

Preliminary communication

PREPARATION AND PROPERTIES OF SOME NEW ALKYL- AND ARYL-
 PALLADIUM COMPLEXES

G. KEVIN TURNER* and HUGH FELKIN

Institut de Chimie des Substances Naturelles, C.N.R.S., 91190 Gif-sur-Yvette (France)

(Received September 1st, 1976)

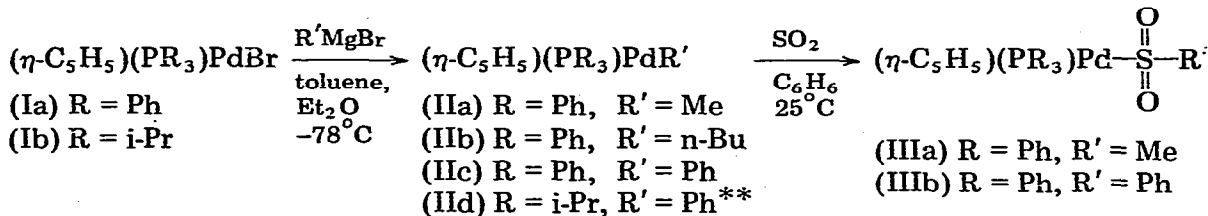
Summary

Complexes of the type $(\eta\text{-C}_5\text{H}_5)(\text{PR}_3)\text{PdR}'$ have been prepared by the reaction of $\text{R}'\text{MgBr}$ with $(\eta\text{-C}_5\text{H}_5)(\text{PR}_3)\text{PdBr}$ in toluene at -78°C .

Several alkyl and aryl complexes of nickel [1] and platinum [2] of the form $(\eta\text{-C}_5\text{H}_5)(\text{PR}_3)\text{MR}'$ are known, but only one arylpalladium compound of this type has been reported, viz. $(\eta\text{-C}_5\text{H}_5)(\text{PEt}_3)\text{PdPh}$, isolated in low yield as an unstable, yellow oil and identified only by its PMR spectrum [2]. We now report the preparation and some properties of a number of alkyl- and aryl-palladium complexes of this type.

Treatment of a green toluene solution of $(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{PdBr}$ (Ia) [2] at -78°C with excess ethereal MeMgBr gave an orange solution after 15 min. The solution was hydrolysed with aqueous NH_4Cl , dried with MgSO_4 , filtered and the solvents removed under vacuum to leave an orange solid. Pure, air-stable, red-orange crystals of $(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{PdMe}$ (IIa) were obtained in 70% yield by crystallisation from toluene/pentane at -30°C (m.p. $130\text{--}132^\circ\text{C}$ (dec); PMR (C_6D_6): $\tau(\text{C}_5\text{H}_5)$ 4.12d ppm, $J(\text{P-H})$ 1.5 Hz; $\tau(\text{CH}_3)$ 9.34d ppm, $J(\text{P-H})$ 4.2 Hz).

The compounds IIb, IIc and IId have been isolated as analytically pure, orange crystals by analogous methods.



*To whom correspondence should be addressed.

**Oily solid, PMR (C_6D_6): $\tau(\text{C}_5\text{H}_5)$ 4.25 ppm, $J(\text{P-H})$ 1.2 Hz.

Complex IIa reacts with SO_2 in C_6D_6 solution to give a red solution of the *S*-methyl sulphinato complex $(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{PdSO}_2\text{Me}$ (IIIa). The PMR spectrum of the product shows the C_5H_5 resonance shifted to higher field (τ 4.60 ppm, $J(\text{P-H})$ 1.5 Hz) than that of the starting material, and the methyl resonance appears as a singlet at τ 7.38 ppm. The infrared spectrum (nujol mull) of the solid, isolated by adding pentane, showed (in addition to bands due to coordinated C_5H_5 and PPh_3) two strong bands at 1199 and 1056 cm^{-1} , assigned to $\nu(\text{SO}_2)$ [3].

Reaction of complex IIc (m.p. 110–115°C (dec); PMR (C_6D_6): $\tau(\text{C}_5\text{H}_5)$ 4.12d ppm, $J(\text{P-H})$ 1.6 Hz) with SO_2 gave the *S*-phenyl sulphinate, IIIb (PMR (C_6D_6): $\tau(\text{C}_5\text{H}_5)$ 4.72d ppm, $J(\text{P-H})$ 1.5 Hz; IR (nujol): $\nu(\text{SO}_2)$, 1181, 1029 cm^{-1}).

The *n*-butyl complex IIb (m.p. 59–62°C (dec); PMR (C_6D_6): $\tau(\text{C}_5\text{H}_5)$ 4.07d ppm, $J(\text{P-H})$ 1.5 Hz) decomposes in CDCl_3 or C_6D_6 under N_2 at 35°C to give but-1-ene, cyclopentadiene and a palladium(0) species. The decomposition probably proceeds by β -hydrogen elimination from the butyl complex to give but-1-ene, and $(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{PdH}$ as an intermediate, which reacts further to give cyclopentadiene and the palladium(0) species. Attempts to isolate the intermediate hydride were unsuccessful. In the presence of PPh_3 decomposition takes place to give $\text{Pd}(\text{PPh}_3)_4$.

Complex IIb also reacts with $(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{PdBr}$ (Ia) in C_6D_6 to give but-1-ene, cyclopentadiene and a quantitative yield of the dimeric palladium(I) complex $[\mu\text{-}(\eta^3\text{-C}_5\text{H}_5)\text{-}\mu\text{-BrPd}_2(\text{PPh}_3)_2]$ [4] presumably by attack of Ia by the palladium(0) species formed from the decomposition of IIb.

We thank the Compagnie des Métaux Précieux (Ivry) for a generous loan of palladium.

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