Inorganica Chimica Acta, 86 (1984) L81–L82

^{195}Pt N.M.R. Spectra of Some [Pt(PR$_3$)$_n$] Complexes

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Received February 24, 1984

Despite the extensive reports of ^{195}Pt chemical shifts in the literature [1], very little attention has been paid to the ^{195}Pt chemical shifts of platinum(0) complexes and especially to platinum(0)–tertiary phosphine complexes [2, 3]. In the course of an investigation of the properties of Pt(PR$_3$)$_n$, we have measured their ^{195}Pt n.m.r. spectra, and the chemical shifts are reported in Table I. $^1J(^{195}\text{Pt}, {}^{31}\text{P})$ were also measured and found to be in good agreement with those reported earlier using ^{31}P n.m.r. spectroscopy [4]. The observation of $^1J(^{195}\text{Pt}, {}^{31}\text{P})$ provides a direct measure of the stoichiometry of the complex. Thus Pt(PMePh$_2$)$_4$ was originally formulated as Pt(PMePh$_2$)$_3$, even in the presence of free PMePh$_2$ [5]. Subsequent ^{31}P n.m.r. measurements showed the compound to be Pt(PMePh$_2$)$_4$ at −17 °C, but relatively fast PMePh$_2$ exchange prevented the unambiguous proof of the existence of Pt(PMePh$_2$)$_4$ in solution at room temperature [4]. The ^{195}Pt n.m.r. spectrum of Pt(PMePh$_2$)$_4$ at room temperature clearly shows a 1:5:10:5:1 quintet due to $^1J(^{195}\text{Pt}, {}^{31}\text{P})$ proving the tetrakis formulation, see Fig. 1.

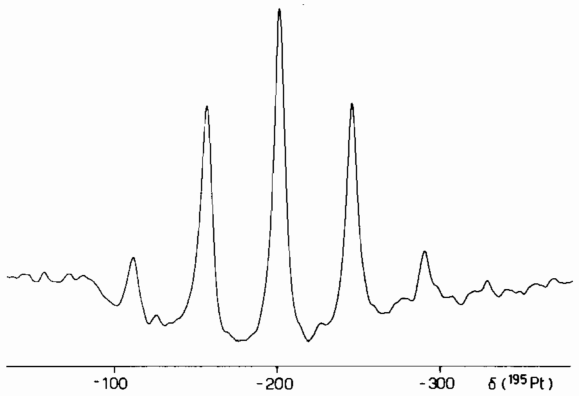

Fig. 1. 85.63 MHz ^{195}Pt n.m.r. spectrum of Pt(PMePh$_2$)$_4$ in toluene-d$_8$–toluene at 23 °C with broadband ^{1}H decoupling.

The ^{195}Pt chemical shifts of Pt(PR$_3$)$_n$ are of considerable interest. The chemical shifts of PtL$_2$, L = PPr$_3{}^i$, P(cyclohexyl)$_3$, or PBu$_2{}^t$Ph, are like lowest frequency ones so far reported, and the chemical shifts follow the order Pt(PR$_3$)$_3$ > Pt(PR$_3$)$_4$ > Pt(PR$_3$)$_2$. These observations can be explained in terms of the paramagnetic shielding term, σ^P, which is believed to be dominant for all nuclei apart from ^{1}H [6]. In a LCAO description, this term is only non-zero between pairs of occupied and empty molecular orbitals containing atomic orbitals having the same angular momentum quantum number. It is on this treatment that the Ramsey equation is based. For d^6 octahedral transition metal complexes, *e.g.*, cobalt(III), it has been shown that there is a linear dependence of the metal chemical shift on ΔE^{-1} where ΔE is the energy separation between the filled t_{2g} orbitals and the empty e_g orbitals [7]. A similar analysis may be applied to platinum(0) complexes with tetrahedral, trigonal, and linear stereochemistry, the molecular orbital diagrams of which are shown in Fig. 2. Examination of the tetrahedral case shows that the first excited state $e^1t_2{}^{*1}$ will mix with the ground state, the degree of mixing depending upon the platinum *d*-orbital content of the $t_2{}^*$ orbital. This *d*-orbital content is to be expected to be sensitive to the ligand, and it is not surprising that there is a substantial chemical shift range for the PtL$_4$ compounds. For the trigonal case, the filled e^1 non-bonding orbital will have some *p*-character, providing a low energy excited state $e'^1a_2''^1$ using the empty a_2'' non-bonding orbital. In contrast, in the linear case, the first excited state to contribute to the paramagnetic term involves the excitation of a *bonding* electron from the $\sigma_u{}^+$ bonding orbital to the $\pi_u{}^+$ empty non-bonding orbital. From electronic spectra, the transition to $e''^1a_2''^1$ (PtL$_3$) is of somewhat lower energy than

TABLE I. ^{195}Pt Chemical Shifts of PtL$_n$ in Toluene at 213 K. Reference ≡ 21.4 MHz.

L	n = 4	n = 3	n = 2
PMe$_3$	−376.1		
PMe$_2$Ph	−309.2		
PMePh$_2$	−250.2		
PEt$_3$	−729.0	6.9	
PBu$_3{}^n$	−822.5	21.7	
P(*p*-tol)$_3$		−55.5	
PBz$_3$		93.9	
PPr$_3{}^i$			−2074.0
P(C$_6$H$_{11}$)$_3$		−33.5	−2021.7
PBu$_2{}^t$Ph			−1993.3

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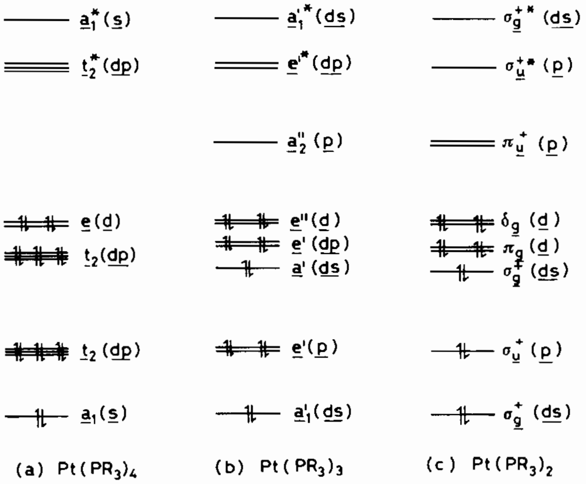

Fig. 2. M.O. diagram for the σ-bonding orbitals in (a) Pt$(PR_3)_4$, (b) $Pt(PR_3)_3$ and (c) $Pt(PR_3)_2$.

the transition to $e^1t_2{}^{*1}$ (PtL_4) [8]. It is therefore clear that the energies of these excited states will follow the order $Pt(PR_3)_3 < Pt(PR_3)_4 < Pt(PR_3)_2$. Applying Ramsey's relationship

$$\sigma^P = A - \frac{B}{\Delta E}$$

where A and B are constant, then the ^{195}Pt chemical shifts follow the observed order.

Experimental

The $Pt(PR_3)_n$ samples are the ones previously used in a ^{31}P n.m.r. study, details of which have been previously published [4]. The ^{195}Pt n.m.r. spectra were measured at 85.63 MHz on a Bruker WH400 n.m.r. spectrometer using CD_3 of the d_8-toluene/toluene solvent as internal ^{2}H lock. The ^{195}Pt chemical shifts are referenced to $\equiv$21.4 MHz with high frequency being taken as positive. Referencing was achieved *via* the ^{2}H signal from the lock.

Acknowledgements

We wish to thank the Science Research Council for a maintenance grant (I.G.), and the provision of the spectrometer. This work is also supported by N.A.T.O. grant No. 1052.

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