1715

Reactions of Palladium(II) Allyl Dimers with Palladium(II) Complexes containing σ -Bonded 1,2-Bis(imino)alkyl Groups. Crystal and Molecular Structure of the Zwitterionic Binuclear Compound [Pd(η^3 -2-MeC₃H₄)-{R¹N=C(PdCl₂L)-CMe=NR²}] (L = PPh₃, R¹ = R² = C₆H₄OMe-*p*)†

By Bruno Crociani • and Roberta Bertani, Istituto di Chimica Generale, Via Archirafi 26, University of Palermo, Italy

Tristano Boschi, Istituto di Chimica, Facolta di Ingegneria, University of Rome, Italy

Giuliano Bandoli, Istituto di Chimica e Tecnologia dei Radioelementi C.N.R., Area di Ricerca, Padova, Italy

The 1,2-bis(imino)alkylpalladium derivatives (A), $R^1N-CL'-CR^3-NR^2$ [$R^1 = R^2 = C_6H_4OMe_{-p}$, $R^3 = Me_{-}L' = R^2$ trans-PdClL₂ (L = para-substituted triarylphosphine or AsPh₃); $R^1 = R^2 = C_b H_4 O Me_p$, $R^3 = H$ or Ph, L' = trans- $PdCl(PPh_3)_2$; $R^1 = C_6H_4OMe_{-p}$, $R^2 = R^3 = Me_{,L'} = trans_PdCl(PPh_3)_2$] react with [{ $PdCl(\eta^3 - 2 - R^4C_3H_4)$ }_2] ($R^4 = R^3 - R^4C_3H_4$) H or Me) in the presence of NaClO₄ to yield the cationic binuclear complexes (B), $[Pd(\eta^3-2-R^4C_3H_4)(R^1N=CL'-1)]$ $CR^3=NR^2$][CIO₄], where the 1,2-bis(imino)alkyl group acts as $\sigma\sigma'$ -NN' chelating ligand. In the absence of NaClO₄, the reaction leads initially to the formation of the ionic compounds (C), $[Pd(\eta^3-2-R^4C_3H_4)(R^1N=CL' CR^3=NR^2)$ [PdCl₂(η^3 -2-R⁴C₃H₄)], which in a subsequent slower stage reacts further with exchange of ancillary ligands between the cationic and anionic species, to give the zwitterionic binuclear complexes (D), [Pd(η^3 -2- $R^4C_3H_4$)($R^1N=CL''-CR^3=NR^2$)] (L'' = cis-PdCl₂L), and [PdCl(η^3 -2-R⁴C₃H₄)L]. A complex of type (C) [$R^1 = R^2 = C_6H_4OM_6-p$, $R^3 = R^4 = Me$, L' = PdCl(dppe), dppe = 1,2-bis(diphenylphosphino)ethane] can be isolated from the reaction of the corresponding derivative (A) with [{PdCl(η^3 -2-MeC_3H_4)}_2]. The rates of ligand exchange depend markedly on the substituents R¹, R², and R³, on the nature of L, and on the solvent. Based on these effects and on ¹H n.m.r. spectral data, a mechanism is proposed, which essentially involves opening the fivemembered 1,2-bis(imino) ring of the cation promoted by interaction with the anionic species in the intermediate (C). The ¹H n.m.r. spectra of (D) indicate the presence of diastereoisomers which interconvert more or less rapidly at room temperature depending on the substituents R² or R³ and on the ligand L. The crystal and molecular structure of a typical complex (D) ($R^1 = R^2 = C_6H_4OMe_p$, $R^3 = R^4 = Me$, $L = PPh_3$) has been determined by X-ray diffraction analysis. Crystals are Orthorhombic, a = 20.224(5), b = 20.073(8), c = 19.829(9) Å, space group *Pbca*, and Z = 8. The structure has been solved by the heavy-atom method and refined by full-matrix least squares to R = 0.086 for 1 795 diffractometer data (Mo-K_x radiation). The structural data show that the η^{3} -allyl group is almost symmetrically bound to palladium and its plane forms a dihedral angle of 107.4° with the planar five-membered ring. The 1,2-bis(imino)propyl group is $\sigma\sigma'$ -*NN'* chelated to the Pd(r_1^3 -2-MeC₃H₄) unit and the mean plane of the cycle makes a dihedral angle of 81.9° with the co-ordination mean plane of the cis- $PdCl_2(PPh_3)$ group. The major features of the structure are represented by a short Pd-C(imino) bond [1.92(3) Å], indicating a relevant π contribution, and by a close approach of the R³ substituent to the metal centre of the *cis*-PdCl₂(PPh₃) unit [Pd · · · C(methyl) 3.19 Å].

In recent years the chemistry of polynuclear compounds has attracted considerable attention for the inherent theoretical interest and for the relevant catalytic implications. A general synthetic route to polynuclear non-cluster compounds involves the co-ordination reaction of metal complexes containing potentially ligating functions, such as C-bonded acetyl,¹ methoxy(imino)methyl,² and pentane-2,4-dione ³ groups or N-bonded pyrazolate ⁴ and P-bonded phosphinoyl ligands,⁵ see following page. Due to our interest in this field, we have previously studied the syntheses ⁶ and the co-ordinating abilities ^{6c,7} of C-bonded 1,2-bis(imino)alkylpalladium(II) derivatives of type (A) (following page).

In general the reactions of (A) with transition metal substrates yield binuclear complexes in which the 1,2-bis(imino)alkyl group acts as a $\sigma\sigma'$ -NN' chelating bidentate ligand.

Only in a few cases, however, are trinuclear complexes obtained, which probably involve a $\sigma\sigma'$ -NN' bridging co-

ordination mode of (A).^{7d} In some binuclear compounds, migration of ancillary ligands between the metal centres is also observed.^{7c.d}

Following up this line of research and with a particular aim of elucidating the factors which affect the exchange of ancillary ligands, we have carried out an investigation of the reactions of (A) with palladium(II) allyl dimers, the results of which are reported herein.

RESULTS AND DISCUSSION

The reactions of various 1,2-bis(imino)alkylpalladium-(II) derivatives with $[\{PdCl(\eta^3-2-R^4C_3H_4)\}_2]$ ($R^4 = H$ or Me) are reported in Schemes 1 and 2. When an excess of NaClO₄ is present, reactions (1) and (3) lead to the formation of intensely coloured (from deep yellow to redorange) cationic binuclear complexes (B) and (28), which behave as mono-monovalent electrolytes in MeOH solutions (Table 1). The presence of an unco-ordinated perchlorate anion in the solid is confirmed by the occurrence of a strong broad band at *ca*. 1 090 cm⁻¹ [ν (Cl-O)] and a sharp strong absorption at *ca*. 625 cm⁻¹ [δ (Cl-O)]. Reaction (1) (Scheme 1) with compounds (5) or (6) yields

 $[\]mu$ -[1',2'-Bis(*p*-methoxyphenylimino)propyl- $C^{1'}(Pd^1):NN'-(Pd^2)$]-1,1-dichloro-2-(1''-3''- η -2''-methylallyl)-1-triphenyl-phosphinedipalladium.

Published on 01 January 1982. Downloaded by Freie Universitaet Berlin on 31/10/2014 10:10:21

cationic complexes of type (B), contaminated by a certain amount of the products of types (D) and (E) of reaction (2). In the preparation of compound (14), the formation of the latter impurities can be minimized when the reaction mixture is worked-up as quick as possible (see Experimental section). The $\sigma\sigma'$ -NN' chelation of the 1,2bis(imino)alkyl group, indicated by the electronic and ¹H n.m.r. spectra, affects the characteristic i.r. bands, aldehyde-N-methylimine).⁹ This is probably related to the presence of stronger Pd-N bonds in the binuclear cationic compounds (9)—(17) and (28), with a consequently higher activation energy for the formation of a monodentate N-ligand intermediate involved in the above dynamic processes.

In the absence of NaClO₄, the reaction of (A) with $[{PdCl(\eta^3-2-R^4C_3H_4)}_2]$ follows a quite different course,



v(C=N) and v(Pd-Cl), of the free ligands (A) in the same way as previously observed 6c,7 for other types of binuclear complexes. In particular, the high-frequency shift of v(Pd-Cl) in (B) is due to the reduced *trans*influence of the σ -bonded organic moiety of (A) upon coordination, as can be inferred from the shortening of the Pd-Cl bond distance of compound (1) in its adducts with CuCl₂ [(1) 2.41; CuCl₂·(1) 2.36 Å]. 6b,7b On the other hand, the v(Pd-Cl) band in compound (27) (294 or 283 cm⁻¹), 7a in which the chloride ligand is *trans* to a phosphorus atom of the chelating group dppe [dppe = 1,2bis(diphenylphosphino)ethane], is essentially unaffected by co-ordination [v(Pd-Cl) = 297 or 285 cm⁻¹ in (28)].



$$\begin{split} R^{1} &= R^{2} = C_{6}H_{11} \text{ or } C_{6}H_{4}X - \rho (X = H, Me, \text{ or OMe}); R^{3} = Me \text{ or Ph} \\ R^{1} &= R^{2} = C_{6}H_{4}OMe - \rho; R^{3} = H \\ R^{1} &= C_{6}H_{11}; R^{2} = C_{6}H_{4}OMe - \rho; R^{3} = Me \\ R^{1} &= C_{6}H_{4}OMe - \rho; R^{2} = R^{3} = Me \end{split}$$

The ¹H n.m.r. spectra (Table 2) show that the allyl groups of (B) are η^3 -bound to the palladium centre which is linked to the imino-nitrogen atoms and do not undergo any dynamic process at an appreciable rate in CD₂Cl₂ or CDCl₃ solutions at 35 °C. This result is in contrast with the fast syn-syn, anti-anti exchange of the allyl protons in the cationic mononuclear complexes, $[Pd(\eta^3-2-RC_3H_4)Y]^+$ (R = H or Me; Y = p-MeOC₆H₄N=CH-CMe=NC₆H₄-OMe-p),⁸ containing an asymmetric 1,2-bis(imino) ligand, and with the fast exchange of the non-equivalent terminal allyl carbons observed at 23 °C for CD₂Cl₂ solutions of $[Pd(\eta^3-C_3H_5)(aqa)]^+$ (aqa = 8-alkylquinoline-2-carb-

which eventually leads to the formation of the binuclear zwitterionic complexes (D) and the well known derivatives (E) [reaction (2)]. Upon mixing of the reactants (1:1 molar ratio), the ionic intermediates (C) are immediately and quantitatively formed, as indicated by the electronic spectra in methanol, characterized by the intense metal-to-ligand charge-transfer (m.l.c.t.) bands of the cationic complexes (B), and by the ¹H n.m.r. spectra in CDCl₃, which exhibit the typical signals of (B) and the anionic compounds $[PdCl_2(\eta^3-2-R^4C_3H_4)]^-$. The only relevant difference occurs in the dynamic behaviour (syn-anti exchange) of the allyl group of the cationic species. The same spectral features are observed when the independently prepared complexes (B) and $[AsPh_{4}]$ - $[PdCl_2(\eta^3-2-R^4C_3H_4)]$ are mixed together in a 1 : 1 molar ratio, under comparable experimental conditions. A typical ¹H n.m.r. spectrum of the initial reaction mixtures $(1)-[{PdCl(\eta^3-C_3H_5)}_2]$, or $(10)-[AsPh_4][PdCl_2(\eta^3-C_3H_5)]$, is reported in Figure 1. The signals H_c , H_s , and H_a are due to the η^3 -C₃H₅ group of the anion and compare well with those of the complex $[AsPh_4][PdCl_2(\eta^3 C_{3}H_{5}$] { $\delta(H_{c}) = 5.5-5.0$ (central proton); $\delta(H_{s}) = 3.93$ [syn protons, ${}^{3}J(H_{c}-H_{s}) = 7.3$]; and $\delta(H_{a}) = 2.85$ p.p.m. [anti protons, ${}^{3}J(H_{c}-H_{a}) = 12.3 \text{ Hz}$]. The syn and anti protons of the allyl groups of the cationic derivative (10) undergo a rather fast exchange, indicated by their appearance as a doublet H' at 3.14 p.p.m. $[^{3}/(H_{c}'-H') = 9.9 \text{ Hz}]$, with a corresponding quintet H_{c}' at 5.70 p.p.m. for the central allylic proton. The same dynamic process is also apparent from the ¹H n.m.r. spectra of the equimolar mixtures (A)-[{PdCl(η^3 -2- $R^{4}C_{3}H_{4}$] {or (B)-[AsPh_4][PdCl_2($\eta^{3}-2-R^{4}C_{3}H_{4}$)]}, if the subsequent ligand exchange reaction leading to (D) and (E) is sufficiently slow. For the initial mixture (1)-[{ $PdCl(\eta^{3}-2-MeC_{3}H_{4})$ }₂] {or (9)-[$AsPh_{4}$][$PdCl_{2}(\eta^{3}-2-MeC_{3}H_{4})$]} in CDCl₃ at 35 °C, the syn and anti proton signals of the cationic species coalesce into a rather broad singlet at 2.93 p.p.m., whereas those of the anion occur as sharp singlets at 3.74 (syn) and 2.73 (anti), with the allyl methyl resonance at 2.02 p.p.m. {In [AsPh₄][PdCl₂(η³-2-

1717



Scheme 1 (i) [{PdCl(η^3 -2-R⁴C₃H₄)}₂], NaClO₄ (excess); (ii) [{PdCl(η^3 -2-R⁴C₃H₄)}₂]; (iii) [AsPh₄][PdCl₂(η^3 -2-R⁴C₃H₄)]

J. CHEM. SOC. DALTON TRANS. 1982



 $\label{eq:scheme 2} \begin{array}{l} \text{Scheme 2} & (i) \; [\{ PdCl(\eta^3 - 2 - MeC_3H_4)\}_2], \; NaClO_4 \; (excess); \; \; (ii) \; [\{ PdCl(\eta^3 - 2 - MeC_3H_4)\}_2] \end{array}$



FIGURE 1 Proton n.m.r. spectrum in $CDCl_3$ at 35 °C of the system (1)-[{ $PdCl(\eta^3-C_3H_5)$ }], or (10)-[$AsPh_4$][$PdCl_2(\eta^3-C_3H_5)$], (1 : 1 molar ratio) after 10 min from mixing

 $MeC_{3}H_{4}$] the corresponding signals are at 3.70, 2.69, and 1.99 p.p.m., respectively.} The characteristic $\delta(O-Me)$ and $\delta(C-Me)$ resonances of the co-ordinated 1,2-bis-(imino)propyl group appear at 3.84, 3.74, and 2.38 p.p.m., respectively, in good agreement with the corresligands in the intermediates (C) of reaction (2). No exchange of ligands was observed in the reaction of (27) with an equimolar amount of $[{RhCl(cod)}_2]$ (cod = cyclo-octa-1,5-diene).^{7d} The formulation of (29) is based on elemental analysis, conductivity, and spectral

 TABLE 1

 Analytical, physical, conductivity, and characteristic i.r. data

	Mad		Analysi	s * (%)		Λ ° (Ω ⁻¹		I.r. absorptio	n (cm ⁻¹)
Compd	(f)_/°C)	C	Н	N	CI	mol^{-1}	M 6,d	ν (C=N) *	v(Pd-Cl)
(9)	185	55 4	3.6	2.4	217	,	1 198	1 620ms 1 564ms	270m
(2)	100	(55.15)	(3.60)	(2.45)	(21.50)		(1 154.4)	1 020110, 1 001110	
(3)	189	68.4	5.9	2.6	3.6		1 015	1 624s, 1 552s	265m
(-)		(68.65)	(5.75)	(2.70)	(3.45)		$(1 \ 031.9)$		
(4)	170	`62.9 ´	5.4	2.5	3.2		`1 118 ´	1 620ms, 1 565s	265m
、 /		(62.80)	(5.25)	(2.50)	(3.15)		(1 127.9)		
(5)	160164	60.5	4.6	2.6	3.6		1 040	1 620s, 1 560ms	274m
		(61.45)	(4.55)	(2.70)	(3.40)		(1 035.6)		
(9)	164	56.6	4.7	2.2	6.0	81.1		1 580m, 1 510 (sh)	309m
		(56.65)	(4.50)	(2.30)	(5.85)				
(10)	163	55.8	4.5	2.3	5.9	81.1		1 580m, 1 510 (sh)	308m
	100	(56.30)	(4.40)	(2.35)	(5.95)	74.1		1 500	010
(11)	193	48.3	3.5	2.0	19.8	74.1		1 560m	312m
(10)	155	(48.35)	(3.40)	(2.0)	(20.05)	70.9		1 590 (ab)	915mg
(12)	175	07.8	0.U (5.15)	2.1	0.0 (5.50)	19.8		1 580 (SII)	310ms
(19)	167	(08.00)	(0.10)	10	(0.00)	75 B		1 568m	310m
(15)	107	(54 50)	(4.80)	(2.00)	(5.10)	10.0		1 50811	51011
(14)	150	55 9	43	2.00)	61	84 9		1 552m	305mw
(1)	105	(56.3)	(4 40)	(2.35)	(5.95)	01.0		1 00211	000111
(15)	164	58 4	4.4	21	57	75.4		1 578m	302m
(10)	101 100	(58,60)	(4.45)	(2,20)	(5,60)				000000
(16)	178	54.9	4.4	2.5	6.5	85.1		1 575m, 1 510 (sh)	300m
(10)		(54.85)	(4.50)	(2.50)	(6.35)				
(17)	179	54.0	4.3	2.5	6.5	81.4		1 575m, 1 510 (sh)	302m
()		(54.45)	(4.40)	(2.55)	(6.45)				
(28)	163	52.5	4.3	2.5	6.6	81.4		1 581m	297m or 285m
· · ·		(52.15)	(4.45)	(2.60)	(6.55)				
(18)	180	52.8	4.5	3.1	8.0	43.9	869	1 580m, 1 515 (sh)	297ms, 280ms
		(53.10)	(4.45)	(3.15)	(8.05)	0.1 1	(882.4)		
(19)	179	52.4	4.2	3.2	8.2	42.6	885	1 580m	300m, 280m
		(52.55)	(4.30)	(3.25)	(8.15)	0.2 5	(868.4)		
(20)	187—189	47.1	3.8	2.8	18.1	51.5		1 565m	300m, 284m
		(47.50)	(3.70)	(2.85)	(18.0)		0.40	1 500 1 500 (1)	007 000 (1)
(21)	183-186	53.9	4.8	3.0	7.6	46.7	946	1 580m, 1 520 (sn)	295s, 280 (sh)
(00)	1.0.4	(04.00)	(4.90)	(3.00)	(7.60)		(924.0)	1 585-	904ma 977ma
(22)	104	01.7	4.0	2.7 (9.00)	(7.3)			1 365111	294ms, 277ms
(99)	171	(01.80)	(4.05)	2.90)	(7.30)	21.6	954	1.580m 1.510 (ch)	901e 980 (eb)
(23)	171	(50 55)	(4.95)	(3,00)	(7.65)	0 15 1	(096 3)	1 00011, 1 010 (51)	2015, 200 (81)
(94)	170-181	52.3	44	32	8.2	39.7	893	1.560m	298ms 276ms
(24)	110101	(52.55)	(4.30)	(3.25)	(8.15)	00.1	(868.4)	1 0001	2001115, 2101115
(25)	145	55.7	4.3	2.8	7.5	47.6	926	1 575m	294ms, 272ms
()		(55,95)	(4.40)	(2.95)	(7.50)		(944.4)		
(26)	160	49.8	4.4	3.4	9.1	44.1	792	1 575mw, 1 520 (sh)	298ms, 273ms
()		(50.15)	(4.45)	(3.55)	(8.95)		(790.3)	. ()	··· • •
(29)	165	50.2	`4 .5	`2.3 ´	`8.5	61.1	. ,	1 581m	298m, 270m,
		(50.40)	(4.55)	(2.30)	(8.75)				255 (sh)

⁶ Uncorrected values, all compounds decompose on melting. ^b Calculated values are given in parentheses. ^c Molar conductivities of 10^{-3} mol dm⁻³ MeOH solutions, 293 K. ^d Molecular weight determinations by osmometry in 1,2-dichloroethane. ^e The assignment of the ν (C=N) band of the binuclear complexes is tentative because of the occurrence of strong absorptions of the *para*-substituted phenyl groups around 1 600 and 1 500 cm⁻¹. ^f Molar conductivities of 10^{-3} mol dm⁻³ 1,2-dichloroethane solutions, 293 K.

ponding chemical shift values of compound (9) (Table 2). The intermediacy of the ionic compounds (C) in reaction (2) is further supported by the isolation of product (29) from reaction (4) (Scheme 2). This can be easily achieved because the exchange of ancillary ligands between the cation containing a chelating dppe ligand and the anion of (29), if it occurs, proceeds at a considerably much slower rate than the exchange of monodentate measurements. The i.r. spectrum in the solid shows two intense v(Pd-Cl) bands of the anionic species at 270 and 255 cm⁻¹, which partly overlap with the v(Pd-Cl) absorption of the cation. The electronic spectrum in MeOH at 25 °C is characterized by strong m.l.c.t. bands with a maximum at 25 900 ($\varepsilon = 4\,900$ dm³ mol⁻¹ cm⁻¹) and shoulders at 22 500 and 20 900 cm⁻¹, and matches very well with the spectrum of (28) in the same solvent. The

¹H n.m.r. spectrum in CDCl₃ confirms the presence of both the cationic and anionic species. Also in this case, the syn and anti allyl protons of the binuclear cation are rapidly exchanging so as to give rise to a slightly broad singlet at 2.92 p.p.m., whereas the η^3 -2-MeC₃H₄ system of the anion remains essentially unchanged. The dynamic behaviour of the allyl groups of the cation in the intermediates (C), as well as in compound (29), may be reasonably accounted for by an interaction with the anion, [PdCl₂(η^3 -2-R⁴C₃H₄)]⁻, probably through bridging chlorides, whereby a short lived σ -allyl is formed ¹⁰ (see below).



This is also supported by the fact that the static η^3 -allyl group of the binuclear cationic complex (28) is promptly turned into a dynamic system, identical to that of (29), upon addition of Cl⁻ ions (see Table 2). The cation-anion interaction in (C) and in (29) does not involve exchange of the Pd(2-R^4C_3H_4) unit between the two allyl species at a significant rate on the n.m.r. timescale, at variance with the behaviour of the systems $Y-[\{PdCl(\eta^3-2-MeC_3H_4)\}_2]$ and $[Pd(\eta^3-2-MeC_3H_4)Y]-[ClO_4]-[AsPh_4][PdCl_2(\eta^3-2-MeC_3H_4)], where Y is an <math display="inline">\alpha$ -di-imine ligand of the type RN=CH-CH=NR (R = Bu^t or C_6H_4OMe-p) or RN=CMe-CMe=NR (R = C_6H_4-OMe-p)^8 [see reaction (5)]. In this case, the ¹H n.m.r.

conductivity is observed, which probably arises from ionic dissociation of the Pd-Cl bonds weakened by the *trans*-influence of L and of the σ -bonded 1,2-bis(imino)alkyl group, and by the presence of a formal negative charge on the palladium atom. The formulation of (D), suggested by spectral data, was confirmed by an X-ray structural analysis of complex (18), which will be discussed later on.

The i.r. spectra in the metal-chloride stretching frequencies region show two v(Pd-Cl) bands in the ranges 300–291 and the 284–272 cm⁻¹ respectively, due to the mutually *cis* chloride ligands of the unit PdCl₂L. The same spectral feature was observed for the related derivatives (see below) [$\mathbf{R} = C_6 \mathbf{H}_4 \text{OMe-}p$; $\mathbf{MX}_n = \text{Rh}(\text{CO})_2$, Rh(cod),^{7d} Pd(S₂C₂NMe₂) and Pt(S₂C₂NMe₂),^{7c} and Pd(pd) and Cu(pd) (pd = pentane-2,4-dionate)¹¹] and appears to be diagnostic for this class of zwitterionic binuclear complexes containing the *cis*-PdCl₂L group.



The course of reaction (2) can be monitored either by ¹H n.m.r. or by visible electronic spectra. The formation of the products (D) and (E) in a 1 : 1 molar ratio is clearly indicated by the integration of the ¹H n.m.r. spectra of the mixtures when reaction (2) is completed. The rates are markedly influenced by the nature of the solvent in the order: benzene > chlorinated solvents (CH₂Cl₂, CHCl₃, 1,2-dichloroethane) \gg alcohols (MeOH, EtOH);

spectra showed a fast scrambling of the $Pd(\eta^3-2-MeC_3H_4)$ group among the different allyl complexes, but gave no evidence of any syn-anti exchange of the allylic protons in $[Pd(\eta^3-2-MeC_3H_4)Y]^+$. Such a difference may be related to the presence of stronger Pd-N bonds in the binuclear complexes (B) (as earlier discussed), which would make the exchange of the $Pd(\eta^3-2-R^4C_3H_4)$ unit between the cation and the anion of (C) energetically less favourable than the dynamic process involving syn-anti exchange in the allyl cation.

Both products (D) and (E) of reaction (2) have been isolated and characterized. The compounds (E) are easily identified by elemental analysis and by comparison of their i.r. and ¹H n.m.r. spectra with those of authentic samples prepared by bridge-splitting reactions of the dimers [{PdCl(η^3 -2-R⁴C₃H₄)}₂] with L. The zwitterionic binuclear complexes (D) are monomers in 1,2-dichloroethane, where they are essentially non-conducting. In MeOH solution, however, an appreciable electrical by the neutral ligand L and the R², R³ substituents in the order: L = AsPh₃ $\geq P(C_6H_4Cl-p)_3 > PPh_3 >$ $P(C_6H_4Me-p)_3 > P(C_6H_4OMe-p)_3$ (when R¹ = R² = C_6H_4OMe-p and R³ = Me); R³ = H > Ph \geq Me (when L = PPh₃ and R¹ = R² = C_6H_4OMe-p); R² = $C_6H_4-OMe-p$, R³ = Me).

While the influence of L essentially reflects the different strength of the Pd-L bonds, the effects of the substituents on the α -di-imine moiety are mainly related to the stability of the five-membered ring of (B)^{8,12} and imply that a Pd-N bond breaking (*i.e.* opening of the ring) is involved in the step (C) \rightarrow (D) + (E) of reaction (2). According to the reaction mechanism which will be reported in detail in a forthcoming paper,¹³ the exchange of ligands occurs preferentially *via* a trinuclear transition state, arising from the slow opening of the five-membered ring of the cationic substrate (B) upon interaction with the anion (see below). An analogous trinuclear transition state (or transient) was proposed for the transfer of ancillary ligands occurring in the reaction of (1) or (8) with $[{\rm RhCl(cod)}_2]^{.7d}$



Proton N.m.r. Spectra.—The ¹H n.m.r. spectra of some representative complexes are reported in Table 2. In general, the signals of the C- and N-substituents of the 1,2-bis(imino)alkyl moieties are shifted downfield on co-ordination. This effect is particularly evident for the R^3 group, when $R^3 = Me$, since for $R^1 = R^2 = C_6H_4$ -OMe-*p* and/or $R^3 = Ph$, the aromatic proton signals are

partially masked by the intense phenyl resonances of L. In the complexes (A) with $\mathbb{R}^3 = Me$, $\delta(\mathbb{R}^3)$ occurs at rather high field, 1.29 - 1.01 p.p.m. [the $\delta(\mathbf{R}^3)$ values of compounds (1), 1.29, and (8), 1.01 p.p.m., are taken from refs. 7(a) and 6(c)], owing to the through-space shielding effect of the phenyl ring current of the two mutually trans-L ligands,66 whereas in the corresponding cationic derivatives (B) they are detected in the range 2.42-2.35 p.p.m. Such a marked downfield shift can be ascribed in part to a σ -N ligating mode of the imino-nitrogens {in the mononuclear compound $[Pd(\eta^3-2-MeC_3H_4)Y]^+$ (Y = $p\text{-MeOC}_{6}H_{4}\text{-}N\text{=}CMe\text{-}CMe\text{=}N\text{-}C_{6}H_{4}OMe\text{-}p) \text{ the } \delta(C\text{-}Me)$ signal of the $\sigma\sigma'$ -NN' chelating α -di-imine at 2.33 p.p.m. is only 0.23 p.p.m. to lower field from that of the free ligand 8} and, to greater extent, to the change of configuration (trans \rightarrow cis) of the 1,2-bis(imino)alkyl unit



'IGURE 2 Electronic spectra in 1,2-dichloroethane at 25 °C of complexes $[Pd(\eta^3-2-MeC_3H_4)(p-MeOC_6H_4N=CMe-CMe=NC_6H_4-OMe-p)][ClO_4]$ (----); (14) (····); (18) (----); (14) (····); (18)

upon chelation, which brings the methyl protons into a position very close to the palladium centre of the *trans*-PdClL₂ group above its co-ordination plane [Pd \cdots C(methyl) distances of 3.37 and 3.19 Å have been observed in CuCl₂·(1) ^{7b} and (18), respectively]. It is well established that protons closely approaching d^8 square planar metal centres above the co-ordination plane undergo large downfield shifts, resulting from the anisotropy in the magnetic susceptibility of the metal.^{9,15}

A further deshielding of the \mathbb{R}^1 , \mathbb{R}^2 , and \mathbb{R}^3 protons is observed on going from (B) to (D) (*i.e.* upon replacement of L by Cl⁻), which is essentially due to the reduced

		1,2	Pis(imino)alkyl group				[1] V	
Compound (9)	Solvent CD ₂ Cl ₂	$\begin{array}{c} P-C_{6}H_{5} \\ \text{or } P-C_{6}H_{4} - \\ 7.7-7.2 \ (m) \ [30] \end{array}$	N-C ₆ H ₄ - 7.2-0.2 (m) [8]	OCH ₃ 3.85 (s) [3] 3.75 (s) [3]	C-R ³ 2.42 (s) [3]		2.93 (s, br) [1]	group C-R ⁴ 1.94 (s) [3]
(18)	CDC1 ₃	7.8—7.0 (m) [17]	6.9—6.7 (m) [6] ^b	3.88 (s) [3] 3.79 (s) [3]	2.96 (s) [3]		2.76 (s, br) [z] 2.80 (s, br) [z] 2.68 (s) [1] 2.66 (s) [1]	$\left[1.96 (s, br) \right] \left[3 \right] \mathfrak{c},\mathfrak{a}$ 1.82 (s, br) $\left[3 \right]$
(18)-AsPh ₄ Cl •	cDC1 ₃			3.89 (s) [3] 3.80 (s) [3]	2.97 (s) [3]		2.00 (S) [I] 2.83 (S) [2] 2.69 (S) [1] 3.61 (S) [1]	1.90 (s) [3]
(2)	cDC13	7.7—7.1 (m) [26]	6.9—5.9 (m) [6] ^b	$\left. \begin{array}{c} 3.81 \\ 2 \\ 7 \\ 0 \end{array} \right \left. \begin{array}{c} (s) \\ (s) \\ (s) \end{array} \right \left[6 \right]$	1.28 (s) [3] f		[T] (S) TO.7	
(11)	cDCl ₃	7.77.0 (m) [26]	7.0-6.2 (m) [6] ^b	3.81 (s) [3] 3.81 (s) [3]	2.35 (s) [3]		$\left. \begin{array}{c} 3.14 \ (\mathrm{sh}) \\ 3.10 \ (\mathrm{s}) \\ 3.01 \ (\mathrm{s}) \ [1] \end{array} \right\} \left[2 ight]$	2.07 (s) [3]
(20)	CD_2Cl_2	7.77.0 (m) [14]	7.0-6.8 (m) [6] ⁶	3.88 (s) [3] 3.78 (s) [3]	2.87 (s) [5] ^g		$\begin{array}{c} 2.91 \ (\rm s, \ br) \ [1] \\ 2.92 \ (\rm sh)^{g} \\ 2.80 \ (\rm s, \ br) \ [1] \\ 5.60 \ (\rm s) \ (\rm r) \end{array}$	$\frac{2.0}{1.87} { m (s, br) \choose m [3]} d$
(13)	cDC1,	7.8—6.5 (m) [30] °	6.4—6.2 (m) [2] "	$\left. \begin{array}{c} 3.86 & (\mathrm{s}) \\ 3.81 & (\mathrm{s}) \end{array} \right\} \left[24 ight]$	2.40 (s) [3]		2.03 (5) [1] 3.04 (5, br) [1] 2.91 (5) [1] 5.63 (5, br) [9]	2.01 (s) [3]
(22)	cDC13	7.86.5	(m) [20]	$\frac{3.85}{3.76} \stackrel{(s)}{(s)} [15]$	2.90 (s) [3]		2.76 (s, br) [2] 2.76 (s, br) [2] 2.67 (s) [1]	$\frac{1.95}{1.79} \begin{pmatrix} s, br \\ s, br \end{pmatrix} [3] d$
(23)	cDC13	7.8—7.0 (m) [17] ^h	6.9-6.6 (m) [6] ^b	3.84 (s) [3] 3.78 (s) [3]	2.99 (s) [3]		2.89 (5, br) [1] 2.64 (s) [1] 2.64 (s) [1]	1.87 (s, br) [3]
(14)	CD ₂ Cl ₂	7.87.0 (m) [32]	6.9-6.5 (m) [6] ⁶	3.87 (s) [3] 3.79 (s) [3]	7.80 (s) [1]		2.94 (s) [J] 3.42 (s, br) [1] 3.13 (s, br) [1] 2.94 (s) [1]	1.99 (s) ⁻ [3]
(24)	CD_2Cl_2	7.7—7.1 (m) [17]	7.1-6.8 (m) [6] ^b	3.94 (s) [3] 3.89 (s) [3]	8.88 (s) [1]		2.86 (s) [1] 3.31 (s, br) [2] 2.95 (s) [1] 2.86 (s) [1]	2.01 (s) [3]
(15)	cDC1 ₃	7.8-6.3	(m) [43]	3.82 (s) [3] 3.65 (s) [3]			2.22 (s) [1] 3.22 (s) [1] 3.15 (s, br) [1] 2.91 (sh) [2]	2.02 (s) [3]
(25)	CDC1 ₃	7.9-6.4	(m) <u>-</u> 28]	3.82 (s) [3] 3.65 (s) [3]	•		2.94 (s, 0r)	1.98 (s) [3]
(26)	CDC13	7.67.0 (m) [17]	6.8 — 6.6 (m) [2]	3.84 (s) [3]	2.98 (s) [3]	3.39 (s) [3] (N-CH ₃)	$\begin{array}{c} 2.79 & (br) \\ 2.79 & (br) \\ 2.79 & (br) \\ 2.65 & (br) \\ \end{array}$	$\left[1.98 \left({ m s, br} ight) ight\} \left[3 ight] { m d}, j$ $\left[1.85 \left({ m s, br} ight) ight\}$
(28) (28)-AsPh ₄ Cl *	cDCI, CDCI,	8.06	3.4 (m)	3.79 (s) 3.75 (s) 3.80 (s) 3.76 (s)	2.33 (s) ^d 2.30 (s) ^d 2.32 (s)	$\begin{array}{c} 3.2-2.0 \text{ (m, br)} ' \\ (P-CH_2^{-}) \\ 3.2-2.0 \text{ (m, br)} \\ (P-CH_{s^{-}}) \end{array}$	3.1-2.7 2.91 (s, br)	2.08 (s, br) ^d 1.81 (s, br) ^d 1.93 (s)
(29)	CDC1 ₃	8.0(3.4 (m)	3.81 (s) 3.77 (s)	2.34 (s)	3.2-2.0 (m, br) (P-CH ₂ -)	$\begin{array}{c} 3.70 \ (\text{s}) \ k \\ 2.69 \ (\text{s}) \ k \\ 2.92 \ (\text{s}, \ \text{br}) \end{array}$	1.94 (s) $k1.94 (s)$
 Chemical shii Cherical shii Overlapping A. At 100 °C in 1, are present (see ' respectively. "A 43, 45 (sh), "3.4 respectively. Th 	tt 8/p.p.m., : A'BB' signal 1,2,2-tetrach text). * Mo >verlapping : 1 (s), 2.97 (ie allylic met	spectra recorded at 35 ls of the C_6H_4OMe - p g ultrocethane, the allyl g ultrartatio (compound): signals. $^{h}AS=C_6H_5+^{h}$ sin, 2.92 (s), 2.85 (s), thyl protons are detect	°C unless stated other roups (\mathbb{R}^1 and \mathbb{R}^2 subs roup signals occur at 2 AsPh_4Cl \geq 20:1. / 1 \mathbb{N} -CeH_4 - protons. i 2.77 (s), and 2.69 (s), ed as two sharp singlet	wisc; $s = singletstituents), the out(S2 (s) [2], 2.70 (s)The \delta(C-R^3) sign.Masked by the P-, and are partials at 2.06 and 1.9$	t, m = multiple the protons of R (he protons of R) [1], 2.62 (s) [1] al of the new c -C ₆ H ₅ + N-C ₆ H IIJ masked by 1 IIJ masked by 1	t, br = broad. Integr ¹ being masked by th ¹ being masked by th ¹ $\beta(CH_2)$; and at 1.80 ¹ $\beta(CH_2)$; and at 1.80 ¹ $\beta(CH_2)$; and $\beta(CH_2)$ ¹ $\beta(N-CH_3)$ and $\beta(C$ ¹ $\beta(N-CH_3)$ and $\beta(N-CH_3)$ and $\beta(C$ ¹ $\beta(N-CH_3)$ and $\beta(C$ ¹ $\beta(N-CH_3)$ and $\beta(N$	ration values are giv e intense phenyl pro $g(s)$ [3], $\delta(C-R^4)$. ^d (5) occurs at 1.17, (5) occurs at 1.17, (3) at -40 °C, the all $\rightarrow R^3$) resonances at MeC ₃ H ₄) ⁻ anion.	en in square brackets. tons resonances of L. Two diastereoisomers 1,22, and 1,21 p.p.m., 1,122, signals occur 3.53 and 3.05 p.p.m.

TABLE 2 Proton n.m.r. data ^a

Published on 01 January 1982. Downloaded by Freie Universitaet Berlin on 31/10/2014 10:10:21.

shielding effect of the phenyl ring current of the single L ligand in the *cis*-PdCl₂L unit,^{6b} and probably also to a different charge distribution in the zwitterionic binuclear complexes. Such a downfield shift is of *ca*. 0.5 p.p.m. for $\mathbb{R}^3 = \mathbb{M}e$ and becomes remarkably large (1.08 p.p.m.) for $\mathbb{R}^3 = \mathbb{H}$. The change in chemical shift of the \mathbb{R}^2 protons (when $\mathbb{R}^2 = \mathbb{M}e$) is illustrated by the sequence: (8) 3.02,^{6c} (16) 3.10, (26) 3.39 p.p.m.

In general, the ¹H n.m.r. spectra of both types of binuclear complexes (B) and (D) indicate the presence of η^3 -allyl groups, characterized by distinct resonances for the syn and anti protons, even though in most cases (for η^3 -2-MeC₃H₄) the assignment proved to be rather difficult for the following reasons.

(a) The syn and anti protons have chemical shifts rather close to each other so that overlapping often occurs.



(b) The asymmetric nature of the 1,2-bis(imino)alkyl group (when $R^1 = R^2 = C_6H_4OMe-p$ and $R^3 = Me$) does not appreciably affect the two CH_2 ends of the η^3 -2-MeC₃H₄ system. For complexes (B) with a 'rigid' η^3 -2-MeC₃H₄ group, one would expect four signals, one for each allyl proton, which may exhibit a fine structure resulting from coupling between non-equivalent protons (ABCD spectrum). Spectra of this type have been observed for compounds (14) and (15), where $R^3 = H$ and Ph respectively, and also for complexes (16), where R^1

 C_6H_4OMe-p and $R^2 = Me$ (see Figure 3). A common feature of these spectra is represented by the presence of two broader bands [at 3.55 and 2.82 p.p.m. for (16)], which upon accurate examination appear as unresolved doublets and are tentatively assigned to the syn protons on the basis of coupling constant considerations (it is generally observed that the more significant coupling in allylic systems is that between the two syn protons ¹⁶). In the analogue (17) the syn, anti assignment results from the different coupling constants with the central allyl proton $[\delta/p.p.m. (^3J/Hz)$ in CD_2Cl_2 , 3.76 (6.4) and 3.19 (6.1) syn protons; 3.07 (13.3) and 2.90 (12.9) anti protons].



SCHEME 3 (i) Interchange of diastereoisomers (1) \rightarrow (11) either through loss of configuration of the *cis*-PdCl₂L unit or through rotation about the Pd-C bond; (*ii*) interchange of diastereoisomers (1a) \rightarrow (11b) and (1b) \rightarrow (11a) through dynamic processes of the allyl group (see text)

(c) Because of restricted rotation about the Pd-C σ bond of the 1,2-bis(imino)alkyl group in the zwitterionic complexes (D), as can be inferred from the structural data of (18) on the basis of steric and electronic (relevant π contribution in the Pd-C bond) considerations, four diastereoisomers may be present in solution (Scheme 3). Due to the asymmetry of the PdCl(dppe) unit relative to the co-ordination plane of the chelating α -di-imine, similar diastereoisomers may also occur for complex (28), whereas for derivatives (B), containing the trans-PdClL, group, only two enantiomers are possible, which are not distinguished by ¹H n.m.r. spectra. The presence of both diastereoisomers (I) and (II) in solution is generally indicated by the occurrence of two signals for the methyl protons of the 2-MeC₃H₄ ligand and, in a few cases, by two very close $\delta(C-R^3)$ resonances [$\delta(C-Me)$ 2.33 and 2.30 p.p.m. for (28) in CDCl₃ at 35 °C; 8(C-H) 8.89 and 8.87 p.p.m. for (24) in CD_2Cl_2 at -50 °C]. The integration and

the broadness of the two allylic methyl bands of (18), (20). (22), (26), and (28) show that isomers (I) and (II) are present in ca. 1:1 ratio and interconvert rather rapidly on the n.m.r. time-scale at 35 °C. For complex (18) a coalescence temperature of ca. 70 °C has been observed in 1,1,2,2-tetrachloroethane. For the binuclear derivatives (23), (24), or (25), however, the interconversion rate is much higher as to give rise to a single $\delta(C-R^4)$ at 35 °C. At a lower temperature $(-50 \, ^{\circ}\text{C})$ the allylic methyl signal of (24) at 2.01 p.p.m. splits into two signals of equal intensity at 2.08 and 1.86 p.p.m., with a concomitant splitting of $\delta(C-R^3)$. Qualitatively, the rates depend on the substituent \mathbb{R}^3 in the order $\mathbb{P}h \simeq \mathbb{H} > \mathbb{M}e$, and on the ancillary ligand L in the order $AsPh_3 > P(C_6H_4Cl-p)_3$ $> PPh_3$, all other things being equal. In the fast exchange limit, the terminal allylic protons of the 2- $MeC_{3}H_{4}$ group appear as three separate resonances (singlets) of relative intensity 2:1:1, the more intense of which being slightly broad. This may be interpreted either as an ABCD spectrum with two coincident signals or as two overlapping AA'BB' spectra. In any case, the (I) \longrightarrow (II) interconversion does not involve any $\eta^3 \implies \sigma$ rearrangement of the allyl moiety. In the slow exchange limit, one would expect two more or less superimposed ABCD patterns, one for each $Pd(\eta^3-2-MeC_3H_4)$ group linked to the asymmetric chelating ligands which are not mirror images. This has been observed for complex (26) $(R^1 = C_6 H_4 OMe-p, R^2 = Me)$ in $CD_2 Cl_2$ at -40 °C, whereas, for the other derivatives with $R^1 = R^2 =$ C_6H_4OMe-p , the differences in chemical shift are so small that large overlapping occurs. The rate of (1) \rightarrow (11) interconversion is very much increased by a small amount of Cl- ions. As discussed earlier, in the system (28)-AsPh₄Cl this proceeds via a fast $\eta^3 \rightleftharpoons \sigma$ dynamic process of the allyl group so that the syn and anti protons, and those of the \mathbb{R}^3 and \mathbb{R}^4 groups of the binuclear cationic complex, coalesce into singlets at 2.91, 2.32, and 1.93 p.p.m., respectively. In the mixture (18)-AsPh₄Cl, however, a different mechanism is operating, since its spectrum at 35 °C (Table 2) is very similar to that obtained for (18) in 1,1,2,2-tetrachloroethane at high temperature. Various mechanisms can be proposed in order to account for the above spectral observations. The (I) \rightleftharpoons (II) interconversion via path (i) of Scheme 3 may involve either rotation of the chelated 1,2-bis-(imino)alkyl group about the Pd-C σ bond or loss of configuration of the cis-PdCl₂L unit probably through a Pd-Cl bond dissociation equilibrium (see previous discussion). The (I) \rightleftharpoons (II) interconversion via path (ii) may involve either rotation of the allyl group around its bond axis to palladium, or cis-trans isomerization of the asymmetric 1,2-bis(imino) ligand through cleavage of one Pd-N bond, or a 'flipping' motion of the allyl ligand. Mechanisms involving complete dissociation of the $Pd(\eta^{3}-2-R^{4}C_{3}H_{4})$ unit or simultaneous occurrence of both path (i) and (ii) at comparable rate can be ruled out as they would lead to one AA'BB' pattern. The catalytic activity of added Cl⁻ ions may take place either by path (i) (attack of Cl^- on the cis-PdCl₂L unit with loss of

configuration at the Pd centre) or by path (*ii*) [cleavage of one Pd-N bond upon attack of Cl⁻ on the Pd(η^3 -2-R⁴C₃H₄) unit, followed by *cis-trans* isomerization].

Crystal and Molecular Structure of Complex (18).—In order to establish definitely the formulation of the zwitterionic binuclear complexes (D), a single-crystal Xray diffraction study of a typical representative compound, (18), was carried out.

A PLUTO drawing ¹⁷ of the molecule is shown in Figure 4, which also gives the labelling scheme. Selected



FIGURE 4 Projection of complex (18) viewed along the normal to the five-membered chelate ring including Pd(2)

intramolecular distances and angles with their estimated standard deviations are listed in Table 3. The standard deviations for all the distances and angles between light atoms are rather high and reflect the low precision of the positional parameters (see Experimental section), owing to the disorder at MeOH-H₂O positions (in the unit cell there are four MeOH and four H₂O molecules of crystallization per eight molecules of complex), the relatively poor quality of the diffraction data, and the limited number of observed reflections. Because of the large uncertainties, comparison of lengths and angles is restricted to the ' inner core ' of the complex. Although both diastereoisomers (1) and (11) of complex (18) are observed in solution (see Scheme 3 and Table 2), only the enantiomers (1) precipitate during the crystallization process. The geometry around the Pd(1) atom is approximately square planar and the five-membered chelate ring, including the Pd(2) atom, shows only very small deviations from planarity. The Pd(2) co-ordination sphere also includes a non-planar 2-methylallyl unit, with C(5)

TABLE 3

Selected intramolecular distances (Å) and angles (°) for complex (18) with estimated standard deviations in parentheses

Pd(1)-Cl(1)	2.36(1)
$\mathbf{D}_{\mathbf{A}}(\mathbf{I}) = \mathbf{C}_{\mathbf{A}}(\mathbf{I})$	0 97(1)
Pu(1) = Ol(2)	2.37(1)
Pd(1) - P	2.26(1)
$\mathbf{P}_{\mathbf{A}}(\mathbf{u}) \sim \mathbf{C}(\mathbf{u})$	1 09/31
	0.15(0)
Pd(2) - C(4)	2.10(3)
Pd(2) - C(5)	2.16(3)
$D_{1}(0) = C(0)$	0 11(9)
Pu(2) = C(0)	2.11(3)
Pd(2) - N(1)	2.07(3)
Pd(2) - N(2)	2 08(2)
1((2)) + ((2))	1.00(2)
N(1) - C(1)	1.29(3)
C(1) - C(2)	1.55(4)
C(2) = N(2)	1 95(3)
O(2) = N(2)	1.25(3)
C(2) - C(3)	1.51(3)
N(1) - C(8)	1.48(3)
C(11) = O(1)	1 94(4)
U(11) = U(1)	1.34(4)
O(1) - C(14)	1.45(4)
$\mathbf{X}(2) - \mathbf{C}(15)$	1 51(3)
C(1) $C(2)$	1 49(4)
C(4) = C(3)	1.4.3(4)
C(4) - C(6)	1.36(4)
C(18) = O(2)	1 20(4)
	1.00(1)
C(2) = C(21)	1.48(3)
C(4) - C(7)	1.53(4)
D = C mean	1 99/9
r-c mean	1.82(2)
C–C(phenyl) mean	1.40(3)
$N(1) \rightarrow N(2)$	2 50(3)
$D_{1}(1) = D_{1}(2)$	4 99(1)
$Pa(1) \cdots Pa(2)$	4.88(1)
$Pd(2) \cdot \cdot \cdot C(1)$	2.98(3)
Cl(1) - Pd(1) - Cl(2)	91.2(3)
Cl(2) - Pd(1) - P	89 2(3)
D D D D D D D D D D	00/1)
P = Pa(1) = C(1)	92(1)
C(1) - Pd(1) - Cl(1)	88(1)
Cl(1) - Pd(1) - P	175 3(3)
C(a) D(b) C(b)	170/0)
CI(2) = Pa(1) = C(1)	179(1)
N(1) - Pd(2) - C(4)	143(1)
N(1) - Pd(9) - C(5)	114(1)
N(1) = D(2) = O(0)	
N(1) - Pd(2) - C(6)	177(1)
N(1) - Pd(2) - N(2)	74(1)
N(2) - Pd(2) - C(4)	137(1)
I(2) I I I(2) C(4)	197(1)
N(2) - Pd(2) - C(5)	170(1)
N(2) - Pd(2) - C(6)	107(1)
$C(A) = D_{1}(A) = C(5)$	20(1)
C(4) = P(12) = C(3)	00(1)
C(4) - Pd(2) - C(6)	37(1)
C(5) - Pd(2) - C(6)	65(1)
$D_1(0) = C(1) = C(0)$	110(0)
$\Gamma^{(2)} - C(4) - C(7)$	110(2)
C(5)-C(4)-C(7)	124(3)
Pd(2) - C(6) - C(4)	73(1)
$D_{1}(2) = C(0) = C(1)$	70(1)
P((2) - C(3) - C(4)	70(1)
C(5)-C(4)-C(6)	110(2)
C(6) - C(4) - C(7)	125(3)
$D_{I}(0) = N(1) = C(1)$	104(0)
Pa(2) = N(1) = C(1)	124(2)
Pd(2)-N(1)-C(8)	123(2)
C(1) - N(1) - C(8)	114(9)
$D_{1}(0) \rightarrow D_{1}(0) = C(0)$	110(0)
Pd(2) - N(2) - C(2)	118(2)
Pd(2) - N(2) - C(15)	119(2)
C(2) - N(2) - C(15)	123(2)
C(2) $R(2)$ $C(10)$	125(2)
N(1) - C(1) - Pd(1)	135(2)
N(1)-C(1)-C(2)	106(2)
Pd(h) - C(h) - C(h)	119(2)
C(1) $C(2)$ $N(2)$	110(2)
U(1) = U(2) = N(2)	118(2)
C(1)-C(2)-C(3)	118(2)
N(2) - C(2) - C(3)	125(2)
C(11) O(1) C(14)	100/0
U(11) = U(1) = U(14)	120(2)
C(18)=C(9)=C(91)	330/01
C(10) - C(2) - C(21)	118(2)
$Pd(1)-C(1) \cdots Pd(2)$	118(2) 169.4(7)
$Pd(1)-C(1) \cdots Pd(2)$ C-C-C(phenyl) mean	$118(2) \\ 169.4(7) \\ 120(2)$
$Pd(1)-C(1) \cdots Pd(2)$ C-C-C(phenyl) mean	118(2) 169.4(7) 120(2)

(0.09 Å) above the chelate ring plane and C(4), C(6) (-0.73, -0.02 Å, respectively) below it. The plane of the allyl group makes an angle of 107.4° with the Pd(2) co-ordinative plane, so that C(4) is tilted away from Pd(2). These structural features are normal for η^3 -2-

methylallyl complexes of palladium.¹⁸ The Pd(1) and Pd(2) co-ordination planes are roughly normal (81.9°) and C(1) links the two planes. The distance between the palladium atoms is 4.88 Å, with a $Pd(1)-C(1)\cdots$ Pd(2) angle of 169.4°. Within the allyl group the bond lengths and angles are similar to those found in the previous 2-methylallyl palladium structures,18.19 and the geometry of the groups out of the 'inner core' of the complex is normal. The two rings of the *p*-methoxyphenyl units are at a dihedral angle of 24.4° and make angles of 53.5 and 71.7° with the chelating ring, in line with the values observed in the adduct $CuCl_{2}$ (1).^{7b} The allyl moiety is η^3 -bonded to Pd(2) in an essentially symmetrical manner. The 1,2-bis(imino)propyl group acts as a $\sigma\sigma'$ -NN' chelating ligand, with Pd(2)-N($s\rho^2$) bond lengths of 2.07 and 2.08 Å, which are rather longer than the predicted value of 2.01 Å [based upon $r(Pd^{II}) =$ 1.31 and r(N) = 0.70 Å (Pauling radii)].²⁰ However, the difference $(ca. 2\sigma)$ is not significant and the observed distances are very close to those reported for other palladium-imino-nitrogen bonds.9,18c The PPh₃ ligand and the chelated 1,2-bis(imino)propyl group have essentially the same structural trans-influence, as indicated by the close Pd(1)-Cl(1) and Pd(1)-Cl(2) distances (2.36) and 2.37 Å, respectively). The Pd(1)-C(1) length [1.92(3)] Å) is considerably shorter than the sum of covalent radii for a Pd- $C(sp^2)$ bond ²⁰ and the values observed in other complexes containing a Pd-C(sp^2) σ -bond.^{66.7d} This may be ascribed to a relevant π contribution (d --- π^*_{imino}) which would reduce the formal negative charge on the cis-PdCl₂(PPh₃) metal centre. In this structure short range palladium-hydrogen interactions are likely to occur, as can be inferred from the $Pd(1) \cdots C(9)$ (3.25 Å) and $Pd(1) \cdots C(3)$ (3.19 Å) distances above and below the mean co-ordination plane. In particular, the interaction of the C(3) methyl protons (which may reach a minimum calculated distance of 2.5 Å) is reflected in the rather low-field chemical shift (2.96 p.p.m.) of this group in the ¹H n.m.r. spectrum of (18).

This study rules out the alternative formulation of complexes (D) (see below) which does not require any



separation of electrical charges and can be related to the structures of other compounds with four-membered N,C-chelating 1,2-bis(imino)alkyl groups.^{21,22}

EXPERIMENTAL

Physical Measurements.—The molecular weights were determined using a Knauer osmometer in 1,2-dichloro-

ethane at 37 °C. Conductivity measurements were carried out with a Philips PR9500 bridge at 20 °C. Proton n.m.r. spectra were recorded on a Varian EM-390 90 MHz spectrometer with SiMe₄ as internal standard. Electronic spectra in solution were recorded with a Bausch-Lomb Spectronic 210UV spectrophotometer in the range 650—250 nm at 25 °C, using quartz cells of 1 cm path length. Infrared spectra were recorded with a Perkin-Elmer 597 instrument, using hexachlorobutadiene mulls and NaCl plates in the range 4 000—1 300 cm⁻¹, and Nujol mulls and CsI plates in the range 1 700—250 cm⁻¹. Microanalyses were performed by A. Berton and G. Biasioli of the Microanalytical Laboratory, Instituto Radioelementi C.N.R., Padua.

Preparation of the 1,2-Bis(imino)alkylpalladium Derivatives (A), (1)—(8) and (27).—The complexes (1), (6)—(8), and (27) have been prepared by previously described methods.^{6a, 6c, 6d, 7a} The new compounds (2)—(5), all containing the 1,2-bis(p-methoxyphenylimino)propyl group, have been obtained by the same synthetic procedure as for (1), using the appropriate ligand L instead of PPh₃. For complex (5) (L = AsPh₃), the reaction takes ca. 12 h for completion, after addition of AsPh₃ to the mixture resulting from the initial reaction between cis-[PdCl₂(CNC₆H₄OMe-p)₂] and HgMe₂ (molar ratio $\simeq 1 : 1.5, 7$ h).

Due to the high solubility of (2) in benzene or CH_2Cl_2 , n-hexane was added for precipitation. In all cases, after elimination of the residual HgMeCl by sublimation, the products were conveniently purified by dissolving in the minimum volume of benzene (or CH_2Cl_2 , depending on solubility) and adding a double volume of ethanol. The mixture was concentrated at reduced pressure until the compounds began to precipitate, and stored at -20 °C to complete the crystallization. [Yields based on theoretical amount: (2) 70; (3) 83; (4) 68; (5) 60%.]

Preparation of the Binuclear Cationic Complexes (B), (9)-(17) and (28).--All these compounds have been prepared by a general method, which is described in detail for compound (9). The dimer $[{PdCl(\eta^3-2-MeC_3H_4)}_2]$ (0.1 g, 0.25 mmol) dissolved in dichloromethane (ca. 40 cm³) was treated with (1) (0.48 g, 0.5 mmol) and then with a solution of NaClO₄·H₂O (0.140 g, 1 mmol) in methanol (5 cm³). A white precipitate of NaCl was immediately formed and the solution became red-orange. After stirring for 15 min the reaction mixture was evaporated to dryness and the residue treated with dichloromethane and charcoal. After filtration, the clear solution was concentrated to a small volume at reduced pressure and the product was precipitated by addition of diethyl ether. The complex was purified by recrystallization * from dichloromethane-diethyl ether (0.46 g, 76%). High yields (75-90%) were also obtained for the other cationic compounds. In the reaction with (6), the reactants were initially mixed together at 0 °C. After stirring for 5 min, the mixture was worked-up at room temperature as quick as possible to give a satisfactorily pure product, (14), in 65% yield.

Preparation of the Binuclear Zwitterionic Complexes (D), (18)---(26).--These compounds can be prepared in good yields from the reactions of the 1,2-bis(imino)alkylpalladium derivatives (A) with [{PdCl(η^3 -2-R⁴C_3H_4)}₂] (R⁴ = H or Me; 1 : 1 molar ratio) either in chlorinated solvents (usually 1,2dichloroethane, but also dichloromethane, and chloroform) J. CHEM. SOC. DALTON TRANS. 1982

View Article Online

or in benzene at room temperature. Since the reaction rates are much higher in benzene, the use of this solvent is particularly convenient for reactions which are exceedingly slow in 1,2-dichloroethane. For instance, the reactions of (4), (8), and (3) require 8, 4, and 3 d respectively for completion in 1,2-dichloroethane, whereas in benzene the reaction times are reduced to 48, 24, and 24 h, respectively. Another advantage of benzene is that the products (D) precipitate on forming. The two general methods will be described in detail for the preparation of compound (18).

(a) Reaction in 1,2-dichloroethane. Compound (1) (0.48 g, 0.5 mmol) dissolved in 1,2-dichloroethane (ca. 40 cm³) was reacted with $[{PdCl(\eta^3-2-MeC_3H_4)}_2] (0.2 \text{ g}, 0.5 \text{ mmol}).$ After 24 h, the reaction mixture was treated with activated charcoal, filtered off, and the resulting orange solution concentrated to a small volume at reduced pressure. The product (18) was precipitated almost quantitatively by addition of diethyl ether. Because of the presence of a small amount of the second product, $[PdCl(\eta^3-2-MeC_3H_4)-$ (PPh₃)] (indicated by the ¹H n.m.r. spectrum), complex (18) was recrystallized twice from the same solvents (0.32 g)72%). The mother-liquor from the first precipitation was concentrated to small volume. Upon addition of n-hexane, a yellow precipitate was obtained which was recrystallized from 1,2-dichloroethane-n-hexane to give an analytically pure sample of $[PdCl(\eta^{3}-2-MeC_{3}H_{4})(PPh_{3})]$ (0.23 g, 50%, based on the theoretical amount) (Found: C, 57.3; H, 4.7; Cl, 7.9. C22H22ClPPd requires C, 57.55; H, 4.85; Cl, 7.70). This compound was further identified by comparing its i.r. and ¹H n.m.r. spectra with those of an authentic sample prepared by the bridge-splitting reaction of [{PdCl(η^3 - $2-MeC_{3}H_{4}$ and with PPh₃. The same procedure was used for the preparation of (19) (reaction time 24 h, yield 75%); (20) (8 h, 84%); (23) (1 h, 70%); (24) (2 h, 76%); and (25) (5 h, 68%). In all cases, the second product (E) of reaction (2), $[PdCl(\eta^3-2-R^4C_3H_4)L]$, was isolated and identified e.g., analysis of $[PdCl(\eta^3-2-MeC_3H_4)\{P(C_6H_4Cl-p)_3\}]$ (Found: C, 46.8; H, 3.3; Cl, 25.0. C22H19Cl4PPd requires C, 46.95; H, 3.40: Cl, 25.20). The binuclear complex (18) can also be prepared from the reaction of the cationic compound (9) (0.6 g, 0.5 mmol) with $[\text{AsPh}_4][\text{PdCl}_2(\eta^3 - 2 - \text{MeC}_3 H_4)]$ (0.31 g,0.5 mmol) in 1,2-dichloroethane (20 cm³). After filtration of the sparingly soluble salt [AsPh₄][ClO₄], the reaction mixture was worked-up as described above.

(b) Reaction in benzene. Complex (1) (0.48 g, 0.5 mmol) was reacted with $[{PdCl(\eta^{3}-2-MeC_{3}H_{4})}_{2}]$ (0.2 g, 0.5 mmol) in benzene (40 cm³). A red-orange solution was initially obtained, from which yellow microcrystals of (18) ·C₆H₆ began to separate after a few minutes. The presence of a molecule of benzene of crystallization was indicated by elemental analysis (Found: C, 56.5; H, 4.8; N, 2.9; Cl, 7.4. C45H45Cl2N2O2PPd requires C, 56.25; H, 4.70; N, 2.90; Cl, 7.40%) and by g.l.c. analysis (gas liquid chromatography) of a dichloromethane solution. The reaction mixture was set aside for 6 h and then diethyl ether (20 cm³) added in order to complete the precipitation. After filtration, the product was recrystallized twice from 1,2-dichloroethane-diethyl ether, whereupon the benzene of crystallization is lost (0.33 g, 75%). The mother-liquor from the first precipitation was worked-up in the same way as for the reaction in 1,2dichloroethane to yield 0.25 g of $[PdCl(\eta^3-2-MeC_3H_4) (PPh_{a})$

The same procedure was followed for the preparation of (21) (reaction time 24 h, yield 80%); (22) (48 h, 78%); and (26) (24 h, 75%).

^{*} General procedure: compounds were dissolved in the minimum volume of chlorinated solvent, the second solvent added until incipient precipitation (stirring), and set aside for 12-24 h.

Preparation of the Ionic Compound (29).—Complex (27) (0.21 g, 0.25 mmol) was reacted with $[\{PdCl(\eta^{3}-2-MeC_{3}H_{4})\}_{2}]$ (0.1 g, 0.25 mmol) in benzene (ca. 20 cm³). An immediate change from vellow to orange occurred. After stirring for 10 min, the yellow product (29) began to precipitate. The mixture was set aside (without stirring) for 30 min, and then the solid was filtered off and washed with cold benzene (0.16)g, 53%). No further purification was required.

TABLE 4

Atomic co-ordinates $(\times 10^4)$ for complex (18), with estimated standard deviations in parentheses

tom	X	У	z
Pd(1)	2.949(1)	8 071(1)	7 487(2)
2d(2)	2 957(1)	6 320(1)	9 196(2)
uni	2 376(5)	8 771(5)	8 244(5)
1(9)	$\frac{2}{3} \frac{010(0)}{054(5)}$	8 950(4)	6 698(5)
>	3 416(4)	7 374(4)	6 739(5)
)(I)	5 957(19)	8 000(13)	8 608(13)
)(1))(9)	190(12)	5 005(11)	0 125(19)
)(2))(2) *	-120(12)	4 791(10)	075(91)
)()) *	4 010(18)	4 731(19)	1 200/221
J(4) *	3 374(24)	4204(24)	1 209(20)
N(1)	3 233(13)	7 109(12)	8 383(14)
N(2)	2131(12)	0 340(11)	8 612(13)
J(I)	2 854(15)	7 371(14)	8 136(17)
$\mathcal{L}(2)$	$2\ 183(14)$	6 998(14)	8 181(16)
2(3)	1.638(15)	7 212(14)	7 710(16)
C(4)	$3 \ 335(20)$	5 474(19)	9.734(21)
C(5)	3 693(16)	6 057(17)	9 938(19)
C(6)	2681(18)	5 551(17)	9.868(21)
C(7)	$3\ 627(19)$	4 913(19)	9 306(22)
C(8)	3899(16)	7 413(16)	8 614(17)
C(9)	4 029(16)	8 080(17)	8 703(17)
C(10)	4676(17)	8 351(15)	8 736(18)
C(11)	$5\ 206(20)$	7 889(20)	8 664(20)
C(12)	5114(16)	7 218(17)	8 598(17)
C(13)	4 451(16)	6 941(16)	8 591(17)
2(14)	5,997(21)	8 792(23)	8 635(22)
(15)	1 509(16)	6144(16)	8 711(17)
(16)	981(17)	6462(16)	9 025(18)
$\Sigma(17)$	421(16)	6 059(17)	9 186(19)
(18)	418(18)	5 416(19)	8 998(20)
	930(15)	5 107(15)	8 705(17)
2(1 <i>0</i>) 2(90)	1 509(17)	5 489(17)	8 531/18)
2(20) 2(91)	799(17)	5 210/16)	0 431(18)
2(21) 2(99)	2 0 0 0 (17)	7 994(15)	6 006(17)
2(22)	2 920(17)	7 224(13)	5 970(20)
ン(ゴラ) こ(コオ)	2 389(17)	7 047(10)	5 900(20)
2(24) 2(95)	2.011(19) 3.169(10)	7 003(19)	0 290(21) 4 945(01)
2(20) 2(90)	2 103(18)	7 037(18)	4 849(21)
2(20) 2(27)	2 094(18)	0.014(17)	4 981(22)
(27)	3 073(20)	6 708(19)	3 301(22)
(28)	4 202(17)	7 698(17)	6 410(20)
(29)	4 410(18)	7 641(18)	5 742(22)
(30)	5 006(22)	7 928(19)	5 539(21)
2(31)	$5\ 394(18)$	8 272(18)	6 005(22)
C(32)	$5\ 186(21)$	8 329(20)	$6\ 674(25)$
C(33)	4 590(18)	8 042(18)	$6\ 876(20)$
C(34)	$3\ 613(16)$	6 514(16)	7 001(18)
C(35)	3 080(19)	$6 \ 085(19)$	7 107(21)
C(36)	3 190(20)	5 440(20)	7 345(23)
C(37)	3833(21)	5 225(19)	7 477(24)
C(38)	4 366(20)	5653(20)	7 371(23)
C(39)	4 256(19)	6 298(19)	7 133(20)
C(40) *	3 830(28)	4 484(29)	1 778(33)
	* Occupat	ncy factor: 0.5.	

X-Ray Crystallography of (18).—Crystals of compound (18) were grown by very slow evaporation of a solution in MeOH-CH₂Cl₂ (3:1 v/v). The plates showed a strong tendency to crack and to twin. Eventually a cubic-shaped crystal was found which was not cracked or twinned which was used for the structural determination [C₃₉H₃₉Cl₂N₂O₂-

For details see Notices to Authors No. 7, J. Chem. Soc., Dalton Trans., 1981, Index issue.

 $PPd_2(0.5MeOH \cdot 0.5H_2O)$, orthorhombic, a = 20.224(5), b = 20.073(8), c = 19.829(9) Å, U = 8.050 Å³, Z = 8, Z $D_{\rm c} = 1.50$ g cm⁻³, $\mu = 10.9$ cm⁻¹ for Mo-K_a radiation $(\lambda = 0.7107 \text{ Å})$, space group *Pbca*]. The cell parameters were obtained with a Philips PW1100 computer-controlled diffractometer from 25 strong reflections at $20 \le 2\theta \le 27^{\circ}$. Intensities were collected from the crystal of dimensions $0.18 \times 0.20 \times 0.18$ mm with graphite monochromated Mo- K_{α} radiation. An unique data set was collected out of $2\theta = 36^{\circ}$ by the ω -scan technique with a scan range of $1.4 \pm 0.3 \tan\theta$ and a scan rate of $0.04^{\circ} \text{ s}^{-1}$; no reflection was sufficiently strong to require the insertion of an attenuator filter. The intensities of 3 256 independent reflections were measured; of these only 1 795 obeyed the condition $I > 3\sigma(I)$ and were used in subsequent calculations. The intensities were processed in the usual manner.23 No extinction or absorption corrections were applied. The structure was solved by the heavy-atom method. In the least-squares refinement the function $\Sigma w (|F_0| - |F_c|)^2$ was minimized, with unit weight to each reflection.

A weighting scheme based on counter statistics was unsuccessful, probably owing to systematic errors. In particular, inspection of F_0/F_c values showed a rather poor agreement among weak reflections attributable to an unsound signal-to-noise ratio of the scintillation counter. The scattering factors used were those of ref. 24. The major calculations for the analysis were made with the SHELX 76 program.²⁵ Calculations were all performed on the Consorzio Interuniversitario Italia Nord-Orientale CDC 7600 computer system. A number of cycles of block-diagonal least-squares refinement with isotropic thermal parameters, followed by difference syntheses, enabled location of all the non-hydrogen atoms and led to convergence with R = 0.12. A difference synthesis at this stage showed evidence of anisotropy in the motion of the heavy atoms together with three unexpected peaks of 1.27, 1.15, and 0.98 e Å⁻³. These peaks were attributed to MeOH and H₂O from the recrystallization mixture and the occupation factors for these sites were fixed at 0.5 in the successive refinement procedure. Thermal motions for these atoms are no greater than those observed in the core of the complex. Further full-matrix refinement, with anisotropic thermal parameters only for the heavy atoms and with the phenyl carbon atoms of the PPh₃ group constrained to fit a rigid regular hexagon to achieve a better 'observations-parameters' ratio, converged to R = 0.086. A final difference synthesis showed maxima no greater than 0.58 e Å⁻³.

Table 4 shows the final position parameters of the atoms; thermal parameters and the observed and calculated structure factors are listed in Supplementary Publication No. SUP 23297 (14 pp.).*

[1/1455 Received, 17th September, 1981]

REFERENCES

¹ C. M. Lukehart and G. P. Torrence, Inorg. Chem., 1979, 18, 3150; D. T. Hobbs and C M. Lukehart, *Inorg. Chem.*, 1980, **19**, 1811, and refs. therein.

² G. Minghetti, F. Bonati, and G. Banditelli, Inorg. Chem., 1976, 15, 2649.

¹⁹ J. Lewis and C. Oldham, J. Chem. Soc. A, 1966, 1456; Y.
 ³ J. Lewis and K. Nakamoto, *Inorg. Chem.*, 1975, 14, 63.
 ⁴ G. Minghetti, G. Banditelli, and F. Bonati, *Chem. Ind.* (London), 1977, 123; J. Chem. Soc., Dalton Trans., 1979, 1851.

⁶ R. P. Sperline and D. M. Roundhill, Inorg. Chem., 1977, 16, 2612.

⁶ (a) B. Crociani, M. Nicolini, and R. L. Richards, J. Organomet. Chem., 1976, 104, 259; (b) B. Crociani, G. Bandoli, and D. A. Clemente, *ibid.*, 1980, 184, 269; (c) B. Crociani and R. L. Richards, *ibid.*, 1978, 154, 65; (d) P. L. Sandrini, A. Mantovani, and B. Crociani, *ibid.*, 1980, 185, C13.

⁷ (a) B. Crociani, M. Nicolini, and R. L. Richards, J. Chem. Soc., Dalton Trans., 1978, 1478; (b) B. Crociani, G. Bandoli, and D. A. Clemente, J. Organomet. Chem., 1980, 190, C97; (c) B. Crociani, M. Nicolini, and A. Mantovani, *ibid.*, 1979, 177, 365; (d) B. Crociani, U. Belluco, and P. L. Sandrini, ibid., 1979, 177,

385.
⁸ B. Crociani, T. Boschi, and P. Uguagliati, *Inorg. Chim. Acta*, 1981, **48**, 9.

⁹ A. J. Deeming, I. A. Rothwell, M. B. Hursthouse, and K. M.

Abdul Malik, J. Chem. Soc., Dalton Trans., 1979, 1899. ¹⁰ K. Vrieze, in 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' eds. L. M. Jackman and F. A. Cotton, Academic Press, New York, 1975, p. 441.

¹¹ B. Crociani, unpublished data.

12 P. L. Sandrini, A. Mantovani, P. Uguagliati, and B. Crociani, Inorg. Chim. Acta, 1981, 51, 71.

¹³ B. Crociani, P. Uguagliati, R. Bertani, and L. Calligaro, Inorg. Chim. Acta, 1980, **45**, L75; B. Crociani, P. Uguagliati, U. Belluco, and M. Nicolini, unpublished data. ¹⁴ H. tom Dieck and I. W. Renk, *Chem. Ber.*, 1971, **104**, 110;

H. tom Dieck, K. D. Franz, and F. Hohmann, ibid., 1975, 108, 163; R. W. Balk, D. J. Stufkens, and A. Oskam, Inorg. Chim. *Acta*, 1978, 28, 133; L. H. Staal, D. J. Stufkens, and A. Oskam, *ibid.*, 1978, 26, 255.
 ¹⁵ H. van der Poel, G. van Koten, K. Vrieze, M. Kokkes, and

C. H. Starn, Inorg. Chim. Acta, 1980, 39, 197, and refs. therein.

¹⁶ I. D. Rae, B. E. Reichert, and B. O. West, J. Organomet. Chem., 1974, 81, 227. ¹⁷ W. D. S. Motherwell, PLUTO Program for Plotting Molecular

and Crystal Structures, Cambridge University, 1976. ¹⁸ (a) C. R. Mason and A. G. Wheeler, *J. Chem. Soc. A*, 1968, 2549; (b) A. E. Smith, *Acta Crystallogr.*, 1965, **18**, 331; (c) B. M. Gatehouse, B. E. Reichert, and B. O. West, *Acta Crystallogr.*, Sect. B, 1974, 30, 2451.

¹⁹ P. M. Bailey, E A. Kelley, and P. A. Maitlis, J. Organomet. Chem., 1978, 144, C52; P. Hendriks, K. Olic, and K. Vrieze, Cryst. Struct. Commun., 1975, 4, 611; H. A. Graf, R. Hüttel, G. Nagorsen, and B. Rao, J. Organomet. Chem., 1977, 136, 389; W. E.
 Oberhannsli and L. F. Dahl, *ibid.*, 1965, 3, 43; M. R. Churchill and R. Mason, Nature (London), 1964, 204, 777; R. Mason and D. R. Russell, Chem. Commun., 1966, 26.
 ²⁰ L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Correct University Decrement these New York, 1960, a, 204

Cornell University Press, Ithaca, New York, 1960, p. 224. ²¹ Y. Yamamoto and Y. Yamazaki, J. Organomet. Chem., 1975,

90, 329.

²² J. M. Bassett, M. Green, J. A. K. Howard, and F. G. A. Stone, J. Chem. Soc., Dalton Trans., 1980, 1779.

²³ J. Hornstra and B. Stubbe, PW1100 Data Processing Program, Philips Research Laboratories, Eindhoven, Netherlands, 1972.

²⁴ D. T. Cromer and J. B. Mann, Acta Crystallogr., Sect. A, 1968, 24, 321.

²⁵ G. M. Sheldrick, SHELX 76, program for crystal structure determination, Cambridge University, 1976.