The Sign of the ^{195}Pt–^{1}H Coupling Constant in Square Planar Complexes of Platinum(II)

By W. McFarlane

(Chemistry Department, Sir John Cass College, Jewry Street, London, E.C.3)

PROTONS attached to transition metals are characterized[1] by large high-field chemical shifts in their n.m.r. spectra, and by large spin–spin coupling constants with the metal atom when this has a suitable nuclear spin.[2] Theoretical rationalisations of the large chemical shifts of the hydrides of platinum(II) and iridium(III) have been presented,[3,4]

and similar studies of spin–spin couplings involving heavy transition metals would contribute to our understanding of the chemical bonding.

Continuing the work described in reference 5, we can extend Pople and Santry's equation[6] for the Fermi contact contribution to directly bonded X–Y coupling constants to obtain

$$J(\text{Pt–H}) \propto \gamma_{\text{Pt}}\, \gamma_{\text{H}} (\Delta E)^{-1}\, \alpha_{\text{Pt}}^2\, \alpha_{\text{H}}^2\, |\psi_{\text{Pt(6s)}}(0)|^2\, |\psi_{\text{H(1s)}}(0)|^2 \qquad \text{(I)}$$

where ΔE is an average excitation energy, α_X^2 is the s-character of the hybrid orbital used by X in the X–Y bond, and the $|\psi(0)|^2$ terms are electron densities of the appropriate orbitals at the nucleus. The hydrides provide a useful test of this equation since α_H^2 can be taken as 1·00, and $|\psi_{H(1s)}(0)|^2$ will be closely related to the polarity of the Pt–H bond. The above equation yields a positive value for $J(^{195}Pt–H)$ (both γ's are positive), and an essential preliminary test is an experimental determination of the sign of this coupling constant.

The hydridic proton resonance of a solution of trans-$[(Et_3P)_2PtHCl]$ in methylene dichloride was recorded in frequency-sweep mode on a Varian HA 100 spectrometer in which the manual oscillator has been replaced by an external one so that the Me_4Si locking signal could be obtained at up to 100,005 kc./sec. The central 1:2:1 triplet $[|^2J(^{31}P \cdots H)| = 14\cdot4$ c./sec.] at τ 27·75 was flanked by satellites arising from molecules containing the isotope ^{195}Pt $[I = \frac{1}{2}$, abundance $= 33\cdot7\%$, $^1J(^{195}Pt–H) = 1307$ c./sec.] Irradiation with a weak "tickling" field at the ^{31}P resonant frequency (ca. 40·48 Mc./sec.) showed that $|^1J(^{195}Pt–^{31}P)| = 2710 \pm 10$ c./sec., and that the high frequency proton satellites were associated with the high frequency ^{31}P lines and vice versa, i.e., $^1J(^{195}Pt–^{31}P)$ and $^1J(^{195}Pt–H)$ are of the same sign. Irradiation at the ^{195}Pt resonant frequency (ca. 21·4 Mc./sec.) confirmed the value of $^1J(^{195}Pt–^{31}P)$ and showed it to be of opposite sign to $^2J(^{31}P \cdots H)$. The numerical value of the platinum–phosphorus coupling constant obtained here differs from that given (3510 c./sec.) by Pidcock et al. in their preliminary Communication[7] for the rather similar complex of tributylphosphine, but is about what would be expected for a complex of platinum(II) containing trans-phosphine groups.[5,8]

The proton spectra of the organic groups in phosphine complexes of transition metals are complicated by P–P spin coupling, and the somewhat involved arguments needed to extract the relative signs of coupling constants from double resonance experiments will be presented in detail elsewhere.[9] In a number of cis- and trans-phosphine complexes of platinum(II), ^{31}P and ^{195}Pt double irradiation showed that $^1J(^{195}Pt–H)$ and $^3J(H \cdots H)$ in ethyl groups attached to phosphorus were of like sign. The latter coupling constant is known to be positive,[10] so that in the hybride $^1J(^{195}Pt–H)$ is positive and $^2J(^{31}P \cdots H)$ is negative.

The positive value of the directly bonded Pt–H coupling constant agrees with the predictions of molecular orbital theory, although a critical evaluation of the parameters in equation (I) would be needed to provide a searching numerical test. The geminal ^{31}P–Pt–H coupling constant ($-14\cdot4$ c./sec.) is rather more negative than geminal ^{31}P –C– H coupling constants in similar molecules, and this may indicate that α^2_P is low for the Pt–P bonds.

Part of this work was carried out at the National Physical Laboratory, Teddington, and I thank Dr. D. H. Whiffen for advice.

[1] (a) J. Chatt, L. A. Duncanson, and B. L. Shaw, Proc. Chem. Soc., 1957, 343; (b) R. J. Cross, Organometallic Chem. Rev., 1967, 2, 97.

[2] (a) J. Chatt and B. L. Shaw, J. Chem. Soc., 1962, 5075; (b) M. L. H. Green and D. J. Jones, Adv. Inorg. Chem. Radiochem., 1965, 7, 115.

[3] A. D. Buckingham and P. J. Stephens, J. Chem. Soc., 1964, 4583.

[4] A. D. Buckingham and P. J. Stephens, J. Chem. Soc., 1964, 2747.

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

[6] J. A. Pople and D. P. Santry, Mol. Phys., 1964, 8, 1.

[7] A. Pidcock, R. E. Richards, and L. M. Venanzi, Proc. Chem. Soc., 1962, 184.

[8] S. O. Grim, W. McFarlane, and R. Keiter, Inorg. Chem., in the press.

[9] W. McFarlane, J. Chem. Soc., to be submitted.

[10] P. C. Lauterbur and R. J. Kurland, J. Amer. Chem. Soc., 1962, 84, 3405.