Synthesis and Reactivity of Neutral and Cationic Pentafluorophenyl Platinum(I) Derivatives

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The synthesis of $[ClPt(\mu\text{-dppm})_2Pt(C_6F_5)]$ (**1**) (dppm = $Ph_2PCH_2PPh_2$) is described. The Cl ligand in (**1**) can be replaced by Br, SCN and by neutral ligands (PPh_3, $AsPh_3$, pyridine, or CO) to give other Pt^I complexes. $MeO_2CC{\equiv}CCO_2Me$, SO_2, $[N_2C_6H_4Me\text{-}p]^+$, and H^+ insert into the Pt–Pt bond to give A-frame Pt^{II} complexes. $SnCl_2$, on the contrary, inserts into the Pt–Cl bond to give Pt–$SnCl_3$ derivatives. t-Butyl isocyanide acts as do other neutral ligands to give cationic complexes $[(Bu^tNC)Pt(\mu\text{-dppm})_2Pt(C_6F_5)]^+$, whereas CNC_6H_{11} and $CNC_6H_4Me\text{-}p$ lead to insertion, co-ordination, or both depending on the conditions of the reaction. The products are characterized by i.r. and ^1H, ^{19}F, and ^{31}P n.m.r. spectroscopy.

The chemistry of binuclear metal–metal bonded platinum(I) complexes with dppm ($Ph_2PCH_2PPh_2$) or related bridging groups and their reactivity with small groups to give the so-called A-frame compounds has attracted much attention,[1–3] but little work has been done on platinum(I) complexes containing Pt–C σ bonds or on the synthesis of cationic species.[4–7]

This paper deals with the synthesis of some pentafluorophenyl platinum(I) derivatives with dppm as bridging ligand and the study of their reactivity, and follows our previous work on palladium(I) derivatives.[8,9]

Results and Discussion

Synthesis and I.r. Spectra.—The pentafluorophenyl platinum(I) complex (**1**) has been prepared by a redox condensation of $[Pt(cod)_2]$[10] (cod = cyclo-octa-1,5-diene) and $[PtCl(C_6F_5)(dppm\text{-}P)_2]$ according to equation (1).

$$[Pt(cod)_2] + [PtCl(C_6F_5)(dppm\text{-}P)_2] \longrightarrow \underset{(\mathbf{1})}{[ClPt(\mu\text{-dppm})_2Pt(C_6F_5)]} + 2cod \quad (1)$$

The chemistry derived from complex (**1**) is illustrated in the Scheme. The analytical, molecular weight and conductivity data and some relevant i.r. absorptions for the complexes are collected in Table 1.

Several reactions lead to the formation of new platinum(I) complexes. Thus, Cl can be replaced by Br or SCN by treatment with the corresponding potassium salt. Treatment with $SnCl_2$ (1:1 ratio) leads to insertion of $SnCl_2$ into the Pt–Cl bond and not into the Pt–Pt bond, similarly to other reactions described before for palladium(I)[11] and platinum(I)[12] complexes. The addition of neutral ligands (L) to methanol suspensions of complex (**1**) in the presence of $NaBPh_4$ affords cationic complexes $[LPt(\mu\text{-dppm})_2Pt(C_6F_5)]BPh_4$ [L = PPh_3 (**5**), $AsPh_3$ (**6**), or pyridine (py) (**7**)].

No reaction is observed when CO is bubbled through a solution of complex (**1**) in benzene but if the reaction is carried out in CH_2Cl_2, the initial yellow colour of the solution becomes deeper and solution i.r. spectra show a strong absorption at 2 052 cm^{-1} but none in the 1 700 cm^{-1} region. This suggests the formation of the complex $[(CO)Pt(\mu\text{-dppm})_2Pt(C_6F_5)]Cl$, though addition of n-hexane to the solution leads only to precipitation of starting material. However, if the reaction is carried out in the presence of $NaBPh_4$ the cationic carbonyl complex (**8**) can be isolated, which shows a strong ν(C≡O) absorption at 2 052 cm^{-1}. Under no condition could products containing CO inserted into the Pt–Pt bond be detected. This behaviour contrasts with that described for $[ClPt(\mu\text{-dppm})_2PtCl]$ which gives complexes with terminal CO[13] or with bridging (inserted) CO[14] depending on the solvent.

The presence of platinum as Pt^I in complexes (**1**)—(**8**) can be verified by n.m.r. (see below) and i.r. spectroscopy. Thus an i.r. absorption for C_6F_5 which is observed above 950 cm^{-1} in platinum(II) complexes is shifted below 950 cm^{-1} in our platinum(I) complexes, reflecting a decrease in the formal oxidation state of the metal.[8,15,16] In addition, complex (**1**) shows a weak absorption at 244 cm^{-1}, assigned to ν(Pt–Cl) in the same range found for ν(Pt–Cl) in $[ClPt(\mu\text{-dppm})_2PtCl]$.[2]

Insertion of a variety of small groups into the Pt–Pt bond leads to the formation of new asymmetric A-frame platinum(II) compounds [reactions (*d*)—(*h*), (*j*), and (*k*) in the Scheme]. Thus, by bubbling SO_2 through a CH_2Cl_2 solution of (**1**), complex (**9**) is formed. Treatment of (**1**) with the diazonium salt $[N_2C_6H_4Me\text{-}p]BF_4$ gives (**10**). $MeO_2CC{\equiv}CCO_2Me$ reacts slowly with complex (**1**), to give (**11**) with the acetylene inserted into the Pt–Pt bond, and a similar reaction is observed starting from (**4**). Finally, treatment of (**1**) in $CHCl_3$ with $HClO_4$ leads to insertion of H^+ into the Pt–Pt bond to give (**13**).

The i.r. spectra of complexes (**9**)—(**13**) generally display new absorptions related to the inserted group or (when this is a cation) to the counter ion, some of which are listed in Table 1. In addition the change in the oxidation state of the platinum atom is expected to produce an increase in the wavenumber of both the C_6F_5 absorption near 950 cm^{-1} and the ν(Pt–Cl) absorption, relative to their values in complex (**1**). This is in fact the case for all the platinum(II) complexes reported here (see Table 1), the increase being bigger for the cationic than for the neutral complexes, as expected.

A more complex and interesting behaviour is observed in the reactivity of complex (**1**) towards isonitriles. Complex (**1**) reacts in benzene with $CNC_6H_4Me\text{-}p$ giving rise to the insertion product (**14**) [Scheme, reaction (*h*)]. On the other hand, when CNC_6H_{11} (C_6H_{11} = cyclohexyl) is added to a yellow solution of complex (**1**) in benzene (1:1 molar ratio) a deep orange colour (usually typical of isonitrile inserted complexes) develops which immediately fades out to yellow, and a pale yellow precipitate, identified as the cationic complex (**15**), is formed; if the same reaction is carried out in toluene at −40 °C an orange solution is formed and some orange solid precipitates which shows i.r. absorptions near 2 100 and 1 600 cm^{-1}. This means

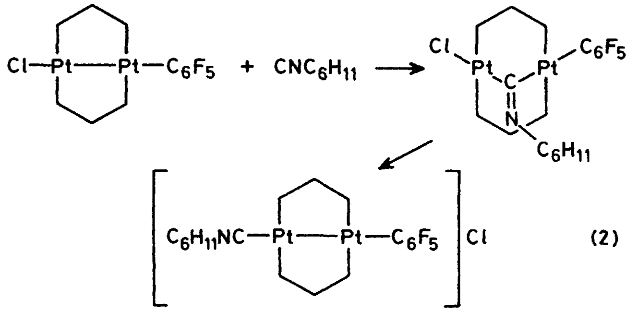
Table 1. Analytical results, molecular weights (calculated values in parentheses), molar conductivities (ohm^{-1} cm^{2} mol^{-1}), and relevant i.r. absorptions (cm^{-1})

	Analysis					I.r.			
Complex	C	H	N	M	Λ_M	C_6F_5	ν(C≡N)	ν(C=N)	Other
(1) $[\mathrm{ClPt}(\mu\text{-dppm})_2\mathrm{Pt}(\mathrm{C_6F_5})]$	48.65	3.15		1 348		947			244^{a}
	(49.40)	(3.25)		(1 361)					
(2) $[\mathrm{BrPt}(\mu\text{-dppm})_2\mathrm{Pt}(\mathrm{C_6F_5})]$	48.25	3.35		1 373		948			
	(47.85)	(3.15)		(1 406)					
(3) $[(\mathrm{SCN})\mathrm{Pt}(\mu\text{-dppm})_2\mathrm{Pt}(\mathrm{C_6F_5})]$	49.25	3.00	1.00	1 426		948			2 106^{b}
	(49.45)	(3.20)	(1.00)	(1 384)					
(4) $[\mathrm{Cl_3SnPt}(\mu\text{-dppm})_2\mathrm{Pt}(\mathrm{C_6F_5})]$	43.45	2.95		*c*		949			317, 290^{d}
	(43.35)	(2.85)							
(5) $[(\mathrm{PPh_3})\mathrm{Pt}(\mu\text{-dppm})_2\mathrm{Pt}(\mathrm{C_6F_5})]\mathrm{BPh_4}$	61.40	4.25			71	953			610^{e}
	(61.70)	(4.15)							
(6) $[(\mathrm{AsPh_3})\mathrm{Pt}(\mu\text{-dppm})_2\mathrm{Pt}(\mathrm{C_6F_5})]\mathrm{BPh_4}$	60.40	3.95			69	951			610^{e}
	(60.30)	(4.10)							
(7) $[(\mathrm{py})\mathrm{Pt}(\mu\text{-dppm})_2\mathrm{Pt}(\mathrm{C_6F_5})]\mathrm{BPh_4}$	60.05	4.10	0.70		74	948			610^{e}
	(59.20)	(4.05)	(0.80)						
(8) $[(\mathrm{CO})\mathrm{Pt}(\mu\text{-dppm})_2\mathrm{Pt}(\mathrm{C_6F_5})]\mathrm{BPh_4}$	57.35	4.00			74	951			610^{e}, 2 052^{f}
	(58.15)	(3.85)							
(9) $[\mathrm{ClPt}(\mu\text{-dppm})_2(\mu\text{-SO}_2)\mathrm{Pt}(\mathrm{C_6F_5})]$	47.65	3.10		1 561		953			1 132, 1 013;^{g} 271^{a}
	(47.20)	(3.10)		(1 425)					
(10) $[\mathrm{ClPt}(\mu\text{-dppm})_2(\mu\text{-N}_2\mathrm{C_6H_4Me}\text{-}p)\text{-}\mathrm{Pt}(\mathrm{C_6F_5})]\mathrm{BF_4}$	47.50	3.05	1.95		111	960			1 059^{h}
	(48.25)	(3.30)	(1.80)						
(11) $[\mathrm{ClPt}(\mu\text{-dppm})_2\{\mu\text{-C}_2(\mathrm{CO_2Me})_2\}\mathrm{Pt}(\mathrm{C_6F_5})]$	49.60	3.65		1 556		953			1 702, 1 691;^{i} 272^{a}
	(49.55)	(3.35)		(1 504)					
(12) $[\mathrm{Cl_3SnPt}(\mu\text{-dppm})_2\{\mu\text{-C}_2(\mathrm{CO_2Me})_2\}\mathrm{Pt}(\mathrm{C_6F_5})]$	43.75	2.90		1 783		954			1 696, 1 678^{i}
	(44.00)	(3.00)		(1 694)					
(13) $[\mathrm{ClPt}(\mu\text{-dppm})_2(\mu\text{-H})\mathrm{Pt}(\mathrm{C_6F_5})]\mathrm{ClO_4}$	45.40	3.10			106	957			1 100, 630;^{j} 331^{a}
	(46.00)	(3.10)							
(14) $[\mathrm{ClPt}(\mu\text{-dppm})_2(\mu\text{-CNC_6H_4Me}\text{-}p)\mathrm{Pt}(\mathrm{C_6F_5})]$	52.40	3.50	1.15			947		1 561 1 610 ^{k}	
	(52.00)	(3.50)	(0.95)						
(15) $[(\mathrm{C_6H_{11}NC})\mathrm{Pt}(\mu\text{-dppm})_2\mathrm{Pt}(\mathrm{C_6F_5})]\mathrm{Cl}$	51.75	3.70	0.70		102	947	2 173		
	(51.45)	(3.75)	(0.95)						
(16) $[(\mathrm{Bu^tNC})\mathrm{Pt}(\mu\text{-dppm})_2\mathrm{Pt}(\mathrm{C_6F_5})]\mathrm{Cl}$	50.60	3.80	0.80		101	948	2 179		
	(50.70)	(3.70)	(0.95)						
(17) $[(p\text{-MeC_6H_4NC})\mathrm{Pt}(\mu\text{-dppm})_2\mathrm{Pt}(\mathrm{C_6F_5})]\mathrm{Cl}$	51.85	3.60	0.80		112	948	2 148		
	(52.00)	(3.50)	(0.95)						
(18) $[(\mathrm{C_6H_{11}NC})\mathrm{Pt}(\mu\text{-dppm})_2\mathrm{Pt}(\mathrm{C_6F_5})]\mathrm{BPh_4}$	60.10	4.30	0.85		80	945	2 173		610^{e}
	(59.55)	(4.30)	(0.80)						
(19) $[(\mathrm{Bu^tNC})\mathrm{Pt}(\mu\text{-dppm})_2\mathrm{Pt}(\mathrm{C_6F_5})]\mathrm{BPh_4}$	58.70	4.00	0.75		79	948	2 163		610^{e}
	(59.05)	(4.25)	(0.80)						
(20) $[(p\text{-MeC_6H_4NC})\mathrm{Pt}(\mu\text{-dppm})_2\mathrm{Pt}(\mathrm{C_6F_5})]\mathrm{BPh_4}$	59.95	4.10	0.80		72	948	2 149		610^{e}
	(59.95)	(4.05)	(0.80)						
(21) $[(\mathrm{C_6H_{11}NC})\mathrm{Pt}(\mu\text{-dppm})_2(\mu\text{-CNC_6H_{11}})\mathrm{Pt}\text{-}(\mathrm{C_6F_5})]\mathrm{Cl\cdot Me_2CO}$	52.90	4.50	1.90		99	948	2 185	1 605 1 620 ^{k}	1 715^{l}
	(53.55)	(4.45)	(1.70)						
(22) $[(p\text{-MeC_6H_4NC})\mathrm{Pt}(\mu\text{-dppm})_2(\mu\text{-CNC_6H_4Me}\text{-}p)\text{-}\mathrm{Pt}(\mathrm{C_6F_5})]\mathrm{Cl}$	53.65	3.60	1.95		103	949	2 158	1 560 1 614 ^{k}	
	(54.20)	(3.65)	(1.75)						
(23) $[(\mathrm{C_6H_{11}NC})\mathrm{Pt}(\mu\text{-dppm})_2(\mu\text{-CNC_6H_{11}})\mathrm{Pt}\text{-}(\mathrm{C_6F_5})]\mathrm{BPh_4}$	61.30	4.95	1.40		80	950	2 185	1 580 1 604 ^{k}	610^{e}
	(60.60)	(4.65)	(1.50)						
(24) $[(p\text{-MeC_6H_4NC})\mathrm{Pt}(\mu\text{-dppm})_2(\mu\text{-CNC_6H_4Me}\text{-}p)\text{-}\mathrm{Pt}(\mathrm{C_6F_5})]\mathrm{BPh_4}$	60.90	4.10	1.35		77	949	2 156	1 561 1 578 ^{k}	610^{e}
	(61.35)	(4.20)	(1.50)						

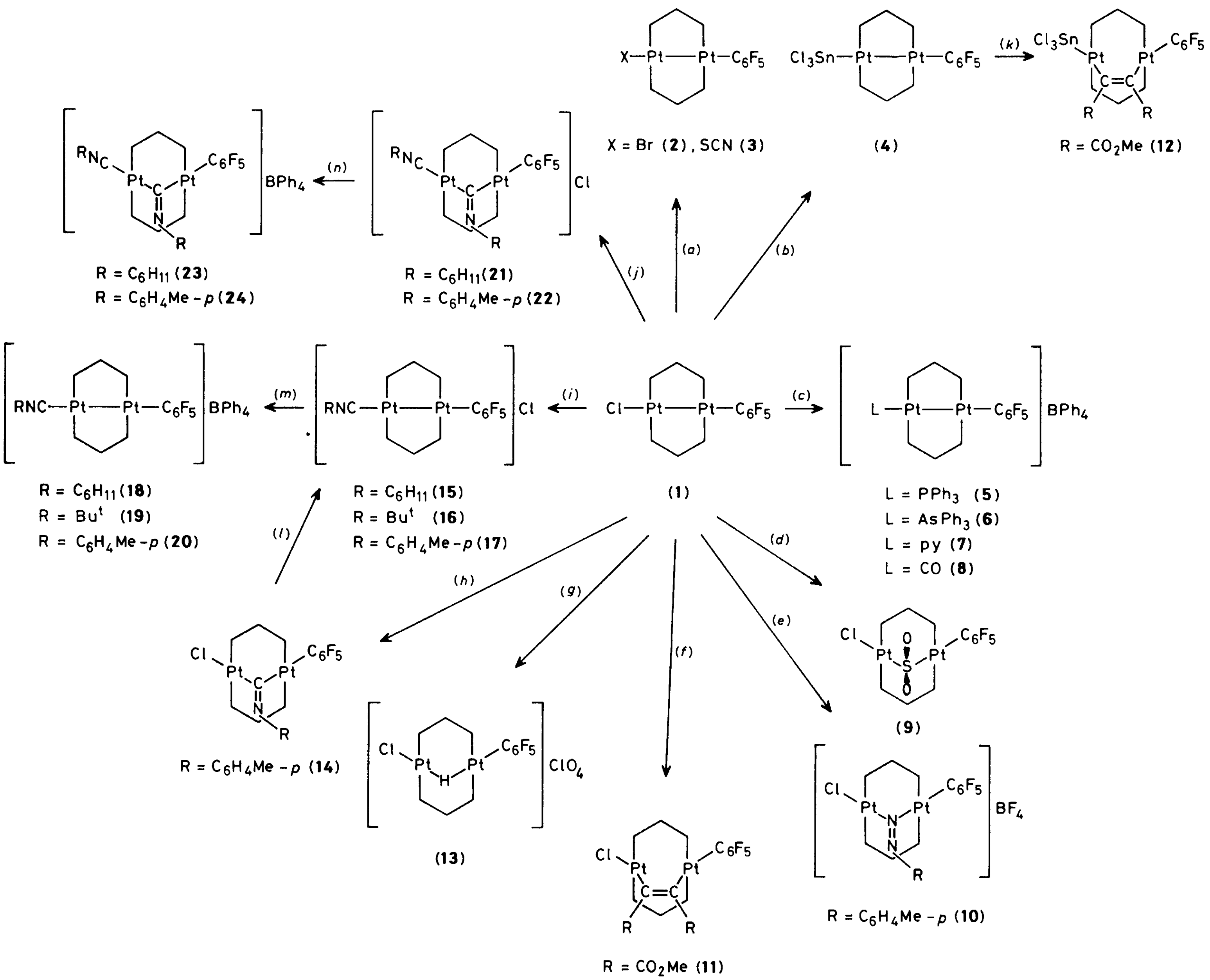
[a] ν(Pt–Cl). [b] ν(C≡N), SCN group. [c] Not soluble enough for molecular weight determination. [d] $SnCl_3$; see D. F. Schriver and M. P. Johnson, *Inorg. Chem.*, 1967, **6**, 1265. [e] BPh_4^-. [f] ν(C≡O). [g] $\nu_{asym}(SO_2)$ and $\nu_{sym}(SO_2)$; see D. M. P. Mingos, *Transition Met. Chem.*, 1978, **3**, 1. [h] BF_4^-; see N. N. Greenwood, *J. Chem. Soc.*, 1959, 3811. [i] ν(C=O). [j] ClO_4^-; see B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 309. [k] Other bands in this region are probably due to the phenyl rings and their intensities are increased upon insertion. We give both absorptions under the heading ν(C=N). [l] ν(C=O), CH_3–CO–CH_3.

that this orange solid most likely consists of a mixture of (**15**) and $[\mathrm{ClPt}(\mu\text{-CNC_6H_{11}})(\mu\text{-dppm})_2\mathrm{Pt}(\mathrm{C_6F_5})]$. At room temperature the colour of the solid changes to pale yellow within minutes and the resulting compound is identified as (**15**). These data support the idea that the insertion of isonitrile is the first step in the reaction, but a rapid isomerization follows to give the cationic complex with co-ordinated isonitrile, equation (2). With $CNBu^t$ in benzene, no change in the colour of the solution of (**1**) is observed and a precipitate of complex (**16**) is obtained.

In a more polar solvent (CH_2Cl_2) not only CNC_6H_{11} and $CNBu^t$, but also CNC_6H_4Me-*p* give solely the cationic complexes, (**15**)—(**17**), with co-ordinated isonitrile [Scheme,



(2)


X = Br (2), SCN (3)
(4)
R = CO$_2$Me (12)
R = C$_6$H$_{11}$ (23)
R = C$_6$H$_4$Me-p (24)
R = C$_6$H$_{11}$ (21)
R = C$_6$H$_4$Me-p (22)
(1)
R = C$_6$H$_{11}$ (18)
R = Bu^t (19)
R = C$_6$H$_4$Me-p (20)
R = C$_6$H$_{11}$ (15)
R = Bu^t (16)
R = C$_6$H$_4$Me-p (17)
L = PPh$_3$ (5)
L = AsPh$_3$ (6)
L = py (7)
L = CO (8)
R = C$_6$H$_4$Me-p (14)
(13)
(9)
R = CO$_2$Me (11)
R = C$_6$H$_4$Me-p (10)
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
(l)
(m)
(n)

Scheme.

Table 2. Fluorine-19 and ^{1}H n.m.r. spectra [δ/p.p.m. referred to $CFCl_3$ and $SiMe_4$ respectively; *J* in Hz; solvent $CDCl_3$]; N(P–H) = ^2J(P–H) + ^4J(P–H)

Complex	F_o	F_p	F_m	$^3J(Pt–F_o)$	$^4J(Pt–F_o)$ or $^5J(Pt–F_o)$	$\delta(CH_2)$	δ(Me) or δ(H)	N(P–H)	^3J(Pt–H)	$^2J(H^\alpha–H^\beta)$
(**1**)	−121.6	−166.7	−166.10	290.5	103.8	4.32		7.9	59.6	
(**9**)	−112.8, −116.6	−163.9	−164.7, −165.6	203.6, 281.5	*a*, *a*	4.39, 2.78		13.9, *a*	*a*, *a*	13.6
(**10**)[b]	−112.8, −117.5	−159.7	−162.8, −163.9	215, 290	*a*, *a*	3.11, 2.86	2.19	*a*, *a*	*a*, *a*	*a*
(**11**)	−109.9, −115.1	−164.4	−165.2, −165.9	213, 285	57.2, *a*	4.15, 3.11	2.49, 2.43	12.9, *a*	*a*, ~64	12.8
(**12**)	−112.2, −114.4	−162.7	−163.8, −165.2	214, 259.8	40, *a*	4.36, 3.17	2.74, 2.20	12.8, *c*	*a*, ~59	12.7
(**13**)	−118.6	−161.7	−163.5	329.5	*a*	4.56	−14.22[c]	7.7	39.2	
(**14**)	−111.3, −114.9	−164.6	−165.3, −165.8	175.3, 220	*a*, *a*	3.2—2.6	1.94	*a*, *a*	*a*, *a*	*a*
(**17**), (**20**)	−119.7	−164.3	to −164.9	273	51.3	4.76	2.15	7.6	54.4	
(**22**), (**24**)[d]	−113.8, −116.1	−162.1	−163.8, −164.4	180, 183	75, *a*	3.42, 3.02		*a*, *a*	*a*, *a*	*a*

[a] Coupling constant(s) not assignable due to overlapping or other reasons. [b] $\delta(^{11}BF_4^-)$ = −153.9, $\delta(^{10}BF_4^-)$ = −153.8. [c] ^1J(H–PtCl) = 910.6, $^1J(H–PtC_6F_5)$ = 496.8. [d] In the presence of added CNC_6H_4Me-*p*.

reaction (*i*)]. In addition, complex (**14**) rearranges slowly to complex (**17**) in CH_2Cl_2 solution [Scheme, reaction (*l*)]. Thus, the formation of inserted neutral rather than co-ordinated cationic complexes takes place only with isonitriles with a high tendency to give insertion (CNC_6H_4Me-*p* > CNC_6H_{11} ≫ $CNBu^t$) and is disfavoured in polar solvents, in agreement with our previous observations on related palladium(I) complexes.[8] By adding $NaBPh_4$ to solutions of complexes (**15**)—(**17**), complexes (**18**)—(**20**) with BPh_4 as counter ion can be isolated [Scheme, reaction (*m*)].

Addition of a large excess of the isonitrile (CNC_6H_{11} or CNC_6H_4Me-*p*) to a CH_2Cl_2 or acetone solution of complex (**1**) gives rise to the formation of cationic complexes with both co-ordinated and inserted isonitrile, $[(RNC)Pt(\mu\text{-}CNR)(\mu\text{-}dppm)_2Pt(C_6F_5)]^+$ which can be isolated directly with Cl as counter ion [(**21**) and (**22**); Scheme, reaction (*j*)], or with BPh_4 if $NaBPh_4$ is added [(**23**) and (**24**); Scheme, reaction (*n*)]. Complex (**21**) crystallizes with acetone which could not be eliminated by heating without decomposition of the complex; the amount of acetone was estimated by ^{1}H n.m.r. integration. Finally, addition of a large excess of $CNBu^t$ to (**1**) gave only complex (**16**).

The i.r. spectra of the isonitrile complexes were very valuable to confirm the presence of co-ordinated [ν(C≡N) = 2 100—2 200 cm^{-1}] and/or inserted [ν(C=N) = 1 550—1 650 cm^{-1}] isonitrile. The C_6F_5 absorption near 950 cm^{-1}, on the contrary, was of little value since it appeared at roughly the same wavenumbers in the platinum(I) and in the platinum(II) complexes.

N.M.R. Spectra.—Proton, ^{19}F, and ^{31}P n.m.r. spectra of representative complexes were recorded; data are given in Table 2 or in the text.

The ^{19}F n.m.r. spectra are particularly interesting for they display two different patterns. All the A-frame platinum(II) complexes [except the hydrido complex (**13**)] show five distinct multiplet signals corresponding to five chemically inequivalent fluorine atoms. This means that the C_6F_5 plane is roughly perpendicular to the P–Pt–P direction and the phenyl groups on the phosphorus atoms hinder the otherwise free rotation around the Pt–C_6F_5 bond, thus giving rise to inequivalence of the two *ortho* fluorines and of the two *meta* fluorines in the C_6F_5 ring. The two F_o signals appear as doublets [due to coupling to the neighbour F_m, $^3J(F_o–F_m)$ ≃ 33 Hz] sometimes broadened by unresolved coupling to other fluorine atoms; platinum satellites due to $^3J(Pt–F_o)$ are always observed, whereas the satellites due to $^5J(Pt–F_o)$ hardly emerge from the central peaks [see Figure 1(*a*)].

On the other hand, the Pt–Pt bonded platinum(I) complexes display only three multiplet signals (2:1:2 ratio) since in these complexes the two *ortho* fluorines are isochronous, and so are the two *meta* fluorines. The F_o signal for one of the complexes, showing $^3J(Pt–F_o)$ and $^4J(Pt–F_o)$ satellites, is shown in Figure 2(*a*).

In the ^{1}H n.m.r. spectra, there is inequivalence of the two protons in each methylene group ($CH^\alpha H^\beta$) for the A-frame platinum(II) complexes, whereas these protons are equivalent for the Pt–Pt bonded platinum(I) complexes. This has been observed before[1–3,17–23] and can also be seen in our complexes. In the platinum(I) complexes [Figure 2(*b*)] the CH_2 signal (containing superimposed components of the four isotopomers ClPt–PtC_6F_5, 43.82%; ClPt–^{195}PtC_6F_5, 22.37%; Cl^{195}Pt–PtC_6F_5, 22.37%; and Cl^{195}Pt–^{195}PtC_6F_5, 11.42%) shows five peaks (1:7.8:17.3:7.8:1) separated by $\frac{1}{2}$ ^3J(Pt–H). The fine structure of each peak is blurred in the satellites due to small differences of ^3J(PtH) to each platinum, but can be clearly seen in the central peak as a pseudoquintet due to virtual coupling to the four P atoms (again the coupling constants to the P atoms on the C_6F_5 side and those on the Cl side are approximately equal); ^2J(PH) + ^4J(PH) values are given in Table 2. In the A-frame platinum(II) complexes two generally well separated signals are observed for H^α and H^β giving rise at 200 MHz to an AX rather than an AB system. Thus each proton should give rise to a doublet [separated by $^2J(H^\alpha H^\beta)$] and each component of the doublet should split, as discussed above, by coupling to ^{31}P and, in some isotopomers, to ^{195}Pt. This usually leads to blurred signals for the high-field proton, but the signal of the low-field proton often allows easy analysis. Thus, the high field proton in Figure 2(*b*) consists basically of a doublet [$^2J(H^\alpha H^\beta)$] of multiplets emerging from a 'hump' containing the signals from isotopomers with one or two ^{195}Pt atoms. On the other hand the low-field proton can be analysed as a doublet [$^2J(H^\alpha H^\beta)$] of pseudoquintets (virtual coupling to four P atoms) emerging from an overlap of the peaks due to coupling to ^{195}Pt, with $^2J(H^\alpha H^\beta) \simeq |^2J(PH^\alpha) + {}^4J(PH^\alpha)|$.

Phosphorus-31 n.m.r. spectra were recorded only for complexes (**1**) and (**9**) and showed the expected pattern. For complex (**9**) the central multiplets of P_A and P_B due to the isotopomer with two inactive platinums are very similar to those reported for $[Pd_2(dppm)_2(\mu\text{-}HC{\equiv}CCO_2H)Cl_2]$[18] and in addition the close and far platinum satellites due to the isotopomers with one ^{195}Pt atom are clearly seen, although there is overlap of the two downfield far satellites of P_A and P_B, and the upfield close satellite of P_A and the low-field close satellite of P_B also overlap in the centre of the spectrum. The following parameters can be easily extracted:[24] $\delta(P_A)$ = 24.1, $\delta(P_B)$ = 21.4; $^1J(PtP_A)$ = 3 335.0, $^1J(PtP_B)$ = 3 814.6, $^3J(Pt\text{-}P_A)$ = 266.6, $^3J(PtP_B)$ = 214.0 Hz; $N = {}^2J(P_AP_B) + {}^4J(P_AP_B)$ = 47.0 Hz (in $CDCl_3$, ref. external 85% H_3PO_4).

For complex (**1**) the central multiplets of P_A and P_B are

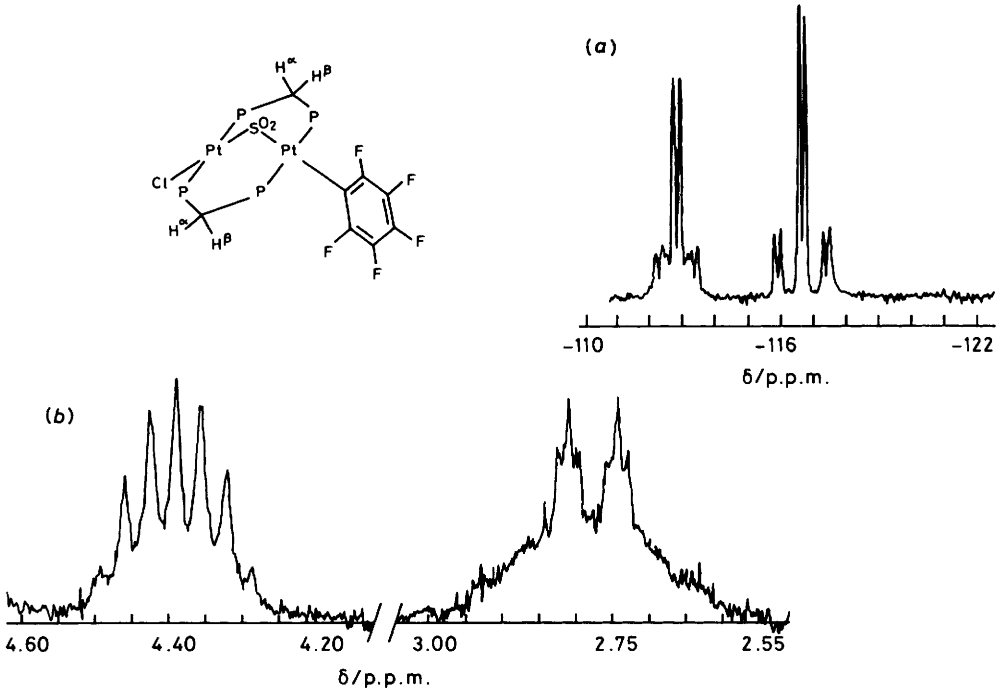


Figure 1. (*a*) ^{19}F N.m.r. spectrum (188.2 MHz) of complex (**9**) in the F_o region; (*b*) ^{1}H n.m.r. spectrum (200 MHz) of complex (**9**) in the methylene region

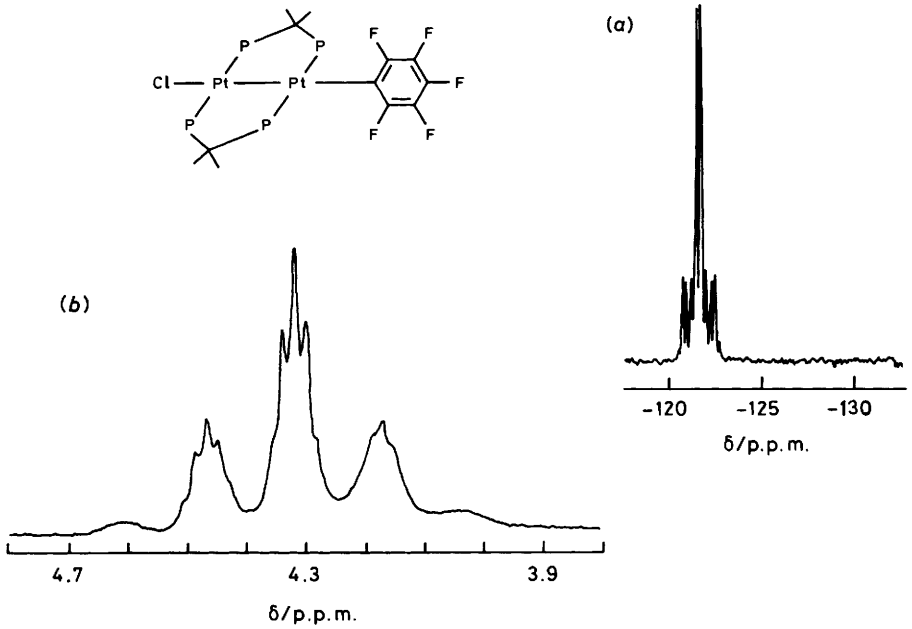


Figure 2. (*a*) ^{19}F N.m.r. spectrum (188.2 MHz) of complex (**1**) in the F_o region; (*b*) ^{1}H n.m.r. spectrum (200 MHz) of complex (**1**) in the methylene region

somewhat complicated as they include the close platinum satellites which do not emerge from the central multiplet; however the two far satellites of each phosphorus are clearly seen and show a pattern very similar to that of complex (**9**). The following parameters are extracted: $\delta(P_A) = 6.3$; $\delta(P_B) = 2.3$; $^{1}J(PtP_A) = 2\,795.1$; $^{1}J(PtP_B) = 3\,161.1$; $N = {}^{2}J(P_AP_B) + {}^{4}J(P_AP_B) = 87.9$ Hz (in $CDCl_3$, ref. external 85% H_3PO_4).

The ^{19}F spectrum of the hydrido complex (**13**) shows only three multiplet signals (2:1:2 ratio) instead of the usual five signals observed in the other A-frame complexes. Moreover, in the ^{1}H n.m.r. spectrum (Figure 3) equivalence of the two methylene protons is seen and the hydride resonance shows two different platinum satellites. This means that a fluxional process is occurring without breaking any H–Pt bond and is in good

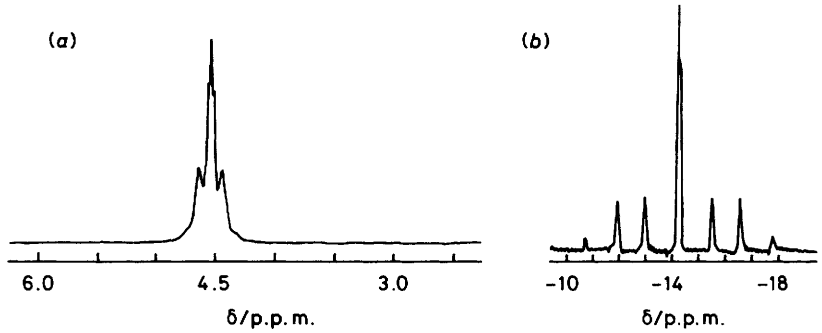
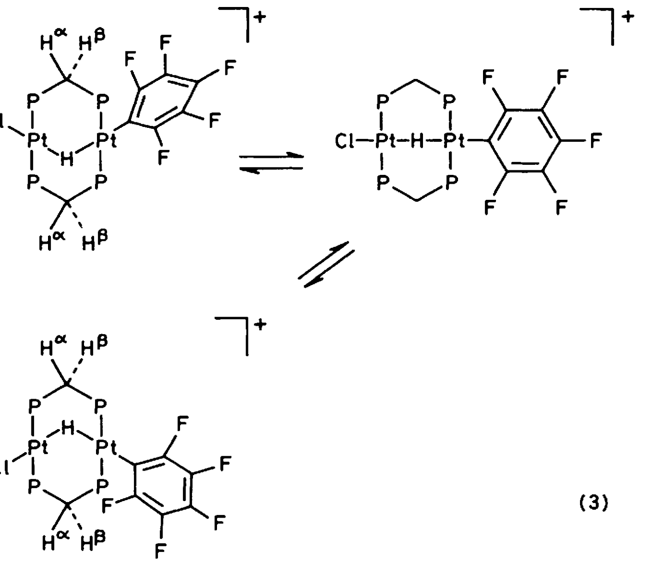


Figure 3. ^1H N.m.r. spectrum (200 MHz) of complex (**13**): (*a*) methylene signal; (*b*) hydrido signal



(3)

agreement with the mechanism depicted in equation (3), which has been proposed before for related hydrido complexes.[23] Since the C_6F_5 group has a higher *trans* influence than the Cl group, a longer average Pt–H distance and a smaller $^1J(^{195}Pt\text{–}H)$ constant throughout the fluxional process is expected for the H–Pt(C_6F_5) than for the H–PtCl bond. The activation energy of the fluxional process seems to be very low since it could not be frozen out on cooling down to −60 °C and only some broadening of the CH_2 signal was noted, possibly due to partial crystallisation in the n.m.r. tube. This observation is in accordance with the high fluxionality observed for $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-dppm})_2]$[23] and suggests that C-bonded ligands lead to low activation energies for this process.

Finally, during the recording of the n.m.r. spectra some conversions in solution were observed. Thus, complex (**14**) leads slowly to (**17**), and its spectra had to be recorded on freshly prepared solutions. In solution, (**22**) and (**24**) were in equilibrium with (**17**) and (**20**), respectively, together with free isonitrile; the n.m.r. spectra were recorded on solutions to which a large excess of CNC_6H_4Me-*p* had been added, to displace the equilibrium to the formation of (**22**) [or (**24**)].

Experimental

The C, H, and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer. Infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene plates. Proton, ^{19}F, and ^{31}P n.m.r. spectra were recorded at room temperature on a Varian XL-200 instrument (200 MHz for ^1H). Molecular weights were determined in $CHCl_3$ solution on a Perkin-Elmer 115 apparatus. Conductivities were measured on *ca.* 10^{-4} mol dm^{-3} solutions in acetone with a Philips PW 9509 conductimeter.

The starting platinum(II) complex $[PtCl(C_6F_5)(dppm\text{-}P)_2]$ was prepared as follows. To a stirred solution of $[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_2(tht)_2]$ (tht = tetrahydrothiophen)[25] (554.3 mg, 0.57 mmol) in benzene (60 cm^3) was added dppm (877.2 mg, 2.28 mmol). After stirring for 3 h the solution was filtered to remove traces of a white precipitate, and then evaporated to dryness. The resulting white residue was stirred in diethyl ether (40 cm^3), filtered off, washed with diethyl ether and dried in an oven (90 °C) for 7 h. Yield: 75% (Found: C, 57.95; H, 3.80. Calc. for $C_{56}H_{44}ClF_5Pt$: C, 57.65; H, 3.80%).

Typical procedures for the synthesis of the complexes are given below.

$[ClPt(\mu\text{-dppm})_2Pt(C_6F_5)]$ (**1**).—To a solution of $[Pt(cod)_2]$ (214.9 mg, 0.522 mmol) in deoxygenated benzene (150 cm^3) *under nitrogen* was added $[PtCl(C_6F_5)(dppm\text{-}P)_2]$ (609 mg, 0.522 mmol). The yellow solution was stirred at room temperature for 4 h. Upon evaporation to *ca.* 2 cm^3 and addition of diethyl ether (20 cm^3) pale yellow crystals of (**1**) were formed which were collected by filtration, washed with Et_2O, and dried in an oven under vacuum at 80 °C. Yield: 85%.

$[XPt(\mu\text{-dppm})_2Pt(C_6F_5)]$ [X = Br (**2**) *or* SCN (**3**)].—A typical experiment is described. To a solution of (**1**) (153 mg, 0.112 mmol) in acetone (30 cm^3) an excess of KSCN (92 mg, 0.946 mmol) was added. The mixture was stirred at room temperature for 20 h and then evaporated to dryness. The residue was extracted with CH_2Cl_2 (60 cm^3) and methanol (10 cm^3) was added to the filtered solution. Upon evaporation to *ca.* 10 cm^3 a solid was obtained which was recrystallised from acetone–methanol to give (**3**). The product was dried in an oven under vacuum at 80 °C to remove crystal acetone. Yield: 70%.

$[Cl_3SnPt(\mu\text{-dppm})_2Pt(C_6F_5)]$ (**4**).—To a solution of (**1**) (100 mg, 0.073 mmol) in CH_2Cl_2 (20 cm^3) was added a solution containing $SnCl_2$ (13.9 mg, 0.073 mmol) in methanol (3 cm^3). After stirring for 45 min at room temperature the resulting deep yellow solution was evaporated to *ca.* 2 cm^3, and Et_2O (10 cm^3) was added to give yellow crystals of (**4**). The product was dried in an oven at 80 °C. Yield: 75%.

$[LPt(\mu\text{-dppm})_2Pt(C_6F_5)]BPh_4$ [L = PPh_3 (**5**), $AsPh_3$ (**6**), py (**7**), *or* CO (**8**)].—A typical preparation was as follows. The addition of PPh_3 (16.4 mg, 0.062 mmol) to a suspension of (**1**)

(85.2 mg, 0.062 mmol) in methanol (25 cm^3) caused the starting material to dissolve within a few minutes. $NaBPh_4$ (33 mg, 0.096 mmol) was added to the solution and the mixture was stirred for 30 min. Evaporation to *ca.* 5 cm^3 gave (**5**) which was filtered off, washed with water, and recrystallised from CH_2Cl_2–n-hexane. Yield: 75%.

For L = py the addition of the ligand did not cause solution of the starting material. For L = CO the reaction was carried out in CH_2Cl_2, CO was bubbled through the suspension containing (**1**) and $NaBPh_4$ for 30 min, and (**8**) was precipitated by adding n-hexane; it was then recrystallised from CH_2Cl_2–MeOH. Yield: 90%.

$[ClPt(\mu\text{-dppm})_2(\mu\text{-}SO_2)Pt(C_6F_5)]$ (**9**).—Sulphur dioxide was bubbled for 1 h through a solution of (**1**) (104 mg, 0.076 mmol) in CH_2Cl_2 (6 cm^3) and then n-hexane was added to precipitate (**9**). Yield: 90%.

$[ClPt(\mu\text{-dppm})_2(\mu\text{-}N_2C_6H_4Me\text{-}p)Pt(C_6F_5)]BF_4$ (**10**).—To a cooled (−25 °C) solution of (**1**) (100 mg, 0.073 mmol) in acetone (20 cm^3) was added $[N_2C_6H_4Me\text{-}p]BF_4$ (15.1 mg, 0.073 mmol). The solution was stirred at −25 °C for 15 min and then allowed to reach room temperature over a period of 30 min. Evaporation to *ca.* 5 cm^3 and addition of Et_2O (15 cm^3) afforded (**10**) which was recrystallised from acetone–ethanol. Yield: 61%.

$[XPt(\mu\text{-dppm})_2\{\mu\text{-}C_2(CO_2Me)_2\}Pt(C_6F_5)]$ [X = Cl (**11**) *or* $SnCl_3$ (**12**)].—To a solution of (**1**) (100 mg, 0.073 mmol) in CH_2Cl_2 (20 cm^3) was added $MeO_2CC{\equiv}CCO_2Me$ (9 μl, 0.073 mmol) and the mixture, protected from light, was stirred at room temperature for 3 d. Upon evaporation to *ca.* 3 cm^3 and addition of Et_2O (20 cm^3) yellow crystals of (**11**) were obtained in 73% yield. Complex (**12**) was obtained similarly from (**4**) in 65% yield.

$[ClPt(\mu\text{-dppm})_2(\mu\text{-}H)Pt(C_6F_5)]ClO_4$ (**13**).— To a solution of (**1**) (110 mg, 0.081 mmol) in $CHCl_3$ (15 cm^3) was added one drop of commercial $HClO_4$ and the mixture was stirred for 15 min. Evaporation to *ca.* 3 cm^3 and addition of n-hexane (20 cm^3) gave an oil which was washed with n-hexane and then stirred in MeOH (2 cm^3) to give (**13**) as a pale yellow solid. Yield: 60%.

$[ClPt(\mu\text{-dppm})_2(\mu\text{-}CNC_6H_4Me\text{-}p)Pt(C_6F_5)]$ (**14**).—To a solution of (**1**) (150 mg, 0.110 mmol) in benzene (50 cm^3) was added $CNC_6H_4Me\text{-}p$ (13.9 μl, 0.110 mmol). The yellow solution was stirred for 4 h and then evaporated to *ca.* 10 cm^3. Addition of Et_2O (15 cm^3) produced yellow crystals of (**14**) which were filtered off, washed with Et_2O, and dried in the oven at 105 °C. Yield: 81%.

$[(RNC)Pt(\mu\text{-dppm})_2Pt(C_6F_5)]Cl$ [R = C_6H_{11} (**15**), Bu^t (**16**), *or* $C_6H_4Me\text{-}p$ (**17**)].—To a stirred solution of (**1**) (200 mg, 0.147 mmol) in benzene (40 cm^3) was added CNC_6H_{11} (17.8 μl, 0.147 mmol) whereupon the initially pale yellow solution changed to orange and, after 1 min to yellow again while a pale yellow precipitate separated. The yellow product was filtered off, washed with benzene, and identified as (**15**). Yield: 80%. Complex (**16**) was obtained similarly in 88% yield. For (**17**) the reaction was carried out in CH_2Cl_2, with stirring for 3 h, and the product was isolated by evaporating to *ca.* 5 cm^3 and adding Et_2O. The product was dried in an oven at 70 °C.

$[(RNC)Pt(\mu\text{-dppm})_2Pt(C_6F_5)]BPh_4$ [R = C_6H_{11} (**18**), Bu^t (**19**), *or* $C_6H_4Me\text{-}p$ (**20**)].—To a stirred solution of (**1**) (141 mg, 0.103 mmol) in CH_2Cl_2 (30 cm^3) was added CNC_6H_{11} (12.5 μl, 0.103 mmol) and then a solution of $NaBPh_4$ (48 mg, 0.140 mmol) in MeOH (2 cm^3). After stirring for 1 h the mixture was filtered and MeOH (10 cm^3) was added to the solution. Upon evaporation to a small volume, pale yellow crystals of (**18**) were obtained. Yield: 73%. Complexes (**19**) and (**20**) were obtained similarly in 70% yield.

$[(RNC)Pt(\mu\text{-dppm})_2(\mu\text{-}CNR)Pt(C_6F_5)]Cl$ [R = C_6H_{11} (**21**) *or* $C_6H_4Me\text{-}p$ (**22**)].—To a solution of (**1**) (125 mg, 0.092 mmol) in acetone (30 cm^3) was added CNC_6H_{11} (32 μl, 0.265 mmol), whereupon the solution became reddish. After stirring for 1 h the solution was evaporated to *ca.* 10 cm^3 and Et_2O (20 cm^3) was added to give (**21**) as red crystals. Yield: 80%.

$[(RNC)Pt(\mu\text{-dppm})_2(\mu\text{-}CNR)Pt(C_6F_5)]BPh_4$ [R = C_6H_{11} (**23**) *or* $C_6H_4Me\text{-}p$ (**24**)].—To a solution of (**1**) (114 mg, 0.086 mmol) in CH_2Cl_2 (25 cm^3) was added CNC_6H_{11} (70 μl, 0.580 mmol) and then a solution of $NaBPh_4$ (29.5 mg, 0.086 mmol) in MeOH (5 cm^3). After stirring for 5 h the mixture was filtered and the solution was evaporated to *ca.* 5 cm^3 to give red crystals of (**23**). Yield: 70%.

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