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Synthesis of cyclometallated compounds of *N*-(3-methoxy)benzylidenecyclohexylamine. Crystal structure of the novel cyclometallated bipalladium(II) complex $[(\text{mbcy-}C6,N)\text{Pd}\{\mu\text{-Ph}_2\text{PC}(=\text{CH}_2)\text{PPh}_2\}(\mu\text{-Cl})\text{Pd}(\text{mbcy-}C6,N)]\text{Cl}\cdot 4\text{CHCl}_3$*

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Abstract

The reaction of palladium(II) acetate with *N*-(3-methoxy)benzylidenecyclohexylamine (Hmbcy) in glacial acetic acid yields the acetato-bridged complex **1**. From this the halide-bridged dimers **2** and **3** are synthesized. Treatment of **2** and **3** with bis(diphenylphosphino)methane (dppm) or 1,1-bis (diphenylphosphino)ethene (vdpp) in a 1:1 molar ratio gives the dinuclear species **4**, **5** and **8** with the two palladium atoms bridged by a diphosphine and a halogen atom. Conductivity measurements show that they are 1:1 electrolytes. Treatment of **2** and **3** with dppm or vdpp and $NaClO_4$ or NH_4PF_6 yields the mononuclear species **6**, **7** and **9** with the diphosphine as a chelating ligand. These complexes are also 1:1 electrolytes. The complexes have been characterized by IR, $^{31}P\{^1H\}$ and ^1H NMR spectroscopies. The crystal structure of the novel bipalladium(II) complex **8** has been determined: $P2_1/n$; $a = 1166.7(3)$, $b = 2314.2(4)$, $c = 2603.3(5)$ pm, $\beta = 100.76(4)°$ and $Z = 4$.

Introduction

Cyclometallated complexes have been extensively studied and reviews covering complexes with different donor atoms have appeared [1–3]. In the past we have studied cyclometallated complexes derived from Schiff base ligands [4] and also from phenylimidazole ligands [5] with different metals in each case. The halide bridged species react with monodentate phosphines to give mononuclear compounds and with bidentate phosphines to give dinuclear compounds with one bridging ligand, i.e. the diphosphine. In the present paper we report a new type of cyclometallated complex with Schiff bases in which the two metal centers are bridged by a diphosphine ligand and a halogen atom to give dinuclear 1:1 electrolyte species. These species are obtained when the halide-bridged dimer/diphosphine ratio is 1:1. When the molar ratio is 1:2 mononuclear complexes are obtained with the phosphine ligand chelated to the metal atom. A crystal structure determination has been carried out for the compound $[(\text{mbcy-}C6,N)\text{Pd}\{\mu\text{-Ph}_2\text{PC}(=\text{CH}_2)\text{PPh}_2\}(\mu\text{-Cl})\text{Pd}(\text{mbcy-}C6,N)]\text{Cl}\cdot 4\text{CHCl}_3$ (**8**).

Experimental

The experimental techniques applied were the same as those reported in recent papers from this laboratory [6].

[Pd(mbcy-C6,N)(O₂CMe)]₂ (1)

In a 100 ml round-bottomed flask, 0.32 g (1.47 mmol) of *N*-(3-methoxy)benzylidenecyclohexylamine and 0.30 g (1.34 mmol) of palladium(II) acetate were added to 25 ml of glacial acetic acid to give an orange solution. After heating under reflux for 2 h the reaction mixture was cooled to room temperature and the acetic acid removed under vacuum. The residue was diluted with water and extracted with dichloromethane. The combined extracts were dried over anhydrous sodium sulfate, filtered and then concentrated *in vacuo* to give an orange solid, which

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was chromatographed on a column of silica gel; elution with dichloromethane removed unchanged starting material, while elution with dichloromethane/1% ethanol gave the desired complex as an orange powder after concentration.

[Pd(mbcy-C6,N)(X)]₂: X=Cl (2); Br (3)

To a solution of 0.32 g (0.42 mmol) of the acetato-bridged dimer in acetone (5 ml) was added a solution of sodium chloride or bromide in water (*c.* 10^{-2} mol l^{-1}). A solid immediately precipitated. After stirring for 1 h at room temperature, the solid was filtered off and dried *in vacuo.*

[(mbcy-C6,N)Pd(μ-Ph₂PCH₂PPh₂)(μ-X)Pd-(mbcy-C6,N)]X: X=Cl (4); Br (5)

To a stirred suspension of **2** (30.55 mg, 0.043 mmol) or of **3** (30.52 mg, 0.038 mmol) in acetone (10 ml) was added $Ph_2PCH_2PPh_2$ in a 1:1 molar ratio (16.39 mg, 0.043 mmol and 14.57 mg, 0.038 mmol, respectively). After stirring for 1 h at room temperature water was added and the resulting precipitate was filtered off and dried *in vacuo.*

[Pd(mbcy-C6,N)(Ph₂PCH₂PPh₂-P,P)]X: X=ClO₄ (6); PF₆ (7)

To a stirred suspension of 30.09 mg (0.042 mmol) of **2** in acetone (10 ml) were added 32.29 mg (0.084 mmol) of $Ph_2PCH_2PPh_2$ and 10.28 mg (0.084 mmol) of $NaClO_4$ (**6**) or 13.69 mg (0.084 mmol) of NH_4PF_6 (**7**). The mixture was stirred at room temperature for 2 h. Water was then added and the mixture stirred for a further 1 h. The resulting precipitate was filtered off and dried *in vacuo.*

[(mbcy-C6,N)Pd{μ-Ph₂PC(=CH₂)PPh₂}(μ-Cl)Pd-(mbcy-C6,N)]Cl (8)

To a stirred suspension of 90.46 mg (0.126 ml) of **2** in acetone (10 ml) was added 50.06 mg (0.126 mmol) of $Ph_2PC(=CH_2)PPh_2$. The mixture was stirred at room temperature for 2 h. Water was added and the resulting precipitate was filtered off and dried *in vacuo.* Recrystallization from chloroform/n-hexane afforded single crystals.

[Pd(mbcy-C6,N)(Ph₂PC(=CH₂)PPh₂-P,P)]PF₆ (9)

The compound was made similarly to **6** or **7** from 30.58 mg (0.038 ml) of **2**, 30.11 mg (0.076 mmol) of $Ph_2PC(=CH_2)PPh_2$ and 12.39 mg (0.076 mmol) of NH_4PF_6.

Analytical data, yields and colors of the complexes as well as conductivity data are given in Table 1.

8 crystallizes in the monoclinic space group $P2_1/n$ with four molecules per unit cell. Crystal data and parameters for data collection and structure determination are summarized in Table 2. Positional parameters are given in Table 3. Cell dimensions were determined on a CAD-4 four circle diffractometer by least-squares fitting of 18 high angle reflections. The intensity measurement in the range of $3<\theta<22°$ with ω/θ-scan and Mo Kα radiation (graphite monochromator) resulted in 8932 intensities. After normal corrections and averaging, 5390 independent intensities with $I>3\sigma(I)$ remained for further calculations. For the structure determination the centrosymmetric space group $P2_1/n$ was assumed due to the observed extinctions. The positions of the Pd atoms were obtained from a Patterson synthesis. The model was then completed by subsequent difference Fourier maps. The hydrogen positions calculated geometrically were included in the refinement with fixed isotropic temperature factors of $B_{iso}=5\times10^4$ pm^2. All non-H atoms were refined with anisotropic thermal parameters resulting in a final R value of 0.041. See also 'Supplementary material'.

Results and discussion

The compounds **1**, **2** and **3** which were necessary precursors for the synthesis of the phosphine complexes were prepared and fully characterized by C, H and N elemental analyses, $^{31}P\{^1H\}$ and ^1H spectroscopies (Tables 1, 4 and 5).

Treatment of *N*-(3-methoxy)benzylidenecyclohexylamine with palladium(II) acetate gave the acetato-bridged dimer as an orange solid. The separation of the ν(COO) vibrations shows that the acetato group is a bridging ligand (Table 5) [10]. The shift of the ν(C=N) vibration towards lower wavenumbers and the shift of the imine proton signal towards lower frequency in the ^1H NMR spectrum indicate that the palladium atom is bonded through the nitrogen atom of the C=N bond (Tables 4 and 5) [11–13]. Compound **1** can in principle exist in either a *cis* or a *trans* arrangement, however the ^1H NMR spectrum shows only one signal for the acetato methyl groups indicating only one isomer present, i.e. *trans*. For the *cis* isomer one would observe two signals for the acetato groups. Similar results have been obtained by us in previous papers where single crystal X-ray determinations have confirmed the spectroscopic data [14].

As we have also described before the ^1H NMR data allow us to determine which phenyl carbon atom is bonded to the metal atom [15]. If metallation takes place through the C(2) atom one would observe a complex multiplet for protons H4, H5 and H6. However, if the metallated carbon atom is C(6), a much more simple spectrum is expected with a doublet of doublets for protons H4 and H5 (AB

TABLE 1. Analytical data, colour and yields of the complexes

Compound	Colour	Yield (%)	Analytical data: found(calc.) (%)			
			C	H	N	Λ_M[a]
1	orange	69	50.2(50.3)	5.3(5.5)	3.8(3.7)	
2	yellow	75	45.7(44.1)	4.9(4.8)	3.6(3.6)	
3	yellow	70	38.4(41.7)	3.2(3.4)	4.9(4.5)	
4	pale yellow	63	57.5(57.8)	5.6(5.3)	2.8(2.5)	104
5	pale yellow	72	52.2(53.5)	5.0(4.9)	2.4(4.3)	110
6	orange	95	57.4(58.0)	5.2(5.0)	1.6(1.7)	101
7	white	95	53.4(54.9)	4.9(4.7)	1.5(1.6)	97
8	yellow	89	58.9(59.3)	5.5(5.3)	2.1(2.5)	102
9	orange	95	58.7(58.6)	4.9(4.9)	1.5(1.7)	98

[a] Λ_M values in ohm^{-1} cm^2 mol^{-1}.

TABLE 2. Data collection and structure refinement parameters

Formula	$C_{54}H_{58}Cl_2P_2O_2N_2Pd_2 \cdot 4CHCl_3$
Molecular weight	1590.24
Space group	$P2_1/N$
Lattice parameters	
a (pm)	1166.7(3)
b (pm)	2314.2(4)
c (pm)	2603.5(5)
β (°)	100.76(4)
Volume, V (10^6 pm^3)	6905.6
Formula units, Z	4
Density, ρ_x (g cm^{-3})	1.529
$F(000)$	3200
Diffractometer used	CAD4, ENRAF-NONIUS
Radiation, λ	Mo Kα (0.71073 Å)
Method of intensity measurements	ω/θ
Absorption coefficient, μ (cm^{-1})	11.461
Method used for absorption correction	DIFABS [7]
Maximum value of sin θ/λ reached in intensity measurement (Å^{-1})	0.5269
Total no. reflections measured	8932
No. observed reflections	5390
Criterion for observed reflections	$I > 3\sigma(I)$
Method used to solve structure	Patterson and subsequent difference Fourier
Method locating hydrogen atoms	calculated geometrically (hydrogen) atoms of methyl, methylen, methine groups and solvent molecules not calculated)
Method refining hydrogen atoms	only included in structure factor calculation
Weighting scheme	$1/\sigma^2$
No. parameters refined	722
R	0.041
R_w	0.044
Computer used	DEC Micro VAXII
Programs used	VAXSDP [8], SCHAKAL [9]

pattern) and a singlet for H2, plus further splitting of the H2 and H4 resonances due to coupling between them. Thus, in the ^{1}H NMR spectrum of **1** we observe a doublet at 6.95 ppm, a doublet at 6.70 ppm and a doublet of doublets at 6.65 ppm (^3J(H4H5) = 7.6 Hz, ^4J(H2H4) = 1.5 Hz) assigned to H5, H2 and H4, respectively (Table 4). This shows that palladation is through the C(6) carbon atom.

Reaction of **1** with sodium chloride or bromide gave the chloro-bridged dimer **2** and the bromo-bridged dimer **3**, respectively, as air-stable solids (see 'Experimental', Table 1 and Fig. 1). The bridging unit (PdX_2Pd) is asymmetric due to the differing *trans* influence of the phenyl carbon atom and of the nitrogen atom and thus two ν(Pd–X) bands appear in the IR spectrum: 319, 257 cm^{-1} (X = Cl)

TABLE 3. Positional and equivalent isotropic displacement parameters B_{eq} along with e.s.d.s for $[Pd_2(\mu\text{-}Cl)\{\mu,\eta\text{-}(Ph_2P)_2C{=}CH_2\}(C_{14}H_{18}NO)_2]Cl\cdot 4CHCl_3$

Atom	x	y	z	B_{eq} (Å^2)
Pd(1)	0.36990(5)	0.06482(3)	0.15481(2)	3.11(1)
Pd(2)	0.13161(5)	0.00849(3)	0.23332(2)	3.26(1)
Cl(1)	0.5105(2)	0.7526(1)	0.01202(9)	561(6)
Cl(12)	0.1888(2)	0.01066(9)	0.14733(7)	3.86(4)
Cl(101)	0.6481(4)	0.3794(2)	0.9123(2)	15.2(2)
Cl(102)	0.7458(4)	0.2703(2)	0.8988(2)	13.1(1)
Cl(103)	0.8112(4)	0.3319(3)	0.9922(2)	17.6(2)
Cl(201)	0.1897(3)	−0.1760(2)	0.4170(1)	8.48(9)
Cl(202)	0.1956(4)	−0.1019(2)	0.5053(1)	10.3(1)
Cl(203)	0.3713(3)	−0.1874(2)	0.5068(1)	8.82(9)
Cl(301)	0.2683(3)	0.8829(2)	0.0472(2)	10.1(1)
Cl(302)	0.3840(3)	0.9161(2)	−0.0360(1)	9.4(1)
Cl(303)	0.4985(3)	0.9271(2)	0.0693(1)	10.9(1)
Cl(401)	0.2533(4)	0.3063(2)	0.8607(1)	12.0(1)
Cl(402)	0.2783(5)	0.1869(2)	0.8520(3)	18.0(2)
Cl(403)	0.9302(4)	0.2418(3)	0.3151(2)	16.9(2)
P(1)	0.4603(2)	0.00776(9)	0.22007(7)	2.98(4)
P(2)	0.2619(2)	−0.06186(9)	0.25985(7)	3.08(4)
O(14)	0.7108(5)	0.2716(3)	0.1744(2)	5.2(2)
O(214)	−0.1707(5)	0.0033(3)	0.4040(3)	7.3(2)
N(1)	0.3133(5)	0.1147(3)	0.0876(2)	3.4(1)
N(2)	0.0163(5)	0.0778(3)	0.2174(3)	4.4(2)
C(1)	0.3837(6)	−0.0608(3)	0.2239(3)	3.1(2)
C(2)	0.4087(7)	−0.1073(4)	0.1976(3)	4.2(2)
C(3)	0.3819(7)	0.1569(3)	0.0821(3)	3.8(2)
C(11)	0.4949(6)	0.1257(3)	0.1668(3)	3.4(2)
C(12)	0.4810(7)	0.1658(3)	0.1265(3)	3.5(2)
C(13)	0.5507(7)	0.2146(3)	0.1264(3)	3.7(2)
C(14)	0.6363(7)	0.2247(3)	0.1690(3)	4.0(2)
C(15)	0.6526(7)	0.1863(3)	0.2104(3)	3.9(2)
C(16)	0.5827(7)	0.1369(4)	0.2089(3)	3.8(2)
C(17)	0.6915(9)	0.3134(4)	0.1333(4)	7.1(3)
C(21)	0.2152(7)	0.1005(4)	0.0449(3)	3.8(2)
C(22)	0.1719(8)	0.1496(4)	0.0075(3)	5.3(2)
C(23)	0.0658(9)	0.1301(5)	−0.0323(4)	6.8(3)
C(24)	0.0935(9)	0.0786(5)	−0.0617(4)	7.1(3)
C(25)	0.1433(8)	0.0295(5)	−0.0260(4)	6.4(3)
C(26)	0.2474(7)	0.0488(4)	0.0154(3)	4.7(2)
C(31)	0.6060(6)	−0.0169(3)	0.2153(3)	3.4(2)
C(32)	0.6628(7)	−0.0588(4)	0.2487(3)	4.3(2)
C(33)	0.7727(8)	−0.0784(4)	0.2435(4)	5.8(2)
C(34)	0.8214(7)	−0.0575(4)	0.2027(4)	5.8(2)
C(35)	0.7650(7)	−0.0175(4)	0.1685(4)	5.3(2)
C(36)	0.6568(7)	0.0027(4)	0.1746(3)	4.1(2)
C(41)	0.4698(6)	0.0447(3)	0.2829(3)	3.4(2)
C(42)	0.3849(7)	0.0862(3)	0.2852(3)	3.7(2)
C(43)	0.3876(8)	0.1192(4)	0.3294(3)	5.1(2)
C(44)	0.4780(9)	0.1129(4)	0.3711(4)	5.9(2)
C(45)	0.5648(8)	0.0727(4)	0.3692(3)	5.3(2)
C(46)	0.5608(7)	0.0383(4)	0.3251(3)	4.2(2)
C(100)	0.6975(9)	0.3160(6)	0.9440(4)	8.1(3)
C(200)	0.2234(8)	−0.1713(4)	0.4856(4)	5.7(2)
C(203)	−0.0477(7)	0.0847(4)	0.2518(4)	4.9(2)
C(211)	0.0496(6)	−0.0009(3)	0.2939(3)	3.2(2)
C(212)	−0.0364(7)	0.0422(4)	0.2942(3)	4.1(2)
C(213)	−0.1076(7)	0.0424(4)	0.3309(3)	5.3(2)
C(214)	−0.0977(7)	0.0003(4)	0.3682(3)	4.6(2)
C(215)	−0.0178(7)	−0.0433(4)	0.3681(3)	4.3(2)
C(216)	0.0544(6)	−0.0443(3)	0.3303(3)	3.8(2)
C(217)	−0.160(1)	−0.0395(5)	0.4443(4)	7.9(3)
C(221)	0.0119(8)	0.1191(4)	0.1739(4)	5.3(2)
C(222)	−0.105(1)	0.1374(5)	0.1484(5)	9.0(3)
C(223)	−0.101(1)	0.1780(5)	0.1020(4)	7.9(3)
C(224)	−0.025(1)	0.2285(4)	0.1183(5)	8.0(3)
C(225)	0.090(1)	0.2107(5)	0.1453(5)	9.4(4)
C(226)	0.0904(9)	0.1690(5)	0.1903(4)	7.2(3)
C(231)	0.3415(6)	−0.0644(3)	0.3268(3)	3.0(2)
C(232)	0.4295(7)	−0.1058(4)	0.3409(3)	4.2(2)
C(233)	0.4945(8)	−0.1062(4)	0.3914(4)	5.2(2)
C(234)	0.4732(8)	−0.0666(5)	0.4276(3)	6.0(2)
C(235)	0.3885(8)	−0.0256(4)	0.4138(3)	5.1(2)
C(236)	0.3227(7)	−0.0234(4)	0.3636(3)	3.9(2)
C(241)	0.1917(6)	−0.1315(3)	0.2451(3)	3.1(2)
C(242)	0.1263(7)	−0.1399(4)	0.1952(3)	4.6(2)
C(243)	0.0642(8)	−0.1903(4)	0.1834(4)	5.8(2)
C(244)	0.0630(8)	−0.2324(4)	0.2200(4)	5.7(2)
C(245)	0.1271(8)	−0.2247(4)	0.2695(4)	5.6(2)
C(246)	0.1918(7)	−0.1746(4)	0.2820(3)	4.4(2)
C(300)	0.4009(9)	0.8843(5)	0.0256(4)	6.3(3)
C(400)	0.3499(9)	0.2490(5)	0.8646(4)	6.6(3)

and 221, 176 cm^{-1} (X=Br) (Table 5). The lower frequency one in each case may be attributed to the Pd–X bond *trans* to the phenyl carbon atom [16, 17].

Reaction of **2** and **3** with bis(diphenylphosphino)methane (dppm) or 1,1-bis(diphenylphosphino)ethene (vdpp) in a 1:1 molar ratio gave the novel species **4**, **5** and **8** in which two palladium atoms are bridged by a diphosphine and a halogen ligand. These are the first examples of cyclometallated complex with Schiff base ligands in which this bridging system appears. The compounds have been fully characterized by their C, H and N elemental analyses, IR and $^{31}P\{^1H\}$, and ^1H NMR spectroscopies (see 'Experimental', Tables 1–3 and Fig. 1). The values of the conductivity data indicate the compounds to be 1:1 electrolytes (Table 1) as expected, in contrast to similar compounds previously obtained in which there are two Pd–Cl terminal bonds and where the molecule is not ionic [18]. The $^{31}P\{^1H\}$ NMR spectra show a singlet for both phosphorus atoms δ28.1 (**4**), δ27.5 (**5**) and δ48.1 (**8**) ppm showing they are equivalent (Table 4). The ^1H NMR spectra show a doublet at δ7.94 (**4**), δ7.98 (**5**) and δ8.18 (**8**) ppm assigned to the imine proton coupled to the ^{31}P atom with $^4J(PH)$ *c.* 7.5 Hz (Table 4). This also indicates that both imine protons are equivalent in each compound with the Schiff base ligands *cis* to each other, i.e. both N atoms are *trans*

TABLE 4. $^{31}P\{^1H\}$ and ^1H NMR data for the ligand and complexes[a]

	δ(H$_i$)	δ(H2)	δ(H4)	δ(H5)	δ(H6)	δ(MeO)	δ(MeCO$_2$)	^4J(H2H4)	^3J(H4H5)	^4J(PH$_i$)	^4J(PH5)[f]	δ(P)	^2J(PP)
a[b]	8.28	m	m	6.95t	m	3.76							
1a	7.31s	6.70d	6.65dd	6.95d		3.76	2.12s	2.7	8.3				
2a	7.81s	6.80d	6.66dd			3.76s		2.9	8.5				
3a	7.85s	6.82d	6.64dd			3.76s		2.9	8.6				
4a[c]	7.94d	6.76d	6.08dd	5.93dd		3.62s		2.9	8.6	7.6	5.9	28.1s	
5a[c]	7.98d	6.80d	6.09d	5.87dd		3.64s		2.9	8.6	7.4	5.9	27.5s	
6a[d]	8.26d		6.45d	6.58st		3.74s			8.4	7.5	15.4	28.7d	62
											8.7	4.0d	
7a[d]	8.24d		6.44d	6.57st		3.74s			8.2	7.2	15.5	28.1d	61
											8.7	4.2d	
8a[e]	8.18d	6.93d	6.04dd	5.84m		3.63s		2.9	8.7	7.4		48.1s	
9a	8.27d		6.5d	6.65st		3.74			8.8	7.6	8.3	12.2d	
												−19.9d	80

[a] s, singlet; d, doublet; dd, doublet of doublets; t, triplet; st, sextuplet; m, multiplet. Coupling constants in Hz. [b] ^3J(H4H5) = ^3J(H5H6) = 7.6. [c] δ(CH$_2$): 4a, 4.83t, ^2J(PH) = 13; 5a, 4.91t, ^2J(PH) = 13. [d] δ(CH$_2$): 6a, 4.31dd, ^2J(PH) = 11, ^2J(PH) = 8; 7a, 4.21dd, ^2J(PH) = 11, ^2J(PH) = 8. [e] δ(C=CH$_2$):5.85 m. [f] The higher value is for *trans*-^4J(PH5) and the lower one for *cis*-^4J(PH5).

TABLE 5. IR data for the ligand and complexes (cm^{-1})[a]

	νC=N	νCH$_3$COO	νPd–X$_b$
Ligand	1645s		
1[b]	1605sh,m	1580, 1415s	
2[c]	1612m		319m, 257m
3[c]	1613m		221m, 176m
4	1629m		235m
5	1624m		200m
6	1621m		
7	1612m		
8	1621m		275m
9	1619m		

[a] s, strong; m, medium; sh, shoulder. [b] The higher value corresponds to ν_{as}(CH$_3$COO) and the lower one to ν_s(CH$_3$COO). [c] The higher value corresponds to ν_{as}(Pd–X$_b$) and the lower one to ν_s(Pd–X$_b$).

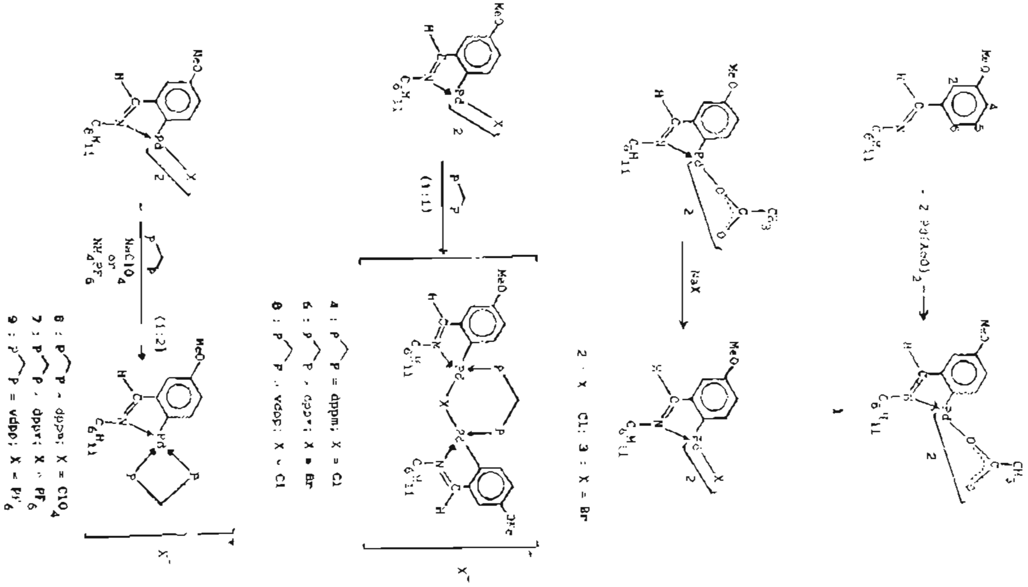

Fig. 1. Reaction scheme.

TABLE 6. Selected bond distances (pm) and angles (°) for $[Pd_2(\mu\text{-}Cl)\{\mu,\eta\text{-}(Ph_2P)_2C{=}CH_2\}(C_{14}H_{18}NO)_2]Cl \cdot 4CHCl_3$

Pd(1)–Cl(12)	243.3(3)	Pd(2)–Cl(12)	245.3(2)
Pd(1)–P(1)	225.3(2)	Pd(2)–P(2)	224.7(3)
Pd(1)–N(1)	209.8(6)	Pd(2)–N(2)	208.4(6)
Pd(1)–C(11)	201.1(7)	Pd(2)–C(211)	200.4(8)
P(1)–C(1)	183.3(8)	P(2)–C(1)	184.2(8)
C(1)–C(2)	134(1)		
N(1)–C(3)	129(2)	N(2)–C(203)	128.(1)
C(3)–C(12)	149(1)	C(203)–C(212)	147(1)
C(11)–C(12)	139(2)	C(211)–C(212)	142(2)
Pd(1)–Pd(2)	397(1)		
Cl(12)–Pd(1)–P(1)	92.06(7)	Cl(12)–Pd(2)–P(2)	90.67(7)
Cl(12)–Pd(1)–N(1)	94.8(2)	Cl(12)–Pd(2)–N(2)	94.5(3)
C(12)–Pd(1)–C(11)	165.4(2)	Cl(12)–Pd(2)–C(211)	166.4(2)
P(1)–Pd(1)–N(1)	169.2(2)	P(2)–Pd(2)–N(2)	173.3(2)
P(1)–Pd(1)–C(11)	94.0(3)	P(2)–Pd(2)–C(211)	94.3(3)
N(1)–Pd(1)–C(11)	81.3(3)	N(2)–Pd(2)–C(211)	81.7(3)
N(1)–C(3)–C(12)	115.3(7)	N(2)–C(203)–C(212)	117.5(7)
C(3)–C(12)–C(11)	117.4(7)	C(203)–C(212)–C(211)	115.7(7)
C(12)–C(11)–Pd(1)	111.2(2)	C(212)–C(211)–Pd(2)	111.2(5)
Pd(1)–N(1)–C(3)	111.7(2)	Pd(2)–N(2)–C(203)	111.7(4)
P(1)–C(1)–P(2)	118.0(4)		
P(1)–C(1)–C(2)	120.9(6)	P(2)–C(1)–C(2)	120.9(7)

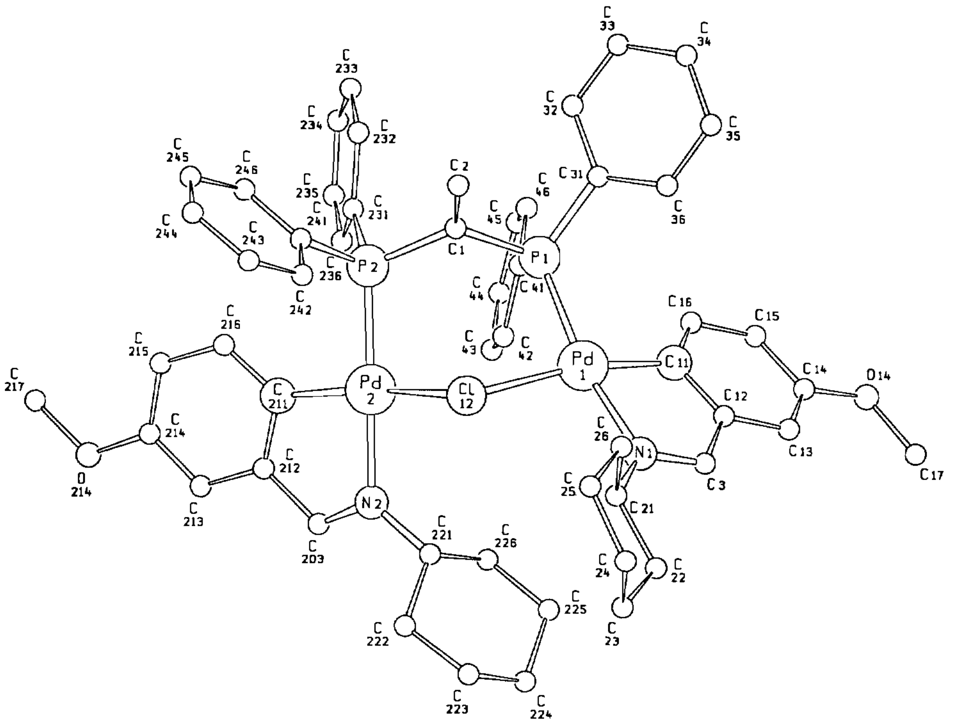

Fig. 2. Plot of the cation of [(mbcy-*C*6,*N*)Pd{μ-Ph$_2$PC(=CH$_2$)PPh$_2$}(μ-Cl)Pd(mbcy-*C*6,*N*)]$^+$ and numbering scheme.

to phosphorus (Fig. 1); otherwise one would be able to see a doublet for the imine proton coupled to the ^{31}P in *trans* and a singlet for the imine proton coupled to the ^{31}P atom in *cis* (*vide infra*). The crystal structure of compound **8** proves this to be correct. A doublet of doublets at δ5.93 (4) and δ5.87 (5) ppm is assigned to H5 coupled to the ^{31}P atom. For **8** this signal results from the vinylidene protons to give a complex multiplet.

We have also synthesized analogous compounds in which the two palladium atoms are bridged by a diphosphine and an acetato ligand [19].

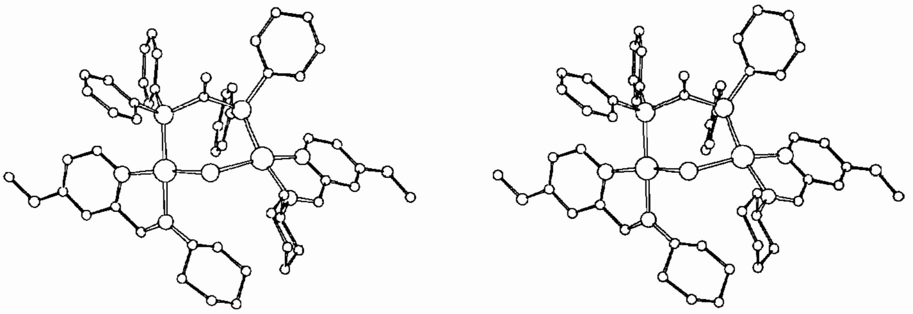

Fig. 3. Stereoview of the cation of $[(\text{mbcy-}C6,N)\text{Pd}\{\mu\text{-Ph}_2\text{PC}(=\text{CH}_2)\text{PPh}_2\}(\mu\text{-Cl})\text{Pd}(\text{mbcy-}C6,N)]^+$.

Treatment of **2** and **3** with dppm or vdpp in a 1:2 molar ratio and $NaClO_4$ or NH_4PF_6 yields the mononuclear species **6**, **7** and **9** as air-stable solids which have been fully characterized (see 'Experimental', Tables 1, 4, 5 and Fig. 1). The conductivity data show them to be 1:1 electrolytes (Table 1). As the counterion is not a halide ion the compounds may be obtained indistinctly from the chloro-bridged or bromo-bridged species (Fig. 1). The $^{31}P\{^1H\}$ NMR spectra show a doublet of doublets in each case δ28.7, 4.0 (**6**); δ28.1, 4.2 (**7**) and δ12.2–19.9 (**9**) ppm for two inequivalent phosphorus atoms.

The ^1H NMR spectra show a doublet at δ8.26 (**6**), δ8.24 (**7**) and δ8.27 (**9**) ppm (Table 4) assigned to the imine proton, which is apparently coupled to only one ^{31}P atom, probably the one *trans* to the imine proton. No coupling of the ^{31}P atom *cis* to it was observed, in which case one would see a doublet of doublets because *trans*-^4J(PH) is usually greater than *cis*-^4J(PH). In **6**, **7** and **9** the imine proton resonance in the ^1H NMR spectra is not significantly shifted to lower frequency with respect to the free ligand in contrast with the dinuclear species; the imine proton is probably under the deshielding influence of a phosphine phenyl ring. A sextuplet at δ6.58 (**6**), δ6.57 (**7**) and δ6.65 (**9**) ppm (Table 4) is assigned to the H5 proton which is coupled to both ^{31}P atoms with *trans*-^4J(PH5) > *cis*-^4J(PH5).

Structure of 8

Selected interatomic distances and angles are given in Table 6. A view of the atomic arrangement of $[(\text{mbcy-C6,N})\text{Pd}\{\mu\text{-Ph}_2\text{PC}(=\text{CH}_2)\text{PPh}_2\}(\mu\text{-Cl})\text{Pd}(\text{mbcy-C6,N})]^+$ with the numbering system used and a stereoview of this cation are given in Figs. 2 and 3. Detailed inspection of Table 6 and Figs. show that no unusual geometrical features are present. In the structure, the fundamental building element is the cation $[\text{Pd}_2(\mu\text{-Cl})\{\mu,\eta\text{-(Ph}_2\text{P)}_2\text{C}=\text{CH}_2\}(\text{C}_{14}\text{H}_{18}\text{NO})_2]^+$ which is a dinuclear complex wherein the coordination around the Pd atoms is square-planar. The angles between neighbouring atoms vary for Pd(1) from 81.3(3) to 94.8(2)° and for Pd(2) from 81.7(3) to 94.5(3)°. N(1) and C(11) are bonded to Pd(1) forming a five-membered metallacycle ($PdNC_3$). The Cl(12) atom is *trans* to the phenyl carbon atom and the P(1) atom is *trans* to the nitrogen atom. The coordination of Pd(2) is similar to the Pd(1) with P(2) and Cl(12) *trans* to N(2) and C(211), respectively. Cl(12) and the diphosphine vdpp act as a connecting bridge between the two Pd atoms which are situated 4.42(6) and 7.83(6) pm outside the least-squares plane formed by the N, C, P and Cl atoms. No Pd–Pd interactions are present as indicated by the metal–metal distance of 397(1) pm.

The distances in the square-planar arrangement around the Pd^{2+} ions reflect the differing *trans* influence of the coordination atoms. The distances Pd–P (av. 225.0(3) pm) are in good agreement with 226.0(2) pm in *cis*-dichlorobis[dimethyl-(phenyl)phosphine]palladium(II) [20] but are significantly longer than Pd–P (av. 222(1) pm) in [bis(diphenylphosphino)ethylamine]dichloropalladium [21]. As expected, the distances Pd–Cl are somewhat longer than terminal Pd–Cl distances (231–237 pm, mean) in these compounds.

Supplementary material

Further details of the structure determination have been deposited as Supplementary Publication No CSD-54038. Copies may be obtained through the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen, F.R.G.

Acknowledgements

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