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Preliminary communication

FACILE INTRAMOLECULAR METALATION OF TRI-t-BUTYLPHOSPHINE IN PALLADIUM(II) HYDRIDE COMPLEXES

HOWARD C. CLARK*, ANIL B. GOEL and SARLA GOEL

Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, University of Guelph, Guelph, Ontario (Canada)

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Summary

Palladium(II) hydride complexes, $PdH(X)(PBu\text{-}t_3)_2$ (I) (where X = Cl, Br or CF_3COO) undergo rapid intramolecular metalation in solution under ambient conditions, producing internally metalated complexes of the type, $PdX(PBu\text{-}t_2CMe_2CH_2)(PBu\text{-}t_3)$ (II). These complexes lose one mol equivalent of phosphine in solution to give the bridged dimeric complexes, $[PdX(PBu\text{-}t_2\text{-}CMe_2CH_2)]_2$ (III).

Reaction of complex I, II or III with sodium borohydride produces bis(tri-t-butylphosphine)palladium(0), which is also obtained when $PdH(X)(PBu\text{-}t_3)_2$ reacts with n-butyllithium.

Comparatively little is known about the chemistry of palladium(II) hydrides [1—3], although recently, Otsuka et al. [4] prepared stable complexes, $PdH(X)L_2$ (I: L = $PBu\text{-}t_2Ph$ or $PBu\text{-}t_3$; X = Cl or CF_3COO). We have now found that although these complexes (I: L = $Bu\text{-}t_3P$) are stable in the solid state for a few days, in solution they undergo rapid intramolecular metalation which also involves the Pd—H bond. The metalation of bulky phosphines in platinum(II) and palladium(II) dichlorides has been widely studied [5,6] but no such metalation process occurring in palladium(II) hydride complexes has been reported previously.

Oxidative addition of HX (X = Cl, Br or CF_3COO) to bis(tri-t-butylphosphine)palladium(0) occurs readily at room temperature in hexane or benzene solutions to give *trans*-$PdH(X)(PBu\text{-}t_3)_2$ (I). These complexes are characterized by elemental analyses, infrared (ν(Pd—H) 2190—2215 cm^{-1}), proton NMR [Pd—H: δ 16.2—18.3(t) ppm; J(P—H) 4.3—6.9 Hz] and ^{31}P NMR (δ 67—79 ppm) spectra. Although these complexes (I) are reasonably stable in the solid state, they undergo intramolecular metalation within a few hours

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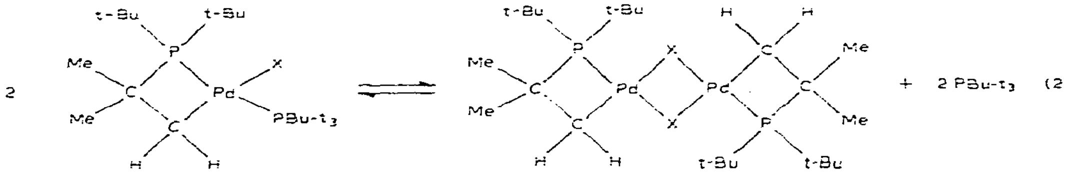
*To whom correspondence should be addressed.

when kept in benzene or methylene chloride solutions to give internally metalated products (II, eq. 1).

$$\underset{\text{(I)}}{\mathrm{PdH(X)(PBu\text{-}t_3)_2}} \rightarrow \underset{\text{(II)}}{\mathrm{PdX(PBu\text{-}t_2CMe_2CH_2)(PBu\text{-}t_3)}} + \mathrm{H_2} \qquad (1)$$

This metalation occurs more rapidly in CH_2Cl_2 *than* in benzene and the rate is markedly enhanced by the addition of a small amount of alcohol and follows the trend Br > Cl > CF_3COO. For example, complex I with X = CF_3COO, in benzene solution containing a small amount of alcohol, was converted into the corresponding complex II within 1 h, while the similar metalation process in complex I (X = Br) was almost instantaneous and the metalated complex II (X = Br) formed, underwent further reaction, producing the dimer complex III by elimination of free phosphine (eq. 2). The completion of the reaction was confirmed by the loss of the ν(Pd—H) band in the infrared spectrum, as well as the signals due to the hydride in the proton NMR spectrum. Furthermore, the proton NMR spectra of the complexes II show the expected three sets of doublets due to the protons of Pd—PBu-t_3, Pd—PBu-t_2 and P—CMe_2 groups. In particular, the spectrum of [Pd(CF_3COO)-(PBu-$t_2CMe_2CH_2$)(PBu-t_3)] shows signals at δ 8.72 (PBu-t_3), 8.55 (PBu-t_2) and 8.62 (P—CMe_2) ppm, in the ratio 9/6/2, with J(P—C—C—H) 12.2, 14.6 and 15.0 Hz, respectively. The proton signals of the C—CH_2—Pd group could not be observed and are probably masked by other strong signals. The ^{31}P NMR spectrum shows two singlets at δ −13.8 (due to metalated phosphine) and 63.9 ppm (due to unmetalated phosphine). These complexes (II) do not show coupling between the two phosphorus nuclei, which may suggest that the coordinated phosphine in the complexes is labile [7].

These complexes (II) are very soluble in benzene and less soluble in hexane from which they could be recrystallized. Because of the rapid conversion of II (X = Br) into III, II (X = Br) could not be isolated in pure form. However, the other complexes were obtained pure by crystallization, and were characterized by elemental analyses and spectroscopic methods. Interestingly, when these complexes were allowed to stand in benzene/hexane solutions for 1 to 2 days, loss of one equivalent of PBu-t_3 occurred (followed by NMR), followed by rearrangement to give halo- or acetato-bridged dimeric complexes [PdX(PBu-$t_2CMe_2CH_2$)]$_2$ (III, eq. 2)*. Interestingly, this reaction is the reverse of the bridge splitting reactions reported earlier by Shaw and coworkers [5], for several other bridged complexes of platinum and palladium.



(II) (III)

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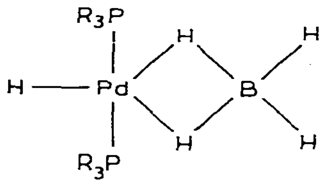
*Compound III (X = Cl) has also been prepared from the reaction of K_2PdCl_4 and PBu-t_3 in DMF [8].

The proton NMR spectra of complexes III invariable show three sets of doublets due to protons of Pd—PBu-t_2, P—CMe_2 and C—CH_2—Pd groups in a 9/3/1 ratio. The ^{31}P NMR spectra contain only one singlet at about δ −13 ppm indicative of metalated phosphine.

The ready conversion of II into III is presumably a consequence of the steric strain at Pd in II due to the presence of both the bidentate, metalated phosphine ligand and the monodentate tertiary phosphine. This is consistent with the observation that II is more stable when the monodentate ligand is less bulky (e.g. Et_3P, Ph_3P or Ph_3As) but more readily dissociates to III with bulky ligands such as Cy_3P, $(o\text{-}CH_3C_6H_4)_3P$, or PBu-t_3.

The reaction of sodium borohydride with palladium(II) hydride complexes (I) in ethanol, expected to yield palladium borohydride complexes of the type IV (PR_3 = PBu-t_3), similar to those obtained previously with tricyclohexylphosphine complexes [1], or the dihydride complex, PdH_2(PBu-$t_3)_2$, surprisingly gave bis(tri-t-butylphosphine)palladium(0). Similarly, when the internally metalated complex (II) was allowed to react with $NaBH_4$, the same palladium(0) complex, (Bu-$t_3)_2$Pd, was obtained.



(IV)

$$PdHX(PBu\text{-}t_3)_2 + NaBH_4 \rightarrow (PBu\text{-}t_3)_2Pd + NaX \quad (3)$$

$$PdX\{PBu\text{-}t_2C(Me)_2CH_2\}(PBu\text{-}t_3) + NaBH_4 \rightarrow (PBu\text{-}t_3)_2 + NaX \quad (4)$$

Sodium borohydride reduction of III also produced the palladium(0) complex as the only stable product. Apparently, if complex IV or the dihydride PdH_2(PBu-$t_3)_2$ (V) is formed, it reductively dissociates to the more stable zerovalent species. This is further supported by the observation that I reacts with n-butyllithium to also give (PBu-$t_3)_2$Pd. A detailed study of these reactions is under investigation.

It has been suggested [5] that intramolecular metalation in the complexes $MX_2(PR_3)_2$ (M = Pd or Pt) occurs by oxidative addition of 2C—H or 3C—H on to the metal, followed by reductive elimination of HX. Kiffen et al. [9] have shown that the complexes $Pt_2Cl_2L_2$ (L = PBu-n_3, PPr-n_3 and PBu-t_2Pr-n) undergo hydrogen—deuterium exchange at the C(3) position of n-butyl or n-propyl groups but also at the C(2) position of t-butyl groups. Moreover, Otsuka et al. [10] have observed the short distance and probable interaction between Pd and the hydrogens of the t-butyl group in Pd(PBu-t_2Ph$)_2$. Hence for PdHCl(PBu-$t_3)_2$, the presence of such an interaction combined with the presence of the hydrido ligand, suggests that intramolecular metalation occurs because of the facile elimination of hydrogen, rather than by oxidative addition of C—H to palladium.

Acknowledgments

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