

PENTAMETHYLCYCLOPENTADIENYLPLATINUM(IV) COMPLEXES

SUSAN H. TAYLOR and PETER M. MAITLIS*

Department of Chemistry, The University, Sheffield S3 7HF
 England.

(Received July 18th, 1977)

SUMMARY

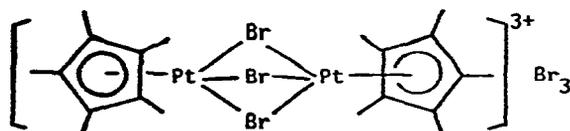
Reaction of dichloro(η^4 -pentamethylcyclopentadiene)platinum with bromine yields a η^5 -pentamethylcyclopentadienylplatinum(IV) complex which is formulated as $[\text{C}_5\text{Me}_5\text{PtBr}_3\text{PtC}_5\text{Me}_5]\text{Br}_3$.

The wide variety of chemistry which has been developed [1] from the pentamethylcyclopentadienyl-rhodium and -iridium chloride complexes $[\text{M}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$ (I) [2] has prompted us to investigate the preparation of pentamethylcyclopentadienyl complexes of other Group VIII metals, and in particular to ascertain whether the high stability and inertness of the $\text{C}_5\text{Me}_5\text{-M}$ bond is a general feature. One obvious direction is to extend this work to complexes of Pt(IV) which would be isoelectronic with the iridium complexes $[\text{Ir}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$.

The convenient and simple synthesis of the very stable dichloro(η^4 -pentamethylcyclopentadiene)platinum, $[\text{Pt}(\text{C}_5\text{Me}_5\text{H})\text{Cl}_2]$ (II), by reaction of hexamethyl bicyclo[2.2.0]diene with K_2PtCl_4 in the presence of acid has been reported previously [3]. When the yellow complex (II) was treated with an excess of bromine in chloroform a complex reaction occurred to give brick-red crystals of $[\text{Pt}(\text{C}_5\text{Me}_5)\text{Br}_3]_n$, (III). The complex was unfortunately very insoluble but a F/T ^1H n.m.r. spectrum in liquid SO_2 at -10°C showed a singlet at δ 2.08, arising from five equivalent methyls, with satellites due to coupling to ^{195}Pt ($I = \frac{1}{2}$, 34%), $J(^1\text{H}-^{195}\text{Pt}) = 12$ Hz.

Further structural information was hard to come by but the far i.r. spectrum showed strong bands, ascribed to $\nu(\text{Pt-Br})$, at 215 and 183 cm^{-1} with a shoulder at 177 cm^{-1} . These bands are below the usual range for terminal

$\nu(\text{Pt-Br})$ [4] but are consistent with the presence of Pt-Br-Pt bridge bonds and we suggest that (III) is ionic with three bromine bridges as shown.



(III)

Recent work has shown that there is a high stability associated with triply bridged binuclear π -complexes of the type $[(\eta^n\text{-C}_n\text{R}_n)\text{MX}_3\text{M}(\eta^n\text{-C}_n\text{R}_n)]^{x+}$, for example $[(\text{Rh}(\text{C}_5\text{Me}_5))_2\text{Cl}_3]^+$ [5], $[(\text{Ir}(\text{C}_5\text{Me}_5))_2\text{H}_3]^+$ [6], and $[(\text{Pd}(\text{C}_4\text{Me}_2\text{Bu}_2^t))_2\text{Cl}_3]^+$ [7], and the suggested formulation for (III) is in accordance with this.

The complex (III) reacted only slowly and decomposition occurred readily. For example, there was negligible reaction during 24 hours when a suspension of (III) was treated with NaBPh_4 in acetone, and only unstable adducts were formed when (III) was reacted with AgPF_6 in the presence of mesitylene or in acetonitrile. Under the latter conditions a wide variety of rhodium and iridium complexes of the type $[\text{M}(\text{C}_5\text{Me}_5)\text{L}_3]^{2+}$ are formed from (I) [1] and it therefore appears that the $\text{C}_5\text{Me}_5\text{-Pt}$ (IV) bond is significantly weaker than that to Rh(III) or Ir(III) .

EXPERIMENTAL

A solution of $[\text{Pt}(\text{C}_5\text{Me}_5\text{H})\text{Cl}_2]$ [3] (0.2 g, 0.5 mmol) in chloroform (15 ml) was refluxed with a large excess of bromine (0.8 ml) under N_2 for 1 hr. The dark-red solution slowly precipitated brick red crystals of (III), which were filtered off, washed with chloroform and dried. Yield. 0.040 g, 14%; decomp $> 250^\circ\text{C}$. Anal: Found, C, 20.9; H, 2.6; Br, 42.0. Calc. for $[\text{C}_{15}\text{H}_{15}\text{Br}_3\text{Pt}]_n$: C, 21.1; H, 2.6; Br, 42.1%. The i.r. spectrum in hexachlorobutadiene mull showed bands at 2965(w), 2910(w), 1642(m), 1480(m), 1418(m), 1370(m), and 1350(w) cm^{-1} .

We thank the Science Research Council for support.

References

- [1] P. M. Maitlis, Trans N.Y Acad. Sci , 33, (1971), 87; C White, S. J. Thompson, and P. M Maitlis, J C S. Dalton, in press; J. Organometallic Chem , 134 (1977) 319.
- [2] J. W. Kang, K. Moseley, and P. M. Maitlis, J Amer. Chem. Soc., 91, (1969), 5970.
- [3] P. V. Balakrishnan and P. M. Maitlis, J. Chem. Soc. (A), (1971) 1715
- [4] See, for example, Specialist Periodical Reports, Chemical Society, London, Vol. 1, p.174, Vol 2, p.287, and Vol. 3, p 277.
- [5] J W Kang and P. M Maitlis, J Organometallic Chem., 30, (1971), 127.
- [6] C. White, A. J. Oliver, and P. M. Maitlis, J.C S Dalton, (1973), 1901.
- [7] E. A. Kelley, P. M. Bailey and P. M Maitlis, J C S Chem Comm , (1977) 289