Dinuclear and Tandem Tetranuclear Palladium(II) Complexes formed by Oxidative Addition of 2,6-Bis(chloromethyl)pyridine to [Pd(PPh$_3$)$_4$]

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2,6-Bis(chloromethyl)pyridine reacts with [Pd(PPh$_3$)$_4$] in toluene at 100 °C to afford two types of oxidative-addition products, C^α,*N*-bridging dinuclear and C^α,*N*,$C^{\alpha'}$-bridging tandem tetranuclear palladium(II) complexes [{PdCl[C$_5$H$_3$(6-CH$_2$Cl)N-2-CH$_2$](PPh$_3$)}$_2$] **1** and [{Pd$_2$Cl$_2$[C$_5$H$_3$N-2,6-(CH$_2$)$_2$]-(PPh$_3$)$_2$}$_2$] **2**. When the reactant molar ratio was 1.3:1 the best yield (56%) of complex **1** was obtained, while that (39%) of complex **2** was obtained using a 1:2 molar ratio. Complex **2** was also obtained in 48% yield by the reaction (1:2 molar ratio) between complex **1** and [Pd(PPh$_3$)$_4$]. With [Pt(PPh$_3$)$_4$], an analogous heteronuclear tetrametal complex was isolated. These were characterized by IR and NMR (^{1}H, ^{13}C and ^{31}P) spectroscopy and mass spectrometry as well as elemental analysis and molecular weight determinations. Complex **2** reacts with excess NaBr and Ag(O$_2$CR) (R = CH$_3$ or CF$_3$) to give the corresponding metathesis and substitution products respectively; diphosphines Ph$_2$PCH$_2$CH$_2$PPh$_2$ or *cis*-Ph$_2$PCH=CHPPh$_2$ partially displace the triphenylphosphine ligands. On the other hand, Tl(acac) (acac = pentane-2,4-dionate) cleaves the tandem tetranuclear structure to afford a dinuclear palladium(II) complex.

Since it was found that a chloro- or bromo-pyridine is oxidatively added to [Ni(PPh$_3$)$_4$] in toluene at room temperature to afford a dinuclear complex [{NiX(C$_5$H$_4$N-C^2)-(PPh$_3$)}$_2$]† (X = Cl or Br),[1] many stable σ-pyridyl, -pyridylmethyl and related complexes of nickel triad metals have been synthesised by analogous reactions.[2–14]

2,6-Dichloropyridine, which is potentially bifunctional in oxidative addition reactions, reacted only with one molecule of [M(PPh$_3$)$_4$] (M = Ni, Pd or Pt) giving [NiCl{C$_5$H$_3$(6-Cl)-N-C^2}(PPh$_3$)}$_2$][1] or *trans*-[MCl{C$_5$H$_3$(6-Cl)N-C^2}(PPh$_3$)$_2$] (M = Pd[3,5,8,12] or Pt[12]).

Oxidative addition of 2-(chloromethyl)pyridine to [Pd(PPh$_3$)$_4$] readily occurred in benzene[6] or toluene[7] to afford a dinuclear complex [{PdCl(C$_5$H$_4$N-2-CH$_2$)(PPh$_3$)}$_2$], analogous to that obtained with 2-chloropyridine.[3] However, the reactions of the potentially bifunctional 2,6-bis(chloromethyl)pyridine [2,6(CH$_2$Cl)$_2$-py] with low-valent metal complexes have not been examined so far. We report here the characterization and some reactions of the two kinds of products [{PdCl[C$_5$H$_3$(6-CH$_2$Cl)N-2-CH$_2$](PPh$_3$)}$_2$] and [{Pd$_2$Cl$_2$-[C$_5$H$_3$N-2,6-(CH$_2$)$_2$](PPh$_3$)$_2$}$_2$] obtained by the reaction of 2,6-CH$_2$Cl-py with [Pd(PPh$_3$)$_4$].

Results and Discussion

When 2,6(CH$_2$Cl)$_2$-py was allowed to react with 1 molar equivalent of [Pd(PPh$_3$)$_4$] in toluene at 100 °C for 1 h, two products [{PdCl[C$_5$H$_3$(6-CH$_2$Cl)N-2-CH$_2$](PPh$_3$)}$_2$] **1** and [{Pd$_2$Cl$_2$[C$_5$H$_3$N-2,6-(CH$_2$)$_2$](PPh$_3$)$_2$}$_2$] **2** were isolated in low yields (17 and 10% respectively). Attempts were made to improve the yields by changing the reaction time and the relative molar ratios of the reactants. The highest yield (56%) for complex **1** was obtained for the reaction of 2,6(CH$_2$Cl)$_2$-py with [Pd(PPh$_3$)$_4$] in a 1.3:1 molar ratio for 2 h. The use of a large excess of 2,6(CH$_2$Cl)$_2$-py, on the contrary, resulted in a lowering of the isolated yield because a large amount of [C$_5$H$_3$(6-CH$_2$Cl)N-2-CH$_2$PPh$_3$]Cl was formed in solution. The formation of the phosphonium chloride was confirmed by comparison of the ^{1}H NMR spectrum with an authentic sample prepared independently. Prolonged heating also lowered the yield through the formation of a by-product *cis*-[PdCl$_2$-(PPh$_3$)$_2$].

The highest yield (39%) of complex **2** was achieved by reacting stoichiometric amounts of the reactants for 2 h. The reaction of the isolated complex **1** with [Pd(PPh$_3$)$_4$] in 1:2 molar ratio also afforded complex **2** in a 48% yield. Similarly, the reaction of complex **1** with 2 mol equivalents of [Pt(PPh$_3$)$_4$] in toluene at 100 °C gave the heteronuclear tetrametal complex [{PdPtCl$_2$[C$_5$H$_3$N-2,6-(CH$_2$)$_2$](PPh$_3$)$_2$}$_2$] **3** in a 48% yield. Such a double oxidative addition has recently been reported to occur in a stepwise manner by Canty and co-workers[15] for the reaction of α,α'-dibromo-*m*-xylene with [PdMe$_2$(bipy)] followed by [MMe$_2$(bipy)] (M = Pd or Pt; bipy = 2,2'-bipyridine) leading to dinuclear complexes with a μ-hydrocarbyl ligand. When we attempted the reaction of 2-(chloromethyl)pyridine with [Pt(PPh$_3$)$_4$] to obtain [{PtCl(C$_5$H$_3$N-2-CH$_2$)-(PPh$_3$)}$_2$], isolation of the desired complex was unsuccessful owing to lack of reaction when 2-(chloromethyl)pyridine was used in a small excess, or decomposition to [PtCl$_2$(PPh$_3$)$_2$] if in large excess. It seems likely that the σ-bonded C$_5$H$_3$N-2-CH$_2$ group enhances the reactivity of a 6-chloromethyl substituent toward oxidative addition to Pt^0.

The analytical and physical data of complexes **1**–**3** are listed in Table 1, together with those of other products derived from complex **2**.

The C^α,*N-Bridging Dinuclear Complex* **1**.—Complex **1** comprises a Cl atom, a C$_5$H$_3$(6-CH$_2$Cl)N-2-CH$_2$ group and a PPh$_3$ ligand per Pd atom, and is dimeric in dichloromethane. The ^{1}H NMR spectrum (Table 2) in CDCl$_3$ showed a triplet at δ 2.26 and a doublet of doublets at δ 4.14. These resonances which are coupled with ^{31}P are assignable to the methylene protons co-ordinated to the metal. Other methylene resonances appeared at δ 5.19 and 5.36 as an AB quartet, suggesting that

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† The chloride-bridging structure proposed for [{NiCl(C$_5$H$_4$N-C^2)-(PPh$_3$)}$_2$] in ref. 1 is suggested in ref. 2 to be better interpreted in terms of a pyridyl-C^2,*N* bridging structure, analogous to that found in [{PdBr(C$_5$H$_4$N-C^2)(PPh$_3$)}$_2$] (ref. 3).

Table 1 Analytical and physical data for the di- and tetra-nuclear palladium(II) complexes

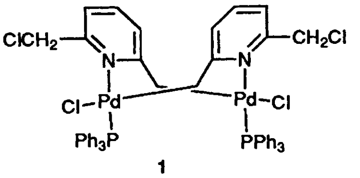
Complex	Yield (%)	M^b	Analysis^a (%) C	H	N
1 $[\{PdCl[C_5H_3(6\text{-}CH_2Cl)N\text{-}2\text{-}CH_2](PPh_3)\}_2]$	56	1160 (1089)	55.0 (55.1)	4.1 (4.1)	2.6 (2.6)
2 $[\{Pd_2Cl_2[C_5H_3N\text{-}2,6\text{-}(CH_2)_2](PPh_3)_2\}_2]$	39,^{c} 48^d	1900 (1827)	56.0 (56.5)	4.1 (4.1)	1.5 (1.5)
3 $[\{PdPtCl_2[C_5H_3N\text{-}2,6\text{-}(CH_2)_2](PPh_3)_2\}_2]$	48		52.0 (51.5)	3.75 (3.70)	1.5 (1.4)
4 $[\{Pd_2Br_2[C_5H_3N\text{-}2,6\text{-}(CH_2)_2](PPh_3)_2\}_2]$	69		51.5 (51.5)	3.7 (3.7)	1.45 (1.40)
5 $[\{Pd_2(CF_3CO_2)_2[C_5H_3N\text{-}2,6\text{-}(CH_2)_2](PPh_3)_2\}_2]$	81	2044 (2137)	52.85 (52.8)	3.4 (3.5)	1.4 (1.3)
6 $[\{Pd_2Cl(CF_3CO_2)[C_5H_3N\text{-}2,6\text{-}(CH_2)_2](PPh_3)_2\}_2]\cdot 0.5CH_2Cl_2$^{e}	73		53.5 (52.8)	3.7 (3.7)	1.4 (1.4)
7 $[\{Pd_2Cl(MeCO_2)[C_5H_3N\text{-}2,6\text{-}(CH_2)_2](PPh_3)_2\}_2]$^{f}	74		56.2 (57.7)	4.3 (4.3)	1.5 (1.5)
8 $[\{Pd_2Cl_2[C_5H_3N\text{-}2,6\text{-}(CH_2)_2](PPh_3)(dppe)\}_2]$^{g}	69		56.4 (58.6)	4.7 (4.4)	1.3 (1.3)
9 $[\{Pd_2Cl_2[C_5H_3N\text{-}2,6\text{-}(CH_2)_2](PPh_3)(dppen)\}_2]$^{g,h}	81		56.9 (58.5)	4.4 (4.2)	1.2 (1.3)
10 $[Pd_2(acac)_2\{C_5H_3N\text{-}2,6\text{-}(CH_2)_2\}(PPh_3)_2]$	51		61.1 (61.2)	5.0 (4.9)	1.35 (1.35)

^{a} Calculated values are given in parentheses. ^{b} In CH_2Cl_2 at 28 °C. ^{c} Method 1. ^{d} Method 2. ^{e} Found: Cl, 5.4. Calc.: 5.2%. ^{f} Found: Cl, 3.9. Calc.: 3.8%. ^{g} Not obtained in an analytically pure state due to a hundred per cent excess diphosphine used. ^{h} Found: P, 8.9. Calc: 8.9%.

Table 2 Proton NMR data (δ) for the complexes *

Complex (Solvent)	$PdCH_2$				C_5H_3N			Others
					H^3,H^5		H^4	
$2,6(CH_2Cl)_2$-py ($CDCl_3$)					7.41 (d) [7.9]		7.73 (t) [7.9]	4.26 CH_2Cl
1 ($CDCl_3$)	2.26 (t) [9.2] {9.2}	4.14 (dd) [9.2] {1.8}			6.83 (d) [7.9]	6.89 (d) [7.9]	7.22 (t) [7.9]	5.19, 5.36 (AB q) [14.7] CH_2Cl
2 ($CDCl_3$)	2.48 (t) [9.2] {9.2}	3.58 (d) [9.2]	2.06 (dd) [7.3] {11.6}	3.36 (dd) [7.3] {4.3}	6.27 (d) [7.3]	5.09 (d) [7.3]	6.31 (t) [7.3]	
3 ($CDCl_3$)	2.49 (t) 2.54 (t) [9.2] {9.2}	3.55 (d) 3.56 (d) [9.2]	2.1 (m)	3.35 (t) 3.37 (t) [9.2] {9.2}	6.32 (d) [7.3]	5.19 (d) 5.09 (d) 4.94 (d) [7.3]	6.29 (t) 6.24 (t) [7.3]	
4 (CD_2Cl_2)	2.71 (t) [8.5] {8.5}	3.69 (d) [8.5]	2.13 (dd) [7.9] {12.8}	3.32 (dd) [7.9] {4.3}	6.26 (d) [7.9]	5.24 (d) [7.9]	6.40 (t) [7.9]	
5 (CD_2Cl_2)	1.72 (t) [9.2] {9.2}	3.13 (d) [9.2]	1.84 (t) [9.2] {9.2}	3.92 (dd) [9.2] {3.6}	6.30 (d) [7.9]	5.59 (d) [7.9]	6.46 (t) [7.9]	
6 (CD_2Cl_2)	2.70 (t) [9.2] {9.2}	3.70 (d) [9.2]	1.97 (dd) [7.9] {12.2}	3.43 (dd) [7.9] {3.7}	6.45 (d) [7.9]	4.37 (d) [7.9]	6.35 (t) [7.9]	
7 ($CDCl_3$)	2.60 (t) [9.2] {9.2}	3.55 (d) [9.2]	1.84 (dd) [7.9] {12.2}	3.26 (dd) [7.9] {3.7}	6.33 (d) [7.9]	4.15 (d) [7.9]	6.23 (t) [7.9]	2.5 (br) CH_3
8 ($CDCl_3$)	2.70 (t) [9.2] {9.2}	3.91 (d) [9.2]	2.04 (br)	2.85 (ddd) [7.3] {11.0, 3.1}	6.30 (d) [7.3]	4.71 (d) [7.3]	6.54 (t) [7.3]	2.4 (br) CH_2
9 ($CDCl_3$)	2.72 (t) [9.2] {9.2}	3.87 (d) [9.2]	2.76 (t) [6.7] {6.7}	2.97 (ddd) [6.7] {11.7, 3.3}	6.37 (d) [7.9]	4.75 (d) [7.9]	6.54 (t) [7.9]	7.13 (ddd) [7.9] {23.2, 11.6} CH
10 ($CDCl_3$)	2.74 (d) {3.7}				7.01 (d) [7.3]		6.94 (t) [7.3]	1.61, 1.84 (br) CH_3 5.16 CH

* Measured at 400 MHz, J(H–H) and J(H–P) values in brackets and braces respectively in Hz.



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one of the originally attached chloromethyl groups remains unaltered but becomes diastereotopic upon N-co-ordination. The $^{13}C\text{-}\{^1H\}$ NMR spectrum (Table 3) showed only one set of resonances assignable to the $PdCH_2$, CH_2Cl, C_5H_3N and PPh_3 groups and the $^{31}P\text{-}\{^1H\}$ NMR spectrum (Table 4) showed a single resonance, both accounting for the presence of a C_2 axis of symmetry in the structure. These results indicate that the structure of complex **1** is as shown, and analogous to that of the 2-pyridylmethyl palladium(II) complex $[\{PdCl(C_5H_4N\text{-}2\text{-}CH_2\text{-}C,N)(PPh_3)\}_2]$.[6,7]

The C^α,N,$C^{\alpha'}$*-Bridging Tandem Tetranuclear Complexes* **2** *and* **3**.—When the un-co-ordinated chloromethyl group in complex **1** is forced to undergo oxidative addition, two possibilities are conceivable for the structure of product complexes; $C^\alpha,C^{\alpha'}$-bridging-structure **I** and $C^\alpha,N,C^{\alpha'}$-bridging structure **II**. Microanalysis and molecular weight measurements (determined in dichloromethane) are compatible with tetranuclear structures composed of two Cl atoms, one pyridine ring and two PPh_3 ligands per two Pd atoms. The fast atom bombardment (FAB) mass spectrum of complex **2** showed a peak for $[M + Na]^+$, with M corresponding to $[\{Pd_2Cl_2[C_5H_3N\text{-}2,6\text{-}(CH_2)_2](PPh_3)_2\}_2]$.

The AB quartet resonances assignable to the CH_2Cl, which was observed in the ^1H NMR spectrum of complex **1**, disappeared in that of complex **2** in $CDCl_3$ (Table 2) and instead, an additional set of methylene resonances appeared at δ 2.06 and 3.36, each as a doublet of doublets with different coupling constants to ^{31}P. Of the three ring-proton resonances of complex **1**, one doublet resonance showed a marked upfield

Table 3 Carbon-13 NMR data (δ) for the complexes[a]

Complex (solvent)	$PdCH_2$		C_5H_3N					PPh_3				Others
			C^2	C^3	C^4	C^5	C^6	C^α	C^β	C^γ	C^δ	
2,6(CH_2Cl)$_2$-py ($CDCl_3$)			156.2	121.9	137.9	121.9	156.2					46.3 CH_2Cl
1 ($CDCl_3$)	28.4		169.1	122.1	137.6	117.2	155.1	130.0 (d) [51.4]	134.7 (d) [10.2]	128.4 (d) [10.3]	130.8	45.9 CH_2Cl
2 ($CDCl_3$)	28.8 (d) [5.0]	31.4	164.5	117.3	135.1	118.0 (d) [3.5]	163.6 (d) [3.0]	130.1 (d) 131.5 (d) [49.9]	134.5 (d) 134.9 (d) [10.3]	138.1 (d) 128.6 (d) [10.3]	130.3 130.8	
3 ($CDCl_3$)	28.9	31.3	*b*					130.2 (d) 131.5 (d) [51.3]	134.5 (d) 134.9 (d) [10.3]	127.8 (d) 128.1(d) 128.6 (d) 128.7 (d) [10.3]	130.3 130.8	
5 (CD_2Cl_2)	28.5	30.3	172.4	123.5	141.1	122.6	170.7	133.3 (d) 133.7 (d) [48.4]	138.8 (d) 139.0 (d) [10.2]	132.9 (d) 133.5 (d) [10.2]	135.6	121.1 (q) {293} CF_3 164.8 (q) {35.2} CO_2 168.5 (q) {38.2} CO_2
6 (CD_2Cl_2)	22.2	29.3	165.5	118.7	136.5	118.6	163.3	130.1 (d) 130.4 (d) [48.4]	134.8 (d) 134.9 (d) [11.7]	128.9 (d) 129.2 (d) [10.3]	131.1 131.5	116.6 (q) {293} CF_3 160.0 (q) {35.2} CO_2
7 ($CDCl_3$)	23.1	28.8	164.5	118.1	135.6	117.5	163.4	130.3 (d) 130.5 (d) [49.9]	134.5 (d) 134.6 (d) [10.3]	128.2 (d) 128.6 (d) [10.2]	130.0 130.1	20.6 CH_3 176.0 CO_2
8 ($CDCl_3$)	28.7		162.9	117.6	135.5	117.2	162.7	*c*				
9 ($CDCl_3$)	28.6	33.3 (d) [83.7]	162.8	117.6	136.4	117.4	162.6	*c*				144.3 (dd) [38.1, 20.6] C=C 147.4 (dd) [46.9, 41.0] C=C
10 ($CDCl_3$)	26.2		164.5	120.0	133.6	120.0	164.5	130.6 (d) [48.4]	134.9 (d) [11.8]	127.9 (d) [10.2]	130.0	27.6 CH_3 99.0 CH

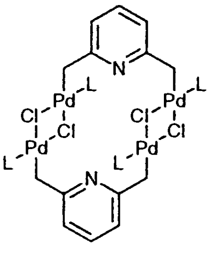
[a] Measured at 100 MHz, J(C–P) and J(C–F) values in brackets and braces respectively in Hz. [b] Well resolved spectrum was not obtained because of low solubility. [c] Not assigned accurately because of the complexity of the spectrum.

Table 4 Phosphorus-31 and ^{19}F NMR data (δ) for the complexes[a]

Complex (Solvent)	^{31}P				
1 ($CDCl_3$)	33.3				
2 ($CDCl_3$)	33.3	37.1			
3 ($CDCl_3$)	12.6 [4061]	16.7 [5128]	33.0	33.3	37.0
4 (CD_2Cl_2)	33.3	35.3			
5[b] ($CDCl_3$)	28.0	37.4			
9 ($CDCl_3$)	33.3	57.3, 65.8 (AB q) {17.1}			
10 ($CDCl_3$)	36.2				

[a] Measured at 24.2 MHz for ^{31}P, δ(P) in ppm from H_3PO_4, J(P–^{195}Pt) and J(P–P) values in brackets and braces respectively in Hz. Measured at 84.2 MHz for ^{19}F, δ(F) in ppm from C_6F_6. [b] δ(^{19}F) 91.8 (br).

shift in the NMR spectrum of complex **2**. These results indicate that structure **II** in which the C_5H_3N-2,6-(CH_2)$_2$ groups co-ordinate unsymmetrically to the palladium atoms is adopted in complex **2**. The conclusion seems reasonable in light of the basicity of the σ-bonded pyridine-ring nitrogen being high enough to split halide bridges.[3,4,7] The presence of two $PdCH_2$ resonances and of two sets of phenyl-ring resonances in the ^{13}C-{^1H} NMR spectrum and of two singlet resonances in the ^{31}P-{^1H} NMR spectrum also support the unsymmetrical structure **II** for complex **2**. Of the two singlet resonances in the ^{31}P-{^1H} NMR spectrum, the higher-field resonance at δ 33.3 is in accord with that in the NMR spectrum of complex **1** and may be assigned to the P atom *trans* to N, while the other resonance at δ 37.1 is assigned to the P *trans* to Cl.



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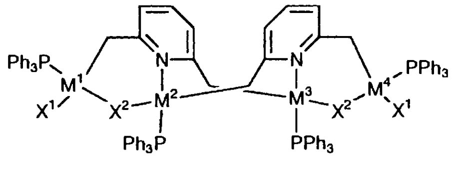


		M¹	M²	M³	M⁴	X¹	X²
2	**II**	Pd	Pd	Pd	Pd	Cl	Cl
3	**III**	Pt	Pd	Pd	Pt	Cl	Cl
	IV	Pd	Pd	Pt	Pt	Cl	Cl
	V	Pd	Pt	Pt	Pd	Cl	Cl
4		Pd	Pd	Pd	Pd	Br	Br
5		Pd	Pd	Pd	Pd	O_2CCF_3	O_2CCF_3
6		Pd	Pd	Pd	Pd	O_2CCF_3	Cl
7		Pd	Pd	Pd	Pd	O_2CMe	Cl

The similarity of the ^1H NMR spectrum (Table 2) of the heteronuclear tetrametal complex **3** in $CDCl_3$ to that of complex **2** suggests that the basic structure of complex **3** is the same as that of **2**. However, complicating features of the signals observed at each resonance field probably arise from the presence of three different isomers **III**–**V** in solution. In the $^{13}C-\{^1H\}$ NMR spectrum of complex **3** in $CDCl_3$, pyridine-ring resonances were not assignable owing to their relatively weak intensity and the poor solubility of the sample. On the other hand, $PdCH_2$ and phenyl-ring resonances were observed as well resolved signals. Moreover, the presence of two kinds of $PhCH_2$ resonances and of two sets of phenyl-ring resonances were clearly perceived, suggesting that the spectral complexity is arising from an isomeric mixture.

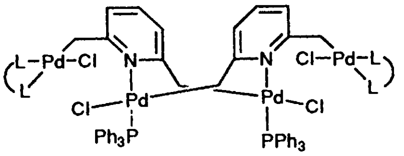
The $^{31}P-\{^1H\}$ NMR spectrum of complex **3** is more informative for calculating the relative molar amounts of the isomers. As shown in Table 4, in $CDCl_3$ there are three singlets at δ 33.0, 33.3 and 37.0, and two singlets flanked by the ^{195}Pt satellites at δ 12.6 and 16.7 [$J(P-^{195}Pt)$ = 4061 and 5128 Hz respectively]. The intensity ratio of the former three singlets was approximately 0.8 : 1 : 1 and that of the latter two is *ca.* 1 : 4. The assignments of these ^{31}P NMR resonances are troublesome since there is no coupling between the ^{31}P nuclei. Hence, we tentatively assigned these resonances as follows by comparison with the data for complex **2**; δ 33.0 (Pd–P *trans* to N for **IV**), 33.3 (Pd–P *trans* to N for **III**), 37.0 (Pd–P *trans* to Cl for **IV** and **V**), 12.6 (Pt–P *trans* to N for **IV** and **V**), 16.7 (Pt–P *trans* to Cl for **III** and **IV**), however it is not possible to assign the resonances at δ 33.0 and 33.3 definitively to **IV** and **III** respectively. The magnitude of the coupling constants to ^{195}Pt however lends strong support for the suggested assignment of the signals at δ 12.6 and 16.7.[14,16] As to why the chemical shifts of Pt–P *trans* to N for **IV** and **V** are identical, while those of Pd–P *trans* to N for **III** and **IV** are slightly different, remains unresolved. However, if the above assignments are correct, the relative molar amounts of the isomers are estimated to be approximately 1 : 1.6 : 0.2 for **III**, **IV** and **V** based on the intensity ratios of three resonances arising from the palladium-co-ordinated phosphorus atoms. These relative molar amounts of the isomers do not necessarily explain the relative resonance intensities of the signals due to Pt–P *trans* to N and Pt–P *trans* to Cl, but all these data indicate that the isomerization from **III** to **IV** or **V** could occur under the synthetic conditions through decomposition and recombination of the tetranuclear structure. Tandem tetrametal complexes like **2** and **3** are relatively unique for palladium. Recently, Nakamura and co-workers[17] reported a rational preparative method of the tandem tetrametal clusters $[Mo_2L_4(MX_n)_2]$ [L = 6-dimethylphosphino-2-pyridyl; MX_n = $Mo(CO)_3$, $PdCl_2$ or $PdBr_2$].

Metathesis and Substitution Reactions of **2**.—The metathesis reaction of complex **2** with a large excess of NaBr proceeded smoothly in dichloromethane–methanol at room temperature to afford $[\{Pd_2Br_2[C_5H_3N-2,6-(CH_2)_2](PPh_3)_2\}_2]$ **4**, for which the ^1H and $^{31}P-\{^1H\}$ NMR spectra (Tables 2 and 4) showed a close resemblance to those of complex **2**.

Chloride abstraction from complex **2** readily occurred by reaction with 4 mol equivalents of $Ag(O_2CCF_3)$ in dichloromethane and afforded a corresponding trifluoroacetato complex $[\{Pd_2(CF_3CO_2)_2[C_5H_3N-2,6-(CH_2)_2](PPh_3)_2\}_2]$ **5**. The use of only 2 molar equivalents of the silver(I) salt resulted in the formation of a chloro–trifluoroacetato mixed-ligand complex $[\{Pd_2Cl(CF_3CO_2)[C_5H_3N-2,6-(CH_2)_2](PPh_3)_2\}_2]\cdot0.5CH_2Cl_2$ **6**. As shown in Table 2, the ^1H NMR spectrum of the mixed-ligand complex **6** in CD_2Cl_2 does not differ appreciably from that of complex **2**. On the other hand, somewhat differing chemical shifts were observed, especially for the $PdCH_2$ resonances, in the ^1H NMR spectrum of complex **5** in CD_2Cl_2. Complex **2** has two terminal and two bridging chlorides. If the terminal and bridging chlorides are sequentially displaced, the CF_3CO_2 groups in complex **6** will probably be *O*-unidentate and co-ordinated to the outer metal centres. In complex **5**, however, in addition to these *O*-unidentate CF_3CO_2 groups, there will be two CF_3CO_2 groups bridging the inner and outer metal centres through two oxygen atoms. This explanation may be conceivable in light of the differing features of the ^1H NMR spectra of **5**. The IR spectrum of complex **6** in Nujol mull showed two bands at 1414 and 1672 cm^{-1}, assignable to $\nu_{sym}(CO_2)$ and $\nu_{asym}(CO_2)$ respectively. Both the band frequencies and the difference $[\nu_{asym}(CO_2) - \nu_{sym}(CO_2)]$ are consistent with unidentate co-ordination of the CF_3CO_2 ligands.[18] In contrast, the IR spectrum of complex **5** showed two sets of $\nu_{sym}(CO_2)$ and $\nu_{asym}(CO_2)$ bands at 1409, 1688 cm^{-1} and 1443, 1642 cm^{-1} respectively. The difference $[\nu_{asym}(CO_2) - \nu_{sym}(CO_2)]$ in the former set is indicative of *O*-unidentate co-ordination, while that in the latter is characteristic of *O,O′*-bridging,[18] consistent with the conclusion drawn from the ^1H NMR data. The $^{13}C-\{^1H\}$ NMR spectrum of complex **5** in CD_2Cl_2 showed two quartet resonances at δ 164.8 and 168.5, assignable to the carboxyl carbons with $^2J(C-F)$ = 35.2 and 38.2 Hz respectively.

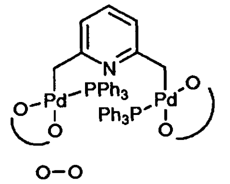
The reaction of complex **2** with 2 molar equivalents of thallium(I) acetate in dichloromethane at room temperature afforded a chloro–acetato mixed ligand complex **7**, analogous to **6**, for which the ^1H and $^{13}C-\{^1H\}$ NMR data could be interpreted in terms of a structure containing only *O*-unidentate acetate ligands. However, the IR data of complex **7** were not conclusive enough to draw such a conclusion. As shown in Table 2, the methyl resonance of the acetate group at δ 2.5 was appreciably broadened. This is due to the exchange of the ligand with OH^- in solution, since the resonance (δ *ca.* 1.1) of water (which was contained in the solvent) was also broadened. The unsatisfactory carbon analysis found for this complex was probably caused by the partial decomposition of the unstable metal–acetate bond during the synthetic procedure. The product obtained using 4 molar equivalents of the thallium(I) salt was even more unstable and did not give satisfactory analysis or NMR data.

Degradation of the Tetranuclear Structure of **2** *by Chelating Reagents*.—In order to obtain dinuclear complexes of the type $[Pd_2Cl_2\{C_5H_3N-2,6-(CH_2)_2\}(L-L)_2]$ [L–L = 1,2-bis(diphenylphosphino)ethane (dppe) or 1,2-*cis*-bis(diphenylphosphino)ethene (dppen)], complex **2** was allowed to react with 4 molar equivalents of dppe or dppen in dichloromethane at room temperature. Microanalysis of the product obtained in each case, however, did not coincide with the above formulation, and was closer to that for $[\{Pd_2Cl_2[C_5H_3N-2,6-(CH_2)_2](PPh_3)(L-L)\}_2]$ (L–L = dppe **8** or dppen **9**). Molecular weight determinations were not performed for either since they could not obtained as analytically pure products. However, the ^1H NMR spectra of complexes **8** and **9** each showed two sets of the $PdCH_2$ resonances, revealing that the tetranuclear structure of complex **2** is still maintained. Owing to the coupling to a geminal proton and *cis* and *trans* phosphorus atoms, one methylene proton of the higher-field set appeared as a doublet of double doublets. This means that the PPh_3 ligands attached to the outer metal centres of complex **2** were displaced by the diphosphine ligands. The $^{31}P-\{^1H\}$ NMR spectrum of complex **9** demonstrated more clearly the displacement of the two PPh_3 ligands in complex **2** by dppen since it showed one singlet and



L–L

8 $Ph_2PCH_2CH_2PPh_2$ (dppe)
9 $Ph_2PCHCHPPh_2$ (dppen)



O–O

10 MeCOCHCOMe (acac)

one AB quartet resonance in an approximately 1:2 intensity ratio. There was no resonance of free diphosphine indicating that the excess diphosphine is removed upon washing with diethyl ether. The carbon analyses for complexes **8** and **9** were 1–2% less than the calculated values. This indicates that the displacement of the PPh_3 ligands attached to the outer metal centres of complex **2** was still incomplete despite the use of a 100% excess of the diphosphines. It is not clear at present why the PPh_3 ligands attached to the inner metal centres were not displaced. Access of the bulky diphosphines to the inner metal centres is presumably sterically hindered.

Chloride abstraction from complex **2** by thallium(I) pentane-2,4-dionate [Tl(acac)], on the contrary, caused degradation of the tetranuclear structure of complex **2** giving the dinuclear complex $[Pd_2(acac)_2\{C_5H_3N\text{-}2,6\text{-}(CH_2)_2\}(PPh_3)_2]$ **10**. In the ^1H NMR spectrum of complex **10** in $CDCl_3$, only one methylene resonance was observed at δ 2.74 as a doublet with $J(H\text{–}P) = 3.7$ Hz and the pyridine-ring protons H^3 and H^5 showed identical chemical shifts, indicating that the structure of complex **10** was symmetrical. In contrast to these sharp resonances, two methyl resonances from the acac ligand were broad at the probe temperature (27 °C) and coalesced at 50 °C. Unfortunately, we could not record a rigid spectrum at lower temperatures because of an unexpected accident to our NMR instrument. However, the above-mentioned fact suggests that complex **10** is stereochemically non-rigid in solution at room temperature and above. Intra- and inter-molecular co-ordination-site exchange of an unco-ordinated pyridine nitrogen atom is well known for the analogous palladium(II) complexes containing a chelate pentane-2,4-dionate anion, carbon-bonded pyridyl ligand and triphenylphosphine.[5]

Experimental

Infrared spectra were obtained in Nujol mulls with a JASCO DS-701G spectrometer. The ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra were recorded on a JEOL JNM GX-400 instrument at 400 and 100 MHz respectively. The $^{31}P\text{-}\{^1H\}$ NMR spectra were measured using a JEOL FX60Q instrument at 24.2 MHz. Internal tetramethylsilane (^1H, $^{13}C\text{-}\{^1H\}$) and external H_3PO_4 ($^{31}P\text{-}\{^1H\}$) were used as references. The FAB mass spectra were obtained with a CONCEPT32 IH instrument in positive-ion mode using 3-nitrobenzyl alcohol as solvent in the presence of NaCl and xenon as bombardment gas. The molecular weight measurements were determined in dichloromethane at 27 °C with a vapour pressure osmometry unit manufactured by Knauer, Berlin. All the reactions were performed under an atmosphere of nitrogen, using solvents which were redistilled under argon. 2,6-Bis(chloromethyl)pyridine was purchased from Tokyo Kasei Kogyo Co. and used without further purification. Thallium(I) acetate (Wako), silver(I) trifluoroacetate (Aldrich) and the diphosphines, dppe and dppen (Alfa) were also purchased. Tetrakis(triphenylphosphine)-palladium(0)[19] and -platinum(0)[20] and thallium(I) pentane-2,4-dionate[21] were synthesised by the published methods.

Preparation of the C^α,N-*Bridging Dinuclear Complex* $[\{PdCl[C_5H_3(6\text{-}CH_2Cl)N\text{-}2\text{-}CH_2](PPh_3)\}_2]$ **1**.—A mixture of $[Pd(PPh_3)_4]$ (3.0 g, 2.60 mmol) and 2,6$(CH_2Cl)_2$-py (0.60 g, 3.38 mmol) in toluene (50 cm^3) was heated at 100 °C for 2 h with stirring. The yellow product **1** and $[C_5H_3(6\text{-}CH_2Cl)N\text{-}2\text{-}CH_2PPh_3]Cl$ which were precipitated from solution were filtered off, washed once with methanol to remove the salt, then with diethyl ether and dried *in vacuo*. The filtrate from the reaction was evaporated to dryness under reduced pressure and the residue was washed with diethyl ether to remove the liberated PPh_3, dried *in vacuo*, then redissolved in dichloromethane (50 cm^3). After filtration, the solvent was reduced to a half or less of its original volume. The yellow product **1** which was precipitated upon addition of diethyl ether was filtered off, washed with methanol and diethyl ether, then dried *in vacuo*. Total yield 0.79 g, 56%. The product obtained in this way was practically pure. It can be recrystallized from dichloromethane–methanol (3:2), if necessary.

Preparation of the C^α,N,$C^{\alpha'}$-*Bridging Tandem Tetranuclear Complexes*.—$[\{Pd_2Cl_2[C_5H_3N\text{-}2,6\text{-}(CH_2)_2](PPh_3)_2\}_2]$ **2**. *Method* 1. A mixture of $[Pd(PPh_3)_4]$ (3.00 g, 2.60 mmol) and 2,6$(CH_2Cl)_2$-py (0.23 g, 1.31 mmol) in toluene (25 cm3) was heated at 100 °C for 2 h with stirring. The yellow product **2** which was precipitated from solution was filtered off, washed with diethyl ether, then dried *in vacuo*. Recrystallization from dichloromethane–methanol (3:2) gave the pure product **2**. Yield 0.46 g, 39%.

Method 2. A mixture of complex **1** (0.28 g, 0.257 mmol) and $[Pd(PPh_3)_4]$ (0.52 g, 0.518 mmol) in toluene (25 cm^3) was heated at 100 °C for 4 h with stirring. The yellow product **2** which precipitated from solution was filtered off, washed with diethyl ether, then dried *in vacuo*. Recrystallization as above gave the pure product **2**. Yield 0.22 g, 48%.

$[\{PdPtCl_2[C_5H_3N\text{-}2,6\text{-}(CH_2)_2](PPh_3)_2\}_2]$ **3**. This complex was prepared in the same way as Method 2 for complex **2**, using $[Pt(PPh_3)_4]$ in the place of $[Pd(PPh_3)_4]$. Yield 48%.

Metathesis and Substitution Reactions of **2**.—$[\{Pd_2Br_2[C_5H_3N\text{-}2,6\text{-}(CH_2)_2](PPh_3)_2\}_2]$ **4**. To a solution of complex **2** (0.084 g, 0.0458 mmol) in dichloromethane (15 cm^3) was added NaBr (0.19 g, 1.81 mmol) in methanol (10 cm^3). The mixture was stirred for 3 h at room temperature, and then the solvent was reduced to a half or less of its original volume. After cooling to 0 °C for 2 h, the yellow product **4** which was precipitated from solution was filtered off, washed with diethyl ether, then dried *in vacuo*. Yield 0.063 g, 69%.

$[\{Pd_2(CF_3CO_2)_2[C_5H_3N\text{-}2,6\text{-}(CH_2)_2](PPh_3)_2\}_2]$ **5**. A mixture of complex **2** (0.12 g, 0.0657 mmol) and $Ag(O_2CCF_3)$ (0.058 g, 0.263 mmol) in dichloromethane (20 cm^3) was stirred for 20 h at room temperature giving AgCl as a white precipitate. After filtration, the solvent was reduced to a half or less of its original volume. The yellow product **5** which was precipitated upon addition of diethyl ether was filtered off, washed with diethyl ether, then dried *in vacuo*. Yield 0.11 g, 81%.

$[\{Pd_2Cl(RCO_2)[C_5H_3N\text{-}2,6\text{-}(CH_2)_2](PPh_3)_2\}_2]$ ($R = CF_3$ **6** *or* Me **7**). These complexes were prepared in the same way as for complex **5** using complex **2** and $Ag(O_2CCF_3)$ or $Tl(O_2CMe)$ in 1:2 molar ratio. In the latter case, TlCl instead of AgCl precipitates. Yields: 76% for **6**, 74% for **7**.

Attempted Degradation Reactions of the Tetranuclear Structure of **2**.—*With diphosphines*. A solution containing complex **2** (0.12 g, 0.0657 mmol) and dppe (0.11 g, 0.254 mmol) in dichloromethane (20 cm^3) was stirred for 4 h at room temperature. The solvent was reduced to a half or less in its original volume and the yellow product $[\{Pd_2Cl_2[C_5H_3N\text{-}2,6\text{-}(CH_2)_2](PPh_3)(dppe)\}_2]$ **8** was precipitated upon addition of diethyl ether. The complex was filtered off, washed with diethyl ether, and dried *in vacuo*. The product was recrystallized from acetone–diethyl ether. Yield 0.091 g, 69%. Similarly, $[\{Pd_2Cl_2[C_5H_3N\text{-}2,6\text{-}(CH_2)_2](PPh_3)(dppen)\}_2]$ **9** was obtained by the reaction with dppen. The product was recrystallized from dichloromethane–diethyl ether. Yield 81%.

With Tl(acac). To a solution of complex **2** (0.19 g, 0.103

mmol) in dichloromethane (20 cm^3) was added Tl(acac) (0.13 g, 0.409 mmol) in dichloromethane (20 cm^3). The yellow suspension thus obtained was stirred for 5 h at room temperature giving TlCl as a white precipitate. After filtration, the solvent was evaporated under reduced pressure. The residue was redissolved in a small volume of benzene and the yellow product [$Pd_2(acac)_2\{C_5H_3N$-2,6-$(CH_2)_2\}(PPh_3)_2$] **10** was precipitated upon addition of hexane. The complex was filtered off, washed with hexane, and dried *in vacuo*. Yield 0.11 g, 51%.

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References

1 K. Isobe, Y. Nakamura and S. Kawaguchi, *Chem. Lett.*, 1977, 1383; *Bull. Chem. Soc. Jpn.*, 1980, **53**, 139.

2 B. Crociani, F. D. Bianca, A. Giovenco and A. Berton, *J. Organomet. Chem.*, 1987, **323**, 123.

3 K. Nakatsu, K. Kinoshita, H. Kanda, K. Isobe, Y. Nakamura and S. Kawaguchi, *Chem. Lett.*, 1980, 913; K. Isobe, K. Nanjo, Y. Nakamura and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 2141.

4 K. Isobe, E. Kai, Y. Nakamura, K. Nishimoto, T. Miwa, S. Kawaguchi, K. Kinoshita and K. Nakatsu, *J. Am. Chem. Soc.*, 1980, **102**, 2475; K. Isobe, Y. Nakamura, T. Miwa and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 149.

5 H. Tanaka, K. Isobe and S. Kawaguchi, *Chem. Lett.*, 1981, 769; *Inorg. Chim. Acta*, 1981, **54**, L201; H. Tanaka, K. Isobe, S. Kawaguchi and S. Okeya, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 456.

6 M. Onishi, K. Hiraki, K. Maeda and T. Itoh, *J. Organomet. Chem.*, 1980, **188**, 245.

7 M. Nakatsu, K. Kafuku, Y. Yamaoka, K. Isobe, Y. Nakamura and S. Kawaguchi, *Inorg. Chim. Acta*, 1981, **54**, L69; K. Isobe, Y. Nakamura and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 1802.

8 K. Isobe and S. Kawaguchi, *Heterocycles*, 1981, **16**, 1603.

9 A. Mantovani and B. Crociani, *J. Organomet. Chem.*, 1982, **236**, C37; B. Crociani, F. Dibianca, R. Bertani and C. B. Castellani, *Inorg. Chim. Acta*, 1985, **101**, 161.

10 R. Bertani, A. Berton, F. D. Bianca and B. Crociani, *J. Organomet. Chem.*, 1986, **303**, 283.

11 B. Crociani, M. Sala, A. Polo and G. Bombieri, *Organometallics*, 1986, **5**, 1369.

12 A. Mantovani, *J. Organomet. Chem.*, 1983, **255**, 385.

13 B. Crociani, F. D. Bianca, A. Giovenco and A. Scrivanti, *J. Organomet. Chem.*, 1983, **251**, 393; 1984, **269**, 295.

14 B. Crociani, F. D. Bianca, A. Giovenco, A. Berton and R. Bertani, *J. Organomet. Chem.*, 1989, **361**, 255.

15 P. K. Byers, A. J. Canty, B. W. Skelton, P. R. Traill, A. A. Watson and A. H. White, *Organometallics*, 1990, **9**, 3080.

16 P. S. Pregosin and R. W. Kunz, *^{31}P and ^{13}C NMR of Transition metal Phosphine Complexes*, Springer, New York, 1979, ch. G, pp. 90–96.

17 K. Mashima, H. Nakano, T. Mori, H. Takaya and A. Nakamura, *Chem. Lett.*, 1992, 185.

18 G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 227.

19 D. R. Coulson, *Inorg. Synth.*, 1972, **13**, 121.

20 R. Ugo, F. Cariati and G. La Monica, *Inorg. Synth.*, 1968, **11**, 105.

21 W. H. Nelson, W. J. Randall and D. F. Martin, *Inorg. Synth.*, 1967, **9**, 52.

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