849(9)
Ru–C(10A)	2.25(2)				

P–Ru–Cl(1)	88.6(1)	P–Ru–N	175.9(2)
P–Ru–Cl(2)	99.0(1)	Cl(1)–Ru–Cl(2)	170.6(1)
Cl(1)–Ru–N	88.7(2)	M(1A)–Ru–M(2A)	167.0(6)
Cl(2)–Ru–N	84.0(2)	M(1B)–Ru–M(2B)	171.3(9)
M(1A)–Ru–P	97.1(4)	M(1B)–Ru–P	89.7(7)
M(1A)–Ru–Cl(1)	82.6(4)	M(1B)–Ru–Cl(1)	93.0(7)
M(1A)–Ru–Cl(2)	90.9(4)	M(1B)–Ru–Cl(2)	81.5(7)
M(1A)–Ru–N	85.5(5)	M(1B)–Ru–N	93.5(7)
M(2A)–Ru–P	94.6(5)	M(2B)–Ru–P	90.8(5)
M(2A)–Ru–Cl(1)	92.2(5)	M(2B)–Ru–Cl(1)	95.7(5)
M(2A)–Ru–Cl(2)	92.8(5)	M(2B)–Ru–Cl(2)	89.9(5)
M(2A)–Ru–N	82.5(5)	M(2B)–Ru–N	86.5(5)
Ru–P–C(12)	114.7(3)	C(12)–P–C(18)	101.9(4)
Ru–P–C(18)	120.6(3)	C(12)–P–C(24)	104.1(3)
Ru–P–C(24)	114.0(3)	C(18)–P–C(24)	99.1(4)

(B) in complex IV

Pd–Cl	2.299(2)	C(2)–C(3)	1.373(5)	C(7)–C(8)	1.276(5)
Pd–N	2.043(3)	C(3)–C(4)	1.363(5)	C(1)–C(9)	1.513(4)
N–C(1)	1.341(3)	C(4)–C(5)	1.379(5)	C(9)–C(10)	1.479(5)
N–C(5)	1.356(4)	C(5)–C(6)	1.497(5)	C(10)–C(11)	1.309(4)
C(1)–C(2)	1.381(5)	C(6)–C(7)	1.483(5)		

Cl–Pd–N	91.2(1)	N–C(5)–C(6)	117.1(3)
Pd–N–C(1)	120.6(2)	C(4)–C(5)–C(6)	122.9(3)
Pd–N–C(5)	119.2(2)	C(5)–C(6)–C(7)	115.5(3)
C(1)–N–C(5)	120.1(3)	C(6)–C(7)–C(8)	125.6(5)
N–C(1)–C(2)	120.9(3)	N–C(1)–C(9)	119.1(3)
C(1)–C(2)–C(3)	119.6(3)	C(2)–C(1)–C(9)	120.1(3)
C(2)–C(3)–C(4)	119.1(4)	C(1)–C(9)–C(10)	112.7(3)
C(3)–C(4)–C(5)	120.4(3)	C(9)–C(10)–C(11)	124.3(4)
C(4)–C(5)–N	120.0(3)		

−anticlinal and C(11) +anticlinal with respect to C(5) and C(1), respectively (τ[C(5)–C(6)–C(7)–C(8)] −124.1(5)°, τ[C(1)–C(9)–C(10)–C(11)] 120.2(5)°). Bond distances and angles in the DAP ligand are similar to those in the rhodium complexes [1], except for the two olefinic bonds (C(7)=C(8) 1.276(5), C(10)=C(11) 1.309(4) Å) not involved in the coordination. The disorder prevents comparison of these bond distances with those in complex III. The shortest interaction between palladium and methylene hydrogen atoms are Pd...H(91) 2.71(4) and Pd...H(61) 2.85(4) Å. The coordination bond distances and angles are normal, and fall in the

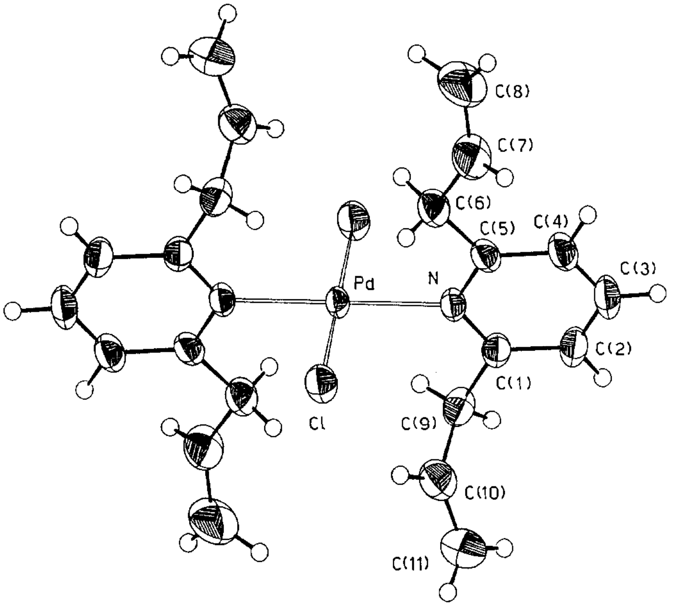

Fig. 2. View of the [$PdCl_2(DAP)_2$] complex with the atomic numbering scheme. Thermal parameters are drawn at the 50% probability level.

range expected for this type of complexes. Extensive use of the Cambridge Structural Database Files was made in the bibliographic search for complexes III and IV.

$PtCl_2$ reacts with DAP in different way to give a complex of formula [$PtCl_2(DAP)$] in which the DAP ligand is probably tridentate. An X-ray structure determination on this compound is in progress.

Experimental

Benzene, hexane, and diethyl ether were dried over sodium wire and distilled from sodium. $RuCl_3 \cdot nH_2O$, $IrCl_3 \cdot nH_2O$, $PdCl_2$, $PtCl_2$ were purchased from Metalli Preziosi S.p.A. (Segrate, Milano). All other chemicals were reagent grade quality and used without further purifications.

Infrared spectra were recorded on a Perkin–Elmer model 337 spectrometer and a polystyrene film was used for calibration. ^1H NMR spectra were recorded on a Varian XL 200 spectrometer with Me_4Si as internal standard.

The preparation of DAP ligand has been described [3]. [$RuCl_2(PPh_3)_3$] [4], [$IrCl(COD)$]$_2$ [5] were also prepared by published methods.

Preparation of compounds

[Ir(COD)(DAP)][IrCl$_2$(COD)]. DAP (50 mg, 0.31 mmol) was added to a solution of [$IrCl(COD)$]$_2$ (100 mg, 0.298 mmol) in benzene (20 ml). The solution was briefly refluxed then cooled, and the yellow crystals formed were filtered off, washed with ether, and dried in vacuo. Typical yields 52%.

[Ir(COD)(DAP)]ClO$_4$. Silver perchlorate (65 mg, 0.31 mmol) was added to a suspension of [$IrCl(COD)$]$_2$ (100 mg, 0.298 mmol) in acetone (15 ml). The mixture

was stirred for 30 min then the AgCl was filtered off and DAP (50 mg, 0.31 mmol) was added. The yellow solution was stirred at room temperature for 30 min then concentrated in vacuo to give yellow crystals. Typical yields 61%.

[IrCl(CO)(DAP)]. A solution of DAP (60 mg, 0.37 mmol) in benzene (10 ml) was added to one of $[IrCl(COE)_2]_2$ (150 mg, 0.33 mmol) in benzene (10 ml). After 15 min refluxing the mixture was cooled to room temperature and the orange-product formed was quickly filtered off and washed with benzene. It was then suspended in 10 ml of benzene and carbon monoxide was bubbled through for 10 minutes at room temperature. The yellow solution obtained was filtered, then concentrated in vacuo, and the yellow crystals obtained by addition of hexane were filtered off, washed with hexane, and dried in vacuo.

$[RuCl_2(PPh_3)(DAP)]$. DAP (50 mg, 0.31 mmol) was added to a solution of 300 mg (0.31 mmol) of $[RuCl_2(PPh_3)_3]$ in 10 ml of benzene. The mixture was refluxed for 4 h then cooled to room temperature, and the red-brown crystals formed were filtered off, washed with benzene, hexane, and dried in vacuo. Typical yields 75–80%. Suitable crystals for the X-ray study were obtained by slow diffusion of hexane into a saturated benzene solution.

$[PdCl_2(DAP)_2]$. DAP (250 mg, 1.57 mmol) was added to a solution of 300 mg (0.78 mmol) of $[PdCl_2(C_6H_5CN)_2]$ in 10 ml of benzene. The mixture was refluxed for 30 min then cooled to room temperature and the yellow precipitate was filtered off, washed with diethyl ether, and dried in vacuo. Crystals for the X-ray study were obtained by slow diffusion of hexane into a saturated benzene solution.

$[PtCl_2(DAP)]$. DAP (110 mg, 0.69 mmol) was added to a solution of 300 mg (0.63 mmol) of $[PtCl_2(C_6H_5CN)_2]$ in 10 ml of benzene. The mixture was refluxed for 3 h then cooled to room temperature and concentrated in vacuo. Diethyl ether was added and the yellow precipitate formed was filtered off, washed with diethyl ether and dried in vacuo.

$[RuCl_2(CO)_2(PPh_3)_2]$. Carbon monoxide was bubbled for 10 min at room temperature through a suspension of $[RuCl_2(PPh_3)(DAP)]$ (100 mg, 0.16 mmol) was in benzene (8 ml). The solution was concentrated in vacuo and diethyl ether was added. The white precipitate was filtered off, washed with diethyl ether, and dried in vacuo.

X-Ray data collections, structure solutions and refinements

Crystal data and data collection parameters for the two compounds are given in Table 4. The structures amplitude were obtained after the usual Lorentz and polarization reduction. A correction for absorption effects was applied for III [6] (maximum and minimum transmission factor values: 1.2351 and 0.7807). Both structures were solved by Patterson and Fourier techniques and refined using the SHELX system of programs [7]. For III, after location of the Ru, Cl, P and N atoms all of the phenyl phosphine C atoms appeared clearly in the Fourier synthesis but the DAP ligand appeared to be distributed between two positions with the N pyridine atom in common. Initially the pyridine rings were refined as rigid bodies to give a better separation of the two locations of the DAP C atoms (s.o.f. 50%), then all the non-hydrogen atoms and the s.o.f. of the disordered C atoms were refined without constraints by isotropic full-matrix least-squares on F. A fifty-fifty distribution was found, in agreement with the values of the electron density found in the ΔF. Then the structure was refined by blocked full-matrix least-squares with

Table 4

Crystal data and details of data collection

	III	IV
Formula	$C_{29}H_{28}Cl_2NPRu$	$C_{22}H_{26}Cl_2N_2Pd$
M.W.	593.497	495.767
Space group	*Pbca*	$P\bar{1}$
a (Å)	11.492(5)	7.950(4)
b (Å)	18.942(3)	8.745(4)
c (Å)	23.083(9)	9.578(4)
α (°)	90	113.02(3)
β (°)	90	90.75(3)
γ (°)	90	116.65(3)
V (Å^3)	5025(3)	533.2(5)
Z	8	1
D_c (Mg m^{-3})	1.569	1.544
Reflections for lattice parameters: number	30	30
Reflections for lattice parameters: θ-range (°)	24–35	10–15
Radiation	Cu-K_α (Ni-filtered)	Mo-K_α (Nb-filtered)
Wavelength (Å)(λ)	1.541838	0.71073
$F(000)$	2416	252
Temperature (K)	295	295
Crystal size (mm^3)	0.16×0.26×0.35	0.14×0.20×0.40
Colour	red	yellow
Diffractometer	Siemens AED	Siemens AED
μ (mm^{-1})	7.930	1.120
θ-range (°)	3.0–70.0	3.0–27.0
h-range	0/14	−9/10
k-range	0/23	−9/0
l-range	0/28	−12/12
Standard reflection checked after every 50	1 10 3	−2 −3 6
Intensity variation	none	none
Scan speed (° s^{-1})	0.20–0.10–0.05	0.20–0.10
Scan width (°)	1.20+0.142 tg θ	1.10+0.346 tg θ
Number of measured reflections	5049	2049
Condition for observed reflections	$I \geqslant 2\sigma(I)$	$I \geqslant 2\sigma(I)$
Number of reflections used in the refinement	2742	1948
Number of refined parameters	356	176
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_0\rvert$ (%)	5.28	2.52
$R_w = [\Sigma w(\Delta F)^2/\Sigma w F_0^2]^{1/2}$ (%)	6.80	3.15
k, g ($w = k[\sigma^2(F_0) + gF_0^2]^{-1}$)	$k = 0.7133$, $g = 0.002348$	$k = 1.0000$, $g = 0.001404$

anisotropic thermal parameters for the Ru, Cl, N, P and phenyl C atoms. A final ΔF synthesis revealed clearly all the phenyl H atoms, and a final blocked full-matrix least-squares was computed with inclusion of these H atoms with isotropic thermal parameters. Data for compound IV were refined by full-matrix least-squares with initially isotropic and then anisotropic thermal parameters. All the H atoms were located from a difference Fourier synthesis and two final full-matrix least-squares cycles were computed with inclusion of the H atoms with isotropic thermal parameters. The atomic scattering factors used, corrected for anomalous dispersion, were taken from International Tables for X-Ray Crystallography [8]. The function minimized in the least-squares calculations was $\Sigma w\lvert\Delta F\rvert^2$; unit weights were used

Table 5

Fractional atomic coordinates (×10^4), equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms in complexes III and IV, and U_{iso} (Å^2 ×10^4) for the disordered atoms in complex III; (e.s.d.'s are given in parentheses)

Atom	x	y	z	B_{eq} or U_{iso}
Complex III				
Ru	2619(1)	205(1)	1272(1)	3.18(1)
Cl(1)	4034(2)	1134(1)	1084(1)	5.24(6)
Cl(2)	1453(2)	−803(1)	1562(2)	7.96(9)
P	1107(2)	1084(1)	1232(1)	2.88(4)
N	3995(5)	−537(3)	1252(3)	3.85(16)
C(12)	1186(7)	1759(4)	1803(3)	3.42(20)
C(13)	442(8)	1730(5)	2279(4)	4.10(29)
C(14)	526(9)	2222(6)	2723(4)	5.21(29)
C(15)	1349(10)	2738(5)	2721(5)	5.55(32)
C(16)	2127(10)	2734(6)	2277(6)	6.92(37)
C(17)	2059(9)	2271(6)	1817(5)	5.73(31)
C(18)	−441(6)	824(4)	1262(3)	3.13(18)
C(19)	−768(8)	125(5)	1169(4)	4.47(25)
C(20)	−1936(8)	−61(5)	1155(4)	4.71(27)
C(21)	−2779(8)	437(6)	1224(4)	5.10(28)
C(22)	−2475(8)	1121(6)	1312(4)	5.06(26)
C(23)	−1301(8)	1328(5)	1326(4)	4.33(23)
C(24)	1083(7)	1598(4)	551(4)	3.80(21)
C(25)	173(9)	1520(6)	155(4)	5.35(29)
C(26)	171(10)	1880(7)	−363(5)	7.14(39)
C(27)	1027(11)	2336(7)	−500(5)	7.05(38)
C(28)	1917(11)	2419(7)	−123(5)	8.45(43)
C(29)	1970(9)	2055(7)	387(5)	6.53(34)
C(1A)	4496(14)	−679(9)	680(7)	488(38)
C(2A)	5302(16)	−1217(10)	604(8)	601(47)
C(3A)	5697(15)	−1552(10)	1063(8)	470(40)
C(4A)	5376(17)	−1396(10)	1615(9)	561(48)
C(5A)	4505(16)	−817(10)	1664(8)	480(44)
C(6A)	4055(15)	−529(9)	2242(7)	556(42)
C(7A)	3708(16)	202(10)	2149(7)	526(40)
C(8A)	2623(16)	593(8)	2279(6)	411(35)
C(9A)	4128(14)	−153(9)	198(7)	573(41)
C(10A)	2970(13)	200(9)	314(7)	445(36)
C(11A)	2043(14)	−304(8)	490(7)	450(37)
C(1B)	4054(14)	−1041(8)	874(7)	482(37)
C(2B)	4969(18)	−1527(11)	873(8)	661(50)
C(3B)	5711(19)	−1513(11)	1355(10)	605(55)
C(4B)	5533(16)	−1056(10)	1798(8)	569(46)
C(5B)	4630(15)	−546(10)	1757(7)	452(43)
C(6B)	4461(18)	36(10)	2174(8)	673(51)
C(7B)	3175(22)	502(12)	2148(10)	730(60)
C(8B)	2269(24)	184(16)	2255(12)	1103(87)
C(9B)	3151(16)	−969(10)	412(8)	680(49)
C(10B)	2848(16)	−166(11)	348(8)	654(49)
C(11B)	1793(16)	27(11)	330(8)	654(51)

Table 5 (continued)

Atom	x	y	z	B_{eq} or U_{iso}
Complex IV				
Pd	0	0	0	2.13(1)
Cl	2843(1)	361(1)	1058(1)	3.24(2)
N	1453(3)	2533(3)	−127(2)	2.39(6)
C(1)	1536(3)	4122(3)	955(3)	2.75(8)
C(2)	2358(4)	5795(4)	798(3)	3.35(10)
C(3)	3116(4)	5837(4)	−475(4)	3.66(11)
C(4)	3046(4)	4221(4)	−1557(3)	3.38(10)
C(5)	2216(3)	2564(4)	−1380(3)	2.74(8)
C(6)	2114(5)	751(4)	−2519(3)	3.50(10)
C(7)	3023(6)	861(5)	−3844(4)	4.65(13)
C(8)	2184(8)	−205(7)	−5284(4)	6.21(22)
C(9)	759(4)	4076(4)	2380(3)	3.27(10)
C(10)	2176(5)	4373(5)	3609(3)	4.10(12)
C(11)	2834(6)	5774(6)	5020(4)	5.49(17)

in the first stages of the refinement, and subsequently weights were applied according to the scheme $w = k[\sigma^2(F_o + gF_o^2]^{-1}$ and the final k and g values as well as the final R are given in Table 4. Final ΔF maps showed no unusual features and the minimum and maximum heights were −1.19 and 0.88 e Å^{-3} for III, and −0.55 and 0.65 e Å^{-3} for IV.

Final atomic coordinates with equivalent isotropic thermal parameters [9] for the non-hydrogen atoms or isotropic U for the disordered C atoms in III are given in Table 5. Lists of atomic coordinates and isotropic thermal parameters for the hydrogen atoms, anisotropic thermal parameters for the non-hydrogen atoms, observed and calculated structure factors for both compounds can be obtained from the authors.

All calculations were performed on the GOULD-SEL 32/77 computer of the "Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma" and on the CRAY X-MP/12 computer of the "Centro di Calcolo Eletronico Interuniversitario dell'Italia Nord-Orientale (Cineca, Casalecchio, Bologna)", with financial support from the University of Parma. The programs PARST [10] and ORTEP [11] were also used.

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