Novel Insertion of Acetylene into σ-Alkynyl Palladium Complexes

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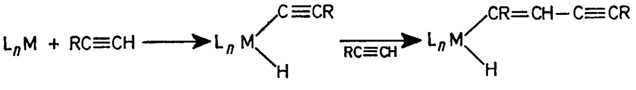
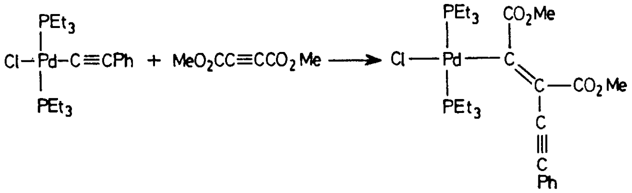
Summary *trans*-$[(PEt_3)_2PdCl(C{\equiv}CPh)]$ reacts with dimethyl acetylenedicarboxylate to give an insertion product, *trans*-$[(PEt_3)_2PdCl\{C(CO_2Me){=}C(CO_2Me)C{\equiv}C\text{-}Ph\}]$, a type important in acetylene catalytic oligomerisation processes.

INSERTION of an acetylene into a transition-metal-alkynyl bond is a critical step in some acetylene oligomerisations with transition-metal catalysts (Scheme 1).[1] No product of insertion into an alkynyl complex has been isolated, although there are many examples of insertion of acetylenes into an alkyl-[2] or alkenyl-metal bond.[3]



SCHEME 1

We report the first example of insertion of acetylene into the alkynyl carbon–palladium bond. Reaction of the acetylide complex, *trans*-$[(PR_3)_2PdX(C{\equiv}CPh)]$ (I; R = Et, X = Cl) with dimethyl acetylenedicarboxylate in dioxan at 85° for 2 h, after chromatography on alumina, gave stable, white crystals of (II),† *trans*-$[(PEt_3)_2PdCl\{C(CO_2Me){=}C(CO_2Me)C{\equiv}CPh\}]$, m.p. 163°; i.r. ν_{Pd-Cl} 298 cm^{-1} (Nujol);



SCHEME 2

Raman $\nu_{C{\equiv}C}$ 2200 cm^{-1}; $M(CH_2Cl_2)$ 612 (calc. 621·4); $\delta(CCl_4)$ 3·69 and 3·64 (CO_2CH_3), and 1·11 (characteristic 1 : 4 : 6 : 4 : 1 quintet[4] for methyl resonances of the *trans*-PEt_3). The mass spectrum of complex (II) shows no parent ion, ready coupling of ligands occurring to give $[Et_3PC(CO_2CH_3){=}C(CO_2CH_3)C{\equiv}CPh]^+$ at *m/e* 361. The compound is thermally stable to *ca.* 220 °C and is unaffected by dry HCl

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† Satisfactory elemental analytical data were obtained.

in ether solution at room temperature. Insertion products† analogous to (II) can be obtained with (I; R = Et, X = Br; and R = Bu, X = Cl, Br, and I) in 8—24% yields. Reaction of the methyl or σ-vinyl palladium complexes, *trans*-[$(PEt_3)_2PdI(Me)$] or *trans*-[$(PBu_3)_2PdBr(CH{=}CPh_2)$]† with dimethyl acetylenedicarboxylate gave similar insertion products, *trans*-[$(PEt_3)_2PdI\{C(CO_2Me){=}C(CO_2Me)(Me)\}$]† and *trans*-[$(PBu_3)_2PdBr\{C(CO_2Me){=}C(CO_2Me)CH{=}CPh_2\}$],† in 40 and 74% yields, respectively. It is interesting that the phenyl or sterically hindered σ-vinyl complexes, *trans*-[$(PEt_3)_2PdClPh$] or *trans*-[$(PEt_3)_2PdBr(CPh{=}CPh_2)$],† gave no insertion product analogous to (II). Since insertion of acetylenes into transition-metal hydrides[5] and alkyls[2] is believed to give *cis*-vinyl derivatives, complex (II) may have the structure shown in Scheme 2.

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