Structure of Bromobis(triphenylphosphine)-(1,2,3,4-tetrakismethoxycarbonylbuta-1,3-dienyl)palladium and Evidence for a C–H · · · Pd Interaction

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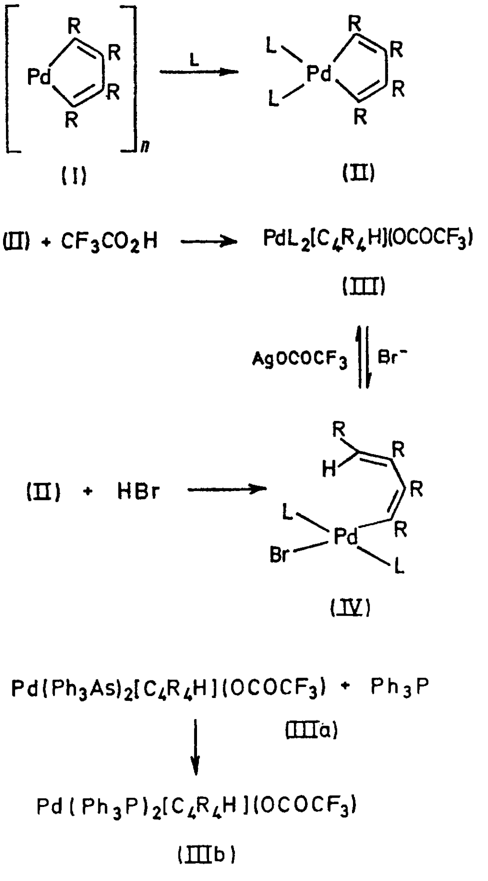
Summary Treatment of $[PdL_2\{C_4(CO_2Me)_4\}]$ with HX gives *trans*-$PdL_2\{C_4(CO_2Me)_4H\}X$; the crystal structure of *trans*-$Pd(Ph_3P)_2\{C_4(CO_2Me)_4H\}Br$ is reported and it is shown that there is an interaction between the δ-butadienyl hydrogen and the metal.

We recently showed that bis(dibenzylideneacetone)palladium(0) reacted with dimethyl acetylenedicarboxylate to give the palladiacyclopentadiene (I) which with a variety of Lewis bases gave the monomeric adducts (II). We here report the acid cleavage reactions of (I).



Scheme

R = CO_2Me, a; L = Ph_3As, b; L = Ph_3P, c; L = Ph_2MeP.

All the complexes (IIa—c) reacted with one equivalent of acid to give adducts [(III)‡ with CF_3CO_2H or (IV)‡ with HBr] which could be interconverted (Scheme). One Pd–C bond of the palladiacyclopentadiene ring has been cleaved in these adducts: for example, the triphenylarsine trifluoroacetate (IIIa) showed resonances in the n.m.r. ($CDCl_3$, 60 MHz) at δ 3·00, 3·41, 3·48, 3·68 (all 3H, s, CO_2Me), 6·44 (1H, s, vinylic H), and 7·4 (30H, m, phenyl). The spectrum of the triphenylphosphine trifluoroacetate (IIIb) was very similar except that the vinylic hydrogen was shifted downfield to δ 8·10 and was now a triplet (*J* 1·4 Hz). The ^{31}P decoupled spectrum of (IIIb) showed a singlet at δ 8·10 indicating that this hydrogen was equally coupled to two phosphorus nuclei. The vinylic proton was also a triplet in (IVb) [δ 8·60]. In the diphenylmethylphosphine complexes (IIIc) and (IVc) it was not observed and was presumably obscured by the phenyl protons. However, here the phosphine methyls (δ 2·00) were observed as triplets (*J* 4 Hz) owing to virtual coupling. This evidence and that from the vinylic hydrogens in (IIIb) and (IVb) indicates that the complexes have the *trans*-configuration.

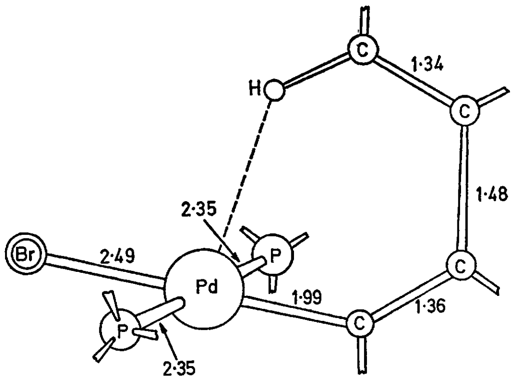


Figure. *The structure of bromobis(triphenylphosphine)-(1,2,3,4-tetrakismethoxycarbonylbuta-1,3-dienyl)palladium; phenyl groups (on the phosphorus atoms) and ester groups (on the butadienyl carbons) are omitted for clarity. Bond lengths are given in* Å. *E.s.d.'s are:* C–C, 0·05 Å (av.); Pd–Br, 0·004 Å; Pd–C, 0·03 Å; and Pd–P, 0·008 Å (av.).

To confirm this the crystal structure of (IVb) was determined. *Crystal data:* $C_{48}H_{43}BrO_8P_2Pd$, $M = 996{\cdot}121$, monoclinic, $a = 12{\cdot}650(5)$, $b = 14{\cdot}141(5)$, $c = 30{\cdot}09(1)$ Å, $\beta = 123{\cdot}7(1)°$, $U = 4478{\cdot}5$ Å^3, $D_c = 1{\cdot}477$ g cm^{-3}, $Z = 4$, $F(000) = 2024$; space group $P2_1/c$ (C_{2h}^5 No. 14).

Three-dimensional *X*-ray data were collected using Zr filtered Mo-K_α radiation ($\lambda = 0{\cdot}7107$ Å); precession methods were used with the crystal in two different orientations and the data were estimated visually. Routine corrections were applied for Lorentz and polarisation effects and the data were scaled together using common reflexions to give 2502 independent reflexions. The structure was solved by standard Patterson and Fourier methods; block-diagonal least-squares refinement reduced *R* to a value of 0·109, allowing anisotropic temperature factors for the Pd, Br, and P atoms.

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‡ All new complexes have been fully characterised by analytical, molecular weight, and spectroscopic measurements.

The essential features are shown in the Figure and comprise an almost planar butadienylpalladium portion (r.m.s. deviation of these atoms from their best plane is 0·03 Å) which is at an angle of 88° to the co-ordination plane of the metals.

The unusual feature of the structure is that the predicted position of the vinylic hydrogen [assuming d(C–H) = 1·08 Å and a trigonal carbon] is in the fifth co-ordination position and at 2·3 Å from the metal. This value is much less than that expected for the sum of the van der Waals radii [r(H) = 1·2 Å; r(Pd) = *ca.* 1·9 Å][2] and suggests that some interaction (hydrogen bonding?) is occurring. This is confirmed by the n.m.r. data which show the vinylic hydrogen at extremely low field and coupled to the phosphorus atoms, presumably by a two-bond H–Pd–P coupling rather than one which proceeds along the butadienyl chain and which would have to be a six-bond interaction. This type of interaction has not been observed before, though Trofimenko noted that the methylene hydrogens of the ethyl groups in $Ni[Et_2B(pz)_2]_2$ are shifted downfield, probably because they occupy axial sites about the metal.[3] The point is also of great interest in relation to the problem of the activation of C–H bonds by metal.

It is also relevant to compare the structure of (IVb) with the one described by Blackmore *et al.* for $Ru(\pi\text{-}C_5H_5)(Ph_3P)\{C_4(CF_3)_4H\}$ which has a butadienylruthenium group.[4] In this complex, however, the terminal double bond is π-bonded to the metal, whereas in ours it is more nearly edge-on to it.

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