A Novel π-Allylic–Palladium Complex derived from Hexamethyl Dewar Benzene

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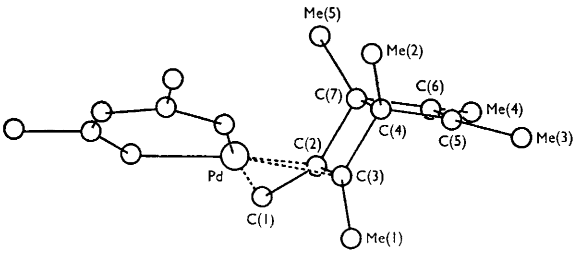
CONSIDERABLE interest has been shown recently in complexes containing the ligand hexamethylbicyclo[2,2,0]hexa-2,5-diene (hexamethyl Dewar benzene, HMDB),[1–5] and also in olefin and allylic complexes of palladium. We now find that treatment of [$PdBr_2$(HMDB)] with an excess of sodium methoxide in methanol gives a yellow crystalline complex [$Pd_2Br_2(C_{12}H_{17})_2$]. [$PdBr_2$(HMDB)] was prepared from the corresponding dichloride[4] by treatment with lithium bromide in acetone. The complex [$Pd_2Br_2(C_{12}H_{17})_2$] undergoes metathesis with sodium iodide to give [$Pd_2I_2(C_{12}H_{17})_2$], and with typical halogen-bridge splitting ligands (L), such as PPh_3, PMe_2Ph, $AsPh_3$ or isoquinoline, it gives mononuclear complexes of the type $[PdBr(C_{12}H_{17})L]$. Treatment with thallous acetylacetonate or cyclopentadienylsodium gives $[PdL'(C_{12}H_{17})]$ (L' = acac or C_5H_5). The i.r. spectra of all these complexes show a weak band at 1680 cm.$^{-1}$ due to C=C stretch (exactly the same as in free HMDB). The ^1H n.m.r. spectrum of $[Pd_2Br_2(C_{12}H_{17})_2]$ shows five methyl resonances per palladium, at τ 8·31, 8·46, 8·57, 8·63 and 8·68, and two doublets (intensities corresponding to one proton per doublet) at 6·15 and 6·65 τ, J = 2 Hz. These and other properties suggested that the $C_{12}H_{17}$ ligand was a π-allylic ligand formed from HMDB by loss of a proton. This has been confirmed by a single-crystal X-ray structural determination of the compound $[Pd(acac)(C_{12}H_{17})]$.

Crystals of the compound are monoclinic, space group $P2_1/n$ with a = 7·43, b = 16·69, c = 14·03 Å β = 99·25°, Z = 4. The intensities of 1325 independent non-zero reflections were measured visually from equi-inclination Weissenberg photographs taken with Mo-K_α radiation. The structure was determined by the heavy-atom method and refined by least squares with allowance for anisotropic temperature factors for all (non-hydrogen) atoms. The refinement converged at R = 7·0%.



FIGURE

A projection of the molecule down the a-axis is shown in the Figure and the principal bond lengths are given in the Table. The distances from the palladium to the allylic carbon atoms C(1), C(2), and C(3) do not differ significantly although our results and previous structural determinations on π-allylic palladium complexes, *e.g.* $[Pd_2Cl_2(C_3H_3)]$,[6] $[Pd_2(MeCO_2)_2(C_3H_5)_2]$,[7] and [Pd(acac)(cyclo-octa-2,4-dienyl)][8] suggest that the central carbon atom is slightly closer to the palladium than the other two. The bond lengths C(1)–C(2) and C(2)–C(3) are not significantly different and the angle C(1)–C(2)–C(3) is 124°. The dimensions of the acetylacetonate group are normal.[8] The dihedral angle between the Pd(acac) plane and the plane C(1)–C(2)–C(3) is 121° {*cf.* $[Pd_2Cl_2(C_3H_5)_2]$, 118°;[6] $[Pd_2(CH_3COO)_2(C_3H_5)_2]$, 125° and 110°;[7] [Pd(acac)(cyclo-octa-2,4-dienyl) 121°}.[8]

Bond lengths (Å) *in* $[Pd(acac)(C_{12}H_{17})]$

Pd–C(1)	2·14	C(1)–C(2)	1·44
Pd–C(2)	2·11	C(2)–C(3)	1·43
Pd–C(3)	2·13	C(4)–C(7)	1·56
		C(5)–C(6)	1·28

* The e.s.d.s are ± 0·02 Å for Pd–C and 0·03 Å for C–C.

The atoms C (2, 3, 4, 7) are accurately coplanar and Me(1) is 0·6 Å below the plane (on the side remote from the Pd atom). Me(2) and Me(4) are in the C (4, 5, 6, 7) plane as might be expected for the free ligand. The dihedral angle between the planes of the Dewar benzene rings is 112° [*cf.* $[Cr(CO)_4(HMDB)]$, 113°][2] and each of these planes makes an angle of 124° with the plane Me(2)–C(4)–C(7)–Me(5).

The organic ligand in the iodo-bridged platinum complex $[Pt_2I_2(C_{12}H_{17})_2]$[9] is of the same type as that shown in the Figure (i.r. and n.m.r. evidence).

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