Tertiary Phosphine–Palladium(0)–Ethylene Complexes

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Summary The synthesis of L_2Pd–ethylene complexes (L = triphenylphosphine, tricyclohexylphosphine, or tri-*o*-tolyl phosphite) and of L_2Pd (L = tricyclohexylphosphine) is reported; these easily accessible compounds may serve as starting materials in oxidative addition reactions.

UNLIKE ethylene complexes of zerovalent nickel,[1] and the bis(triphenylphosphine)-ethylene complex of platinum(0),[2] no similar complexes of zerovalent palladium with simple nonactivated olefins have, to our knowledge, been reported.[3] The latter compounds can, however, be synthesized in fairly good yields by reduction of palladium acetylacetonate with (ethoxy)diethylaluminium in ether solution at room temperature in the presence of ethylene and an appropriate ligand (2 mol.). The ethylene complexes thus obtained are air-sensitive, white, crystalline solids; they were characterized by palladium analysis and i.r. spectra (Table). In all three cases the stoicheiometric amount of ethylene was evolved upon addition of excess of triphenyl phosphite.

TABLE

Analysis and i.r. data of L_2Pd–ethylene *complexes*

L	Yield (%)	Palladium Calc. (%)	Palladium Found (%)	I.r. absorptions tentatively assigned to complexed ethylene (cm^{-1})
Triphenylphosphine	77	16·1	16·2	† 1488 (ν C=C), 1203 (δ CH_2), 388 (ν PdC)
Tricyclohexylphosphine	63	15·3	15·5	3048, 2980 (ν CH), 1483 (ν C=C), 1202, 1195 (δ CH_2) 350 (ν PdC)
Tri-o-tolylphosphite	47	12·6	12·6	†

† Absorptions obscured by bands of L.

The reduction of palladium acetylacetonate in the presence of the bidentate ligand $R_2PCH_2CH_2PR_2$ (R = cyclohexyl) (1 mol.) does not lead to the ethylene complex; here the very stable diethyl compound ($R_2PCH_2CH_2PR_2$)-$PdEt_2$ was isolated [Pd calc. 18·1% found 18·1%; i.r. 2320(νCH) and 530(νPdC) cm^{-1}]. The ethylene complexes dissociate in solution in benzene, the triphenylphosphine complex disproportionating with precipitation of metallic palladium. For the tricyclohexylphosphine compound a molecular weight of 550 at $2·2 \times 10^{-2}$ mol l^{-1} was found (calc. 695·3) from freezing point measurements (benzene), indicating that dissociation is appreciable. This complex, when suspended in ether, loses ethylene readily upon evacuation or passage of argon through the suspension.

$$(R_3P)_2Pd(C_2H_4) \rightleftarrows (R_3P)_2Pd + C_2H_4$$

$$2\,(R_3P)_2Pd \rightarrow (R_3P)_4Pd + Pd \quad (R = \text{phenyl})$$

From the resulting pale yellow solution $(R_3P)_2Pd$ (R = cyclohexyl)[4] may be isolated as a stable, air-sensitive, white, crystalline solid by evaporation *in vacuo* (Pd calc. 16·0%, found 16·1%; i.r. ethylene absorptions (see Table) absent; νPdP 395 cm^{-1}). This compound reacts with acids to form hydridopalladium complexes.

$$(R_3P)_2Pd + HX \rightarrow \textit{trans}\text{-}(R_3P)_2Pd(H)X \quad (R = \text{cyclohexyl})$$

For X = Cl, we obtained *trans*-$[(C_6H_{11})_3P]_2Pd(H)Cl$ in almost quantitative yield [i.r. (KBr) 2002 cm^{-1} (νPdH); ^1H n.m.r. (220 MHz; C_6D_6) $\tau H = 27·4$; $J_{HP} = 4·5$ Hz. This complex has recently been reported by Munakata and Green,[5] though its synthesis seems more convenient by this route.

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