Tetrahedron Letters No.2, pp. 48-50, 1961. Pergamon Press, Inc. Printed in the United States of America.

STRUCTURES OF CYCLOOLEFIN COMPLEXES OF TRANSITION METALS

D. Jones, G.W. Parshall, L. Pratt and G. Wilkinson

Department of Chemistry, Imperial College, London

(Received 10 January 1961)

IN a continuation of the spectral study of cyclopentadiene complexes of transition metals,[1] we have determined the proton magnetic resonance spectrum (at 56.4 Mc/sec) of the product from reaction of cyclopentadiene and nickel carbonyl.[2] The spectrum indicates unequivocally that this compound is π-cyclopentadienyl π-cyclopentenyl nickel (I) rather than bis(cyclopentadiene)nickel, the isomeric structure originally proposed. The spectrum contains peaks whose position and relative intensities confirm the assignment to five equivalent π-cyclopentadienyl protons ($\tau = 4.79$),[3] three "olefinic" protons ($\tau = 4.95$, 6.12) and four aliphatic protons ($\tau = 8.92$). The cyclopentenyl ring presumably contains and is bound to the metal by a delocalized "π-allylic" system similar to that suggested for allylcobalt and manganese carbonyls.[4]

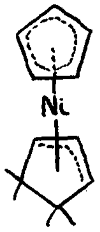
---

[1] M.L.H. Green, L. Pratt and G. Wilkinson, J. Chem. Soc. 3753 (1959); 989 (1960).

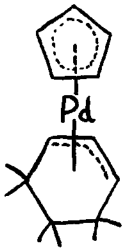
[2] E.O. Fischer and H. Werner, Chem. Ber. 92, 1423 (1959).

[3] Location of the resonance lines is in terms of $\tau = 10.000 - (H_{Me_4Si} - H_{sample})(H_{Me_4Si})^{-1}$ where H_{Me_4Si} is the field of resonance of tetramethylsilane inserted as an internal standard.

[4] W.R. McClellan, H.H. Hoehn, H.N. Cripps, E.L. Muetterties and B.W. Howk, J. Amer. Chem. Soc. In Press, and references given therein.



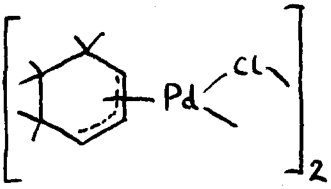
I



II

Similarly the palladium complex previously designated as 1,3-cyclohexadiene cyclopentadiene palladium[5] is found to be cyclohexenyl π-cyclopentadienyl palladium(II). The proton resonance spectrum contains peaks assignable to five equivalent π-cyclopentadienyl protons (τ 4.22), three "π-allylic" protons (τ 5.04, 5.18) and six aliphatic protons (τ 8.56).

The present spectral study also confirms the recent suggestion[6] that the product obtained by reaction of 1,3-cyclohexadiene with palladium carbonyl chloride[5] is bis(π-cyclohexenylpalladium chloride)(III).



III

---

[5] E.O. Fischer and H. Werner, Chem. Ber. 93, 2075 (1960).

[6] E.O. Fischer, H.P. Kogler and P. Kuzel, Chem. Ber. 93, 3006 (1960).

Presumably the structure is analogous to that of allylpalladium chloride which has been the subject of a recent nuclear magnetic resonance study.[7] As in allylpalladium chloride, the resonance of a single "olefinic" proton occurs at lowest field (τ 4.49) followed by a peak assignable to two equivalent "olefinic" protons (τ 4.78). The resonance of the six aliphatic protons is noted at highest field (τ 8.20).

Details of this work and the extension to other systems will be presented shortly.

---

[7] H.C. Dehm and J.C.W. Chien, *J. Amer. Chem. Soc*. **82**, 4429 (1960).