Disproportionation of a Halogen-bridged Complex containing Platinum and Palladium

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^{31}P N.m.r. spectroscopy shows that complexes of the type [$PdPtCl_4L_aL_b$] [L_a and L_b are either the same or different tertiary-phosphine ligands (PPr_3 or PBu_3)] are formed in chloroform solution when equimolar amounts of [$Pd_2Cl_4(L_a)_2$] and [$Pt_2Cl_4(L_b)_2$] are mixed at room temperature. All three complexes are in dynamic equilibrium, and a kinetic study indicates that the exchange occurs *via* a tetrameric intermediate involving four metal centres. Attempts to isolate the mixed metal complexes have proved unsuccessful. The first measurement of platinum–platinum coupling constants is reported for the complexes [$Pt_2Cl_4(PBu_3)_2$] and [$Pt_2I_4(PBu_3)_2$].

ALTHOUGH complexes containing different transition metals have recently attracted much attention,[1-5] most work has concentrated on preparative routes and little is known about the chemistry and dynamic behaviour of such complexes.

Observation of the ^{31}P n.m.r. spectrum of an equimolar mixture of [$Pt_2Cl_4(PBu_3)_2$] and [$Pd_2Cl_4(PBu_3)_2$] in deuteriochloroform shows that mixing solutions of these two complexes at room temperature leads to the immediate formation of the mixed metal complex

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[1] R. J. Haines, R. Mason, J. A. Zubieta, and C. R. Nolte, *J.C.S. Chem. Comm.*, 1972, 990.

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[3] A. R. Dias and M. L. H. Green, *J. Chem. Soc.* (*A*), 1971, 1951.

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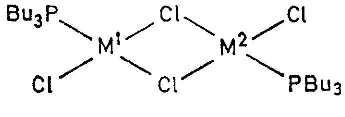
$[PtPdCl_4(PBu_3)_2]$. All three complexes have the structure A.



A

(I) $M^1 = M^2 = Pt$
(II) $M^1 = M^2 = Pd$
(III) $M^1 = Pt$; $M^2 = Pd$

If the fine structure is ignored,* the ^{31}P n.m.r. spectrum † of (I) consists of a strong singlet, with satellites due to the direct $^{195}Pt-^{31}P$ coupling, while that of (II) shows simply a singlet. In the ^{31}P n.m.r. spectrum of the mixture two new phosphorus resonances are present.‡ One of these new signals has platinum satellites, and this we assign to the phosphorus nucleus bound to platinum in (III). The remaining signal is assigned to the phosphorus nucleus bound to palladium in (III). Integration of the n.m.r. spectrum shows that the three species are present in the ratio (I) : (II) : (III) = 1 : 1 : 2.3, indicating that the equilibrium constant for equilibrium (a) is 5.3.

$$[Pt_2Cl_4(PBu_3)_2] + [Pd_2Cl_4(PBu_3)_2] \rightleftharpoons 2[PtPdCl_4(PBu_3)_2] \quad \text{(a)}$$

However, since the accuracy of the integral is not better than ±10% this deviation from the statistically expected distribution may not be significant.

In Figure 1(a) we show an expansion of the phosphorus–palladium and phosphorus–platinum sections of the ^{31}P n.m.r. spectrum of the mixture, labelled, respectively, A and B. It can be seen that at 30 °C the signals due to the phosphorus nuclei bound to palladium are considerably broader than those due to the phosphorus nuclei bound to platinum. Also, at this temperature the expected $^4J(^{31}P-^{31}P)$ couplings on the signals due to P_a and P_b in structure (IV) are not resolved. When the sample is cooled to −16 °C the (expanded) ^{31}P n.m.r. spectrum shows complete resolution of all the expected couplings [see Figure 1(b)]. The ^{31}P n.m.r. data are given in Tables 1 and 4, both for this system and for that obtained by mixing equimolar amounts of $[Pt_2Cl_4(PBu_3)_2]$ and $[Pd_2Cl_4(PPr_3)_2]$ in deuteriochloroform solution.

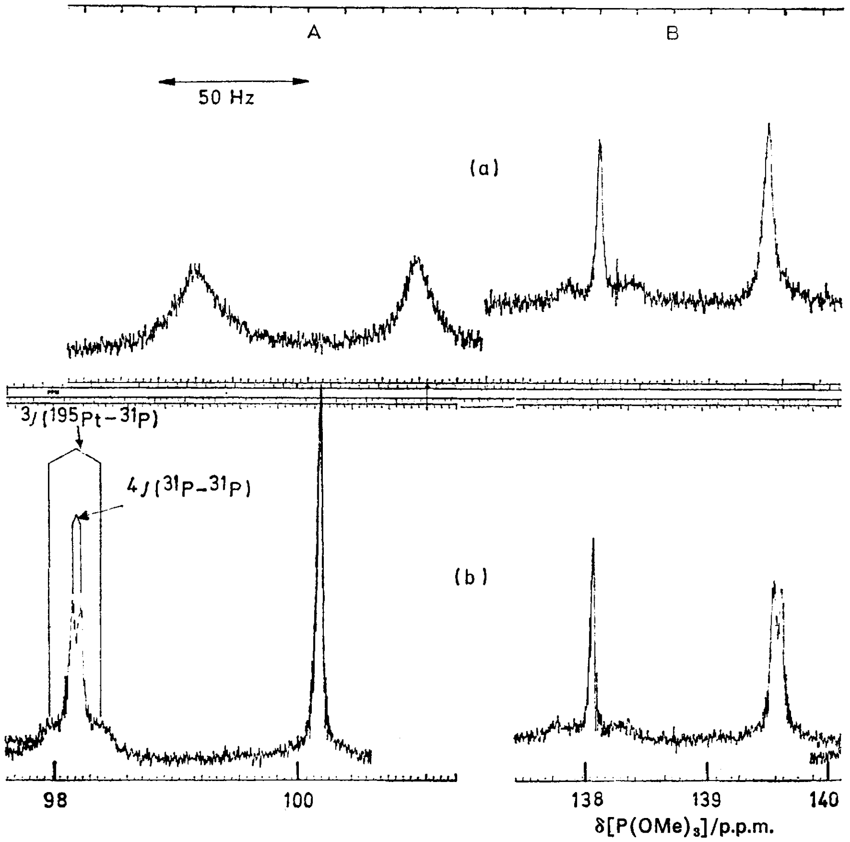


FIGURE 1 Expanded (proton-decoupled) ^{31}P n.m.r. spectrum of a 1 : 1 mixture of $[Pt_2Cl_4(PBu_3)_2]$ and $[Pd_2Cl_4(PBu_3)_2]$ recorded in deuteriochloroform at 40.5 MHz and at a temperature of (a) 30 °C and (b) −16 °C. The phosphorus–palladium and phosphorus–platinum resonances are labelled A and B, respectively. Shifts are relative to trimethyl phosphite

The temperature-dependence of the ^{31}P n.m.r. spectrum indicates that species (I), (II), and (III) are in dynamic equilibrium. We have undertaken a kinetic study of this system, employing n.m.r. line-broadening tech-

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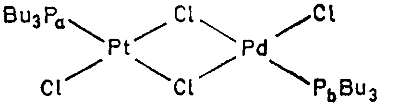
* A discussion of the complete ^{31}P n.m.r. spectrum of a complex of the type $[Pt_2X_4L_2]$ (X = halogen, L = tertiary phosphine) is given later in the paper.

† In all the ^{31}P n.m.r. spectra quoted, proton coupling was removed using a random-noise decoupler.

‡ While this work was in progress other workers independently observed the same phenomenon.[6]

[6] B. T. Heaton, personal communication.

niques.[7] A preliminary report of this work has already appeared.[8]



(IV)

Kinetic Measurements.—We have established that the observed broadening of the signals is not due to dissociation of the tertiary-phosphine ligand.† Thus, the exchange phenomenon observed may be represented by:

$$\mathrm{P^*PdPdP^* + PPdPtP \longrightarrow P^*PdPdP + P^*PdPtP} \quad \text{(b)}$$

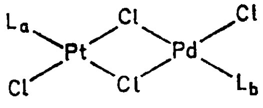
and

$$\mathrm{P^*PtPtP^* + PPdPtP \longrightarrow P^*PtPtP + P^*PtPdP} \quad \text{(c)}$$

where P*PtPtP*, P*PdPdP*, and PPtPdP represent complexes (I), (II), and (III), respectively. Exchange (b) leads to broadening of the phosphorus–palladium resonances (*i.e.* section A of the spectrum, Figure 1) and exchange (c) to broadening of the phosphorus–platinum resonances (*i.e.* section B of the spectrum, Figure 1). The parameter obtained from the n.m.r. studies is the mean lifetime (τ) of a particular site, which is inversely proportional to the rate of site exchange.[9] Using a ratio of $[Pt_2Cl_4(PBu_3)_2]$ to $[Pd_2Cl_4(PBu_3)_2]$ of 1 : 1, we have measured τ^{-1} as a function of temperature over the range −16 to +55 °C at four different initial concentrations of dimer. The results are given in Table 2. The activation energies for the two processes [represented by equations (b) and (c)] were calculated from a plot of $\ln \tau^{-1}$ *vs.* T^{-1} as being 46 ± 8 kJ mol^{-1} for (b) and 59 ± 17 kJ mol^{-1} for (c). The rate order in palladium dimer [*i.e.* complex (I)] for the exchange represented by (b) was determined from a linear plot of $\ln \tau_{Pd_2}^{-1}$ *vs.* $\ln [Pd_2Cl_4(PBu_3)_2]$ at a given temperature. A least-squares analysis of these data, at 285 and 303 K, gave a gradient of 1.17 ± 0.19, indicating that the exchange, (b), is first-order in palladium dimer. This implies that the exchange proceeds *via* attack of a dimer on a dimer rather than *via* dissociation of the dimeric complexes into monomers.‡

TABLE 1

^{31}P N.m.r. data * for complexes of the type



	$\delta(L_a)$ †/p.p.m. ($\pm$0.2 p.p.m.)	$\delta(L_b)$ †/p.p.m. ($\pm$0.2 p.p.m.)	$^1J(^{195}Pt-^{31}P)$/Hz ($\pm$0.2 Hz)	$^3J(^{195}Pt-^{31}P)$/Hz ($\pm$0.2 Hz)	$^4J(^{31}P-^{31}P)$/Hz ($\pm$0.2 Hz)
$L_a = L_b = PBu_3$	+139.6	+98.2	3 841.0	17.0	2.5
$L_a = PBu_3$ $L_b = PPr_3$	+139.4	+99.4	3 844.0	17.0	2.0

* Spectra were recorded in deuteriochloroform at −16 °C with complete (random noise) proton decoupling. The chemical shifts relative to trimethyl phosphite for the phosphorus nuclei in $[Pd_2Cl_4(PPr_3)_2]$ and $[Pd_2Cl_4(PBu_3)_2]$ are 101.2 and 100.2 p.p.m., respectively, recorded under the same conditions. † Relative to trimethyl phosphite.

On the basis of this observation we suggest that the exchange proceeds *via* a bimolecular process involving the interaction of two dimers to form an intermediate tetramer of the type (V) [for exchange (b)] which then disproportionates.

TABLE 2

^{31}P N.m.r.* kinetic data for the system:

$$[Pt_2Cl_4(PBu_3)_2] + [Pd_2Cl_4(PBu_3)_2] \rightleftharpoons 2[PdPtCl_4(PBu_3)_2]$$

Initial dimer † concentration

Temp./K	0.09M		0.11M		0.15M		0.2M	
($\pm$2.0 K)	$\tau_{Pd_2}^{-1}$	$\tau_{Pt_2}^{-1}$	$\tau_{Pd_2}^{-1}$	$\tau_{Pt_2}^{-1}$	$\tau_{Pd_2}^{-1}$	$\tau_{Pt_2}^{-1}$	$\tau_{Pd_2}^{-1}$	$\tau_{Pt_2}^{-1}$
257							1.6	
265							3.1	
273	1.6		1.6		1.6		4.7	
279	3.1		4.7		4.7		7.9	
285	6.3		7.4		8.4		12.6	1.6
303	22.0		24.2	3.1	29.3	3.1	42.4	4.7
313	39.6	9.0	42.4	9.4	45.6	9.4	61.3	14.1
321	55.0	15.3	70.7	22.0	73.5	17.7		23.6
328		23.9		25.1		28.3		

* The spectra were recorded in deuteriochloroform solution with complete (random noise) proton decoupling. $\tau_{Pd_2}^{-1}$ and $\tau_{Pt_2}^{-1}$ were calculated from the line widths at half peak height of the signals due to the phosphorus nuclei in $[Pd_2Cl_4(PBu_3)_2]$ and $[Pt_2Cl_4(PBu_3)_2]$, respectively. † $[Pt_2Cl_4(PBu_3)_2]$ or $[Pd_2Cl_4(PBu_3)_2]$.

A similar tetrameric intermediate has also been proposed[10] for the exchange of 2-methylallylpalladium groups in thiocyano- and halogeno-bridged dimers of the type $[(C_4H_7PdX)_2]$, where X = SCN, Cl, or I.

Since both of the ^{31}P n.m.r. signals due to the phosphorus nuclei bonded to the platinum show coupling (see Figure 1), accurate line-width analysis was impossible and a treatment analogous to that outlined above for the palladium case proved inconclusive. Knowledge

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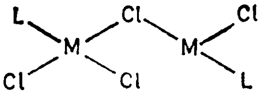
† Since the ^{31}P n.m.r. spectrum of a mixture of $[Pt_2Cl_4(PBu_3)_2]$ and $[Pd_2Cl_4(PPr_3)_2]$ in $CDCl_3$ shows no signals arising from either PBu_3 bonded to Pd or PPr_3 bonded to Pt we consider that the observed broadening is not due to dissociation of the tertiary phosphine ligands.

‡ Clearly this analysis does not exclude the possibility of partial rupture of the chloro-bridge to give a species such as



which is then active in the exchange sequence.

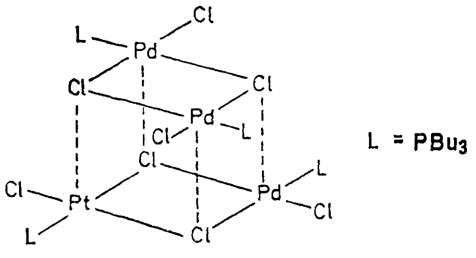
[7] J. A. Pople, W. G. Schneider, and J. H. Bernstein, 'High Resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959.

[8] C. Masters and J. P. Visser, *J.C.S. Chem. Comm.*, 1974, 932.

[9] K. Vrieze, H. C. Volger, and P. W. N. M. van Leeuwen, *Inorg. Chim. Acta*, 1969, **3**, 109.

[10] D. L. Tibbetts and T. L. Brown, *J. Amer. Chem. Soc.*, 1969, **91**, 1108.

of the rate order of the reaction allows the activation entropy to be calculated using the appropriate relationship for reactions in solution. The thermodynamic data



(V)

for this system and the $[Pd_2Cl_4(PPr_3)_2]/[Pt_2Cl_4(PBu_3)_2]$ system are summarized in Table 3. We suggest that

TABLE 3

Thermodynamic data for the $[Pd_2Cl_4L_2]/[Pt_2Cl_4(PBu_3)_2]$ systems

Exchange process	Activation energy (E_a/kJ mol^{-1})
Pd–P (L = PPr_3) *	34 ± 8
Pd–P (L = PBu_3) *	46 ± 8
Pt–P (L = PPr_3) †	80 ± 17
Pt–P (L = PBu_3) †	59 ± 17

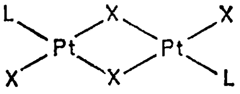
* $P^*PdPdP^* + PPdPtP \longrightarrow P^*PdPtP + P^*PdPdP$
† $P^*PtPtP^* + PPdPtP \longrightarrow P^*PdPtP + P^*PtPtP$

For the palladium exchanges (*i.e.* *) (L = PPr_3 or PBu_3) the activation entropies are -80 ± 17 J mol^{-1} K^{-1} and -50 ± 17 J mol^{-1} K^{-1}, respectively. For the platinum exchange (*i.e.* †) the experimental error in the data is too great to allow a meaningful value for the activation entropy to be calculated.

the higher activation energy found for the platinum–phosphorus exchange, *i.e.* reaction (c), compared to that of the palladium-phosphorus exchange, *i.e.* reaction (b), reflects the greater strength of the chloro-bridge in (I) compared to that in (II).

Attempted Isolation.—When set aside, a chloroform solution containing $[Pt_2Cl_4L_2]$ and $[Pd_2Cl_4L_2]$ (L = PEt_3, PPr_3, or PBu_3) in the ratio 1 : 1 produces crystals the analysis (C, H, Cl) for which is consistent with their formulation as $[PtPdCl_4L_2]$ and which are made up of molecules having the corresponding molecular weight (osmometric determination). Although only a complete *X*-ray diffraction study would provide definitive evidence, we suggest that these crystals are probably mixed crystals containing all three species (*i.e.* $[Pt_2Cl_4L_2]$, $[Pd_2Cl_4L_2]$, and $[PtPdCl_4L_2]$) since *X*-ray powder photographs show that $[Pd_2Cl_4(PPr_3)_2]$, $[Pt_2Cl_4(PPr_3)_2]$, and the crystals (when L = PPr_3) are all isomorphous. The ^{31}P n.m.r. spectrum shows that in solution the three species are present in the expected statistical amounts (±10%).

Complete ^{31}P *N.m.r. Spectra of* $[Pt_2X_4(PBu_3)_2]$ (X = Cl *or* I).—Although platinum has a naturally occurring isotope with a nuclear spin of one half (^{195}Pt, 33.7% abundance), and although many complexes containing two platinum nuclei are known, hitherto no platinum–platinum coupling has been reported. A complex of the type (B) exists as a mixture of three magnetic isomers:



(B)

L = tertiary phosphine
X = halogen

one in which both platinum nuclei have *I* (spin quantum number) = 0, one in which one platinum has *I* = 0, and the other $I = \frac{1}{2}$, and finally one isomer in which both platinum nuclei have $I = \frac{1}{2}$.

By examination of the proton-decoupled ^{31}P n.m.r. spectrum of this complex, when L = PBu_3 and X = I, we have been able to detect all the lines predicted for the three aforementioned magnetic isomers (see Figure 2). Previously, for this type of complex, only three of the expected 19 lines have been reported.[11] The isomer with both platinum nuclei having *I* = 0 gives rise to a single line (Δ in Figure). The second isomer, in which $I\{Pt(1)\} = 0$ and $I\{Pt(2)\} = \frac{1}{2}$, gives rise to an AA′X pattern (O in Figure) with well resolved $^1J(^{31}P\text{–}^{195}Pt)$, $^3J(^{31}P\text{–}^{195}Pt)$, and $^4J(^{31}P\text{–}^{31}P)$. The third isomer, in which both platinum nuclei have $I = \frac{1}{2}$, gives rise to an AA′XX′ pattern in which all of the ten predicted[12] lines are observed (X in Figure). From the positions of these latter lines $^2J(^{195}Pt\text{–}^{195}Pt)$ is readily calculated. Further, the observation that the most intense lines in the AA′XX′ spectrum (*i.e.* at ±1 751 Hz) fall inside the $^1J(^{31}P\text{–}^{195}Pt)/^4J(^{31}P\text{–}^{31}P)$ doublet of doublets at ±1 764 Hz indicates that $^1J(^{31}P\text{–}^{195}Pt)$ and $^3J(^{31}P\text{–}^{195}Pt)$ are opposite in sign.

TABLE 4

^{31}P N.m.r. data for $[Pt_2X_4(PBu_3)_2]$ (X = Cl or I) from 40.5 MHz spectra recorded at *ca.* 40 °C

	Chemical shift and coupling constants			Position of lines arising from AA′XX′ pattern centred about $\delta(PBu_3)$	
X =	Cl	I		Cl	I
$\delta(PBu_3)$/p.p.m.*	+138.6	+140.3	±0.1	±1 823 †	±1 595
$^1J(^{31}P\text{–}^{195}Pt)$/Hz	3 822	3 528	±0.2	±1 898	±1 600
$^3J(^{31}P\text{–}^{195}Pt)$/Hz	23.5	26.0	±0.2	±2 022 †	±1 751
$^4J(^{31}P\text{–}^{31}P)$/Hz	2.8	5.1	±0.2		±1 975
$^2J(^{195}Pt\text{–}^{195}Pt)$/Hz	199 ± 2	380	±1		±1 980

* Relative to trimethyl phosphite. † Expected doublet not resolved.

All proton–phosphorus couplings were removed by noise decoupling. Chloroform containing *ca.* 10% hexadeuteriobenzene (^2H field frequency lock used) was used as solvent for $[Pt_2I_4(PBu_3)_2]$ and deuteriochloroform for $[Pt_2Cl_4(PBu_3)_2]$.

A similar analysis of the ^{31}P n.m.r. spectrum of $[Pt_2Cl_4(PBu_3)_2]$ in deuteriochloroform gives a value of 199 Hz for $^2J(^{195}Pt\text{–}^{195}Pt)$ in this complex. The ^{31}P spectroscopic data are given in Table 4.

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[11] A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.* (*A*), **1966**, 1707.

[12] F. A. Bovey, ' Nuclear Magnetic Resonance Spectroscopy,' Academic Press, New York and London, **1969**, p. 117.

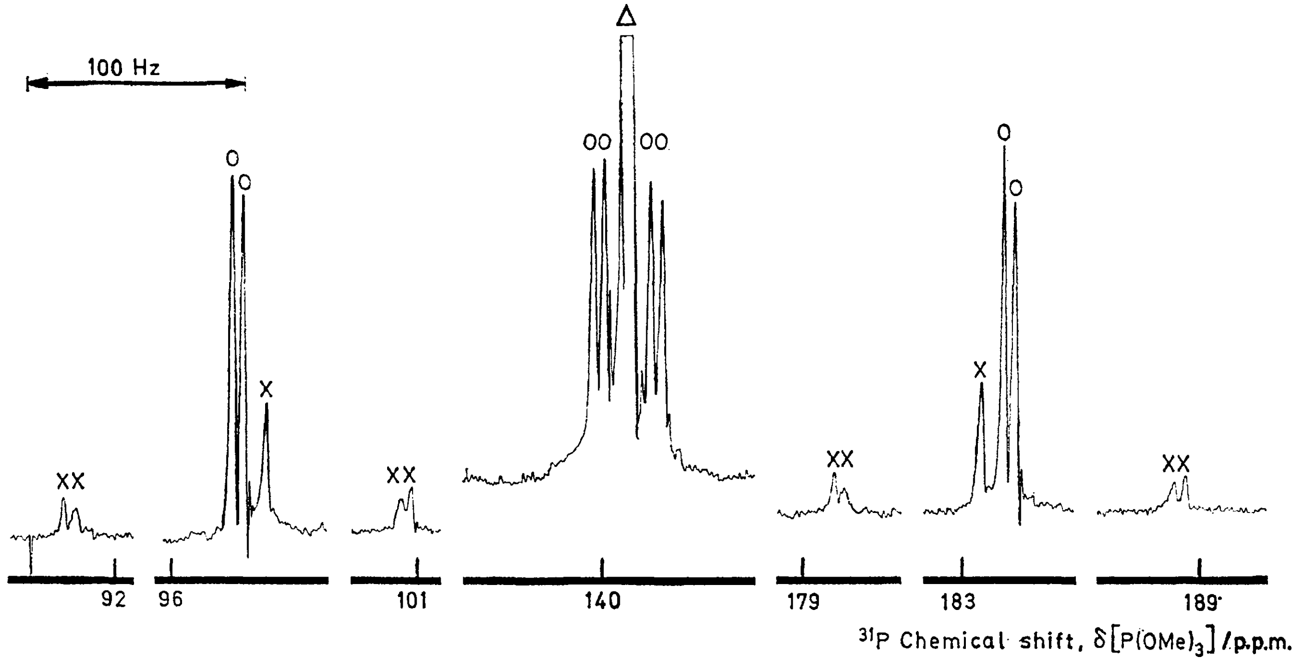

FIGURE 2 $^{31}P\{^1H\}$ N.m.r. spectrum of [$Pt_2I_4(PBu_3)_2$] recorded at 40.5 MHz in chloroform, with complete proton decoupling

EXPERIMENTAL

Complexes of type [$M_2Cl_4L_2$] (M = Pd or Pt and L = PEt_3, PPr_3, or PBu_3) were prepared using previously published procedures.[13-15] ^{31}P N.m.r. spectra of solutions in deuteriochloroform were recorded at 40.5 MHz using a Varian XL 100 spectrometer. Either hexadeuteriobenzene or deuteriochloroform was used to provide a ^2H field-frequency lock. Shifts are quoted with respect to *ca.* 25% trimethyl phosphite in deuteriochloroform. All proton couplings were removed using a random noise decoupler.

Molecular weights were measured using a Mechrolab vapour-pressure osmometer, model 301 A, for solutions in chloroform at 30 °C.

[4/2041 *Received, 4th October,* 1974]

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[15] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 2351.