Synthesis and Reactivity of Platinum–Formaldehyde Complexes [Pt(PR$_3$)$_2$(CH$_2$O)]

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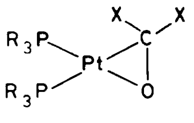
Sodium dihydronaphthylide reduction of [PtCl$_2$(PR$_3$)$_2$] (R$_3$ = Et$_3$, Pr$^i_3$, Ph$_3$, Et$_2$Ph, or $\frac{1}{2}$Ph$_2$PCH$_2$CH$_2$PPh$_2$) under an ethylene atmosphere gives [Pt(PR$_3$)$_2$(C$_2$H$_4$)] in quantitative yield as shown by ^{31}P n.m.r. spectroscopy. Reactions of the ethylene complexes with CO, CH$_2$I$_2$, (CF$_3$)$_2$CO, (CO$_2$Et)$_2$CO, and CH$_2$O are described. Monomeric formaldehyde reacts to give the first platinum–formaldehyde complexes, [Pt(PR$_3$)$_2$(CH$_2$O)], decomposition of which produces [Pt$_3$(CO)$_3$(PR$_3$)$_n$] (n = 3 or 4) and a complex tentatively assigned as [{PtH(PR$_3$)$_2$}$_2${C(=O)-OCH$_2$}].

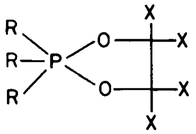
It is apparent from the great deal of research into alternative routes to organic chemicals using Synthesis Gas (CO–H$_2$) that formaldehyde plays a very important role. The use of formaldehyde in the formation of styrene, methacrylates, ethylene glycol, and other C$_2$ compounds is well documented and recently Fahey [1] has proposed that formaldehyde is an intermediate in the homogeneous synthesis of oxygenated organics directly from CO–H$_2$. The present work was undertaken to prepare formaldehyde complexes of platinum and investigate their chemistry.

RESULTS AND DISCUSSION

The compounds [Pt(PR$_3$)$_3$] (R = Et or Pr^i) [2] react rapidly with both hexafluoroacetone and diethyl oxomalonate to give high yields of the side-bonded ketone complexes (1)—(4) and the corresponding phospholane (5).[3] In contrast, monomeric formaldehyde is less able to displace a phosphine ligand with little reaction occurring after 1 h as evidenced by ^{31}P n.m.r. spectroscopy and as such resembles ethylene.[4] With this in mind it was decided to study the reactions of formaldehyde with [Pt(PR$_3$)$_2$(C$_2$H$_4$)] where the ethylene is a more easily displaced ligand.



(1) R = Et, X = CF$_3$
(2) R = Et, X = CO$_2$Et
(3) R = Pr^i, X = CF$_3$
(4) R = Pr^i, X = CO$_2$Et



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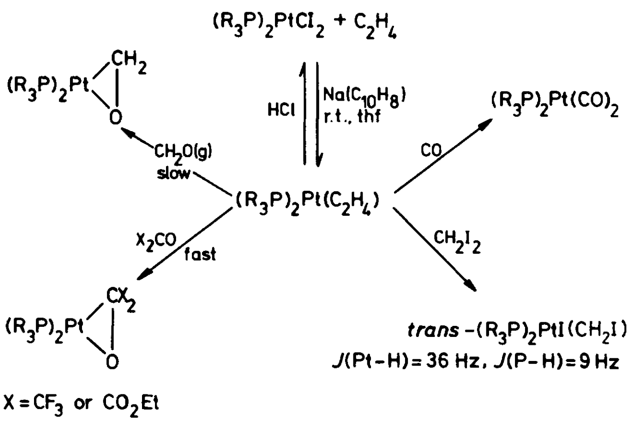
Published syntheses of ethylene complexes containing trialkylphosphines are rather inconvenient as they include the reaction of the very sensitive [Pt(C$_2$H$_4$)$_3$] with phosphines [5] and the thermal decomposition of [Pt(C$_2$H$_5$)$_2$(PR$_3$)$_2$].[6] It is now found that sodium dihydronaphthylide, Na(C$_{10}$H$_8$), reduction of the readily available [PtCl$_2$(PR$_3$)$_2$] under an ethylene atmosphere provides a clean, high-yield synthesis of a range of ethylene complexes which have been characterised by ^{31}P n.m.r. spectroscopy (Table). Solutions of these materials are colourless or pale yellow and if saturated with ethylene are stable at room temperature for long periods. Attempts to isolate crystalline products, however, have failed with the solutions irreversibly turning red-brown in colour when concentrated or warmed. Nevertheless they are very reactive and can be conveniently used *in situ* (Scheme 1). Thus with methylene iodide the orange, crystalline complex *trans*-[PtI-

Phosphorus-31 n.m.r. data

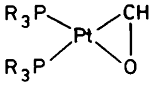
Complex	Shift (p.p.m.)	J(Pt–P)/ Hz	J(P–P)/ Hz
[Pt(PEt$_3$)$_2$(C$_2$H$_4$)]	20.4	3 520	—
[Pt(PPr$^i_3$)$_2$(C$_2$H$_4$)]	53.4	3 657	—
[Pt(PEt$_2$Ph)$_2$(C$_2$H$_4$)]	23.2	3 574	—
[Pt(dppe)(C$_2$H$_4$)] *	54.5	3 300	—
[Pt(PPh$_3$)$_2$(C$_2$H$_4$)]	32.0	3 660	—
[Pt(PPr$^i_3$)$_2${OC(CO$_2$Et)$_2$}]	39.8	4 848	19.6
	38.6	3 422	
[Pt(PEt$_3$)$_2${OC(CO$_2$Et)$_2$}]	11.7	3 418	11.0
	5.9	4 565	
[Pt(PEt$_3$)$_2$(CH$_2$O)]	19.0	2 119	12.0
	4.3	3 346	

Tetrahydrofuran solutions, shifts relative to 85% H$_3$PO$_4$.
* dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$.



SCHEME 1 r.t. = Room temperature

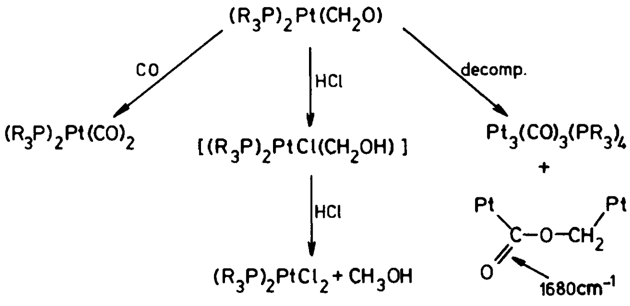
$(CH_2I)(PEt_3)_2]$ is obtained, which has ^1H n.m.r. signals arising from CH_2I at δ 2.97 [$^2J(^1HC^{195}Pt) = 36.6$, $^3J(^1HCPt^{31}P) = 9.1$ Hz, CD_2Cl_2 solvent] similar to that recently reported by Lappert and co-workers [7] for *trans*-$[PtI(CH_2I)(PPh_3)_2]$. Both hexafluoroacetone and diethyl oxomalonate react rapidly with elimination of ethylene to give (1)—(4) in almost quantitative yield.



(6)

The assignments of (1)—(4) as η^2-bonded complexes have been made by comparing their spectroscopic properties with related molecules known to have this structure. For instance the ^{19}F n.m.r. spectrum of (1) exhibits a doublet of doublet of triplets centred at 65.8 p.p.m. (relative to $CFCl_3$) with coupling constants of $^3J(^{19}FCC^{195}Pt) = 75.9$, $^4J[^{19}FCCPt^{31}P(trans)] = 12.1$, and $^4J[^{19}FCCPt^{31}P(cis)] \approx 1$ Hz compared with 66.9 p.p.m., 70.5, 11.3, and 1.3 Hz, respectively for $[Pt(PPh_3)_2\{(CF_3)_2CO\}]$.[8] Complexes (2) and (4) also have similar spectral properties to those of the triphenylphosphine analogues reported by Kemmitt and co-workers.[9]

Monomeric formaldehyde undergoes a slow reaction with $[Pt(PR_3)_2(C_2H_4)]$ to give colourless solutions of $[Pt(PR_3)_2(CH_2O)]$ (6), the first reported platinum formaldehyde complex. The only previous formaldehyde complexes are $[Os(CH_2O)(CO)_2(PPh_3)_2]$ [10] and $[Fe(CH_2O)(CO)_2\{P(OMe)_3\}_2]$.[11] The ^{31}P n.m.r. spectrum shown in the Figure was recorded after passage of CH_2O through a solution of $[Pt(PEt_3)_2(C_2H_4)]$ for 45 min at room temperature and consists of (6) together with some unreacted ethylene complex. The formaldehyde is considered to be co-ordinated *via* the p_π–p orbitals of the carbonyl group in a similar fashion to (1)—(4). This is supported by the very similar ^{31}P n.m.r. spectra (Table) as well as the ease with which the formaldehyde is displaced (Scheme 2). Thus passage of CO through a solution of (6) rapidly produces the dicarbonyl complex $[Pt(PR_3)_2(CO)_2]$. Addition of HCl affords $[PtCl_2(PEt_3)_2]$ and CH_3OH, presumably *via* protonation at oxygen to form the intermediate $[PtCl(CH_2OH)(PEt_3)_2]$ (*cf.* ref. 11). Attempts to isolate the hydroxymethyl complex by use of 1 equivalent of HCl proved unsuccessful.



SCHEME 2

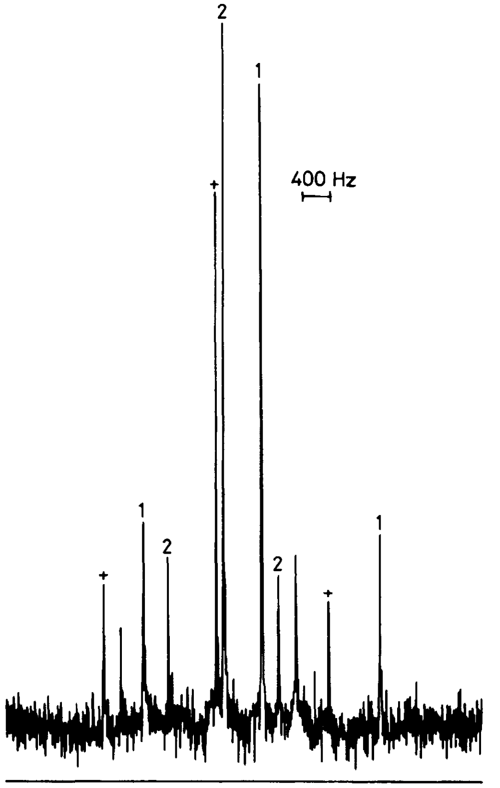
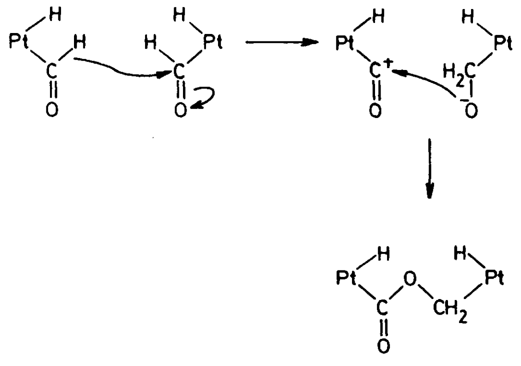


FIGURE Phosphorus-31 n.m.r. spectrum of $[Pt(PEt_3)_2(CH_2O)]$ (1 and 2); the crosses indicate unreacted ethylene complex

Complex (6) is stable in solution at room temperature for a few hours although the solution slowly turns red in colour. Decomposition proceeds rapidly during attempts to isolate a crystalline product, as shown by the formation of a deep red solution from which essentially two products can be isolated. The major product is the hexane-soluble, red cluster $[Pt_3(CO)_3(PR_3)_n]$ ($n = 3$ or 4) in >90% yield. Small amounts of a colourless, crystalline, hexane-insoluble material (≈5%) are also obtained which has a strong i.r. band at 1 680 cm^{-1} and tentatively formulated as $[\{PtH(PR_3)_2\}_2\{C(=O)OCH_2\}]$ (7). The mechanism of decomposition is thought to involve an unstable formylhydrido-complex $[PtH(CHO)(PR_3)_2]$. This is analogous to the decomposition [10] of $[Os(CH_2O)(CO)_2(PPh_3)_2]$ to $[OsH(CHO)(CO)_2(PPh_3)_2]$ and Thorn [12] has recently obtained $[IrH(CHO)(PMe_3)_4]^+$ from the reaction of $[Ir(PMe_3)_4]^+$ with paraformaldehyde, $(CH_2O)_n$. The intermediate formyl complex then eliminates H_2 with subsequent formation of $[Pt_3(CO)_3(PR_3)_n]$ ($n = 3$ or 4) {*cf.* decomposition [10] of $[OsH(CHO)(CO)_2(PPh_3)_2]$ to give H_2 and $[Os(CO)_3(PPh_3)_2]$} or alternatively undergoes a hydrogen-transfer [13] reaction to produce (7) as shown below. The formulation of (7) is supported by the detection of small amounts of methyl formate during the decomposition of (6). Attempts to synthesise a more stable formyl complex by treating $[PtCl(CO)(PEt_3)_2]^+$ with KH or $Na[AlH_2(OCH_2CH_2OMe)_2]$ also led to mixtures of (7) and the trinuclear clusters.



(7)

EXPERIMENTAL

Solvents were dried prior to use and all manipulations were carried out under dry dinitrogen atmospheres. Spectra, n.m.r. and i.r., were recorded using a JEOL FX100 spectrometer and a Perkin-Elmer 197 spectrophotometer respectively. Gas–liquid chromatographic (g.l.c.) analyses were carried out using a Pye Unicam GCD equipped with a 9-ft Porapak Q column isothermal at 175 °C.

General Procedures.—(*a*) *Preparation of complexes* [Pt-$(PR_3)_2(C_2H_4)$]. A known amount of $[PtCl_2(PR_3)_2]$ ($\approx$0.5 g) was suspended in tetrahydrofuran (thf) (60 cm^3) saturated with ethylene. A solution of sodium dihydronaphthylide (2 equivalents) was slowly added *via* a syringe through a Suba Seal. An instant reaction occurred on mixing the two solutions, the deep green colour of the reducing agent being destroyed and the suspension gradually dissolving to give solutions of $[Pt(PR_3)_2(C_2H_4)]$. Addition of excess of $Na(C_{10}H_8)$ produced a brown-red solution; the reaction could be reversed by adding a few crystals of $[PtCl_2(PR_3)_2]$.

(*b*) *Syntheses of* (1)—(4). A solution of $[Pt(PR_3)_2(C_2H_4)]$ was prepared as outlined above and an excess of X_2CO, *e.g.* $(CF_3)_2CO$, added and the mixture stirred at room temperature for 1 h. The solvent was removed and the naphthalene isolated by sublimation. Recrystallisation of the product from methylene chloride–hexane gave (1)—(4) in high yields as colourless or pale yellow crystalline solids. Analysis: (1) Found: C, 28.3; H, 5.3. $C_{15}H_{30}F_6OP_2Pt$ requires C, 28.7, H, 5.2%; (2) Found: C, 38.0; H, 6.4. $C_{19}H_{40}O_5P_2Pt$ requires C, 37.7; H, 6.6%; (3) Found: C; 35.5; H, 6.1. $C_{21}H_{42}F_6OP_2Pt$ requires C, 35.9; H, 6.3%; (4) Found: C, 44.1; H, 7.4. $C_{25}H_{52}OP_2Pt$ requires C, 43.5; H, 7.6%.

(*c*) *Preparation and attempted isolation of* $[Pt(PR_3)_2(CH_2O)]$ (6). Monomeric formaldehyde, prepared by thermal decomposition of $(CH_2O)_n$, was bubbled into a solution of $[Pt(PR_3)_2(C_2H_4)]$ as prepared in (*a*) using dry dinitrogen. After $\approx$1 h the cloudy solution was filtered to give a clear colourless solution of (6) which slowly turned red on standing.

Evaporating a solution of (6) to dryness gave a deep red oil. Hexane extraction afforded a deep red solution which was shown to contain $[Pt_3(CO)_3(PR_3)_n]$ (n = 3 or 4) by i.r. spectroscopy. The colourless solid remaining after extraction was dissolved in toluene, filtered, and taken to dryness to give colourless crystals of (7), m.p. >150 °C. In addition to a strong band at 1 680 cm^{-1} the i.r. spectrum of (7) also exhibits a band of weak to medium intensity at 2 040 cm^{-1} tentatively assigned to ν(Pt–H).

The author wishes to thank Mr. M. I. Tabb for experimental assistance and ICI PLC for permission to publish.

[2/047 *Received*, 11*th January*, 1982]

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