A Dehydro-hexamethyl Dewar Benzene Complex of Platinum(II)

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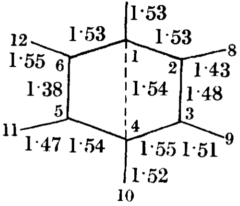
THERE has been much recent interest in transition metal complexes formed from hexamethyl Dewar benzene (HMDB).[1–5] We now describe some novel platinum complexes derived from HMDB.

The reaction of HMDB with sodium chloroplatinite in ethanol gives a white complex, $[PtCl_2(C_{12}H_{18})]$, which, from its properties, is clearly analogous to the palladium complex $[PdCl_2(C_{12}H_{18})]$ in which the HMDB ligand is acting as a chelating diolefin.[5] When treated with sodium methoxide in methanol $[PtCl_2(C_{12}H_{18})]$ is converted into a yellow dehydro-complex $[Pt_2Cl_2(C_{12}H_{17})_2]$ in 70—80% yield. This complex is dimeric in benzene; the far i.r. spectrum shows only a terminal platinum–chlorine stretching frequency (316 cm.$^{-1}$) and the ^{1}H n.m.r. spectrum indicates the presence of five non-equivalent methyl groups per platinum atom (each resonance has accompanying satellites due to coupling with ^{195}Pt, $I = \frac{1}{2}$).

The structure of the dehydro-HMDB complex has been determined by *X*-ray diffraction analysis. The crystals are monoclinic with $a = 13{\cdot}33$, $b = 10{\cdot}88$, $c = 17{\cdot}60$ Å, $\beta = 100{\cdot}6°$; $Z = 4$, space group $C2/c$. The refinement of atomic parameters has reached the point where the discrepancy index for the 1349 independent reflexions, measured on a Pailred diffractometer and having $F^2_{\text{obs}}/\sigma(F^2_{\text{obs}}) \geqslant 3{\cdot}0$, is 0·065; the average e.s.ds. in the bond lengths given in the Figure are 0·008 (Pt–Cl), 0·026 (Pt–C), 0·04 Å (C–C).

The dimeric molecule has precise C_2 symmetry. A dehydrohexamethyl Dewar benzene ligand bridges two platinum atoms, being co-ordinated *via* a σ-bond from the methylene carbon atom to one platinum and to the other *via* two π-olefin bonds. The platinum–carbon (methylene) bond length of 2·10 Å is close to the sum of covalent radii—it is identical, within experimental error, with, for example, the mean Pt–C (methyl) bond length of 2·05 ± 0·02 Å in trimethyl(acetylacetonyl)-2,2′-bipyridylplatinum[6] and with that of 2·11 Å in the bisacetylacetonylchloroplatinate(II) cation.[7] The platinum–olefin bonds *trans* to the chlorines and *trans* to the σ-bonded carbon atoms are significantly different. The difference of 0·19 Å between the two pairs of platinum–carbon (olefin) bond lengths is identical, within one standard deviation, with that of 0·17 Å between the platinum–chlorine bond length *trans* to a σ-bonded carbon and that *trans* to a π-bonded olefin in [PtCl(OMe)(dicyclopentadiene)].[8] The implication is that the *trans*-bond lengthening effect of a π-bonded olefin is very small indeed. The difference in the carbon–carbon (olefin) bond lengths reflects the variation in the platinum–carbon bonds and is consistent with the i.r. spectrum of the complex in that there are two C=C stretching frequencies at 1570 and 1497 cm.$^{-1}$.

The dihedral angle between the planes containing the atoms C(1), C(2), C(3), C(4) and C(1), C(4), C(5), C(6) is 111° compared with the corresponding value of 113° in tetracarbonyl(hexamethylbicyclo[2,2,0]hexa-2,5-diene)chromium.[2] As in the chromium complex, the methyl groups are not coplanar with the carbon atoms of the Dewar benzene but their distances from the planes vary in a way which reflects the asymmetric metal to olefin bonding.



The presence of a bridging allylic system in the dehydro-hexamethyl Dewar benzene complex is noteworthy in the light of suggestions[9] relating to the role of bridging allylic groups as intermediates in allyl transfer reactions between metals.

The complexes $[Pt_2X_2(C_{12}H_{17})_2]$ (X = Cl or Br) are recovered unchanged after treatment with triphenylphosphine, isoquinoline, thallous acetylacetonate or cyclopentadienylsodium. $[Pt_2Cl_2(C_{12}H_{17})_2]$ reacts with dry hydrogen chloride to give $[PtCl_2(C_{12}H_{18})]$ and gives the iodo-complex $[Pt_2I_2(C_{12}H_{17})_2]$ when treated with sodium iodide in acetone. The chemical properties, i.r. and n.m.r. spectra of the iodo-complex show that it has an iodo-bridged π-allylic structure in which the $C_{12}H_{17}$ ligand is bonded to the metal in a completely analogous way to that observed in $[Pd(acac)(C_{12}H_{17})]$.[10] Thus, the iodo-complex undergoes reactions typical of a halogen-bridged structure, for example, bridge fission reactions with tertiary phosphines and amines.

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[1] E. O. Fischer, W. Berngruber, and C. G. Kreiter, *Chem. Ber.*, 1968, **101**, 824.
[2] G. Huttner and O. S. Mills, *Chem. Comm.*, 1968, 344.
[3] H. Hogeveen and H. C. Volger, *Chem. Comm.*, 1967, 1133.
[4] B. L. Booth, R. N. Haszeldine, and M. Hill, *Chem. Comm.*, 1967, 1118.
[5] H. Dietl and P. M. Maitlis, *Chem. Comm.*, 1967, 759.
[6] A. G. Swallow and M. R. Truter, *Proc. Roy. Soc.*, 1962, *A*, **266**, 527.
[7] R. Mason, P. Pauling, and G. B. Robertson, in the press.
[8] W. A. Whitla, H. M. Powell, and L. M. Venanzi, *Chem. Comm.*, 1966, 310.
[9] J. Powell and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 583.
[10] J. F. Malone, W. S. McDonald, B. L. Shaw, and G. Shaw, following Communication.