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Study of the interaction of platinum hydride complex $[(PPh_3)_3PtH]^+$ with carbon monoxide and ethylene in trifluoroacetic acid solutions

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Abstract

The most probable intermediate formed by interaction of CO and C_2H_4 with $[(PPh_3)_3PtH]^+$ (I), in the synthesis of diethyl ketone from C_2H_4, CO and H_2 under action of the catalytic system $(PPh_3)_2Pt(OAc)_2/PPh_3/CF_3COOH$ has been studied by ^1H, ^{13}C, ^{31}P NMR spectroscopy. Complex I readily reacts with CO in CF_3COOH solutions to form a carbonyl hydride complex *trans*-$[(PPh_3)_2Pt(CO)H]^+$ (II). In contrast to I, II undergoes ethylene insertion at the Pt–H bond in the presence of a catalytic additive $Sn(OAc)_2$. The carbonyl ethyl complex *trans*$[(PPh_3)_2Pt(CO)(C_2H_5)]^+$ (III) formed quantitatively from this insertion is stable to isomerization to the corresponding complex indicating that the carbonylation of the Pt–ethyl bond is the rate-determining step of the diethyl ketone synthesis.

Introduction

We recently studied the catalytic system "$Pd(OAc)_2$–PPh_3" in the synthesis of diethyl ketone from ethylene, carbon monoxide and dihydrogen in CF_3COOH solutions at 70 °C and 1 atm [1]. The hydride complex $[(PPh_3)_3PdH]^+$ has been shown to be the key palladium compound in this reaction, and is formed both by the interaction of H_2 with the phosphinepalladium(II) complex, and by protonation of the phosphinepalladium(0) complex in aqueous CF_3COOH solutions [2]. The hydride complex readily undergoes the sequential insertion of C_2H_4 into the Pd–H bond and then of CO into the Pd–C bond to give the propionylpalladium derivative, which reacts with the second C_2H_4 molecule in the rate-determining steps to give diethyl ketone [2–4].

Under similar conditions for ethylene carbonylation catalysed by phosphine complexes of other platinum metals, it was found that diethyl ketone synthesis also takes place slowly in the presence of $(PPh_3)_2Pt(OAc)_2$ [5].

Here we report the results of ^1H, ^{13}C and ^{31}P NMR spectroscopic studies of the important features of the interaction of carbon monoxide and ethylene with the platinum hydride complex $[(PPh_3)_3PtH]^+$ (as the most probable, catalytically active

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intermediate) in order to determine the composition and structure of the resulting platinum compounds and to elucidate the mechanism by which the platinum system operates and why its catalytic activity in the synthesis of diethyl ketone is low.

Results and discussion

Protonation of $Pt(PPh_3)_4$ by trifluoroacetic acid in benzene solutions results in a cationic hydride complex $[(PPh_3)_3PtH]^+$ (I) having a square-planar structure [6]. The hydride complex of the same composition and structure (from the ^1H and ^{31}P NMR data in Table 1) is readily and quantitatively formed during the dissolution of $Pt(PPh_3)_4$ in pure CF_3COOH. We believe that in catalytic system for diethyl ketone synthesis [5] I may be generated either by the interaction of H_2 with initial phosphineplatinum(II) complex or during the reduction of the latter by CO and further protonation of the phosphineplatinum(0) complex formed. It was of interest to determine the sequence in which complex I reacts with CO and C_2H_4 to give diethyl ketone. Complex I reacts readily with CO in CF_3COOH to give the cationic carbonyl hydride complex *trans*-$[(PPh_3)_2Pt(CO)H]^+$ (II), the spectral parameters of which are presented in Table 1. A similar reaction took place quantitatively in benzene solution only upon addition of large amounts ($\gtrsim 25$ mol/g-at. Pt) of CF_3COOH, indicating that the excess of triphenylphosphine is probably removed by protonation.

The hydride complexes I and II, do not react with ethylene in CF_3COOH solutions at 25–70 °C to any noticeable extent. The inertness of I towards CO and C_2H_4 in aprotic solvents was noted earlier [6,7]. However, in contrast to I, the reactivity of II towards ethylene changed significantly when tin(II) acetate was added to the solution. Though the tin concentration in the solution was less than 1% relative to platinum owing to its low solubility, it catalyzed the rapid and complete transformation of II into the new compound III, identified as carbonylethylplatinum derivative from its spectral data (Table 1). The ^1H and ^{13}C NMR spectra indicate the presence of ethyl and carbonyl groups in the composition of III. The resonances of CO and CH_2 groups in the ^{13}C NMR spectrum, in contrast to the CH_3 group, show triplet splitting of the signals from the two equivalent phosphorus nuclei of PPh_3 ligands, which are *trans* to each other. Furthermore, the value of J(C–Pt) for the CO group is less than double that for the CH_2 group whereas the J(C–Pt) values for the CH_3 and CH_2 groups differ by a factor of at least 15. Thus, both carbonyl and ethyl groups are bonded directly with platinum (but not as a propionyl ligand) and III is actually *trans*-$[(PPh_3)_2Pt(CO)(C_2H_5)]^+$. This complex has been prepared previously [8] by the reaction of propionyl chloride with $Pt(PPh_3)_4$ in ethanol in the presence of $AgPF_6$. We succeeded in preparing it by means of an important catalysed reaction, that of olefin insertion into the Pt–H bond of the carbonyl hydride complex II.

Phosphine complexes of platinum(II), for example $(PPh_3)_2PtCl_2$, are known to be the active catalysts of homogeneous hydrogenation, hydroformylation and isomerization of olefins in the presence of $SnCl_2$. The catalytically active intermediate in hydroformylation is suggested to be $Pt(H)(CO)(PPh_3)(SnCl_3)$ [9]. The $SnCl_3^-$ ligand is regarded as the promoter owing to its ability to stabilize five-coordinated Pt^{II} species [10,11], which facilitates olefin insertion into a Pt–H bond via trigonal bipyramidal intermediates [7].

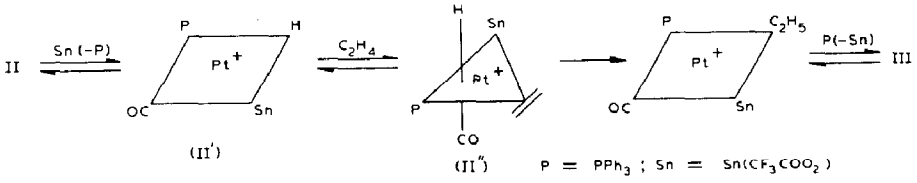
Table 1

NMR data for the triphenylphosphine platinum complexes [a]

Platinum complexes	Observed ligands	Chemical shifts, δ(ppm) [b]			Coupling constants (Hz)
		^1H	$^{31}P\{^1H\}$	$^{13}C\{^1H\}$	
$[(PPh_3)_3PtH]^+$ (I)	H^-	−5.86(dt)			$^1J(H-Pt)$ 771;
	trans-$PPh_3(P^1)$		24.3(t) [c] (dt) [d]		$^2J(P^1-P^2)$ 18; $^2J(H-P^1)$ 160;
	cis-$PPh_3(P^2)$		23.3(d) [c,e] (dd) [d]		$^2J(H-P^2)$ 13; $^1J(P^1-Pt)$ 2217; $^1J(P^2-Pt)$ 2816
trans-$[(PPh_3)_2Pt(CO)H]^+$ (II)	H^-	−4.37(t)			$^1J(H-Pt)$ 907;
	PPh_3		24.1(s) [c] (d) [d]		$^2J(H-P)$ 10; $^1J(P-Pt)$ 2529;
	CO			186.2(t) [c] (dt) [d]	$^2J(C-P)$ 6; $^2J(C-H)$ 63; $^1J(C-Pt)$ 998
trans-$[(PPh_3)_2Pt(CO)(C_2H_5)]^+$ (III)	PPh_3		21.3(s) [c] (t) [d]		$^3J(H-H) \approx 8$; $^3J(P-H_{CH_2}) 10$;
	CO [f]			181.7(m)	$^2J(C_{CH_2}-P) \approx 5$;
	CH_2-group [g]	1.15(m)		20.7 [h]	$^2J(C_{CO}-P) \approx 10$;
	CH_3-group [g]	−0.16(t) [i]		16.7(s)	$^2J(C_{CO}-C_{CH_2})$ 24; $^1J(P-Pt)$ 2842; $^1J(C_{CO}-Pt)$ 886; $^1J(C_{CH_2}-Pt)$ 496; $^2J(C_{CH_3}-Pt)$ 29; $^2J(H_{CH_2}-Pt) \approx 61$; $^3J(H_{CH_3}-Pt) = 37$
trans-$[(PPh_3)_2Pt(NO_2)(C_2H_5)]$ (IV) (?)	CH_2-group	2.56(q)			$^3J(H-H) \approx 7$;
	CH_3-group	0.36(t) [i]			$^2J(H_{CH_2}-Pt) \approx 66$

[a] Measured at 25 °C in concentrated CF_3COOH ($[H_2O] \lesssim 0.5\%$), [Pt] = 0.04–0.08 mol/l. [b] Designations (taking no account of ^{195}Pt-satellites): s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dt, doublet of triplets; q, quartet; m, multiplet. [c] Recorded with proton noise decoupling. [d] Recorded with selective decoupling of the phenyl protons. [e] Integral intensity ratio $P^2/P^1 = 2$. [f] ^{13}C NMR spectra were recorded for samples prepared using ^{13}C labelled CO (75% labelled). [g] Idem $^{13}CH_2{=}CH_2$ (86% labelled). [h] Superposition of triplet (25%) and doublet of triplets (75%). [i] Integral intensities of the resonances of the CH_2 and CH_3 groups related as 2/3.

From the evidence we have presented here and the fact that no intermediate square-planar hydride-olefin platinum complex was observed by us, C_2H_4 insertion into the Pt–H bond of II probably proceeds by associative mechanism. The complex catalytically active for insertion is II′ (present in very low concentration), which transforms into III via a five-coordinated intermediate (II″):



The higher reactivity of II towards C_2H_4 insertion compared with I is probably determined by the presence of a strong π-acceptor ligand (CO in the case of II), which promotes ethylene coordination to platinum.

Various decomposition routes of complex III were monitored by ^1H NMR and indicate the alkyl (not the acyl) nature of this complex. The hydrogen present decomposes III, to liberate ethane and regenerates II. The interaction of III with nitrous acid results in the formation of ethyl trifluoroacetate via the intermediate IV. The ^1H NMR spectrum of IV (Table 1) reveals that its ethyl group is bonded with the platinum atom. Complex IV is probably formed as a result of replacement of the carbonyl ligand by nitrite anion, followed by decomposition via intramolecular redox decay.

Complex III is rather stable in CF_3COOH solution at room temperature and remains relatively stable in solution during one week, slowly decomposing with formation of ethane and small amounts of propionic acid. Upon heating (70 °C) solutions of III under ethylene for 1 h leads to the appearance of diethyl ketone in solution as observed from the ^1H NMR spectrum. This suggests very slow isomerization of carbonyl ethyl complex to a propionyl complex, which then reacts with ethylene to form diethyl ketone, or undergoes hydrolysis to give propionic acid. The metal–carbon bond carbonylation step, which was the most rapid in the case of the palladium system for the diethyl ketone synthesis [3,4], in the case of the platinum system was the slowest and probably the rate-determining step. In this connection it is of interest that the carbonylation rates of the complexes, *trans*-$[MBr(Ph)(PPh_3)_2]$ for M = Pt, Pd, Ni are related in the ratio 1/184/115, respectively [12]. The low rate shown for Pt is probably due (i) to the slower (relative to Pd and Ni) ligand substitution in the initial complex with formation of carbonyl phenyl derivative and (ii) to the slower isomerization of the latter into the corresponding acyl complex. Carbonyl ethyl complex III, that forms in our system, has the *trans*-located CO and C_2H_5 ligand configuration, which is unfavourable for insertion. Carbonyl insertion into the Pt–C bond becomes successful once the isomerization of *trans*-complex III (very slow under the conditions used) to the corresponding *cis*-derivative, had taken place.

Experimental

Reagent grade trifluoroacetic acid ($[H_2O] \lesssim 0.5\%$), tin(II) acetate and triphenylphosphine (twice recrystallized from ethanol) used.

Tetrakis(triphenylphosphine)platinum(0). A solution of H_2PtCl_6 (1 g, 1.9 mmol) in 5 ml of water was added to a stirred warm (60 °C) solution of PPh_3 (3.55 g, 13.5 mmol) and LiOH (0.32 g, 13.5 mmol) in a water (50 ml)/ethanol (150 ml) mixture. After 1–2 min $Pt(PPh_3)_4$ separates as a bright-yellow sediment. The mixture was kept at 60 °C for some minutes and then the $Pt(PPh_3)_4$ was filtered off, washed successively with warm aqueous ethanol, cold ethanol, pentane, and then dried in vacuum. All operations were carried out under argon in deaerated solvents. Yield of $Pt(PPh_3)_4$ 90%. The samples of $Pt(PPh_3)_4$ prepared by this method gave satisfactory elemental (Pt, C, H) analyses. ^{31}P NMR spectra of the CF_3COOH solutions of $Pt(PPh_3)_4$ revealed the presence of the only platinum compound $[(PPh_3)_3PtH]^+$.

Tin(II) acetate was used as a saturated solution in CF_3COOH (≈ 0.1 mmol/l). Hydrogen (for reduction) and nitrous acid (for oxidation) were generated in situ by adding either magnesium powder or $NaNO_2$, respectively, to the solutions of complex III in CF_3COOH.

For the NMR spectroscopic investigation of the reactivity of complex I, solutions of which (40–80 mmol/l) were prepared by dissolution of weighed amounts of

$Pt(PPh_3)_4$ in concentrated CF_3COOH under argon. For the reactions, the gases CO and C_2H_4 were bubbled at atmospheric pressure through solutions of the platinum complexes (at 25–70 °C) contained in the NMR ampoule before recording the NMR spectra was begun.

^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker CXP-300 spectrometer at 300, 75 and 121 MHz, respectively. ^{13}C and ^{31}P NMR spectra were recorded with proton noise decoupling or with selective decoupling of the phenyl protons. Proton chemical shifts were measured against acetone as internal standard (2.08 ppm relative to TMS), ^{13}C chemical shifts were compared with those of the carboxyl group of CF_3COOH (166.0 ppm relative to TMS). In both cases the shifts were referred to TMS. ^{31}P chemical shifts were referred to external 85% H_3PO_4. For all NMR spectra, downfield shifts are positive.

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