

## Phosphorus-Hydrogen Interactions in the $^1\text{H}$ Nuclear Magnetic Resonance Spectra of Some Organo-cobalt, -nickel, and -platinum Complexes

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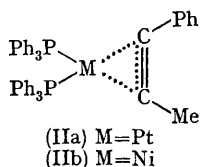
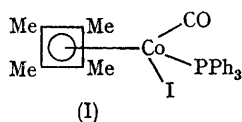
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THE recent reports of large long-range phosphorus-hydrogen interactions observed in the  $^1\text{H}$  n.m.r. spectra of tertiary phosphine-cobaloxime complexes<sup>1,2</sup> prompt us to report on some other unusually large P-H coupling constants in a tetramethylcyclobutadienecobalt(I) complex and in

methylphenylacetylene-platinum and -nickel complexes.

The 100 Mc./sec. spectrum of the recently reported<sup>3</sup> iodocarbonyltriphenylphosphine- $\pi$ -tetramethylcyclobutadienecobalt (I) in  $\text{CH}_2\text{Cl}_2$ - $\text{CDCl}_3$  at  $22.5^\circ$  showed a multiplet at  $\tau$  2.6 due to the

triphenylphosphine protons and a sharp symmetrical doublet at  $\tau$  8.52 due to the methyl protons. This doublet arises from coupling between the twelve equivalent methyl protons and the phosphorus ( $J_{\text{PH}} = 3.8$  c./sec.) and is unchanged in the 60 Mc./sec. spectrum at 34°.



This result is in contrast to the previously reported values of  $J_{\text{PH}}$  in  $\pi$ -complexes; for example, in  $\pi$ -cyclopentadienyl complexes such as  $[\pi\text{-C}_5\text{H}_5\text{NiPR}_2]_2$ , where the nuclei which couple (P and the H's of the cyclopentadienyl ring) are separated by one less atom than in (I), values of  $J_{\text{PH}}$  from 0 to 1.7 c./sec. have been reported.<sup>4</sup> No coupling was observed between the methyl protons and the phosphorus in ( $\pi$ -methallyl)-PdPPh<sub>3</sub>·Cl.<sup>5</sup>

The 60 Mc./sec. <sup>1</sup>H n.m.r. spectrum of methylphenylacetylenebis(triphenylphosphine)platinum (IIa), prepared by the method of Chatt *et al.*,<sup>6</sup> showed a multiplet at *ca.*  $\tau$  2.7 (phenyl protons) and a doublet centred at  $\tau$  7.88 due to the methyl protons coupling with a phosphorus ( $J_{\text{PH}} = 6.2$  c./sec.). Two pairs of satellite peaks due to coupling of the methyl protons with <sup>195</sup>Pt (34% abundance) were also observed ( $J_{\text{PtH}} = 41.5$  c./sec.).<sup>†</sup> The 100 Mc./sec. spectrum of (IIa) at 22.5° showed the same coupling constants; it was however now possible to observe that the resonances noted above were further split into symmetrical doublets due to coupling with the second phosphorus ( $J_{\text{PH}} \sim 1.2$  c./sec.). Since it is generally agreed that *trans*-couplings in octahedral or square-planar complexes are larger than *cis*-couplings,<sup>7,8</sup> we assign the larger,  $J_{\text{PH}}$ , to the coupling with the *trans*-phosphorus and the smaller,  $J_{\text{PH}}$ , to coupling with the *cis*-phosphorus. Our observation of both *cis*- and *trans*-coupling implies that the rate of rotation of the acetylene about the Pt-acetylene axis is very slow on the n.m.r. time-scale (less than about 1.2 sec.<sup>-1</sup>),<sup>9</sup> that this process therefore has a fairly high activation energy and that the molecule is constrained to an approximately planar geometry

<sup>†</sup> The spectrum of (IIa) when run in chlorinated solvents was complicated by the slow appearance of a new peak at  $\tau$  7.94; this was shown to be due to the formation of free methylphenylacetylene.

<sup>‡</sup> This still leaves open the question of whether the bonding in (IIa) is best considered as consisting of a  $\mu$ -bond from the acetylene to the Pt (and back-bonding from Pt to the acetylene), or two C-Pt  $\sigma$ -bonds in a "platinocyclopropene" ring. We have therefore chosen to formulate the bonding as shown.

even in solution. This agrees with the type of structure originally suggested by Chatt *et al.*,<sup>6</sup> and with the recent X-ray structure determination of the diphenylacetylene analogue of (IIa), which showed that in the solid the two P atoms, the two acetylenic C atoms and the Pt are nearly coplanar.<sup>10‡</sup>

Similar considerations appear to hold for the methylphenylacetylenenickel complex (IIb)<sup>11</sup> the spectrum of which we examined at 60 Mc./sec. in benzene at 34°. This showed the methyl protons as a symmetrical doublet centred at  $\tau$  7.86 ( $J_{\text{PH}} = 4.5$  c./sec.), and again each resonance appeared to be further split into a doublet ( $J \sim 1$  c./sec.) due to coupling with the *cis*-phosphorus.

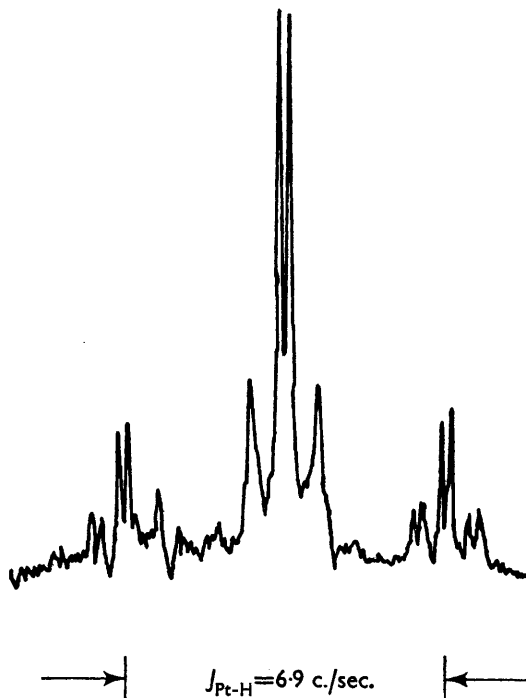


FIGURE. 100 Mc./sec. spectrum of *cis*-(Ph<sub>3</sub>P)<sub>2</sub>PtMe<sub>2</sub> in CDCl<sub>3</sub>-CH<sub>2</sub>Cl<sub>2</sub> at 22.5°.

The 60 and 100 Mc./sec. spectra of *cis*-dimethylbis(triphenylphosphine)platinum<sup>12</sup> were also measured. The methyl resonances were observed as a quartet at  $\tau$  9.63 with two satellite quartets on either side due to coupling with <sup>195</sup>Pt ( $J_{\text{PtH}} = 69$  c./sec.) (see Figure). This spectrum is clearly

not susceptible to first-order analysis and is an example of an  $AA'MX_3X'$  spectrum. Due to the limited solubility of the complex, and to the fact that further significant peaks may be hidden under the noise or under the satellite peaks, calculation of *cis*- and *trans*-P-H coupling constants was not

attempted, but they appeared to be of comparable magnitude to each other.

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