Synthesis, Reactions, and *X*-Ray Structure of η^2-Ethene(diop)palladium: a Useful Synthetic Equivalent for (diop)Pd^0†

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The synthesis and crystal structure of η^2-ethene-4,5-[bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane]palladium(0) (**1**) is reported; the complex undergoes alkene displacement and oxidative addition reactions of relevance to catalytic processes involving palladium bisphosphine complexes.

Palladium bisphosphine complexes are important catalysts for many significant transformations including catalytic allylic alkylation,[1] cross-coupling reactions,[2] and catalytic alkene hydrocyanation.[3] Such reactions are subject to 'chelate control'; the most reactive catalysts in the latter processes involve seven-membered-ring P_2-palladium chelates.[4,5] During studies directed towards the elucidation of the mechanism of catalytic asymmetric hydrocyanation,[5] we sought a convenient precursor for (diop)palladium(0).† Procedures have been devised for the synthesis of the related (diop)platinum ethene complex[6] in which the ethene ligand is readily displaced. We report the synthesis and *X*-ray structure of the complex (**1**), which is the first structurally characterised ethene complex of palladium, and some of its reactions which are of relevance to the catalytic transformations involving chelate bisphosphine palladium complexes.

Reduction of (*R*)-[Pd(diop)Cl$_2$] with sodium borohydride at −40 °C in ethene-saturated dichloromethane/ethanol (1 : 5) yielded a colourless crystalline solid (**1**) on gently warming to room temperature [70%, m.p. 80 °C (decomp.), $\delta_P(CD_2Cl_2)$ +6.8 p.p.m.]. The complex is unstable in solution in the

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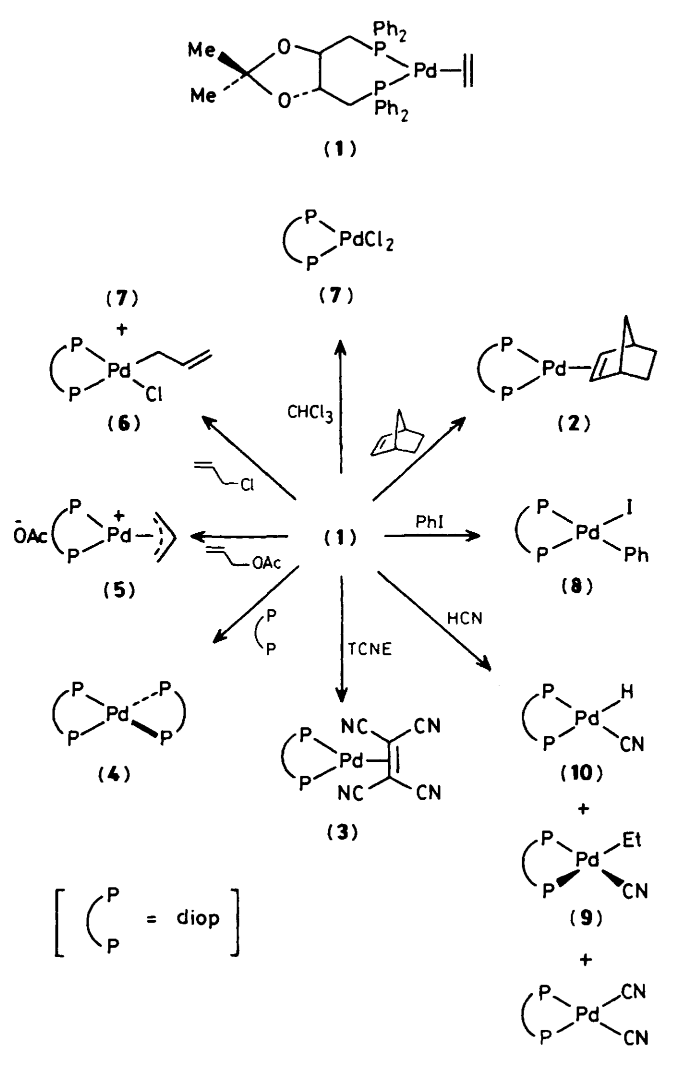
† Diop is 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane.



Scheme 1. TCNE = tetracyanoethylene.

absence of ethene,[7] but exhibits reasonable stability in air. In the ^{1}H n.m.r. spectrum of (**1**) (298 K; CD_2Cl_2), in the presence of ethene, broad signals for free and bound ethene were observed at +5.2 and +2.9 p.p.m., which sharpened under higher partial pressures of ethene indicative of dissociative alkene exchange. Smoky-grey crystals of (**1**) were isolated from the reaction mixture; an ORTEP diagram of the molecule is shown in Figure 1.‡ The co-ordination geometry about the palladium(0) centre is trigonal, with only a small torsion angle between the P(1)–P(2)–Pd and Pd–C(1)–C(2) planes, as observed in a fulvene complex of palladium(0).[8] The carbon–carbon bond length in the co-ordinated ethene is 1.366(11) Å, consistent with a rather weak palladium–ethene bond and in accord with the ease of dissociation of ethene in

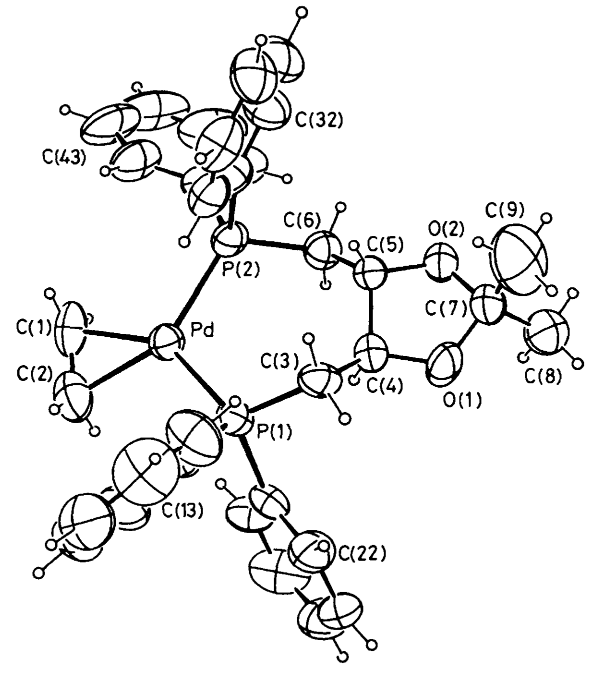


Figure 1. Molecular structure of (**1**); key dimensions Pd–C(2) 2.119(8), Pd–C(1) 2.122(8), C(1)–C(2) 1.366(11), Pd–P(1), Pd–P(2) 2.289(2) Å; P(2)–Pd–P(1) 106.4, C(1)–Pd–C(2) 37.6(3), Pd–C(1)–C(2) 71.1, P(1)–Pd–C(1) 145.2, P(1)–Pd–C(2) 108°.

solution. Generally, in lower-valent alkene complexes of Group VIII metals, the degree of back donation is fairly extensive and the alkene bond length in several Pt^0 alkene complexes is increased by as much as 0.2 Å on co-ordination.[9] For comparison, in $[PtC_2H_4(PPh_3)_2]$ and $[NiC_2H_4(PPh_3)_2]$ the carbon–carbon bond length for bound ethene is 1.43 Å.[10] The chelate 'bite' angle in (**1**) is 106.4°; *cf.* 96° for the square planar $[Pd(diop)Cl_2]$.[11]

The ethene ligand in (**1**) may be displaced readily by strained or electron-poor η^2-donors: reaction with an excess of norbornene in dichloromethane gives the η^2-norbornene complex (**2**) (δ_P +6.2 p.p.m.) although cyclopentene fails to react under similar conditions. Tetracyanoethene cleanly displaces ethene to give the complex (**3**) (δ_P +9.2 p.p.m.) which may also be formed by reaction of $[(diop)_2Pd]$[12] (**4**) with tetracyanoethene. Reaction with allyl acetate gives the cationic palladium(II) allyl complex (**5**) (δ_P +8.1 p.p.m.) rapidly, presumably *via* an S_N2 pathway, while oxidative addition of allyl chloride gave not only the η^1-allyl chloride complex (**6**) (δ_P 28.2 and 2.0 p.p.m.; J_{PP} 40 Hz) but also $[Pd(diop)Cl_2]$ (**7**) (δ_P +16.1 p.p.m.). Given that (**1**) also abstracts chlorine from chloroform and carbon tetrachloride to give $[Pd(diop)Cl_2]$, it seems likely that this oxidative addition involves direct halogen abstraction to form a $[(diop)Pd^{I}Cl]$ radical intermediate.[13] Only the formation of (diop)Pd(η^1-allyl) chloride is inhibited by the presence of 5 mol % duroquinone, suggesting that $[Pd(diop)Cl_2]$ may be formed *via* competitive interception of the radical cage pair by further allyl chloride, or at least that halogen abstraction by [Pd(diop)Cl] and its reaction with additional allyl chloride are competitive. The ethene ligand in (**1**) is also rapidly displaced by phenyl iodide to give the *cis*-aryl iodide complex (**8**) (δ_P +13.2 and −3.2 p.p.m.; J_{PP} 41 Hz), a plausible intermediate in aryl coupling reactions.[2]

Chiral palladium bisphosphine complexes are efficient catalysts for the asymmetric hydrocyanation of alkenes.[3,5]

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‡ *Crystal data* for (**1**): $C_{33}H_{36}PdO_2P_2$, M = 633, monoclinic, space group $P2_1$, a = 10.664(3), b = 11.023(4), c = 13.926(2) Å, β = 109.41(2)°, U = 1543.9 Å^3, Z = 2, D_c = 1.36 g cm^{-3}, $F(000)$ = 652, T = 296 K, λ = 0.71073 Å, μ(Mo-K_α) = 7.2 cm^{-1}. Data were collected with an Enraf-Nonius CAD-4 diffractometer, and at convergence R was 0.034 (R_w 0.037) for the 2220 unique observed reflections. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Reaction of (**1**) with HCN in toluene gives two major species (δ_P +4.0 and −6.3 p.p.m.; J_{PP} 13 Hz; δ_P +18.2 and −1.4 p.p.m.; J_{PP} 40 Hz); the former is generated selectively by reaction of HCN with the preformed η^2-norbornadiene complex (**2**). Both species slowly react in solution to form [Pd(diop)$(CN)_2$] (δ_P +17.6 p.p.m.) irreversibly, a reaction which may be associated with catalyst deactivation. The former species is [PdH](diop)(CN)] (**10**) and exhibits ^{31}P and ^1H n.m.r. characteristics similar to those of [Pt(H)(diop)CN][5] {δ_P +11.5 (J_{PtP} 2840) and 9.69 (J_{PtP} 1725 p.p.m.), J_{PP} 15 Hz; δ_H −3.99 [J_{PtH} 967, J_{HP} 187 (*trans*), J_{HP} 16 Hz (*cis*)]}. The latter transient species is probably the cyanoethyl complex (**9**), from which a product nitrile may be derived by reductive elimination.[14]

In summary, the dissociatively labile d^{10} complex (**1**) undergoes alkene displacement reactions with strained or electron-poor alkenes and is sensitive to oxidative addition reactions with certain alkyl, allyl, or aryl halides and esters, some of which may involve single electron transfer and palladium(I) intermediates.[13] The complex (**1**) is therefore a useful synthetic equivalent for the 14-electron (diop)Pd^0 species,[15] on account of the ease of ethene dissociation.

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