Preparation and Fluxional Behaviour of α,1,2-η-Triphenylmethyl-palladium and -platinum Complexes

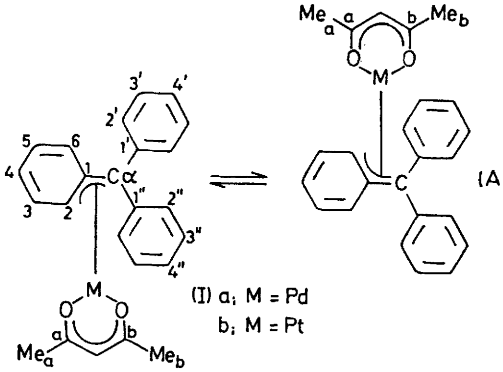
By AKIO SONODA, BRIAN E. MANN, and PETER M. MAITLIS*
(*Department of Chemistry, The University, Sheffield* S3 7HF)

Summary $[M(CPh_3)Cl]_n$, obtained by oxidative addition of Ph_3CCl to $M(dibenzylideneacetone)_n$ (M = Pd or Pt), was converted into $[M(CPh_3)(acac)]$ (I); three independent types of fluxional behaviour have been observed for (I).

REACTION of bis(dibenzylideneacetone)palladium(0) or tris(dibenzylideneacetone)platinum(0)[1] with chlorotriphenylmethane in chloroform gave the rather insoluble yellow-orange complexes, $[M(CPh_3)Cl]_n$ (M = Pd or Pt), in 80—100% yield.† The chlorides were converted into the soluble, monomeric, and crystalline acetylacetonates $[M(CPh_3)(acac)]$, (I)†, by reaction with Tl(acac) in benzene.

The following conclusions concerning the complexes (Ia and b) were drawn from their ^{1}H and ^{13}C n.m.r. spectra at different temperatures. (i) In the platinum complex (Ib) at all accessible temperatures a fluxional process (A) occurs in which the metal is interacting strongly with (C-α), (C-1), (C-2), and (C-6) on the n.m.r. time-scale. (ii) The same features are shown by the palladium complex (Ia) at low temperatures. (iii) At higher temperatures an additional process (B) occurs for (Ia) in which the palladium becomes associated on average with (C-α), (C-1), (C-1′), and (C-1″) and all the *ortho*-carbons of the three phenyl rings. (iv) At higher temperatures the ^{1}H n.m.r. spectra of (Ia) show that the acac ligand is undergoing exchange (process C) at a different rate to (B).

Thus, at +30 °C the ^{1}H n.m.r. spectrum of (Ib) showed resonances at: δ 1·76 (3H, acac Me; the satellites due to coupling to ^{195}Pt could not be resolved), 1·89 [t, 3H, acac Me, J(H–Pt) 7 Hz], 5·30 [t, 1H, acac H, J(H–Pt) 11 Hz], 6·13 [m, 2H, (H-2 + H-6), J(H-2–H-4) 2, J(H-2–H-3) 7, J(H-2–Pt) 27 Hz], and 7·1—7·5 (m, 13H, Ph). The significant features are that the two methyls of the acac are non-equivalent and that the phenyl proton resonances have become separated into a multiplet of relative intensity 13 and a multiplet of relative intensity 2 (H-2 + H-6) which

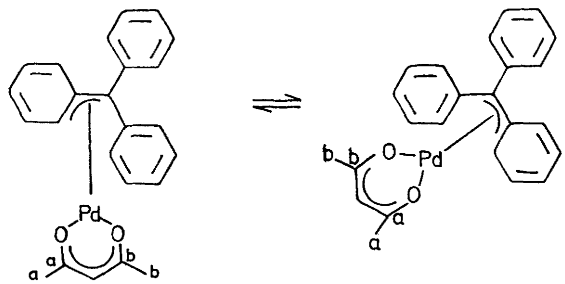


(I) a; M = Pd
b; M = Pt

---

† Satisfactory elemental analyses [and molecular weights for (Ia and b)] were obtained.

now appears at higher field. The latter observation is consistent with a situation where two H's (on average) have become allylic in nature and we propose that it is due to the dynamic rearrangement (A), which is fast on the n.m.r. time-scale. This resembles the behaviour of η^3-benzyl complexes such as $[M(\alpha,1,2\text{-}\eta\text{-}CH_2C_6H_4\text{-}p\text{-}Me)(CO)_2(\eta\text{-}C_5H_5)]$ (M = Mo or W).[2]



(B)

This proposal is **supported by** the ^{1}H-decoupled ^{13}C n.m.r. spectrum {(1b at +30 °C; coupling to ^{195}Pt in Hz in parentheses); δ 56·8 [t, C-α (375)] 104·0 [t, C-1, (96)], 92·9 [t, (C-2 + -6), (66)], 135·8 [t, (C-3 + -5), (26)], 125·3 (C-4‡), 145·0 [t, (C-1′ + -1″) (40)], 129·7 [t, (C-2′ + -2″), (15)], 128·1 (C-3′ + -3″),‡ 125·8 (C-4′ + -4″),‡ 27·5 and 28·1 (acac Me's), 100·5 [t, acac CH, (83)], and 184·4 and 186·3 [t, acac CO's (46), (29)]} which shows that the molecule has an apparent plane of symmetry. Although attempts to 'freeze out' the exchange process have not yet been successful broadening of the signal at δ 92·9 [due to (C-2 + -6)] was observed at −81 °C.

The palladium complex (Ia) showed similar spectra at low temperatures: ^{1}H n.m.r. at −40 °C, δ 1·83 (s, 3H, acac Me), 1·89 (s, 3H, acac Me), 5·19 (s, 1H, acac H), 6·64 [m, 2H, *J*(H-2–H-3) 8 Hz] and 7·4 (m, 13H); ^{13}C n.m.r. at −19 °C δ 73·3 (C-α), 116·0 (C-1), 102·3 (C-2 + -6), 133·7 (C-3 + -5), 143·1 (C-1′ + 1″), 129·9 (C-2′ + -2″), 127·9 (C-3′ + -3″), 126·7 (C-4′ + -4″), 28·3 (acac Me's), 98·8 (acac CH), and 187·1 (acac CO's)§. At high temperatures two new types of fluxional behaviour were observed; one in which the phenyls all became equivalent and one in which the acac resonances coalesced. Thus, at +50 °C the ^{1}H n.m.r. showed resonances at δ 1·86 (s, 6H, acac Me's), 5·16 (s, 1H, acac H), and 7·32 (m, 15H, Ph). In the ^{13}C n.m.r. spectrum at +61 °C coalescence had occurred between (C-2 + -6) and (C-2′ + 2″) (δ 120, broad); C-4 and (C-4′ + -4″) (δ 127·2); and (C-3 + -5) and (C-3′ + -3″) (δ 130·0); with C-α now at δ 73·0. The doublet owing to the two acac CO groups was only just resolvable at δ 186·9 and 187·4.

These changes can be accounted for by fluxional behaviour of type (B) where the triphenylmethyl ligand "rotates" with respect to the metal somewhat in the manner of a three-bladed propeller, and (C) in which there is scrambling of the acac resonances.

For complex (Ia) at 30 °C process (B) is *ca.* 80 times faster than process (C), while (A) is obviously several orders of magnitude more rapid still. This appears to rule out a mechanism for either type (A) or (B) dynamic behaviour in which a 3-co-ordinate $(acac)Pd\text{-}CPh_3$ is intermediate, though a short-lived transition state of this type which retains its configuration at the metal is not excluded. The platinum complex (Ia) did not exhibit fluxional behaviour of types (B) or (C) below its decomposition temperature.

The complexes described here are closely analogous to the $Ni(CPh_3)X$ (X = halide or CPh_3) complexes reported[3] and it is probable that similar bonding and similar dynamic behaviour will be observed there.

We thank the S.R.C. for support of this work and I.C.I., Ltd. for a grant.

(*Received*, 29*th October* 1974; *Com.* 1331.)

‡ Owing to poor signal:noise the coupling to ^{195}Pt could not be determined with certainty for these signals; t is used to denote a 1:4:1 triplet arising from coupling to Pt.

§ The signal due to C-4 could not clearly be distinguished owing to overlapping with (C-4′ + -4″) or (C-3′ + -3″); the signals arising from the acac CO's are accidentally coincident at this temperature and separate at both higher and lower temperatures.

[1] Y. Takahashi, T. Ito, S. Sakai, and Y. Ishii, *Chem. Comm.*, 1970, 1065; K. Moseley and P. M. Maitlis, *Chem. Comm.*, 1971, 982; *J.C.S. Dalton*, 1974, 169; M. C. Mazza and C. G. Pierpont, *J.C.S. Chem. Comm.*, 1973, 207; T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet, and J. A. Ibers, *J. Organometallic Chem.*, 1974, 65, 253.

[2] F. A. Cotton and J. J. Marks, *J. Amer. Chem. Soc.*, 1969, **91**, 1339.

[3] G. Wilke and H. Schott, *Angew. Chem. Internat. Edn.*, 1966, **5**, 583; see also R. B. King, 'Annual Surveys of Organometallic Chemistry,' Elsevier, Amsterdam, Vol. 3, 1967, p. 403; and P. M. Maitlis, 'Organometallic Chemistry of Palladium,' Academic Press, New York, Vol. 1, 1971, p. 74.