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Chemistry of Metal–Diene Complexes; a New Convenient Synthesis of Palladium(II) Hydride Complexes

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The chemistry of palladium hydrides has been studied in less detail than that of platinum hydrides probably due to the lack of a convenient synthetic route to these complexes [1]. Since the first report on stable palladium(II) hydrides appeared in 1970 [2], only a few complexes of the type *trans*-PdHXL$_2$ (I), (X = halide, NO$_3$ or other anionic ligand and L = tertiary phosphine) have been reported [3]. During the course of our investigations on the metal–diene complexes, we have discovered that such complexes (I) can be prepared rapidly and in excellent yields by the reaction of phosphine with bis[(2-methoxy-5-cyclooctenyl)chloropalladium], (II) [4].

For the present studies, bis[(2-methoxy-5-cyclooctenyl)chloropalladium], [(C$_8$H$_{12}$OCH$_3$)PdCl]$_2$ is obtained from the equimolar reaction of (COD)-PdCl$_2$ (COD = cyclooctadiene) with NaOH in aqueous methanol (eqn. 1).

$$(C_8H_{12})PdCl_2 \xrightarrow[CH_3OH]{NaOH} \tfrac{1}{2}[(C_8H_{12}OCH_3)PdCl]_2 + NaCl \qquad (1)$$

Addition of a tertiary phosphine ligand to a suspension of (II) in methanol in a molar ratio of 4:1 results in a clear solution, from which crystalline solid *trans*-PdH(Cl)L$_2$, (I), (L = PCy$_3$, PPr$^i_3$, PBu$^t_2$Me, PBu$^t_2$Bu^n) is precipitated in almost quantitative yield within a few minutes (eqn. 2).

$$\underset{\text{(II)}}{[(C_8H_{12}OCH_3)PdCl]_2} + 4L \rightarrow \underset{\text{(I)}}{2PdH(Cl)L_2} + 2C_8H_{11}OCH_3 \qquad (2)$$

However, when PBu$^t_3$ is used in metalated complex [PdCl(Bu$^t_2$PCMe$_2$CH$_2$)]$_2$ (III), is the main product and only a small amount of the hydride complex (I; L = PBu$^t_3$) is obtained. It appears that the palladium hydride complex (I) is formed first and undergoes metalation of *t*-butylphosphine to give the metalated complex(III), as we have shown previously [5, 6].

$$2PdH(Cl)(PBu^t_3)_2 \rightarrow \underset{\text{(III)}}{[PdCl(Bu^t_2PCMe_2CH_2)]_2} + 2Bu^t_3PHCl \qquad (3)$$

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TABLE I. Analytical Data for the Complexes [(C$_8$H$_{12}$OCH$_3$)PdCl]$_2$, PdH(Cl)L$_2$ and [Pd(Bu$^t_2$PCMe$_2$CH$_2$)Cl]$_2$.

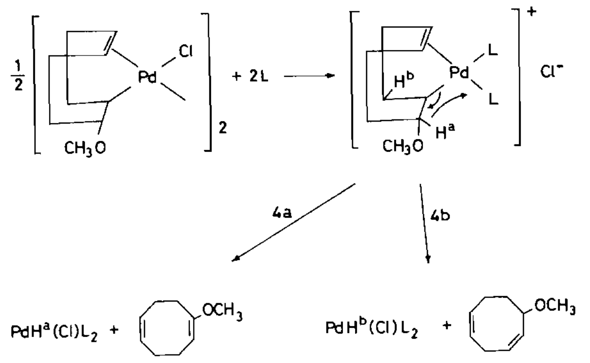
Complex	Analyses (%) Found (Calcd.)			
	C	H	Cl	P
[C$_8$H$_{12}$OCH$_3$)PdCl]$_2$	38.8 (38.5)	5.42 (5.35)	12.5 (12.7)	
PdH(Cl)L$_2$				
L = Cy$_3$P	61.2 (61.5)	9.69 (9.54)	5.17 (5.05)	8.61 (8.83)
Pr$^i_3$P	46.4 (46.7)	9.54 (9.30)	7.56 (7.68)	13.6 (13.4)
Bu$^t_2$Bu^{n}P	52.9 (52.7)	10.0 (10.1)	6.66 (6.50)	11.5 (11.3)
Bu$^t_2$MeP	46.8 (46.7)	9.38 (9.30)	7.72 (7.68)	13.4 (13.4)
[Pd(Bu$^t_2$PCMe$_2$CH$_2$)Cl]$_2$	42.0 (42.0)	7.57 (7.59)	10.3 (10.4)	9.12 (9.05)

The same complex (III) is formed in quantitative yield when the above reaction (eqn. 2) is carried out in 1:2 molar ratio.

The crystalline products (I) obtained from the reaction (1), are found to be analytically pure without recrystallization. They can be recrystallized from benzene/hexane or benzene/methanol. They have been fully characterized analytically (Table I) as well as spectroscopically. The infrared spectrum of complex I (L = PCy_3, PPr^i_3, PBu^t_2Me, $PBu^t_2Bu^n$) shows a νPd–H band in the region 1995–2040 cm^{-1}. Proton NMR spectra contains a triplet at δ 13.7–14.5 ppm (J_{P-H} = 4.1–4.6 Hz) due to the hydridic proton suggesting the *trans*-disposition of phosphines in that complex. This is further supported by the ^{31}P NMR spectrum which shows only one singlet at δ 41.1–54.0 ppm. ^1H and ^{31}P NMR spectra of the metalated complex(III) are consistent with those reported earlier [5, 6].

The organic products formed as in eqn. 2, were isolated by g.l.c. and found to be an isomeric mixture of methoxy-cyclooctadienes $C_9H_{14}O$ by elemental analysis, mass spectrum (obs. m/e = 138.1) and proton NMR spectrum. On the basis of the formation of these isomeric dienes a mechanism involving β-H transfer from the 2-methoxy-5-cyclooctenyl group to the palladium can be proposed as is shown in the scheme (*e.g.* 4a and 4b).

The involvement of the ionic intermediate is suggested by the fact that a polar solvent such as methanol or ethanol is required for these reactions. Thus, palladium hydride complexes (I) can be obtained conveniently and in high yields from the reaction of sodium hydroxide with $(COD)PdCl_2$ in methanol followed by the addition of a tertiary phosphine.



Scheme

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