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ELECTROPHILIC ATTACK ON [1,2-BIS(DIPHENYLPHOSPHINO)ETHANE] (2-NORBORNANONE)PALLADIUM(II) CHLORIDE

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Summary

The protonolysis of the complex [1,2-bis(diphenylphosphino)ethane](2-norbornanone)palladium(II) chloride(I) has been studied. Comparison of the ^{13}C NMR spectra of samples of 2-norbornanone obtained by treatment with HCl or DCl, unambiguously reveals that the carbon of the ketone was previously coordinated to the palladium(II). Kinetic results for the electrophilic cleavage of I are also reported. The rate law and the deuterium isotope effect suggest a rate-determining proton transfer to the palladium–carbon σ-bond, which takes place through a symmetrical three-centre transition state.

Introduction

We recently described the formation of [1,2-bis(diphenylphosphino)ethane](2-norbornanone)palladium(II) chloride, through a Wacker-related process involving a palladium(II) assisted intramolecular hydride migration from an alcohol substituent to an adjacent olefinic carbon atom [1]. Although the formation of the σ-coordinated 2-norbornanone was unambigously demonstrated by GC analysis of the product produced by acid cleavage the spectroscopic evidence did not show which carbon of the organic moiety became σ-bonded to the metal, coordination of either C(5) or C(6) being consistent with the ^{13}C data (Fig. 1). We desribe here an experiment carried out to remove this doubt. Furthermore, since only a few results relating to protonolysis of palladium(II) compounds have previously appeared [2], we also report kinetic data for the attack of the proton on the palladium(II) σ-coordinated 2-norbornanone, in order to clarify the influence of the metal on the mechanism of this electrophilic attack.

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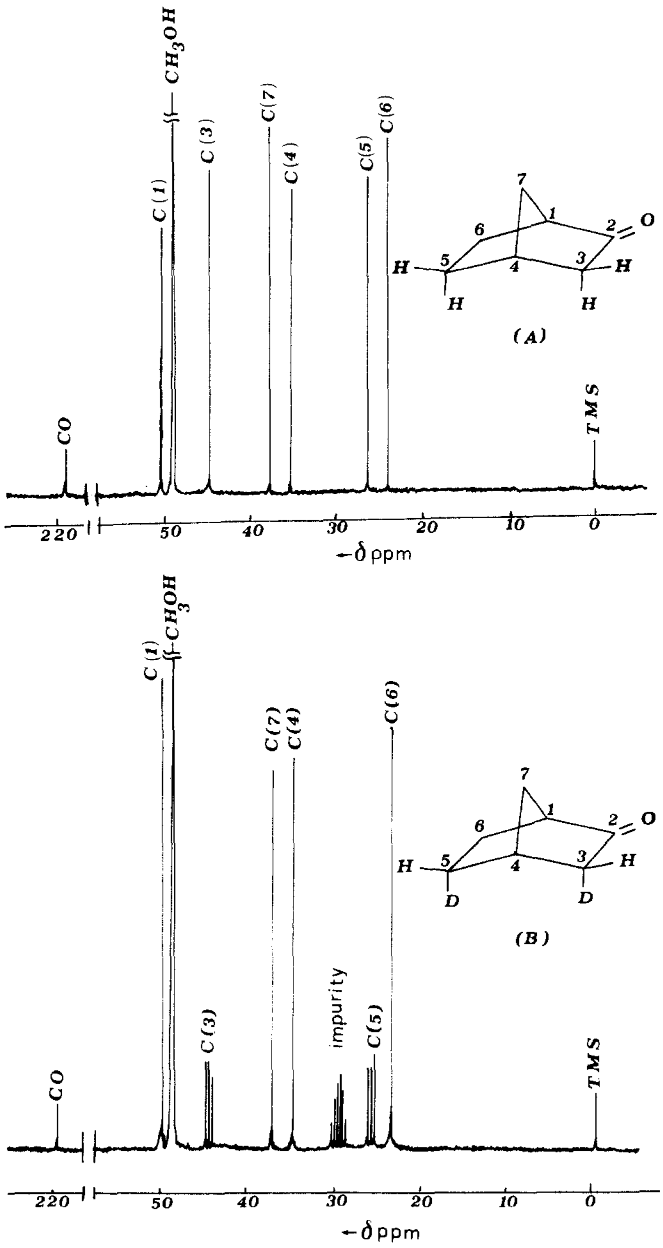


Fig. 1. ^{13}C hydrogen decoupled NMR spectra of: (A) $C_7H_{10}O$, obtained by protonolysis of 1,2-bis(diphenylphosphino)ethanepalladium(II) chloride; and of (B) $C_7H_8D_2O$, obtained by deuterolysis of 1,2-bis(diphenylphosphino)ethane(2-norbornanone)palladium(II)chloride.

Results and discussion

As previously described [1] when the chloride of 5-methoxynortricyclenyl derivative $[Pd(C_7H_8OCH_3)(P{-}P)Cl]$ (P–P = 1,2-bis(diphenylphosphino)ethane) is quantitatively removed by $AgNO_3$, subsequent treatment with an equimolar amount of

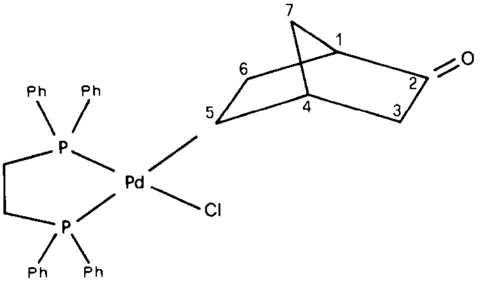


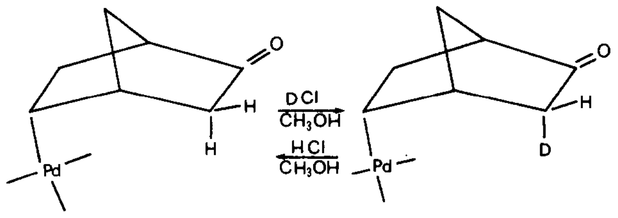
Fig. 2. Formulation of the palladium complex (2-norbornanone)[1,2-bis(diphenylphosphino)ethane]palladium(II) chloride.

HCl in CH_3OH/H_2O gives a white organometallic compound. The ^{13}C NMR spectrum of this compound, (2-norbornanone)[1,2-bis(diphenylphosphino)ethane]palladium(II) chloride, shows six signals in addition to the resonances of the carbons of the coordinated diphosphine and carbonyl ligands. In particular the doublet of doublets centred at 23 ppm is consistent with a carbon atom σ-coordinated to palladium(II) coupled with two non-equivalent phosphorus atoms *trans* and *cis*, respectively, to it (J_A (P) 24.3 cps; J_B (P) 40.7 cps). Comparison of this spectrum with that of an authentic sample of 2-norbornanone did not reveal which carbon was coordinated to palladium, coordination of either C(6) or C(5) (Fig. 1) both being consistent with the spectroscopic data [1].

These possibilities have now been distinguished by recording the hydrogen-decoupled ^{13}C NMR spectra of two samples of 2-norbornanone obtained by cleavage of the palladium by HCl in CH_3OH or DCl in CH_3OD. The spectrum of the former sample is identical with that of an authentic sample of 2-norbornanone, whereas that of the latter shows (as the only difference) the two signals at 27.5 and 48.5 ppm, corresponding respectively to the C(3) and C(5) carbons, split into two triplets by coupling with two deuterium atoms (Fig. 1). On the basis of these findings alone the carbon σ-coordinated to the palladium undergoing the electrophilic attack could either be C(3) or C(5), but the ^{13}C NMR spectrum of the palladium complex excludes the possibility that C(3) is involved in coordination [1]. Thus the only possible formulation of the palladium complex is as shown in Fig. 2.

Quantitative formation of B (Fig. 1), by deuterolysis of this complex suggests that the equilibrium shown in Scheme 1, involving a palladium intramolecular activation of a C–H bond, exists in solution.

Kinetic data for the protonolysis shown in eq. 1, where (P–P) = 1,2-



SCHEME 1

TABLE 1

VALUES OF OBSERVED RATE CONSTANTS, k_{obs} (s^{-1}) FOR THE ACID CLEAVAGE REACTION OF [1,2-BIS(DIPHENYLPHOSPHINO]ETHANE(2-NORBORNANONE)PALLADIUM(II) CHLORIDE IN METHANOL (5%) AT VARIOUS PROTON OR DEUTERIUM ION AND CHLORIDE ION CONCENTRATIONS

10^2 [H^+]	10^2 [Cl^-]	10^2 [ClO_4^-]	$10^4 k_{obs}$ (s^{-1})
50.00	–	50.00	10.00
50	4.92	45.08	9.60
50	10.00	40.00	9.80
50	24.60	25.4	10.00
50	50.00	–	19.60
4.92	50.00	–	0.90
9.8	50.00	–	1.73
17.5	50.00	–	3.52
24.5	50.00	–	4.25
33	50.00	–	6.10
40	50.00	–	7.75
10^2 [D^+] [a]			
5	50.00	–	0.25
11.50	50.00	–	0.59
29.00	50.00	–	1.48
40	50.00	–	1.85
50	50.00	–	2.40

[a] Experiments carried out in CH_3OD containing [D_2O] 2.77 *M*.

bis(diphenylphosphino)ethane and $C_7H_{10}O$ = 2-norbornanone are listed in Table 1.

$$Pd(C_7H_9O)(P\text{–}P)Cl + H^+ + Cl^- \rightarrow Pd(P\text{–}P)Cl_2 + C_7H_{10}O \quad (1)$$

No firm evidence has been found for a path involving Cl^-, the rate being independent of the concentration of the chloride. However reaction in the absence of Cl^- is about four times faster than its presence, suggesting that the cleavage of a more reactive solvated species [Pd(P–P)(2-norbornanone)(CH_3OH)]$^+$ takes place under these conditions; unfortunately, in these particular experiments the nature of the final product could not be unambigously identified.

The linear depencence of k_{obs} (s^{-1}) on the analytical concentration of H^+ (upper line) at [Cl^-] 0.5 is shown in Fig. 3. These results fit the following general expression:

$$k_{obs} = k[H^+]$$

This result together with the large kinetic isotope effect $k_H/k_D = 4$, and the rate law indicate that the rate-determining step of the acidolysis of II (Scheme 2) is electrophilic attack of a proton on the substrate. In keeping with this, there is a marked decrease of rate on going from methanol to methanol containing 5% by volume of water, because of the more effective solvation of the proton in the latter medium. Further increase in the water content does not cause a large change in the rate. The absence of any observable increase of the rate in the presence of chloride implies that the anion does not provide any nucleophilic assistance to the reaction.

In our opinion consideration of which end of the Pd–C bond is first attacked by the proton is largely a matter of semantics. Much more important is to establish

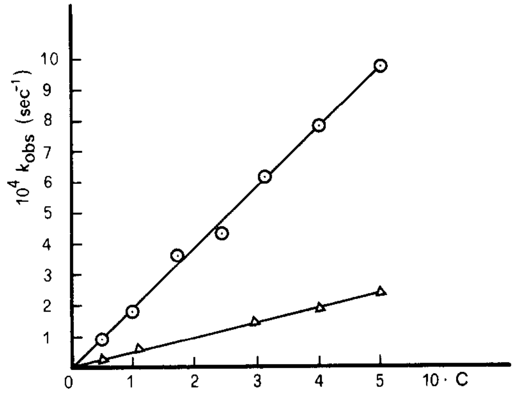
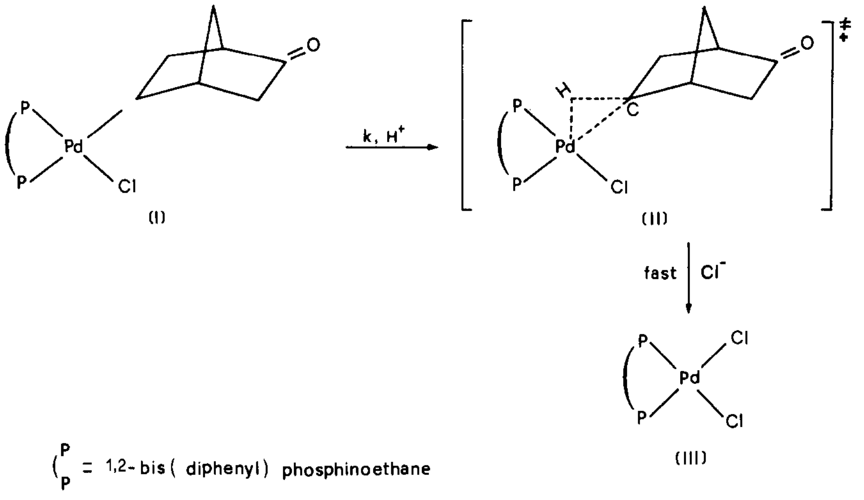


Fig. 3. Plot of first-order rate constant, k_{obs} (s^{-1}), against the analytical concentration of H^+ (○) or D^+ (△) at constant Cl^- concentration, [Cl^-] 0.5 *M*.

whether or not an intermediate is formed. The large kinetic isotope effect and the absence of nucleophilic assistance by Cl^- makes formation of an intermediate palladium(IV) hydride unlikely and so we favour a single bimolecular rate-limiting proton transfer involving a three-centre transition state (S_E2) (see Scheme 2).

The exact position of the hydrogen in the transition state is a matter of speculation; it has been suggested [3] that if the proton undergoes quantum mechanical tunnelling through the energy barrier then the isotope effect is expected to be larger for an almost symmetrical transition state. Moreover reactions which proceed through a rate-limiting proton transfer do not always show large primary isotope effects; small isotope effects are observed when the transition state is strongly product-like or reactant-like.

Mechanisms analogous to the one we propose have been postulated for protonolysis of some alkyl- and aryl-platinum(II) derivatives [4,5]. However, the electrophilic cleavage of the *trans*-$Pt(PEt_3)_2(CH_3)Cl$ has been reported to occur through pre-



SCHEME 2

liminary oxidative addition of H^+ to the substrate followed by reductive elimination of methane and there is compelling evidence for the formation of palladium(IV) intermediates in the electrophilic attack of methyl iodide on σ-alkyl-palladium(II) substrates [6,7]. The available experimental results do not permit generalizations about the nature of the attack of electrophiles on σ-alkylpalladium(II) derivatives, and both oxidative addition to the metal, with only moderate changes in the metal–carbon bond, and reactions involving substantial modification of the metal–carbon bond can occur.

Experimental

Materials

[(2-norbornanone)(1,2-bis(diphenylphosphino)ethane]palladium chloride and (1,2-bis(diphenylphosphino)ethane)palladium dichloride, were prepared by published procedures [1].

Acid cleavage of [(2-norbornanone)(1,2-bis(diphenylphosphino)ethane]palladium chloride. The organometallic compound (300 mg) was suspended in 3 ml of CH_3OH or CH_3OD and 2 ml of a concentrated solution (37%) of HCl in H_2O or concentrated DCl (38%) in D_2O was added. The 1,2-bis(diphenylphosphino)ethane)palladium dichloride formed was filtered off. The ^{13}C NMR spectra of the methanolic solutions were recorded; deuterium locking was achieved by addition of a suitable amount (~ 30%) of CD_3OD to the methanolic solutions.

Kinetics

The reactions were carried out in methanol containing 2.77 mol/l of H_2O at 35°C. The ionic strength was mantained constant at 0.5 *M* by adding suitable amounts of $LiClO_4$. The concentrations of chloride and acid were determined by titration.

A freshly-made solution containing the complex $Pd(C_7H_8OCH_3)(P\text{-}P)Cl$ ($\sim 10^{-4}$ *M*) and a solution of the acid HA ($A^- = Cl^-$, ClO_4^-) containing lithium chloride and/or lithium perchlorate were placed in a thermostat. The reactions were started by mixing known volumes of the two solutions in a 1-cm quartz cell which was then placed in a thermostatted compartment of an OPTICA CF 4R double beam recording spectrophotometer. The progress of the reaction was monitored by recording the UV spectral change. A large excess of lithium chloride and/or acid was used to assure pseudo-first-order conditions and to drive the reaction to completion. The final spectra agreed with those of an authentic sample of $Pd(P\text{-}P)Cl_2$ under the same conditions.

Pseudo-first order rate constants, k_{obs} (s^{-1}), were determined from slopes of plots of log ($A_t - A_\infty$) against time (A_t and A_∞ are the optical densities after time t and 10 half-lives, respectively, at the chosen wavelength λ 300 nm). The spectra during the reaction showed well-defined isosbestic points, indicating that only two absorbing species, the substrate and the product, were present in detectable amounts during the reaction. For measurements of isotopic effect, runs were carried in the presence of DCl and LiCl in CH_3OD/D_2O ($[D_2O]$ 2.77).

Physical measurements

Electronic spectra were recorded on an Optica CF4R spectrophotometer. IR spectra were recorded as Nujol mulls (CsI discs on a Perkin–Elmer 437 spectrometer). The ^1H and ^{13}C NMR spectra were recorded at 80.13 and 20.15 MHz respectively, on a Bruker WP 80 SY (80 MHz) recording spectrometer; the chemica shifts are relative to TMS.

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