Preparation and Crystal Structure of μ-Cyclopentadienyl-μ-bromo-bis-(tri-isopropylphosphinepalladium)

By Arnaud Ducruix, Hugh Felkin, Claudine Pascard,* and G. Kevin Turner*
(*Institut de Chimie des Substances Naturelles, C.N.R.S., 91190 Gif-sur-Yvette, France*)

Summary $[(\eta\text{-}C_5H_5)(PPr^i_3)PdBr]$ reacts with magnesium in tetrahydrofuran to give the novel dimeric complex $[\mu\text{-}(C_5H_5)\text{-}\mu\text{-}BrPd_2(PPr^i_3)_2]$, the crystal structure of which shows that the two palladium atoms are bridged by the bromine atom and the C_5H_5 ring, which has unequal C–C bonds.

During our investigations into the reaction of magnesium with transition-metal complexes, we have isolated the dimeric palladium complex $[\mu\text{-}(C_5H_5)\text{-}\mu\text{-}BrPd_2(PPr^i_3)_2]$. This is the first example of a compound with a bridging cyclopentadienyl ring for which it has been possible to determine the structure of the bridging group.†

Reaction of $[(\eta\text{-}C_5H_5)Pd(PPr^i_3)Br]$ (I)[2] with excess of magnesium in dry THF under nitrogen at room temperature consumed 0·5 mol of magnesium per mol of palladium complex, and yielded a deep red solution after *ca.* 1 h. Dark-red, air-stable crystals of the title complex were isolated from this solution, and recrystallisation from toluene–hexane at −30 °C gave the pure product, m.p. 144 °C (decomp.) in 80% yield. Its ^1H n.m.r. spectrum in $CDCl_3$ showed a triplet due to the C_5H_5 group at τ 4·67, *J* (P–H) 2·1 Hz. The ^{13}C n.m.r. spectrum in $[^2H_8]$toluene showed a singlet for the C_5H_5 group at δ 88·19 p.p.m. (relative to Me_4Si), which remained unchanged at −60 °C.

The compounds $[\mu\text{-}(C_5H_5)\text{-}\mu\text{-}XPd_2(PR_3)_2]$ ($R = Pr^i$ X = Cl or I; R = Ph or cyclohexyl, X = Br) have been prepared by the same method from the complexes $[(\eta\text{-}C_5H_5)Pd(PR_3)X]$, and characterised by n.m.r. spectroscopy and elemental analysis. It is interesting to note that the analogous complexes $[(\eta\text{-}C_5H_5)(PR_3)NiBr]$ and $[(\eta\text{-}C_5H_5)(\text{diphos})FeBr]$ (diphos = $Ph_2PCH_2CH_2PPh_2$) react with magnesium under the same conditions to give inorgano-Grignard reagents.[3]

The title complex reacts with TlSPh in benzene to give $[\mu\text{-}(C_5H_5)\text{-}\mu\text{-}SPhPd_2(PPr^i_3)_2]$ in quantitative yield, and with CS_2 to give (I) and Pd metal.

Crystal data: Crystals of the title complex are monoclinic, space group $P2_1$, $a = 13{\cdot}002(2)$, $b = 15{\cdot}551(2)$, $c = 15{\cdot}734(2)$ Å, $\beta = 116{\cdot}7(1)°$, $Z = 2$. 2672 independent reflections,

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† The crystal structure of only one other compound containing a bridging C_5H_5 group has been reported,[1] *viz.* $[\mu\text{-}(C_5H_5)\text{-}\mu\text{-}(C_4H_7)\text{-}Pd_2(PPh_3)_2]$, in which the methylallyl and C_5H_5 groups were disordered, making it impossible to determine their geometries.

collected with monochromated Mo-K_α radiation on a Phillips automatic diffractometer, were used to solve the structure by standard Patterson, Fourier, and least-squares methods. The final R value is 3·5%.

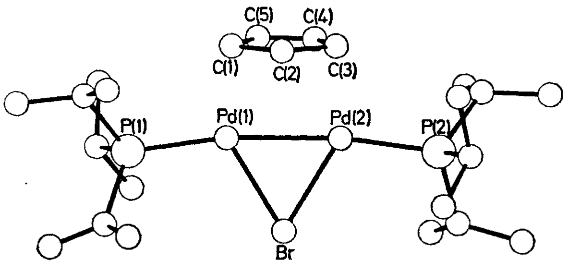

FIGURE. Structure of μ-cyclopentadienyl-μ-bromo-bis(tri-isopropylphosphinepalladium). Bond lengths (Å): Pd(1)–Br, 2·512(1); Pd(2)–Br, 2·504(1); Pd(1)–C(1), 2·124(11); Pd(2)–C(3) 2·140(11); Pd(1)–C(2), 2·568(11); Pd(2)–C(2), 2·615(11); Pd(1)–C(5), 2·788(11); Pd(2)–C(4), 2·720(11); C(1)–C(2), 1·485(17); C(2)–C(3), 1·522(17); C(3)–C(4), 1·455(18); C(5)–C(1), 1·512(15), C(4)–C(5), 1·331(18); Pd(1)–Pd(2), 2·609(1).

The molecular structure of the complex is shown in the Figure. The P(1), P(2), Pd(1), Pd(2), Br, C(1), and C(3) atoms are very nearly coplanar, as are the carbon atoms of the cyclopentadienyl ring, which is inclined at an angle of 82° to the plane containing the Br and Pd atoms. The distance between the two palladium atoms is short (2·609 Å), showing that a Pd–Pd bond exists. The co-ordination of the palladium atoms is distorted square-planar and resembles that in $[\mu\text{-}(C_5H_5)\text{-}\mu\text{-}IPd_2(PPh_3)_2].C_6H_6$[4] and $[\mu\text{-}(C_5H_5)\text{-}\mu\text{-}(C_4H_7)Pd_2(PPh_3)_2]$.[1]

Within the cyclopentadienyl ring four C–C bond distances are approximately equal (1·46–1·52 Å, σ 0·018), but the C(4)–C(5) bond is much shorter (1·33 Å), showing that the π-electron density is only partially delocalised in the ring. The C_5H_5 bridge can therefore be regarded as an allyl plus alkene group, as suggested for some non-bridging systems.[5]

The C(1)–Pd(1) and C(3)–Pd(2) distances are 2·12 and 2·14 Å respectively, and the inclination of the cyclopentadienyl ring puts the C(2) atom at about the same distance (2·23 Å) from the middle of the Pd–Pd bond. These distances fall within the range (2·02–2·22 Å)[6] found for the C–Pd distances in simple η-allyl-Pd complexes.

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[1] H. Werner, D. Tune, G. Parker, C. Krüger, and D. J. Brauer, *Angew. Chem. Internat. Edn.*, 1975, **14**, 185.

[2] R. J. Cross and R. Wardle, *J. Chem. Soc.* (*A*), 1971, 2000.

[3] H. Felkin and P. J. Knowles, *J. Organometallic Chem.*, 1972, **37**, C14; H. Felkin, P. J. Knowles, B. Meunier, A. Mitschler, L. Ricard, and R. Weiss, *J.C.S. Chem. Comm.*, 1974, 44.

[4] Y. Kobayashi, Y. Iitaka, and H. Yamazaki, *Acta Cryst.*, 1972, **B28**, 899.

[5] M. J. Bennett, M. R. Churchill, M. Gerloch, and R. Mason, *Nature*, 1964, **201**, 1318.

[6] P. M. Maitlis, 'The Organic Chemistry of Palladium', Academic Press, New York, 1971, Vol. I, p. 38.