Preparation and Co-ordination Properties of *trans*-Chloro-[1-(*p*-methoxyphenylimino)-2-(methylimino)propyl]bis(triphenylphosphine)-platinum. Crystal and Molecular Structure of the Ionic Compound $[PtCl\{C(=NR)CMe=NMe[Rh(CO)_2]\}(PPh_3)_2][RhCl_2(CO)_2]$ (R = C_6H_4OMe-*p*) †

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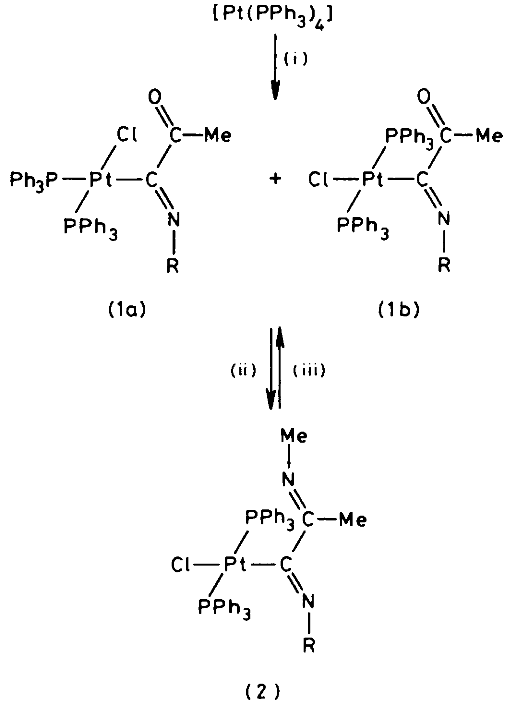
The 1,2-bis(imino)propyl complex *trans*-$[PtCl\{C(=NR)CMe=NR'\}(PPh_3)_2]$ (2) (R = C_6H_4OMe-*p*, R' = Me) can be prepared by the condensation reaction of monomethylamine with the carbonyl group of $[PtCl\{C(=NR)CMe=O\}(PPh_3)_2]$ (1). Complex (2) reacts with MCl_2 and $K[PtCl_3(CH_2=CH_2)]$ to give the adducts $[PtCl\{C(=NR)CMe=NMe(MCl_2)\}(PPh_3)_2][ClO_4]$ (3) (M = Cu, Zn, or Pt), and with chloro-bridged dimers $[\{M'ClL_2\}_2]$ in the presence of $NaClO_4$ (molar ratio Pt:M' = 1:1) to give the cationic complexes $[PtCl\{C(=NR)CMe=NMe(M'L_2)\}(PPh_3)_2][ClO_4]$ (4) [$M'L_2$ = Pd(η^3-2-MeC_3H_4) or Rh(cod) (cod = η^4-cyclo-octa-1,5-diene)]. In the binuclear complexes (3) and (4) the 1,2-bis(imino)-propyl group of (2) is $\sigma:\sigma'$-*N,N'*-chelated to the metal centres M and M' respectively. The reaction of (2) with $[\{M'ClL_2\}_2]$ (molar ratio Pt:M' = 1:2) yields the $[PtCl\{C(=NR)CMe=NMe(M'L_2)\}(PPh_3)_2]$-$[M'Cl_2L_2]$ (5), which are characterized in solution by conductivity measurements and ^1H and ^{31}P n.m.r. spectroscopy. The ^1H n.m.r. data indicate an interaction between the cationic and the anionic species of (5) which involves breaking of one of the $M'-N_{imino}$ bonds in the binuclear cation, without exchange of PPh_3 and chloride ligands between the Pt and M' metal centres. When $M'L_2$ = $Rh(CO)_2$, the reaction affords the complex $[PtCl\{C(=NR)CMe=NMe[Rh(CO)_2]\}(PPh_3)_2][RhCl_2(CO)_2]$ (5c) as a red-brown microcrystalline product, which is partially associated in solution. The crystal and molecular structure of (5c) has been determined by *X*-ray diffraction analysis. Crystals are monoclinic, space group $P2_1/a$, with a = 19.521(3), b = 17.212(7), c = 15.910(3) Å, β = 104.11(2)°, and Z = 4. The structure has been determined by the heavy-atom method and refined to the conventional R of 0.055 for 3 892 counter reflections (up to 2θ = 43°, Mo-K_α radiation). The structure consists of discrete, well separated cationic binuclear species and distorted square-planar *cis*-$[RhCl_2(CO)_2]^-$ anions. In the cation the rhodium co-ordination plane forms a dihedral angle of 81° with the platinum co-ordination plane, with bond distances in the normal range (mean values: Rh–Cl 2.342, Pt–P 2.330, Rh–N 2.07, Rh–CO 1.81, Pt–Cl 2.375, Pt–C(sp^2) 1.97 Å). In the solid state there are no unusually short intermolecular contacts.

1,2-Bis(imino)alkylpalladium(II) derivatives with identical *N*-substituents are readily obtained by successive migratory insertion reactions of two isocyanide molecules into Pd–Me, Pd–Ph, or Pd–H σ bonds, which can be either present in the starting compound {*e.g.* in *trans*-$[PdI(Me)L_2]$ (L = tertiary phosphine) [1]} or be formed *in situ* at the initial stage of the reaction sequence {*e.g.* in the reaction of $[PdX_2(CNR)_2]$ (X = Cl or I, R = aryl) with $HgMe_2$ followed by addition of two equivalents PPh_3,[2] or in the oxidative addition of HCl to the system $[Pd(PPh_3)_4]$–$2CNC_6H_4OMe$-*p*}.[3] Two synthetic routes have been developed for the preparation of C-bonded 1,2-bis(imino)alkyl groups with different *N*-substituents: (*i*) reaction of $[PdCl_2(CNR)(CNR')]$ (R = aryl, R' = cyclo-C_6H_{11}) with $HgMe_2$ followed by addition of two equivalents of PPh_3;[4] (*ii*) the condensation reaction of NH_2Me with the carbonyl function of *trans*-$[PdCl\{C(=NC_6H_4OMe\text{-}p)CR'=O\}(PPh_3)_2]$ (R' = H or Me).[3,4]

In general, migratory insertion reactions of isocyanides into Pt–C or Pt–H σ bonds of platinum(II) complexes proceed at a comparatively lower rate and involve only one CNR molecule.[5,6] All our attempts to prepare 1,2-bis(imino)alkylplatinum(II) derivatives by the 'double' insertion method, successfully employed for the palladium(II) analogues, failed due to the reluctance of the initially formed platinum-1-iminoalkyl bond to undergo further insertion. However, the availability of a complex of the type $[PtCl\{C(=NR)CMe=O\}(PPh_3)_2]$ (R = C_6H_4OMe-*p*) [7] prompted us to study its condensation reaction with NH_2Me. As reported herein, the synthesis of *trans*-$[PtCl\{C(=NR)CMe=NMe\}(PPh_3)_2]$ gave us the opportunity of investigating some co-ordination properties of the 1-(*p*-methoxyphenylimino)-2-(methylimino)propyl group linked

† 2',2'-Dicarbonyl-1'-chloro-μ-[1-(*p*-methoxyphenylimino)-2-(methylimino)propyl-C^1(Pt),*N*(Rh),*N'*(Rh)]-1',1'-bis(triphenylphosphine)platinumrhodium(1+) dicarbonyldichlororhodate(1−).

Supplementary data available (No. SUP 23960, 26 pp.): structure factors, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.



Scheme 1. Reactions: (*i*) RN=C(Cl)–C(Me)=O (R = C_6H_4OMe-*p*); (*ii*) $MeNH_2$; (*iii*) H_3O^+, NEt_3

to platinum(II), in comparison with those of the same organic moiety in the palladium analogue, *trans*-[PdCl{C(=NR)CMe=NMe}$(PPh_3)_2$].[4,8]

Results and Discussion

The title platinum complex (2) can be prepared by the reaction sequence shown in Scheme 1. The oxidative addition (i) yields the α-ketoimidoyl derivative with a *cis*: *trans* isomer ratio (1a):(1b) of ⩾9:1. In the condensation reaction (ii), a *cis* → *trans* isomerization occurs since complex (2) is obtained only in the *trans* configuration. As for the corresponding palladium compounds,[3,9] complex (2) undergoes acidic hydrolysis at the imino group not directly bound to the metal centre. Subsequent deprotonation with NEt_3 regenerates the α-ketoimidoyl intermediate with a *cis*: *trans* isomer ratio (1a):(1b) of ≃ 4:6. The different isomer distribution in the final product appears to be kinetically controlled in the course of the different reactions (i) and (iii). The (1a) ⇄ (1b) interconversion is in fact extremely slow and is not catalyzed by the presence of free PPh_3 or chloride anions [the isomer ratio remains practically unchanged after several days at room temperature in CD_2Cl_2 solutions of the products of both reactions (i) and (iii)].

The two isomers (1a) and (1b) have quite distinct i.r. and ^{1}H and ^{31}P n.m.r. spectral features (Tables 1 and 2). In particular the ν(Pt–Cl) band in (1b) occurs at lower frequency (10 cm^{-1}) than ν(Pt–Cl) in (1a), indicating a somewhat larger *trans* influence of the α-ketoimidoyl group compared to PPh_3. The high *trans* influence of such an organic moiety is also reflected by the low ^1J(Pt–P) value (1 732 Hz) for the phosphine ligand *trans* to the Pt–$C_{imidoyl}$ bond in (1a).[10] In line with previous results,[2-4] a large *trans* influence is also exerted by the 1,2-bis(imino)propyl group of (2) [ν(Pt–Cl) = 283 cm^{-1}]. The i.r. spectra in CH_2Cl_2 and the ^{1}H and ^{31}P n.m.r. spectra of (1a), (1b), and (2) in CD_2Cl_2 indicate that in solution the α-ketoimidoyl and 1,2-bis(imino)propyl groups assume only one of their possible configurations resulting from *cis* or *trans* arrangement of the two conjugated double bonds and from different orientation (*syn* or *anti*) of imino-nitrogen substituents. The structure of the α-ketoimidoyl ligand with a planar O=C–C=N unit oriented perpendicularly to the metal co-ordination plane and with *anti* *N*-substituents has been previously proposed for related complexes,[7] and can be reasonably assigned to complexes (1a) and (1b). This would account for the equivalence of ^{31}P nuclei of the mutually *trans* PPh_3 ligands in (1b) and for the upfield shift of the α-ketoimidoyl proton resonances on going from (1b) to (1a), particularly large (*ca.* 0.8 p.p.m.) for the δ(C–Me) signal due to a decreased shielding of phenyl ring currents of the two PPh_3 ligands on passing from a *trans* to a *cis* geometry.[11]

Steric and electronic factors suggest that the 1,2-bis(imino)propyl group of (2) has a configuration (*trans* planar N=C–C=N unit with *anti* *N*,*N*-substituents) analogous to that of free,[12] σ-*N*-monodentate,[13] and σ:σ′-*N*,*N*′ bridging bidentate[14] α-di-imines, and to that of the corresponding group in *trans*-[PdCl{C(=NR)CMe=NR}$(PPh_3)_2$] (R = C_6H_4OMe-*p*).[1] Also in the case of complex (2), the ^{31}P n.m.r. spectrum is consistent with a *trans*-P–Pt–P arrangement and with a planar σ-bonded α-di-imino moiety lying perpendicular to the metal co-ordination plane.

To the best of our knowledge, this is the first example of a 1,2-bis(imino)alkyl-platinum(II) derivative. Its remarkable stability towards decomposition both in the solid and in solution shows that the failure to prepare complexes of this type by successive migratory insertion of two isocyanide molecules into the Pt–Me bond is essentially due to kinetic factors.

Some co-ordination reactions of (2) are reported in Scheme 2. The binuclear 1:1 adducts (3) are monomers in 1,2-dichloroethane, whereas the cationic complexes (4) behave as uni-univalent electrolytes in methanol. In these reactions, the ligating complex (2) retains its *trans*-Ph_3P–Pt–PPh_3 configuration. As shown by ^{1}H n.m.r. data, electronic spectra and *X*-ray structure analyses of (5c) (see below), the 1,2-bis(imino)propyl group is σ:σ′-*N*,*N*′-chelated to the metal centres M and M′ of compounds (3) and (4), respectively. This bonding mode affects the typical i.r. bands of (2), ν(C=N) and ν(Pt–Cl), in the same way as previously observed for the palladium analogue.[4,8b] In addition, chelation brings about a marked decrease (490—580 Hz) in ^1J(Pt–P) coupling constants. As proposed for *trans*-[PtBr(L′)L_2] (L = tertiary phosphine, L′ = 2-pyridyl) and the corresponding *N*-protonated and -methylated derivatives,[15] the latter effect may be essentially related to a decreased σ-donor/π-acceptor ratio of the C(sp^2)-bonded planar ligand, with a delocalized π-electron system, upon co-ordination. In line with this suggestion, a decrease in ^1J(Pt–P) is also observed when the *N*-methylimino group of (2) is replaced by the more electronegative ketonic oxygen of (1b) and when the η^4-cyclo-octa-1,5-diene (cod) ligand of (4b) is replaced by the more π-accepting carbonyl ligands of (4c).

A distorted pseudo-tetrahedral configuration around the copper centre can be assigned to the binuclear complex (3a) on the basis of the value of the magnetic moment in CH_2Cl_2 (1.82 B.M.) and the position of the typical *d*–*d* transitions in the electronic spectrum in the same solvent ($\tilde{\nu}_{max.}$ = 12 340 cm^{-1}; ε = 161 dm^3 mol^{-1} cm^{-1}).[4,16]

In (3c), the δ(N–Me) and δ(C–Me) signals are flanked by ^{195}Pt satellites, with ^3J(Pt–H) = 33.0 Hz for N–Me and ^4J(Pt–H) ⩽ 7 Hz for C–Me protons, which support the σ-*N*-co-ordination of the CMe=NMe group.

The σ:σ′-*N*,*N*′-chelation of the 1,2-bis(imino)propyl group in (3) and (4) is further confirmed by the occurrence of intense metal to ligand charge-transfer bands [*d*(M) or

Table 1. Analytical, physical, and characteristic i.r. data

Compound	Colour	M.p.[a] (θ_c/°C)	Analysis[b] (%) C	H	N	Cl	Λ[c]/ Ω^{-1} cm^2 mol^{-1}
(1a) + (1b)	Pale yellow	209[f]	58.9	4.3	1.4	3.8	
		217[g]	(59.3)	(4.35)	(1.50)	(3.80)	
(2)	Pale yellow	215	59.5	4.7	2.9	3.9	
			(59.8)	(4.60)	(2.95)	(3.75)	
(3a)	Red-brown	198	52.5	4.1	2.5	10.0	
			(52.35)	(4.00)	(2.60)	(9.85)	
(3b)	Yellow	>270	52.2	3.9	2.5	9.7	
			(52.25)	(4.00)	(2.60)	(9.85)	
(3c)	Orange-brown	219	46.7	3.6	2.2	8.9	
			(46.65)	(3.60)	(2.30)	(8.80)	
(4a)	Deep yellow	247	50.4	4.2	2.2	5.9	97.2
			(50.80)	(4.20)	(2.30)	(5.90)	
(4b)	Dark green	267	52.2	4.4	2.2	5.5	96.3
			(52.65)	(4.40)	(2.25)	(5.65)	
(4c)	Red	261	48.8	3.7	2.2	6.0	93.3
			(48.95)	(3.60)	(2.35)	(5.90)	
(5c)	Red-brown	161	46.0	3.3	2.0	7.9	60.0
			(45.95)	(3.25)	(2.10)	(8.00)	

Compound	M[b,d]	I.r.[e] (cm^{-1}) ν(C=N)	ν(Pt–Cl)	ν(M–Cl)	Other bands
(1a) + (1b)		1 570ms,[h] [1 568]	295ms[h]		1 680s,[h] [1 578] ν(C=O)
		1 550ms,[i] [1 548]	285m[i]		1 680s,[i] [1 578] ν(C=O)
(2)	905	1 628s, [1 630]	283ms		
	(944.3)	1 556s, [1 550]			
(3a)	1 070	1 584m	305s[j]	325m,	
	(1 078.7)			305s[j]	
(3b)	1 094	1 578mw	298ms	327ms,	
	(1 080.6)			315 (sh)	
(3c)	1 183	1 587m	303ms	336ms,	
	(1 210.3)			320 (sh)	
(4a)		1 575mw	299ms		
					1 090vs ν(Cl–O)
(4b)		1 588m	300ms		623s δ(Cl–O)
					1 085vs ν(Cl–O)
(4c)		1 580mw	300m		622s δ(Cl–O)
					2 086s, [2 090] ν(C≡O)
					2 024s, [2 032] ν(C≡O)
(5c)	950[k]	1 580mw	300ms[j]	328m,	2 091s,[l] [2 092] ν(C≡O)
	(1 333.1)			300ms[j]	2 031s,[l] [2 033] ν(C≡O)
					2 060s,[m] [2 071] ν(C≡O)
					1 979s,[m] [1 992] ν(C≡O)

[a] Uncorrected values; all compounds decompose on melting. [b] Calculated values are given in parentheses. [c] Molar conductivities of MeOH solutions (10^{-3} mol dm^{-3}); at 293 K. [d] Molecular weight determinations by osmometry in 1,2-dichloroethane. [e] In Nujol mulls; the values in square brackets refer to CH_2Cl_2 solutions. [f] Mixture of isomers (1a) : (1b) ≈ 9 : 1. [g] Mixture of isomers (1a) : (1b) ≈ 4 : 6. [h] *cis* Isomer (1a). [i] *trans* Isomer (1b). [j] Overlapping ν(Pt–Cl) and ν(M–Cl) bands [M = Cu for (3a) and Rh for (5c)]. [k] Experimental molecular weight for a 5 g dm^{-3} solution; a value of 930 was found for a 3.7 g dm^{-3} solution. [l] Bands of the binuclear cation. [m] Bands of the mononuclear anion.

$d(M') \longrightarrow \pi^*$(α-di-imine)] in their electronic spectra in CH_2Cl_2 solution (33 000—15 000 cm^{-1}, see Experimental section), which are characteristic for the five-membered metallocycle chromophore present in these and related complexes.[3,4,8a,8b]

In the syntheses of (3) and (4) (Scheme 2), the platinum(II) derivative (2) exhibits the same co-ordination properties as its palladium(II) analogue.[4,8b] In contrast is the formation of ionic compounds (5), which do not undergo subsequent exchange of the ancillary ligands PPh_3 and Cl^- between the cationic and anionic species, as in the case of the reactions of [PdCl{C(=NR)CMe=NMe}(PPh_3)$_2$] with [{RhCl(cod)}$_2$][8b] or [{PdCl(η^3-2-MeC$_3$H$_4$)}$_2$].[8b,8c] Such a different reactivity is mainly related to an increased metal–phosphorus bond strength in the order Pt–PPh_3 ≫ Pd–PPh_3 in derivatives of type (5). In the reactions of [PdCl{C(=NR)CMe=NR}L_2] (R = C_6H_4OMe-*p*) with [{PdCl(η^3-2-MeC$_3$H$_4$)}$_2$], the rate of ligand exchange was found to decrease in the order L = P(C_6H_4Cl-*p*)$_3$ > PPh_3 > P(C_6H_4Me-*p*)$_3$ > P(C_6H_4OMe-*p*)$_3$, *i.e.*, with increasing Pd–P bond strength, whereas no exchange occurred when L_2 was the chelating 1,2-bis(diphenylphosphino)ethane.[8b,8c] On the other hand, the lack of ancillary ligand migration in the formation of (5) cannot be ascribed to the presence of much more stable α-di-imino five-membered rings in these compounds, since, as will be discussed later, the cationic species of these compounds undergo dynamic processes in solution, in which a fast α-di-imino ring opening is involved.

The compounds (5a) and (5b) are characterized in solution by conductivity measurements and ^1H and ^{31}P n.m.r. spectroscopy, whereas (5c) can be isolated as a red-brown crystalline solid. The molar conductivity in methanolic solution (10^{-3} mol dm^{-3}) decreases from 81.2 for (5a), to 73.8 for (5b),

Table 2. Characteristic ^1H and $^{31}P-\{^1H\}$ n.m.r. data [a]

Compound	^1H (δ/p.p.m.) C_6H_4O–*Me*	N–Me [b]	C–Me [b]	Other signals	^{31}P (δ/p.p.m.)	Solvent
(1a)	3.96(s)		2.18(s)		18.91(td) 13.39(td) ^1J(Pt–P) = 1 732 ^1J(Pt–P) = 5 401 ^2J(P–P) = 17.7	CD_2Cl_2
(1b)	3.86(s)		1.37(s)		19.79(t) ^1J(Pt–P) = 3 180	CD_2Cl_2
(2)	3.89(s)	3.08(s)	1.08(s)		19.90(t) ^1J(Pt–P) = 3 343	CD_2Cl_2
(3b)	3.84(s)	2.68(s)	1.98(s)		15.70(t) ^1J(Pt–P) = 2 845	CD_2Cl_2
(3c)	3.86(s)	3.09(t) ^3J(Pt–H) = 33.0	1.82 [c]		15.69(t) ^1J(Pt–P) = 2 816	CD_2Cl_2
(4a)	3.86(s)	3.15(s)	2.43(s)	3.56(d,br), 2.74(d,br) } CH_2(*syn*) ^4J(H–H) = 2 2.90(s,br), 2.64(s,br) } CH_2(*anti*)	16.18(t) ^1J(Pt–P) = 2 852	$CDCl_3$
(4b)	3.83(s)	2.51(s)	2.38(s)	4.0(s,br), 3.3(s,br) } CH(olefinic) 2.5–1.5(m,br) CH_2	16.53(t) ^1J(Pt–P) = 2 853	$CDCl_3$
(4c)	3.87(s)	3.05(s)	2.56(s)		15.02(t) ^1J(Pt–P) = 2 764	CD_2Cl_2
(5a)	3.83(s)	3.24(s)	2.47(s)	~3.15(br) CH_2(*syn*) [d] 2.80(br) CH_2(*anti*) [d] 3.72(s) CH_2(*syn*) [e] 2.72(s) CH_2(*anti*) [e] 2.04(s) C–Me [d] 2.01(s) C–Me [e]	16.18(t) ^1J(Pt–P) = 2 856	$CDCl_3$
(5b)	3.80(s)	2.55(s)	2.42(s)	4.18(s,br) CH(olefinic) [f] 3.63(s,br) CH(olefinic) [d] 2.6—1.5(m,br) CH_2	16.60(t) ^1J(Pt–P) = 2 857	$CDCl_3$
(5c)	3.82(s)	3.02(s)	2.54(s)		15.04(t) ^1J(Pt–P) = 2 766	CD_2Cl_2

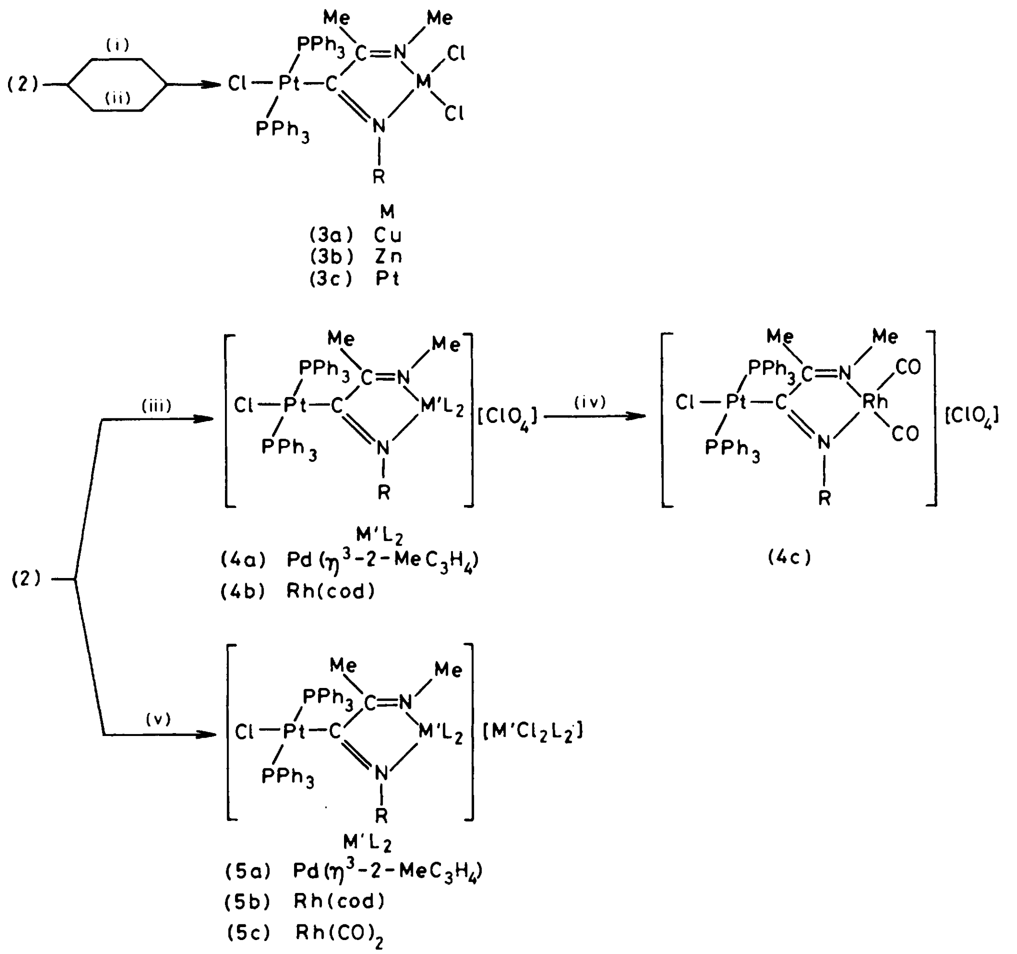
[a] ^1H Chemical shift from $SiMe_4$ at 30 °C; ^{31}P chemical shifts from external 85% H_3PO_4 (down-field shifts taken as positive); coupling constants in Hz; s = singlet, d = doublet, t = triplet, td = triplet of doublets, m = multiplet, br = broad; satisfactory integration values have been obtained. [b] Slightly broad singlets, sometimes with some fine structure due to small ^5J(H–H) coupling. [c] Poorly resolved triplet, with ^4J(Pt–H) ≤ 7 Hz. [d] Signals of the binuclear cationic species. [e] *syn*, *anti*, and 2-Me protons of the anion $[PdCl_2(\eta^3\text{-}2\text{-}MeC_3H_4)]^-$; in $[AsPh_4]$-$[PdCl_2(\eta^3\text{-}2\text{-}MeC_3H_4)]$ these protons resonate at 3.70, 2.69, and 1.99 p.p.m. respectively. [f] Olefinic protons of the anion $[RhCl_2(cod)]^-$; in $[AsPh_4][RhCl_2(cod)]$ these protons resonate at 4.15 p.p.m.

and 60.0 Ω^{-1} cm^2 mol^{-1} for (5c); in any case these values are significantly reduced relative to those of the corresponding perchlorate derivatives (4). Furthermore, the experimental molecular weight of (5c) in 1,2-dichloroethane is markedly higher than that expected for a completely dissociated ionic compound, and appears to increase with increasing concentration (see Table 1). These data indicate a fair degree of association between the cationic and anionic species of (5), the extent of which probably depends on the nature of the $M'L_2$ unit, as suggested by the observed trend in molar conductivity values. The cation–anion interaction is also apparent from the ^1H n.m.r. spectra of (5a) and (5b) in $CDCl_3$ at 30 °C (Table 2 and Figure 1). Figure 1(*a*) clearly shows that the allyl group is η^3-bonded to the palladium centre of the binuclear cationic complex (4a) and does not undergo any dynamic process at a significant rate under the given experimental conditions. Replacement of perchlorate by the $[PdCl_2(\eta^3\text{-}2\text{-}MeC_3H_4)]^-$ anion [Figure 1(*b*)] brings about only minor chemical shift changes in the typical signals of both the chelate 1,2-bis(imino)propyl moiety of (4a) and the allylic anion, whereas the $Pd(\eta^3\text{-}2\text{-}MeC_3H_4)$ unit of the cationic species is now turned into a dynamic system, in which a fast *syn–syn*, *anti–anti*, and a slow *syn–anti* proton exchange occur. The simultaneous presence of the latter process is demonstrated by spin-saturation transfer experiments: as can be seen from Figure 1(*c*), the signal of the *anti* protons of (5a) (2.80 p.p.m.) disappears upon irradiation of the broad resonance of the *syn* protons at *ca.* 3.15 p.p.m. A similar behaviour is shown by compounds (4b) and (5b). Due to the asymmetric nature of the 1,2-bis(imino)propyl ligand, the ^1H n.m.r. spectrum of (4b) exhibits the olefinic protons of the cod group as two separate signals at 4.0 and 3.3 p.p.m., which coalesce into a single absorption at 3.63 p.p.m. in the spectrum of (5b) (see Table 2).

As noted previously for similar ionic compounds derived from 1,2-bis(imino)alkyl-palladium(II) complexes,[8b] the cation–anion interaction in the systems (5a) or (5b) does not involve exchange of the $M'L_2$ fragment between the two ionic species at an appreciable rate on the n.m.r. time-scale. However, the occurrence of a rather slow exchange of this type is confirmed when a $CDCl_3$ solution of (4a) is treated with an equimolar amount of $[AsPh_4][RhCl_2(cod)]$. After filtration of the poorly soluble $[AsPh_4]ClO_4$ salt, the ^1H n.m.r. spectra of the reaction mixture, taken at successive intervals (*ca.* 3 h), indicate the slow establishment (*ca.* 24 h) of the equilibrium in Scheme 3.

Integration of the ^1H and ^{31}P n.m.r. spectra of the equilibrium mixture gives an (A) : (C) ratio of *ca.* 1 : 1, thus indicating comparable stability for both cationic complexes.

By taking into account the equilibria in the systems RN=CR^1CR^2=NR/[{$M'ClL_2$}$_2$] [molar ratio 1 : 1; R = alkyl or aryl; R^1 = R^2 = H or Me; R^1 = H, R^2 = Me; $M'L_2$ = Pd-



Scheme 2. Reactions: (*i*) MCl_2 (M = Cu or Zn); (*ii*) $K[PtCl_3(CH_2{=}CH_2)]$; (*iii*) $\frac{1}{2}[\{M'ClL_2\}_2]$, $NaClO_4$ (excess); (*iv*) (4b), CO; (*v*) $[\{M'ClL_2\}_2]$

(η^3-2-MeC_3H_4) or $Rh(CO)_2$] [17,18] and also the mechanism of ancillary ligand migration in the reactions of 1,2-bis(imino)-alkylpalladium(II) complexes with [{PdCl(η^3-2-MeC_3H_4)}$_2$],[8b,8c] the solution behaviour of compounds (5) and the mechanism of Scheme 3 can be interpreted on the basis of the equilibria reported in Scheme 4. By fast cation–anion association, a non-conducting intermediate (E) is formed, probably through a weak chloride bridge,[8c] which can further rearrange with different rates to other short-lived species, such as (F), (G), and (H). The (E) $\rightleftharpoons$ (F) equilibrium, which involves opening of the five-membered α-di-imino ring, is fast on the n.m.r. time-scale at 30 °C and accounts for the dynamic processes observed in (5a) and (5b). A σ-allyl species of type (G) is likely to be formed, at lower rate, in $CDCl_3$ solutions of (5a), as can be inferred from the slow *syn–anti* allylic proton exchange observed in this system. [Such a process occurs at much higher rate in related palladium(II) derivatives under comparable experimental conditions.[8b]] The formation at even lower rate of a labile transient (H) with a σ : σ′-*N*,*N*′-bridging α-di-imino moiety would account for the rather slow exchange of the $M'L_2$ grouping between the ionic reactants (A) and (B) of Scheme 3.

Crystal and Molecular Structure of (5c).—In order to establish definitely the formulation of complexes (5) in the solid state, also in relation to the versatile co-ordinating ability of α-di-imino ligands, we have carried out a single-crystal *X*-ray diffraction analysis of (5c). The crystal structure consists of discrete well separated cationic binuclear species and *cis*-dichlorodicarbonylrhodate(I) anions. Selected bond lengths and angles are listed in Table 3. The distances are of the magnitude expected for the packing of discrete anionic and cationic components and the shortest separations between the metal centres are presented in Table 4. The molecular structure with atom labelling is shown in Figure 2.

Co-ordination around the platinum atom is essentially square planar with mutually *trans* triphenylphosphine ligands [P(1)–Pt–P(2) 172.3°, with slight lengthening of the Pt–P bonds [19]]. The least-squares plane (Table 4) through P(1), P(2), Cl(1), and C(1) shows that the P atoms are below, while Cl(1) and C(1) are above the mean equatorial plane and the deviations are rather large (±0.07 Å). The C(1) atom exhibits sp^2 hybridization (the sum of the angles about it is 359.9°) and the Pt–Cl(1) distance (2.375 Å) is within the range for a Cl atom *trans* to a sp^2 C.[20] The Pt–C(1) distance (1.97 Å) is similar to those observed for Pt–C(sp^2) bonds in square-planar Pt^{II} systems, where Cl lies opposite carbene ligands.[21] If a standard value of 2.08 Å is assumed for a Pt^{II}–C(sp^3) σ bond,[22] a value of 2.04 Å is predicted for Pt–C(sp^2), which is significantly greater than most platinum–carbene distances. The strictly planar N(1)–C(1)–C(11)–N(2) moiety forms a dihedral angle of 81.3° with the platinum co-ordination plane; the C(1)–N(1) distance (1.32 Å) is indicative of a high degree of double-bond character and is similar to the C–N distances found in a variety of aminocarbene complexes.[23] Both rhodium atoms have essentially square-planar co-ordination geometries. Whereas Rh(1)

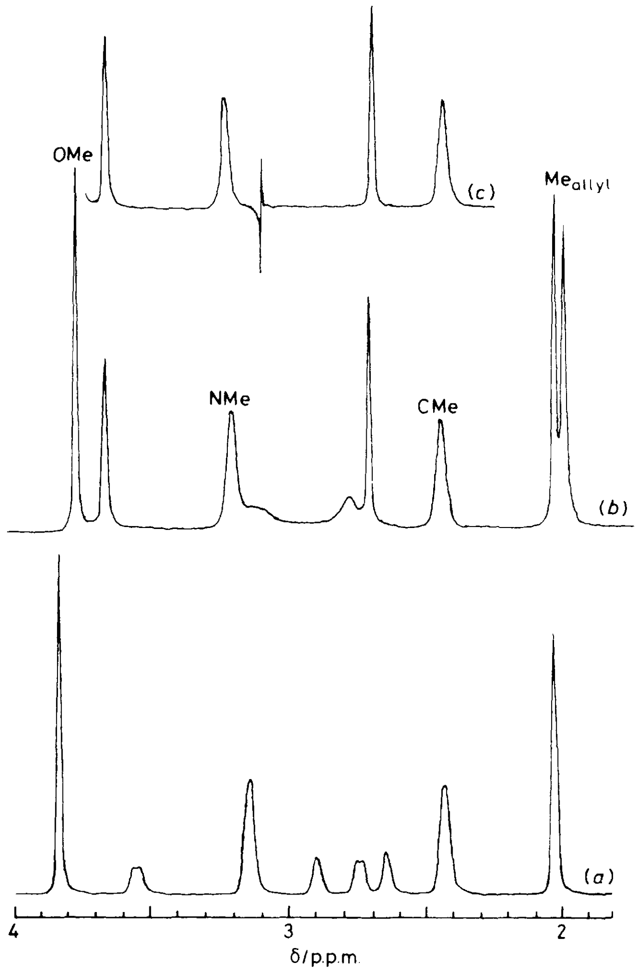
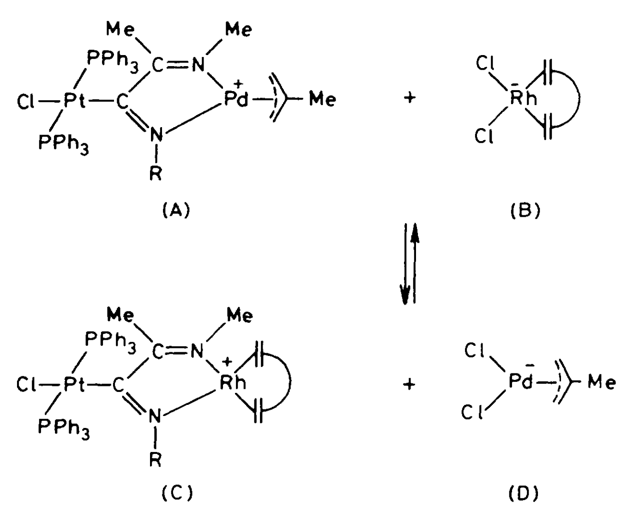
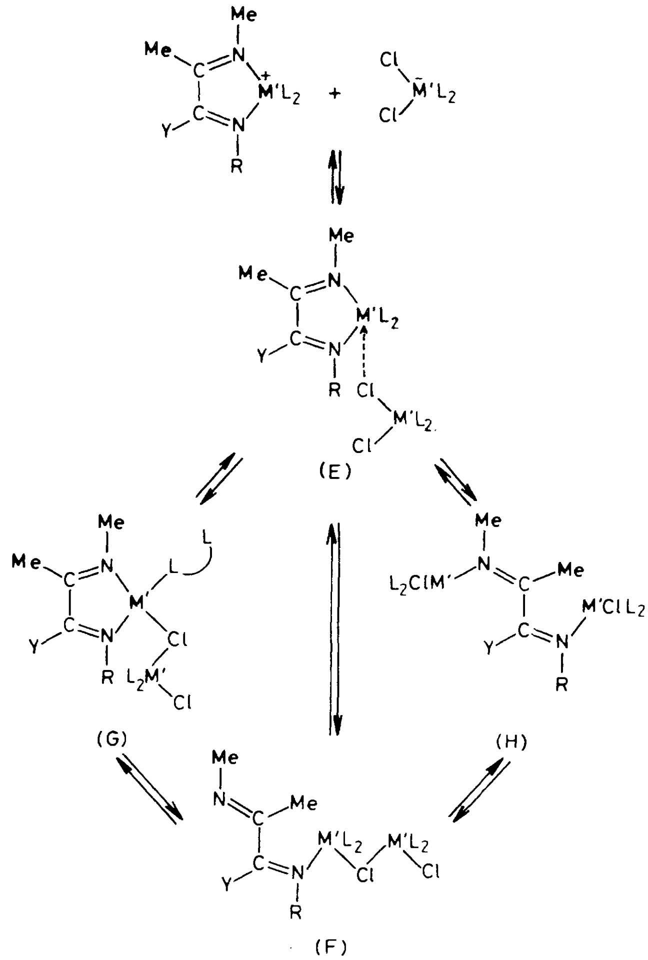


Figure 1. Proton n.m.r. spectra in $CDCl_3$ at 30 °C: (*a*) complex (4a); (*b*) complex (5a); (*c*) complex (5a) upon irradiation of the resonance at 3.15 p.p.m.



Scheme 3.

lies nearly exactly in the plane of its ligands, a slight distortion from planarity is observed for the anionic Rh(2) complex (Table 4). The four independent Rh–CO distances are in the



Scheme 4. Proposed solution equilibria for compounds of type (5): Y = *trans*-$PtCl(PPh_3)_2$, L–L = σ-2-MeC_3H_4

expected range,[24] the average length being 1.81(2) Å. The values of the Rh(1)–N(1) and Rh(1)–N(2) bonds are 2.09(1) and 2.06(1) Å, respectively, slightly shorter than those in the cationic species of the related compound $[Rh(CO)_2(dmpie)]$-$[RhCl_2(CO)_2]$ [dmpie = 1,2-bis(2,4-dimethylpentyl-3-imino)-ethane].[25] Furthermore, in the cation (5c) the two Rh–C–O units exhibit Rh–C and C–O bond lengths shorter and longer, respectively, than the corresponding distances in $[Rh(CO)_2$-$(dmpie)]^+$ suggesting an increased Rh–C π-bonding character in the binuclear cationic complex. This could be related to the better electron-donating capacity of the 2-metallated α-di-imine (2). However, steric factors, arising from bulkiness of *N*-substituents, may also be important; in fact, whereas the N(1)–Rh(1)–N(2) bite angle is almost the same in both compounds (*ca.* 78°), the OC–Rh(1)–CO angle is significantly reduced on going from (5c) (88.6°) to $[Rh(CO)_2(dmpie)]^+$ (83.2°).

The structural analysis of (5c) definitely confirms the σ : σ'-*N*,*N*'-chelating mode of the 1,2-bis(imino)propyl group of (2). The *cis* arrangement of this organic moiety brings the C(3) and C(12) atoms rather close (3.23 and 3.28 Å, respectively) to the platinum atom. Such distances are somewhat shorter than the sum of the van der Waals radii and may be of structural and chemical significance. As a matter of fact, in the ^1H n.m.r. spectra the δ(C–Me) signal of (2) undergoes a considerable downfield shift upon chelation (see Table 2).

The ionic structure of (5c) is in accordance with the solid-

Table 3. Bond lengths (Å) and angles (°) with e.s.d.s in parentheses

Pt–Cl(1)	2.375(3)	Rh(1)–C(10)	1.82(2)	C(4)–C(5)	1.36(2)	C(14)–O(3)	1.00(3)
Pt–P(1)	2.329(4)	C(10)–O(2)	1.15(2)	C(5)–O(5)	1.47(2)	Rh(2)–C(15)	1.81(2)
Pt–P(2)	2.332(4)	N(2)–C(13)	1.52(2)	O(5)–C(8)	1.39(3)	C(15)–O(4)	1.14(2)
Pt–C(1)	1.97(1)	N(2)–C(11)	1.28(2)	C(5)–C(6)	1.38(2)	P(1)–C(16)	1.83(1)
C(1)–N(1)	1.32(2)	C(11)–C(12)	1.48(2)	C(6)–C(7)	1.45(2)	P(1)–C(22)	1.83(1)
N(1)–Rh(1)	2.09(1)	C(1)–C(11)	1.55(2)	C(7)–C(2)	1.37(2)	P(1)–C(28)	1.79(1)
Rh(1)–N(2)	2.06(1)	N(1)–C(2)	1.45(2)	Rh(2)–Cl(2)	2.348(5)	P(2)–C(34)	1.82(1)
Rh(1)–C(9)	1.78(2)	C(2)–C(3)	1.41(2)	Rh(2)–Cl(3)	2.336(5)	P(2)–C(40)	1.83(1)
C(9)–O(1)	1.18(2)	C(3)–C(4)	1.45(2)	Rh(2)–C(14)	1.84(2)	P(2)–C(46)	1.82(1)
C–C (phenyl) mean 1.41[3] *							

Cl(1)–Pt–P(1)	87.6(1)	Rh(2)–C(15)–O(4)	175.8(1.9)	Rh(1)–N(2)–C(13)	123.8(9)
P(1)–Pt–C(1)	93.5(4)	Pt–P(1)–C(16)	111.9(5)	N(2)–C(11)–C(1)	114.7(1.5)
C(1)–Pt–P(2)	91.5(4)	Pt–P(1)–C(22)	117.6(4)	C(13)–N(2)–C(11)	118.4(1.4)
P(2)–Pt–Cl(1)	87.6(1)	Pt–P(1)–C(28)	110.6(4)	N(2)–C(11)–C(12)	128.2(1.6)
P(1)–Pt–P(2)	172.3(1)	Pt–P(2)–C(34)	111.7(3)	C(12)–C(11)–C(1)	117.1(1.4)
Cl(1)–Pt–C(1)	178.1(4)	Pt–P(2)–C(40)	114.4(5)	C(11)–C(1)–N(1)	112.9(1.2)
N(1)–Rh(1)–C(9)	97.0(7)	Pt–P(2)–C(46)	115.6(5)	Rh(1)–N(1)–C(2)	123.0(1.0)
C(9)–Rh(1)–C(10)	88.6(8)	C(16)–P(1)–C(22)	103.5(6)	C(1)–N(1)–C(2)	120.9(1.2)
C(10)–Rh(1)–N(2)	96.6(7)	C(16)–P(1)–C(28)	106.6(6)	N(1)–C(2)–C(3)	120.5(1.5)
N(2)–Rh(1)–N(1)	77.7(5)	C(22)–P(1)–C(28)	105.8(6)	N(1)–C(2)–C(7)	116.6(1.4)
N(1)–Rh(1)–C(10)	173.9(7)	C(34)–P(2)–C(40)	104.8(6)	C(7)–C(2)–C(3)	122.8(1.5)
C(9)–Rh(1)–N(2)	174.3(7)	C(34)–P(2)–C(46)	106.0(6)	C(2)–C(3)–C(4)	116.2(1.5)
Cl(2)–Rh(2)–C(15)	89.5(6)	C(40)–P(2)–C(46)	103.2(7)	C(3)–C(4)–C(5)	118.6(1.7)
C(15)–Rh(2)–C(14)	92.5(9)	Pt–C(1)–N(1)	125.5(1.0)	C(4)–C(5)–C(6)	127.2(1.9)
C(14)–Rh(2)–Cl(3)	87.7(7)	Pt–C(1)–C(11)	121.5(1.0)	C(5)–C(6)–C(7)	113.7(1.7)
Cl(3)–Rh(2)–Cl(2)	90.4(2)	Rh(1)–C(9)–O(1)	176.6(1.8)	C(6)–C(7)–C(2)	121.1(1.5)
C(15)–Rh(2)–Cl(3)	178.3(6)	Rh(1)–C(10)–O(2)	175.8(1.8)	C(4)–C(5)–O(5)	109.7(1.7)
C(14)–Rh(2)–Cl(2)	175.3(7)	Rh(1)–N(1)–C(1)	116.1(9)	C(6)–C(5)–O(5)	123.1(1.8)
Rh(2)–C(14)–O(3)	177.0(2.3)	Rh(1)–N(2)–C(11)	117.8(1.2)	C(5)–O(5)–C(8)	113.2(1.7)
C–C–C (phenyl) mean 120.0[2.1] *					

* Standard deviation calculated as $[\Sigma(\bar{x})^2/(n-1)]^{\frac{1}{2}}$.

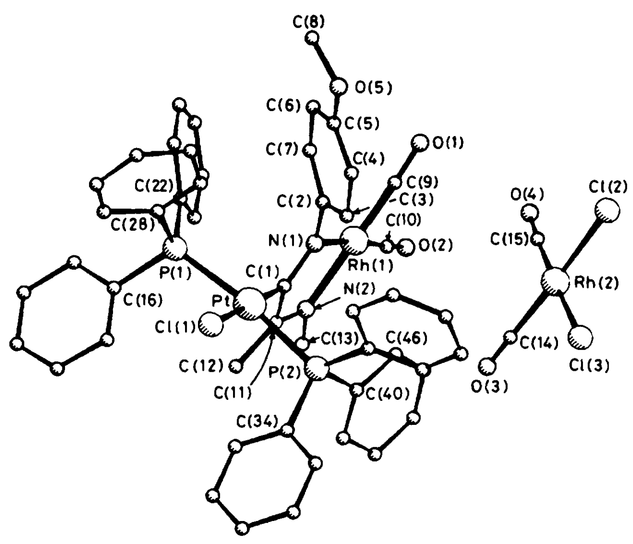


Figure 2. Numbering scheme and view of the molecular structure of (5c)

state i.r. spectrum, which shows two ν(C⩵O) bands of the cation at 2 091 and 2 031 cm^{-1}, and two ν(C⩵O) bands of the anion at 2 060 and 1 979 cm^{-1}, comparing well with those of the cationic binuclear complex (4c) (2 086 and 2 024 cm^{-1}) and those of the anionic derivative $[NPr^n_4][RhCl_2(CO)_2]$ (2 069 and 1 996 cm^{-1}).[26] In the far-i.r., two Rh–Cl stretching vibrations are observed (see Table 1), in agreement with the *cis* configuration of the anion. The same ionic structure is retained in CH_2Cl_2 solution, as can be inferred from the fact that the ν(C⩵O) pattern of (5c) practically results from the superimposition of the ν(C⩵O) bands of (4c) and $[NPr^n_4]$-$[RhCl_2(CO)_2]$ in the same solvent. Although the conductivity and molecular weight measurements of (5c) indicate a fair degree of association, the i.r. spectrum in CH_2Cl_2 (at con-

Table 4. Some geometrical features

(*a*) Shortest distances (Å) between metal centres

	Pt	Rh(1)	Rh(2)
Pt	9.78 [a]		
Rh(1)	4.84	10.81 [b]	
Rh(2)	6.95 [c]	5.20	9.90 [a]

(*b*) Some intramolecular contacts (Å) and torsion angles (°)

Pt ··· C(3)	3.23	O(3) ··· C(42)	3.67
Pt ··· C(12)	3.28	O(2) ··· O(4)	3.29
Rh(1) ··· C(1)	2.92	Pt–C(1)–N(1)–Rh(1)	7.6
Rh(1) ··· C(11)	2.89	N(1)–C(1)–C(11)–N(2)	9.4
O(3) ··· C(43)	3.52		

(*c*) Least-squares planes [d]

Plane	Atoms defining plane	Deviations (Å) of atoms from the plane
1	P(1), Cl(1), P(2), C(1)	P(1) −0.08, Cl(1) 0.07, P(2) −0.07, C(1) 0.08, Pt 0.04
2	N(1), N(2), C(10), C(9)	N(1), N(2), C(10), C(9) 0.00; Rh(1) −0.04, O(1) −0.04, O(2) −0.05, C(13) −0.06; C(12) −0.05
3	Cl(2), Cl(3), C(14), C(15)	Cl(2) −0.05, Cl(3) 0.05, C(14) −0.06, C(15) 0.06, Rh(2) 0.02, O(3) −0.07, O(4) 0.16
4	N(1), C(1), C(11), N(2)	N(1) −0.02, C(1) 0.04, C(11) −0.04, N(2) 0.03, Rh(1) 0.08, C(12) −0.19, C(13) 0.01

Plane	*P*	*Q*	*R*	*S*
1	4.600	9.035	11.706	17.676
2	9.892	12.603	−8.987	7.080
3	8.258	13.462	5.419	13.668
4	8.766	13.365	−8.562	7.708

(*d*) Dihedral angles (°) between planes

1—2	82.4	3—4	53.5	7—8	72.1
1—3	27.8	1—5	60.4	9—10	85.7
1—4	81.3	2—5	64.3	9—11	77.0
2—3	54.6	6—7	80.0	10—11	62.0
2—4	4.2	6—8	87.4		

Plane	Atoms	Plane	Atoms
5	C(2)—(7)	9	C(34)—(39)
6	C(16)—(21)	10	C(40)—(45)
7	C(22)—(27)	11	C(46)—(51)
8	C(28)—(33)		

[a] At $\frac{1}{2}+x, \frac{3}{2}-y, z$. [b] At $1-x, 2-y, 2-z$. [c] At $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$. [d] Equations of planes in direct space given by $Px + Qy + Pz = S$.

centrations comparable with those used in the molecular weight determination) shows no ν(C⩶O) bands attributable to associated species of type (E) in Scheme 4.

This could be interpreted in terms of a weak cation–anion interaction in (E), which would not affect appreciably the structural and electronic configuration of the free ions. Consistently, the ^{1}H and ^{31}P n.m.r. spectra of (5a) and (5b) show no substantial differences from those of the systems (4a)/[$AsPh_4$][$PdCl_2(\eta^3$-2-$MeC_3H_4)$] and (4b)/[$AsPh_4$][$RhCl_2$(cod)], respectively, apart from the dynamic processes involving the M′L_2 unit in the cationic species of (5).

In the light of the present *X*-ray results for (5c), an analogous ionic structure can be also assigned to complexes obtained from the reactions of *trans*-[PdCl{C(=NR)CMe=NR^1}($PPh_3)_2$] (R = R^1 = C_6H_4OMe-*p*; R = C_6H_4OMe-*p*, R^1 = Me) with [{RhCl(CO)$_2$}$_2$] (molar ratio 1 : 1), which were originally formulated as trinuclear derivatives with a bridging 1,2-bis(imino)propyl group on the basis of their solution behaviour.[8a]

Experimental

Physical Measurements.—Infrared spectra were recorded with a Perkin-Elmer 597 instrument, using Nujol mulls and CsI plates in the range 4 000—250 cm^{-1}. The molecular weights were determined in 1,2-dichloroethane at 37 °C with a Knauer osmometer.

Conductivity measurements were carried out with a Philips PR 9500 bridge at 20 °C. The ^{1}H and ^{31}P-{^{1}H} n.m.r. spectra were recorded with a Varian FT 80A spectrometer operating at 79.542 and 32.203 MHz, respectively, at 30 °C. Electronic spectra in CH_2Cl_2 solution were recorded with a Bausch-Lomb Spectronic 210 UV and with a Cary model 14 Recording spectrophotometer in the ranges 40 000—15 000 and 17 000—5 000 cm^{-1}, respectively, using quartz cells of 1-cm path length. Magnetic moments in CH_2Cl_2 solution were measured by published methods.[27]

Preparation of the α-Ketoimidoyl Chloride, *p*-$MeOC_6H_4N$=CCl–CMe=O.—This compound was prepared by α-addition of acetyl chloride to CNC_6H_4OMe-*p*.[28] The isocyanide (2.23 g, 16.7 mmol) dissolved in *ca.* 50 cm^3 of anhydrous benzene was treated with freshly distilled acetyl chloride (2.62 g, 33.4 mmol) under dinitrogen, and the mixture was heated at 80 °C. The course of the reaction was monitored by i.r. spectroscopy from the disappearance of the isocyanide ν(C⩶N) band at 2 120 cm^{-1} and the concomitant appearance of ν(C=N) and ν(C=O) of the product at 1 638 and 1 725 cm^{-1}, respectively. The α-addition was complete in 12 h. The solution was concentrated to a small volume (*ca.* 10 cm^3) at reduced pressure and then diluted with anhydrous benzene (50 cm^3). These operations were repeated three times, until the i.r. spectrum showed no trace of acetyl chloride. The volume was eventually adjusted to 100 cm^3 with anhydrous benzene and this solution was used in the preparation of complex (1) (for a 100% yield, the concentration of the α-ketoimidoyl chloride would be 0.167 mol dm^{-3}).

Preparation of the α-Ketoimidoyl Derivative (1).—A suspension of [$Pt(PPh_3)_4$] (2.5 g, 2 mmol) in anhydrous benzene (*ca.* 80 cm^3) was treated with an excess of the α-ketoimidoyl chloride (18 cm^3 of the above solution) under dinitrogen. The reaction mixture was stirred at 60 °C and the course of the oxidative addition was followed by i.r. spectra [decreasing ν(C=O) band of α-ketoimidoyl chloride at 1 725 cm^{-1} and increasing ν(C=O) of (1) at 1 680 cm^{-1}]. The reaction was complete in *ca.* 2 h. After treatment with charcoal and filtration, the clear solution was concentrated to a small volume at reduced pressure and the product was precipitated by addition of diethyl ether. The crude compound was dissolved in C_6H_6–CH_2Cl_2 (4 : 1 v/v). After treatment with charcoal and

Table 5. Final fractional positional parameters ($\times 10^4$) with e.s.d.s in parentheses

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Pt	4 555(0)	7 676(0)	7 424(0)	Rh(2)	1 864(1)	12 026(1)	6 966(1)
Cl(1)	5 671(2)	7 120(2)	7 438(3)	Cl(2)	2 336(4)	12 765(4)	8 213(4)
P(1)	4 349(2)	6 607(2)	8 227(3)	Cl(3)	2 806(3)	12 386(4)	6 383(4)
P(2)	4 800(2)	8 624(2)	6 492(3)	C(14)	1 557(14)	11 393(16)	6 015(19)
Rh(1)	2 541(1)	9 156(1)	7 802(1)	O(3)	1 365(10)	11 057(11)	5 498(13)
C(1)	3 646(8)	8 168(8)	7 431(11)	C(15)	1 121(13)	11 772(14)	7 404(16)
C(2)	4 061(10)	8 721(11)	8 855(14)	O(4)	640(11)	11 658(12)	7 669(13)
C(3)	4 714(10)	9 055(11)	8 835(13)	C(26)	2 447(10)	6 993(10)	8 803(13)
C(4)	5 228(12)	9 121(13)	9 662(16)	C(27)	2 971(9)	6 882(10)	8 295(12)
C(5)	5 049(13)	8 864(13)	10 385(16)	C(28)	5 127(8)	6 364(9)	9 038(11)
C(6)	4 403(12)	8 571(13)	10 442(15)	C(29)	5 454(9)	6 969(10)	9 565(12)
C(7)	3 884(10)	8 530(11)	9 614(13)	C(30)	6 080(11)	6 825(12)	10 263(14)
C(8)	5 555(15)	8 562(17)	11 867(21)	C(31)	6 388(11)	6 064(13)	10 288(15)
C(9)	2 706(12)	9 737(14)	8 756(17)	C(32)	6 067(11)	5 491(12)	9 738(14)
C(10)	1 678(13)	9 618(13)	7 455(16)	C(33)	5 426(10)	5 600(11)	9 121(13)
C(11)	2 985(12)	8 053(13)	6 675(15)	C(34)	5 146(6)	8 203(7)	5 632(6)
O(1)	2 801(10)	10 093(11)	9 407(13)	C(35)	4 901(6)	7 475(7)	5 307(6)
O(2)	1 121(9)	9 891(9)	7 279(11)	C(36)	5 125(6)	7 158(7)	4 612(6)
O(5)	5 656(10)	8 934(10)	11 134(13)	C(37)	5 593(6)	7 569(7)	4 242(6)
C(12)	3 038(8)	7 475(9)	6 003(11)	C(38)	5 838(6)	8 297(7)	4 567(6)
C(13)	1 796(10)	8 428(11)	5 980(14)	C(39)	5 614(6)	8 614(7)	5 262(6)
N(1)	3 522(8)	8 602(9)	8 060(11)	C(40)	4 031(9)	9 193(10)	5 930(12)
N(2)	2 457(7)	8 477(8)	6 715(9)	C(41)	3 759(10)	9 754(10)	6 407(13)
C(16)	4 109(9)	5 742(10)	7 550(12)	C(42)	3 125(11)	10 158(11)	5 972(14)
C(17)	4 363(10)	5 646(11)	6 812(14)	C(43)	2 812(11)	10 004(12)	5 126(14)
C(18)	4 181(11)	4 934(12)	6 314(15)	C(44)	3 070(12)	9 460(13)	4 640(15)
C(19)	3 804(12)	4 366(13)	6 579(16)	C(45)	3 708(12)	9 008(12)	5 085(16)
C(20)	3 551(10)	4 463(11)	7 311(14)	C(46)	5 433(9)	9 365(10)	6 998(12)
C(21)	3 692(12)	5 172(13)	7 818(15)	C(47)	5 412(10)	10 132(11)	6 662(13)
C(22)	3 642(8)	6 686(9)	8 794(11)	C(48)	5 931(12)	10 687(13)	7 066(16)
C(23)	3 779(9)	6 591(10)	9 692(12)	C(49)	6 445(12)	10 467(14)	7 800(16)
C(24)	3 228(11)	6 665(11)	10 134(13)	C(50)	6 488(13)	9 719(15)	8 143(17)
C(25)	2 592(13)	6 882(14)	9 670(17)	C(51)	5 970(12)	9 151(13)	7 738(15)

filtration, the more volatile CH_2Cl_2 solvent was slowly evaporated at slightly reduced pressure until some precipitate appeared, and precipitation was completed by dropwise addition of diethyl ether (yield 1.42 g, 76%).

Preparation of the 1,2-*Bis(imino)propyl Complex* (2).—Complex (2) was prepared by condensation of NH_2Me with (1), according to the procedure described for the preparation of the 1,2-bis(imino)propyl-palladium(II) analogue.[4] In this case, the condensation rate was much slower and, even after prolonged reaction times (24—72 h), the final product contained a small amount of starting material. The compound was purified by chromatography on a 20-cm Florisil column (60—100 mesh), using CH_2Cl_2–Et_2O (5 : 1 v/v) as eluant. Two yellow fractions were separated, the first consisting of unreacted complex (1) and the second one of product (2). Starting from 1.86 g of (1), a final quantity of 1.10 g of pure complex (2) was obtained. This compound underwent acidic (HCl) hydrolysis in the same way as reported previously for related 1,2-bis(imino)alkyl-palladium(II) derivatives,[3,9] yielding complex (1) with a different (1a) : (1b) isomer ratio (see Results and Discussion section).

Preparation of the Binuclear Complexes (3) *and* (4).—The compounds (3a)—(3c) and (4a) were prepared by the same methods as for the corresponding 1,2-bis(imino)alkyl-palladium(II) adducts,[4,8b,29] with yields in the range 80—90%. The complex (4b) was prepared from the reaction of the dimer [{RhCl(cod)}$_2$] (0.123 g, 0.25 mmol) dissolved in CH_2Cl_2 (*ca.* 40 cm^3) with (2) (0.472 g, 0.5 mmol) and then with a solution of $NaClO_4 \cdot H_2O$ (0.14 g, 1 mmol) in methanol (5 cm^3). A white precipitate of NaCl was immediately formed and the solution became dark green. The reaction mixture was worked up in the same way as for (4a),[8b], yielding the product (4b) (0.49 g, 78%). Complex (4c) was obtained from the reaction of carbon monoxide with a stirred suspension of (4a) (0.314 g, 0.25 mmol) in toluene–n-hexane (4 : 1 v/v; 10 cm^3). Carbon monoxide was initially bubbled through the suspension for 15 min, then the mixture was kept under a CO atmosphere for 1 h. The red product (4c) was filtered off and washed with the same mixture of solvents (0.28 g, 93%). Electronic spectra [$\tilde{\nu}_{max.}$/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1})] in CH_2Cl_2 solution at 20 °C in the range 33 000—15 000 cm^{-1}: (3a) 20 400 (1 015), 25 580 (4 900), 28 570 (sh); (3b) 26 250 (4 180); (3c) 30 860 (sh), 29 070 (sh), 28 090 (11 080), 25 440 (sh), 23 310 (8 310), 21 980 (sh); (4a) 24 510 (3 380), 24 100 (sh), 22 200 (sh); (4b) 25 840 (6 930), 25 120 (sh), 17 390 (420).

Preparation of the Ionic Compounds (5).—Compounds (5a) and (5b) were prepared *in situ* in $CDCl_3$ for ^1H and ^{31}P n.m.r. spectra, and in MeOH for conductivity measurements. The n.m.r. solutions were obtained by mixing (2) (0.047 g, 0.05 mmol) with [{PdCl(η^3-2-MeC$_3$H$_4$)}$_2$] (0.020 g, 0.05 mmol) or with [{RhCl(cod)}$_2$] (0.025 g, 0.05 mmol) in $CDCl_3$ (1 cm^3). The methanolic solutions (10^{-3} mol dm^{-3}) were obtained by mixing (2) (0.047 g, 0.05 mmol) with an equimolar amount of palladium or rhodium dimer in methanol (50 cm^3).

Compound (5c) was prepared by the reaction of (2) (0.472 g, 0.5 mmol) with [{RhCl(CO)$_2$}$_2$] (0.195 g, 0.5 mmol) in toluene (20 cm^3) under dinitrogen. After stirring for 1 h, the mixture was left to stand for 2 h at −5 °C, then the product was filtered off, washed with cold toluene and dried *in vacuo* (yield, 0.60 g, 90%).

Reaction of (4a) *with* $[AsPh_4][RhCl_2(cod)]$.—Complex (4a) (0.063 g, 0.05 mmol) dissolved in $CDCl_3$ (1.5 cm^3) was treated with $[AsPh_4][RhCl_2(cod)]$ (0.033 g, 0.05 mmol). After filtering off the insoluble salt $[AsPh_4]ClO_4$, the course of the reaction was monitored by ^1H n.m.r. spectroscopy (see Results and Discussion section).

X-*Ray Crystallography of* (5c).—Diethyl ether was carefully added to a CH_2Cl_2 solution of (5c) under dinitrogen until incipient precipitation. After storing for 48 h at -10 °C, the red-brown shiny crystals were collected, washed with diethyl ether and dried *in vacuo*. The unit-cell dimensions and the symmetry were determined with an automatic Philips PW 1100 diffractometer. The collection of *X*-ray data was carried out at room temperature (25 °C) with graphite-monochromated Mo-K_α radiation ($\lambda = 0.7107$ Å).

Crystal data. $C_{51}H_{43}Cl_3N_2O_5P_2PtRh_2$ $M = 1\,332.6$, monoclinic, space group $P2_1/a$, $a = 19.521(3)$, $b = 17.212(7)$, $c = 15.910(3)$ Å, $\beta = 104.11(2)°$, $U = 5\,184.4$ Å^3, $Z = 4$, $D_c = 1.708$, D_m (by flotation in CH_3Br–CCl_4) = 1.70 g cm^{-3}, $F(000) = 2\,608$, μ(Mo-K_α) = 35.6 cm^{-1}.

A total of 6 247 independent reflections was collected in the range $3 < 2\theta < 43°$; of these, 3 892 were considered observed $[F^2 > 3\sigma(F^2)]$ and used in the analysis. The usual Lorentz polarisation and absorption [30] corrections were applied to the intensities. The structure was solved by a combination of direct methods and an origin-removed, sharpened Patterson synthesis and refined by full-matrix least squares, with a weighting scheme automatically chosen such that the average values of $w\Delta F^2$ for ranges of increasing $|F_o|$ were almost constant. The residual index R was 0.055, while the weighted R' was 0.059.

Final positional parameters are given in Table 5. Most of the calculations were carried out using the SHELX 76 program system,[31] on a CDC CYBER 70 model 76 computer system.

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