Inorganic Disproportionation. A ^{31}P Nuclear Magnetic Resonance Study of a Bi-hetero-metallic System containing Platinum and Palladium

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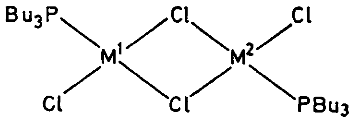
Summary ^{31}P N.m.r. spectra show that on mixing chloroform solutions of $[Pt_2Cl_4(PBu_3)_2]$ and $[Pd_2Cl_4(PBu_3)_2]$ bi-hetero-metallic complexes of type $[PdPtCl_4(PBu_3)_2]$ are formed; the three complexes are in dynamic equilibrium and a kinetic study indicates that the exchange occurs *via* a tetrameric intermediate involving four metal centres.

THE ^{31}P n.m.r. spectrum of an equimolar mixture of $[Pt_2Cl_4PBu_3)_2]$ (I) and $[Pd_2Cl_4(PBu_3)_2]$ (II) in $CDCl_3$ shows that mixing of solutions of these two complexes at room temperature leads to the immediate formation of the mixed metal complex $[PtPdCl_4(PBu_3)_2]$ (III). Ignoring the fine structure† the ^{31}P n.m.r. spectrum of (I) consists of a singlet with ^{195}Pt satellites and that of (II) simply of a singlet. In the ^{31}P n.m.r. spectrum of the mixture two new phosphorus resonances are present, one of which has ^{195}Pt satellites. These new signals are assigned to complex (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.



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

At temperatures above *ca.* −10 °C the resonances due to the phosphorus nuclei bonded to the palladium in (II) and (III) begin to broaden, indicating that complexes (II) and (III) are in exchange. An analogous broadening is observed above *ca.* +10 °C for the phosphorus nuclei bonded to the platinum in (I) and (III). We consider that this broadening does not arise from tertiary-phosphine exchange since on mixing solutions of $[Pt_2Cl_4(PBu_3)_2]$ and $[Pd_2Cl_4(PPr_3)_2]$ no signals arising from either PBu_3 bonded to Pd or PPr_3 bonded to Pt were observed.

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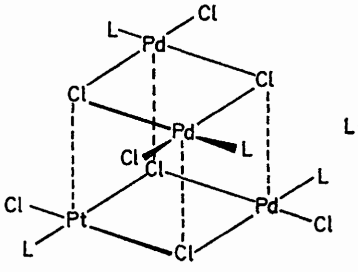
† Careful examination of the spectrum reveals the expected 19 lines arising from the three magnetic isomers, containing 0, 1, or 2 magnetic ($I = \frac{1}{2}$) platinum nuclei $\delta[P(OMe)_3]$ for PBu_3 + 140·3 p.p.m.; $^1J(^{31}P-^{195}Pt)$ 3528·0 Hz; $^3J(^{31}P-^{195}Pt)$ 26·0 Hz; $^4J(^{31}P-^{31}P)$ 5·1 Hz; $^2J(^{195}Pt-^{195}Pt)$ 380 Hz.

‡ While this work was in progress other workers independently observed this phenomenon.[1]

A kinetic study, employing n.m.r. line-broadening techniques, shows that the exchange between (II) and (III) is first order in complex (II) and that, similarly, the exchange between (I) and (III) is first order in complex (I). This implies that the observed exchange process, represented by reaction (1), is first order in both components, as is that represented by reaction (2), *i.e.* the exchanges proceed *via* attack of a dimer on a dimer rather than *via* dissociation of the dimeric complexes.



L = PBu_3

(IV)

$$Pd_2 + Pd^*Pt \rightarrow PdPd^* + PdPt \qquad (1)$$

$$Pt_2 + PdPt^* \rightarrow PtPt^* + PdPt \qquad (2)$$

On the basis of the above results we propose that the exchange proceeds by a bimolecular process involving the interaction of two dimers to form an intermediate of type (IV) [for exchange (1)]. Although a similar tetrameric intermediate has been proposed[2] for the exchange of 2-methylallyl-palladium groups in thiocyano- and halogeno-bridged dimers of the type $[(C_4H_7PdX)_2]$ where X = SCN, Cl, or I, the above is, to our knowledge, the first example of a simple bi-hetero-metallic system containing platinum and palladium.

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

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