Journal of Organometallic Chemistry, 284 (1985) 409–419
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE $PtP(C_6H_{11})_3(C_2H_4)_2$ MEDIATED ACTIVATION OF ALDEHYDE C–H BONDS VIA CHELATE-ASSISTED OXIDATIVE ADDITION REACTIONS

JAE J. KOH, WOOK-HWAN LEE, PAUL G. WILLIARD and WILLIAM M. RISEN*, Jr.
Department of Chemistry, Brown University, Providence, RI 02912 (U.S.A.)

(Received August 21st, 1984)

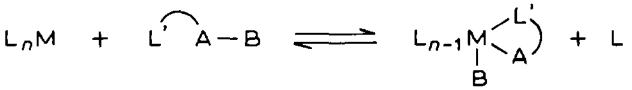
Summary

Hydrocarbon solutions of $PtPCy_3(C_2H_4)_2$ (Cy = cyclohexyl) react rapidly with 8-quinolinecarboxaldehyde (1 equiv.) to yield tricyclohexylphosphine quinolinecarboxyl platinum hydride (**1**) and CH_2CH_2 (2 equiv.). Compound **1** reacts with CCl_4 in hydrocarbons to give $PtPCy_3(NC_9H_6CO)Cl$ (**2**) and $CHCl_3$. The compound $PtPCy_3(C_2H_4)_2$ also reacts with $Ph_2P(C_6H_4$-*o*-CHO) and $Ph_2As(C_6H_4$-*o*-CHO) to give $PCy_3PtPh_2P(C_6H_4$-*o*-CO)(H) (**3**) and $PCy_3PtPh_2As(C_6H_4$-*o*-CO)(H) (**4**), respectively. Compounds **1**, **2**, **3**, and **4** were characterized by infrared and ^1H NMR spectra, and the crystal structure of **3** was determined by X-ray diffraction. Crystals of **3** are monoclinic, with space group $P2_1/n$ and $Z = 4$ with the unit cell dimensions *a* 9.7936(17), *b* 14.844(35), *c* 23.530(64) Å, *β* 91.817 (18)°, and *V* 3419.09(1.36) Å^3. The structure is refined to final discrepancy factors of $R = 0.055$, and $R_w = 0.064$. The molecular structure of **3** is that ligating atoms are in a plane containing Pt. The position of the hydride was not located crystallographically, but the ^1H NMR spectrum of **3**, supports the presence of a terminal hydride that is *cis* to the carbonyl. The IR band of **3** at 2023 cm^{-1}, which is assigned to ν(Pt–H), and the hydride cleavage reaction of **1** with CCl_4, provide evidence for the Pt–H bond.

Introduction

Transition metal acyl hydride compounds are known or postulated to be key intermediates in catalyzed hydroformylation reactions [1] and metal-catalyzed carbonylation processes [2]. In addition, formation of coordinatively unsaturated acyl metal hydride intermediates through the oxidative addition of aldehydes to metal centers is thought to be involved in metal catalyzed decarbonylations of aldehydes. Stable transition metal acyl hydrides have been obtained through reactions involving the scission of C–H bonds in cases where a coordinating group on the metal is available to form a five-membered chelate and where the transition metal precursor is strongly nucleophilic [3]. Acyl hydride compounds of rhodium(III) [4–6] and iridium(III) [7,8] have been prepared through chelate-assisted oxidative

0022-328X/85/$03.30 © 1985 Elsevier Sequoia S.A.



(1)

addition reactions of the form of eq. 1. However, similar acyl hydrides of platinum, which have been synthesized in this work, have not been obtained previously, despite their relevance to Pt-catalyzed reactions of the types mentioned above.

To achieve the synthesis of the initial platinum acyl hydride, the zero-valent platinum compound, $PtPCy_3(C_2H_4)_2$ [9], was selected as a candidate for the metal-containing species represented in eq. 1, because it is coordinatively unsaturated, it has readily displaceable ethylene ligands, and provides a nucleophilic metal center. This is quite different from the recently reported approach to the reactions of platinum(III) and platinum(II) compounds, such as $PdCl_4^{2-}$, with aldehydes to yield cyclic acyl complexes [10]. We describe here the reactions between $PtPCy_3(C_2H_4)_2$ and the aldehydes, 8-quinolinecarboxaldehyde, $Ph_2P(C_6H_4$-*o*-CHO), and $Ph_2As(C_6H_4$-*o*-CHO), which lead to C–H activation through formation of stable four-coordinate platinum(II) acyl hydride compounds.

Experimental

All synthetic procedures were carried out with use of standard Schlenk techniques under a dry and oxygen free atmosphere of N_2. The $PtPCy_3(C_2H_4)_2$ [9], $(C_6H_5)_2PC_6H_4$-*o*-CHO [11], $(C_6H_5)_2AsC_6H_4$-*o*-CHO [11], and 8-quinolinecarboxaldehyde [10a], were prepared according to literature methods. The benzene, hexane and pentane were dried over sodium, distilled under nitrogen from sodium/benzophenone, and deaerated by the freeze-thaw cycle technique before use. The infrared spectra were recorded on a Digilab FTS-15B from Nujol mulls between KBr plates. The ^1H NMR spectra were measured on a Bruker WM250. Elemental analyses were performed by Galbraith Labs., Knoxville, TN.

Syntheses

Triscyclohexylphosphine quiloline carboxylplatinum hydride, $Cy_3PPt(NC_9H_6CO)(H)$, (1). To a stirred benzene (15 ml) solution of $PtPCy_3(C_2H_4)_2$ (2.35 mmol) 8-quinolinecarboxaldehyde (2.35 m mol) was added dropwise under nitrogen. The reaction was continued for 3 h at toom temperature. The volume was reduced and pentane was added. The solution was held at −40°C for 4 h and the supernatant liquid was decanted from the solid with use of a curved Schlenk tube. The brown solid was dried in vacuo. Yield: 21%. Analyses Found: C, 52.59; N, 2.18; H, 6.29. $PtPC_{28}H_{40}NO$ calcd.: C, 53.25; N, 2.21; H, 6.37%. ^1H NMR data obtained from solution in benzene-d_6 at +16°C; δ in ppm relative to Me_4Si: 8.43 (1H, d, J 3.5 Hz, α-H on quinoline ring) 8.28 (1H, d, J 4.8 Hz, α-3H on quinoline ring), −2.86 (1H, overlapping, d of d, J(P–H) 23 Hz, J(Pt–H) 1170.). Infrared data: 2201m; 1637vs; 1601s; 1574s; 1502s; 1224w; 11762; 1160w; 1136w; 1108w; 1080w; 1160w; 900m; 864m; 834m; 786m; 786m; 764m; 724m; 520m; 500w cm^{-1}.

Triscyclohexylphosphine(o-formylphenyl)(diphenyl)phosphine platinum hydride, $Cy_3PPt[(C_6H_5)_2PC_6H_4$-o-CO](H) (3). To a stirred benzene solution of $Cy_3PPt(C_2H_4)_2$ (2.34 mmol) was added $PPh_2C_6H_4$-*o*-CHO (2.34 mmol) dropwise under nitrogen. The color changed immediately to orange. The reaction was continued for 4 h. The volume was reduced and pentane was added. After filtering it off, the orange solid was washed with cold pentane and dried in vacuo. Yield: 91%. Analyses Found: C, 57.49; H, 6.39. $PtP_2C_{37}H_{48}O$ calcd.: C, 58.03; H, 6.32%. ^1H NMR ($CDCl_3$): 7.75, 7.43 (featureless), 1.90–0.08 (br, Cy), −2.17 (d of t of d, J(H–P), *cis* 17 Hz, J(H–P) *trans* 190 Hz; J(H–Pt) 1370 Hz; 1H, Pt–H). Infrared data: 2023s; 1608vs; 1580s; 1310w; 1270w; 1180w; 1163m; 1120m; 1103m; 882w; 870w; 850w; 818w; 765s; 753m; 735m; 702m; 620w; 590w; 555m; 523m; 500m cm^{-1}. M.p.; 157°C (dec.).

Triscyclohexylphosphine(o-formylphenyl)(diphenyl)arsenic platinum hydride, $Cy_3PPt[(C_6H_5)_2AsC_6H_4\text{-}o\text{-}CO](H)$ (4). To a stirred benzene (15 ml) solution of $Cy_3PPt(C_2H_4)_2$ (1.87 mmol) $(C_6H_5)_2AsC_6H_4CHO$ (1.87 mmol) was added dropwise under nitrogen. After the reaction (4 h), the volume was reduced and pentane was added. The solution was recrystallized at −30°C for 5 h and the supernatant was decanted. The resulting orange solid was washed with cold pentane and dried in vacuo. Yield: 85%. M.p.: 123°C (dec.). Analyses Found: C, 54.67; H, 4.89. $PtPAsC_{37}H_{48}P$ calcd.: C, 54.88; H, 5.97%. ^1H NMR ($CDCl_3$); 7.70, 7.35 (Featureless), 1.80–0.09 (br, Cy), −2.24 (1H, d of t, J(P–H) 26 Hz, Pt–H). Infrared data: 2046m; 1606vs; 1576m; 1308m; 1270m; 1180m; 1160m; 1118m; 1080m; 1002m; 892m; 855m; 818s; 740s; 730m; 700m; 680m; 610s; 540w; 520m; 495br cm^{-1}.

Tricyclohexylphosphine quinoline carboxyl platinum chloride, $Cy_3PPt(NC_9H_6CO)Cl$ (2). To a stirred benzene solution of $Cy_3PPt(NC_9H_6CO)(H)$ (3.20 mmol) was added CCl_4(0.5 ml). The color of the solution immediately changed to yellow. The reaction was continued for 2 h. The volume was reduced and pentane was added. The resulting yellow solid was filtered off and dried in vacuo. Yield: 95%. Analyses Found: C, 49.89; H, 5.64; Cl, 5.57. $PtPC_{28}H_{39}NOC$ calcd.: C, 50.41; H, 5.89; Cl, 5.31%. M.p.: 123°C (dec.). ^1H NMR (C_6D_6): 8.91 (1H, d, J 3.8 Hz, α-H on quinoline ring), 8.33 (1H, d, J 5.1 Hz, α-3H on quinoline ring). Infrared data: 1643s; 1595m; 1577m; 1508m; 1301m; 1273s; 1240w; 1210br; 1180s; 1136w; 1116w; 1080w; 1060w; 1030w; 1008m; 977w; 920w; 903m; 850m; 786m; 740m; 723m; 540w; 520m; 490w; 458w; 327m cm^{-1}.

Structural determination and refinement

The orange crystals of **3**, grown by diffusing pentane into a benzene solution of **3**, were mounted on the Nicolet R3m/E diffractometer. X-rays of wavelength 7.1069 nm (Mo-K_α radiation) were used with a graphite monochromator. The crystal was found to belong to the monoclinic system and to have the following cell dimensions: a 9.7936(17), b 14.8441(35), c 23.5305(64) Å, β 91.817 (18)°, and V 3419.09(1.36) Å^3. The standard deviations of the least significant digits are in parentheses. The number of molecules per unit cell is $Z = 4$, and the space group is $P2_1/n$. Some 2284 unique reflections were observed. Reflections were scaled according to the intensities of 3 standard reflections measured after every 97 reflections. The standard intensities decreased to 92% of their original values in the course of data collection. An ellipsodal empirical absorption correction was applied, based on psi scans of 8 strong representative reflections. The structure was determined by the direct multi-solution method to locate Pt. A difference map was used to find the other non-hydrogen atoms. The structure was refined by a least-squares refinement on F. The structure factors were weighted according to $w = 1/[\sigma^2(F) + 0.0010F^2]$, where $\sigma^2(F)$ was evaluated from counting statistics. The positions of Pt, P(1) and P(2) were treated anisotropically, but all others isotropically. The hydrogen atoms were added to the phenyl and cyclohexyl rings in their theoretical positions. The structure was refined to final discrepancy factors of $R = 0.055$, and $R_w = 0.064$. The position of the H atom, postulated to be bound to Pt on the basis of infrared and NMR data, was not located because of the very strong scattering of Pt.

Results and discussion

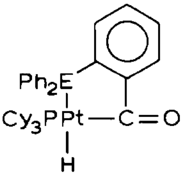
Syntheses and reactivity patterns

The platinum acyl hydrides have been prepared according to the general eq. 2.

$$PtPCy_3(CH_2CH_2)_2 + RCHO \rightarrow PCy_3PtE(C_6H_4\text{-}o\text{-}CO)(H) \qquad (2)$$

Where: $R = Ph_2PC_6H_4\text{-}o$, $Ph_2AsC_6H_4\text{-}o$, 8-quinolinecarboxyl, E = P, As, N.

The addition of equimolar quantities of a $PPh_2C_6H_4\text{-}o\text{-}CHO$ or $AsPh_2C_6H_4\text{-}o\text{-}CHO$ to a stirred benzene solution of $Cy_3PPt(C_2H_4)_2$ affords an orange solution. The resulting orange compounds, $Cy_3PPtPh_2P(C_6H_4\text{-}o\text{-}CO)(H)$ (**3**), and $Cy_3PPtPh_2As(C_6H_4\text{-}o\text{-}CO)(H)$ (**4**), were isolated as air-sensitive crystalline solids in 91 and 85% yield, respectively. The structures of compounds **3** and **4**, were deduced from their ^1H NMR and IR spectra. The structure of compound **3** was determined by X-ray diffraction.

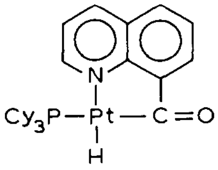


(**3**, E = P;
4, E = As)

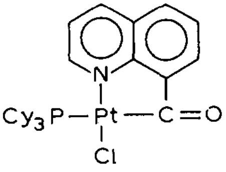
The ^1H NMR spectrum of **3** taken in $CDCl_3$ at room temperature exhibits resonances of Pt–H centered at $\delta -2.17$ (1H, J(H–P)*cis* 17 Hz, J(H–P)*trans* 197 Hz, J(H–Pt) 1370 Hz). Its pattern consists of two doublets of triplets due to the spin coupling between the platinum and hydride, and the phosphorus and hydride. The values are very close to those of the compound *cis*-$[PtH(CH_3)(PPh_3)_2]$ reported by Halpern et al. [12]. The hydrido and carbonyl ligands, therefore, are *cis*, since only this pattern is consistent with a structure containing a triphenylphosphine ligand *trans* to the hydride. This assignment has been confirmed by a single-crystal X-ray structure determination. In addition to that, there are two broad peaks at δ 7.90–6.90 and 1.90–0.08, assigned to benzylic hydrogens and tricyclohexyl hydrogens, respectively.

The infrared spectrum of **3** in Nujol clearly indicates the presence of the Pt–H bond. The intense peak at 2023 cm^{-1} is assigned to the Pt–H stretching mode, which is expected to exhibit a band with stretching frequency in the region 2300–1900 cm^{-1} [13,14]. It is interesting to note that the Pt–H stretching frequency of **3** is relatively low, in spite of the presence of the carbonyl group, compared with the compound $[PtH(SiMe_2Ph)\{P(C_6H_{11})_3\}PMe_3]$ [13b] and t-$PtH(CH_2CN)(PPh_3)_2$ [14], which occur near 2100 and at 2027 cm^{-1}, respectively. The low value is assumed to be related to the slight interaction between the oxygen of the carbonyl group and the hydride, as shown in the longer C–O bond length. The multicenter interaction was assumed in the diplatinum complexes [{Pt(μ-H)(SiR_3)(PR_3')}$_2$] from the low chemical shift for the Pt(μ-H)Pt resonance [13b]. The peak at 1608 cm^{-1} is assigned to ν(C=O), which is shifted to a lower frequency than that found for the free ligand, 1685 cm^{-1}, due to the backbonding of the Pt(d) to CO(π^*). The infrared and ^1H NMR spectrum of **4** are quite similar to those of **3**. This is to be expected from the similarity of phosphorus and arsenic chemistry.

The tricyclohexylphosphine quinoline carboxyl platinum hydride (**1**) was prepared through the addition of $PtPCy_3(C_2H_4)_2$ to a stirred solution of 8-quinolinecarboxaldehyde. The brown acyl platinum(II) hydride is relatively stable in the solid state. The infrared spectrum of **1** gave a high value for the Pt–H stretching frequency (2201 cm^{-1}) compared with those of other platinum(II) hydrides. It may be related to steric effects of the surrounding ligands, which prevent effective interaction between the carbonyl group and the hydride. The peak at 1621 cm^{-1} is assigned to the ν(C=O) mode, and that at 1601 cm^{-1} is assigned at the ν(N=C) mode of the quinoline ring. The ^1H NMR spectrum **1** clearly shows the presence of the coordinated chelating acyl and the Pt–H. The Pt–H signal centered at $\delta - 2.86$ (1H, J(P–H) 23 Hz, J(Pt–H) 1170 Hz) exhibits a pattern that is very similar to that of compound **3**.



(**1**)



(**2**)

In an attempt to cleave the Pt–H bond, compound **1** was reacted with CCl_4. The reaction produced the yellow chlorine-substituted platinum complex **2** in quantitative yield. It exhibits a strong band at 325 cm^{-1}, assigned to a ν(Pt–Cl) stretching mode. The shift of the carbonyl ν(C=O) stretch to a significantly higher frequency (1643 cm^{-1}) than that of compound **1** clearly are consistent with the formulation of **2** with a Pt–Cl bond.

When the process was driven further by refluxing **1** in CCl_4, a band appeared in the infrared spectrum at 2085 cm^{-1}, which may be assigned to the ν(C≡O) mode of a Pt–CO moiety. Even though the exact identity of the resulting compound is not clear, decarbonylation of the acyl moiety may be occurring to yield a platinum carbonyl, with accompanying hydrogen transfer to the ligand.

Solid-state molecular structure of 3

The determination of the crystal structure of compound **3** yielded the atomic coordinates and temperature factors given in Table 1. The related bond lengths, angles, and anisotropic temperature factors are given in Tables 2, 3, and 4 respectively. The hydrogen coordinates and temperature factors are given in Table 5. Two computer-generated views of the molecule **3** are given in Fig. 1.

The primary structure of molecule **3** is that of a Pt atom surrounded by ligands whose ligating atoms are in a plane containing the Pt. Thus, Pt is bonded to the P atom, P(1), of the tricyclohexylphosphine ligand and to the P(2) and C(37) atoms, on the ligand derived from the *o*-formylphenyldiphenylphosphine molecule. The C(37) carbon is in a carbonyl group that is bridge-bound to Pt. These three atoms, P(1), P(2) and C(37) are approximately in the positions to be three of the four atoms around the Pt in a square planar complex. The total of the three angles C(37)–Pt–P(1) (171.2°), P(2)–Pt–C(37) (82.9°) and P(1)–Pt–P(2) (105.3°) taken from Table 3, is 359.4°. The C(37), Pt, P(1) and P(2) atoms are essentially coplanar.

TABLE 1

ATOM COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS ($\text{Å} \times 10^3$)

Atom	*x*	*y*	*z*	*U*
C(1)	4866(14)	7286(11)	1205(7)	44(4)
C(2)	4962(16)	8313(11)	1320(8)	55(5)
C(3)	6380(18)	8593(15)	1524(9)	85(7)
C(4)	7452(20)	8306(14)	1117(9)	85(7)
C(5)	7385(19)	7347(15)	981(9)	85(6)
C(6)	5926(15)	7009(12)	759(8)	64(5)
C(7)	2205(15)	7542(11)	563(7)	44(4)
C(8)	1701(17)	8477(12)	763(8)	60(5)
C(9)	827(18)	8940(14)	319(8)	79(6)
C(10)	1514(20)	9013(14)	−248(9)	83(6)
C(11)	2001(18)	8092(13)	−465(8)	69(5)
C(12)	2924(15)	7641(12)	−3(7)	55(5)
C(13)	3277(15)	5772(11)	796(7)	50(5)
C(14)	1906(17)	5368(13)	564(8)	75(6)
C(15)	2095(20)	4438(15)	301(8)	86(6)
C(16)	2831(21)	3806(16)	691(10)	98(7)
C(17)	4141(20)	4181(14)	918(9)	90(7)
C(18)	3969(18)	5105(13)	1213(8)	71(6)
C(19)	4272(15)	7819(11)	2908(7)	46(5)
C(20)	3753(15)	8655(11)	2742(7)	46(5)
C(21)	4349(16)	9451(14)	2957(7)	63(5)
C(22)	5465(16)	9407(14)	3311(7)	63(5)
C(23)	5990(18)	8614(13)	3466(8)	65(5)
C(24)	5401(16)	7805(13)	3277(7)	60(5)
C(25)	4567(14)	5912(10)	2672(6)	38(4)
C(26)	4095(16)	5014(11)	2803(7)	46(5)
C(27)	4917(16)	4271(13)	2715(7)	58(5)
C(28)	6200(17)	4423(13)	2517(7)	62(5)
C(29)	6722(18)	5247(13)	2444(8)	66(5)
C(30)	5888(15)	5989(12)	2521(7)	49(5)
C(31)	2275(15)	6546(10)	3264(7)	40(4)
C(32)	2783(18)	6363(12)	3823(8)	64(5)
C(33)	1813(19)	6078(13)	4227(9)	78(6)
C(34)	483(19)	6036(13)	4095(9)	76(6)
C(35)	−55(18)	6263(12)	3566(8)	60(5)
C(36)	890(15)	6545(11)	3140(7)	41(4)
C(37)	405(16)	6763(11)	2561(7)	48(5)
O(1)	−845(12)	6963(8)	2490(5)	75(4)
P(1)	3094(4)	6885(3)	1120(2)	41(2) [a]
P(2)	3333(4)	6823(3)	2679(2)	40(2) [a]
Pt	1790(1)	6858(1)	1931(1)	35(1) [a]

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor.

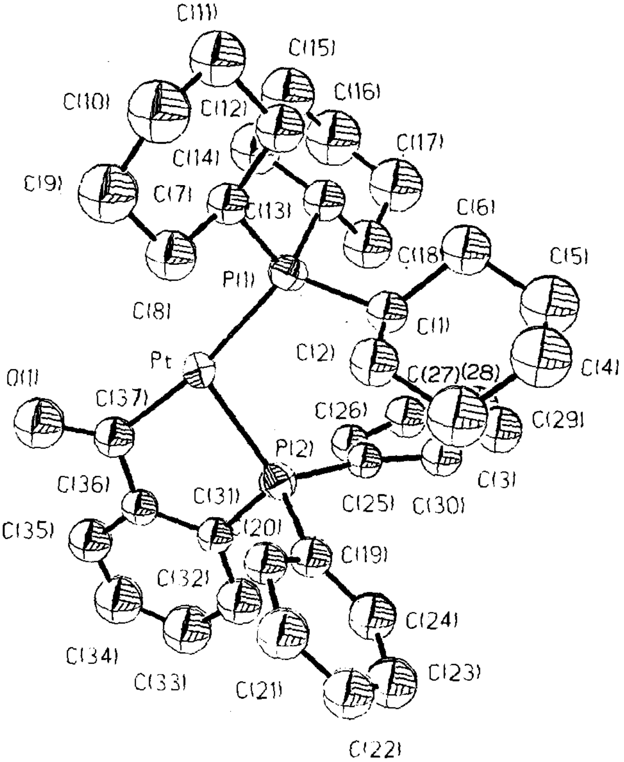


Fig. 1. A computer-generated view of the $PCy_3PtPh_2P(C_6H_4\text{-}o\text{-}CO)(H)$ molecule showing the atom numbering scheme.

TABLE 2

BOND LENGTHS (Å)

C(1)–C(2)	1.551(23)	C(1)–C(6)	1.554(23)
C(1)–P(1)	1.840(15)	C(2)–C(3)	1.513(24)
C(3)–C(4)	1.505(29)	C(4)–C(5)	1.461(30)
C(5)–C(6)	1.587(25)	C(7)–C(8)	1.551(24)
C(7)–C(12)	1.532(22)	C(7)–P(1)	1.833(16)
C(8)–C(9)	1.497(25)	C(9)–C(10)	1.516(28)
C(10)–C(11)	1.541(28)	C(11)–C(12)	1.544(24)
C(13)–C(14)	1.554(23)	C(13)–C(18)	1.536(24)
C(13)–P(1)	1.831(17)	C(14)–C(15)	1.526(29)
C(15)–C(16)	1.483(30)	C(16)–C(17)	1.483(29)
C(17)–C(18)	1.548(29)	C(19)–C(20)	1.392(23)
C(19)–C(24)	1.384(22)	C(19)–P(2)	1.814(16)
C(20)–C(21)	1.404(25)	C(21)–C(22)	1.355(23)
C(22)–C(23)	1.331(27)	C(23)–C(24)	1.398(27)
C(25)–C(26)	1.446(22)	C(25)–C(30)	1.358(21)
C(25)–P(2)	1.815(15)	C(26)–C(27)	1.384(24)
C(27)–C(28)	1.373(23)	C(28)–C(29)	1.339(27)
C(29)–C(30)	1.386(25)	C(31)–C(32)	1.417(24)
C(31)–C(36)	1.378(20)	C(31)–P(2)	1.798(16)
C(32)–C(33)	1.429(27)	C(33)–C(34)	1.332(26)
C(34)–C(35)	1.378(27)	C(35)–C(36)	1.447(24)
C(36)–C(37)	1.465(22)	C(37)–O(1)	1.266(20)
C(37)–Pt	2.046(16)	P(1)–Pt	2.329(4)
P(2)–Pt	2.284(4)		

TABLE 3

BOND ANGLES (deg.)

C(2)–C(1)–C(6)	109.9(13)	C(2)–C(1)–P(1)	112.9(10)
C(6)–C(1)–P(1)	119.3(11)	C(1)–C(2)–C(3)	112.1(14)
C(2)–C(3)–C(4)	111.8(17)	C(3)–C(4)–C(5)	112.8(17)
C(4)–C(5)–C(6)	114.4(16)	C(1)–C(6)–C(5)	107.9(14)
C(8)–C(7)–C(12)	109.7(14)	C(8)–C(7)–P(1)	114.0(11)
C(12)–C(7)–P(1)	116.9(11)	C(7)–C(8)–C(9)	112.3(15)
C(8)–C(9)–C(10)	112.8(15)	C(9)–C(10)–C(11)	112.3(17)
C(10)–C(11)–C(12)	109.3(15)	C(7)–C(12)–C(11)	112.2(13)
C(14)–C(13)–C(18)	109.5(14)	C(14)–C(13)–P(1)	113.6(11)
C(18)–C(13)–P(1)	111.3(12)	C(13)–C(14)–C(15)	112.1(14)
C(14)–C(15)–C(16)	112.6(17)	C(15)–C(16)–C(17)	112.5(19)
C(16)–C(17)–C(18)	112.9(17)	C(13)–C(18)–C(17)	109.8(15)
C(20)–C(19)–C(24)	117.7(15)	C(20)–C(19)–P(2)	117.8(11)
C(24)–C(19)–P(2)	124.2(13)	C(19)–C(20)–C(21)	120.4(14)
C(20)–C(21)–C(22)	119.9(18)	C(21)–C(22)–C(23)	120.6(18)
C(22)–C(23)–C(24)	121.4(17)	C(19)–C(24)–C(23)	120.0(17)
C(26)–C(25)–C(30)	116.6(14)	C(26)–C(25)–P(2)	117.9(11)
C(30)–C(25)–P(2)	125.4(12)	C(25)–C(26)–C(27)	120.7(14)
C(26)–C(27)–C(28)	117.5(17)	C(27)–C(28)–C(29)	123.4(18)
C(28)–C(29)–C(30)	118.7(16)	C(25)–C(30)–C(29)	122.5(16)
C(32)–C(31)–C(36)	120.7(15)	C(32)–C(31)–P(2)	124.1(12)
C(36)–C(31)–P(2)	115.1(12)	C(31)–C(32)–C(33)	116.9(16)
C(32)–C(33)–C(34)	121.6(19)	C(33)–C(34)–C(35)	122.9(19)
C(34)–C(35)–C(36)	117.4(16)	C(31)–C(36)–C(35)	120.0(14)
C(31)–C(36)–C(37)	119.0(14)	C(35)–C(36)–C(37)	120.7(14)
C(36)–C(37)–O(1)	117.4(14)	C(36)–C(37)–Pt	119.1(11)
O(1)–C(37)–Pt	123.2(12)	C(1)–P(1)–C(7)	109.3(7)
C(1)–P(1)–C(13)	103.4(7)	C(7)–P(1)–C(13)	103.4(7)
C(1)–P(1)–Pt	117.2(5)	C(7)–P(1)–Pt	109.6(5)
C(13)–P(1)–Pt	112.9(5)	C(19)–P(2)–C(25)	106.2(7)
C(19)–P(2)–C(31)	105.0(7)	C(25)–P(2)–C(31)	103.6(7)
C(19)–P(2)–Pt	121.9(5)	C(25)–P(2)–Pt	115.8(5)
C(31)–P(2)–Pt	102.3(5)	C(37)–Pt–P(1)	171.2(5)
C(37)–Pt–P(2)	82.9(4)	P(1)–Pt–P(2)	105.3(1)

The position of the hydride H atom was not located crystallographically, but there clearly is a vacant site in the square plane, opposite to P(2), where it must be located. Although the Pt–H bond length was not determined for this compound, the final difference map showed several peaks near Pt. Modern diffraction studies show

TABLE 4

ANISOTROPIC TEMPERATURE FACTORS (Å × 10^3) [a]

Atom	U	U	U	U	U	U
P(1)	43(2)	44(3)	34(3)	−2(3)	3(2)	4(2)
P(2)	41(2)	36(3)	43(3)	−1(3)	4(2)	3(2)
Pt	31(1)	38(1)	37(1)	−1(1)	3(1)	3(1)

[a] The anisotropic temperature factor exponent takes the form: $-2\pi^2(h^2a^{\star 2}U_{11} + k^2b^{\star 2}U_{22} + \ldots + 2hka^{\star}b^{\star}U_{12})$.

that metal–hydrogen bond lengths normally are in the range 2.15–1.7 Å [15,16] as expected from the sum of covalent bond radii. We may estimate the Pt–H bond length to be ca. 1.7–1.9 Å and its approximate position to be *trans* to P(2), but its

TABLE 5

HYDROGEN COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS (Å$\times 10^3$)

Atom	*x*	*y*	*z*	*U*
H(1)	5147	6946	1535	51
H(2a)	4325	8469	1606	68
H(2b)	4732	8630	975	68
H(3a)	6578	8321	1888	101
H(3b)	6406	9237	1562	101
H(4a)	8336	8436	1285	107
H(4b)	7327	8643	771	107
H(5a)	8030	7225	692	104
H(5b)	7634	7014	1318	104
H(6a)	5932	6366	717	77
H(6b)	5696	7284	399	77
H(7)	1429	7162	483	54
H(8a)	2481	8849	852	71
H(8b)	1179	8397	1098	71
H(9a)	−6	8605	265	92
H(9b)	622	9536	450	92
H(10a)	875	9263	−522	102
H(10b)	2289	9405	−204	102
H(11a)	1224	7714	−549	83
H(11b)	2508	8176	−804	83
H(12a)	3728	8003	58	67
H(12b)	3180	7054	−133	67
H(13)	3846	5864	476	59
H(14a)	1524	5765	279	88
H(14b)	1290	5318	872	88
H(15a)	2606	4502	−38	104
H(15b)	1212	4191	206	104
H(16a)	3017	3261	488	117
H(16b)	2259	3672	1004	117
H(17a)	4531	3764	1190	108
H(17b)	4749	4253	609	108
H(18a)	4851	5332	1331	84
H(18b)	3415	5033	1539	84
H(20)	2984	8688	2480	56
H(21)	3966	10026	2853	76
H(22)	5880	9952	3452	76
H(23)	6789	8596	3712	78
H(24)	5779	7241	3403	71
H(26)	3202	4933	2952	55
H(27)	4600	3672	2790	72
H(28)	6753	3912	2426	77
H(29)	7655	5323	2341	81
H(30)	6259	6580	2464	59
H(32)	3734	6428	3926	76
H(33)	2129	5912	4603	94
H(34)	−129	5840	4380	95
H(35)	−1020	6235	3482	72

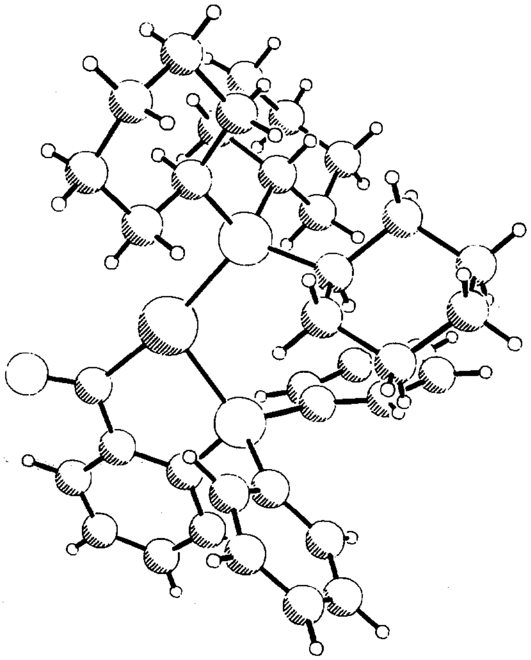


Fig. 2. Configuration of the $PCy_3PtPh_2P(C_6H_4$-*o*-CO)(H) molecule with hydrogen atoms.

angular position is unknown. However, if the angle P(1)–Pt–H is taken to be 90°, in the absence of reasons to expect it to be determined by interactions between H and tricyclohexylphosphine, then the C(37)–Pt–H angle would be ca. 81°. This would place the H somewhat closer to the C=O bond than it would be if the complex were a ML_4 square plane with all L–M–L angles of 90°. The hydride ligand is shown at an assumed position with other hydrogen atoms (Fig. 2).

The inability to locate the position of the H atom in this case is not surprising since the application of X-ray diffraction to metal hydrides is difficult, in general. The scattering of X-rays is roughly proportional to the number of electrons in an atom, so it is very high at the position of a metal atom and very low at the position of a hydrogen atom. Therefore, the problem of locating the hydrogen attached to a metal requires determining the scattering due to the metal with such high accuracy that the residual scattering due to the hydrogen can be analyzed to find its position. This problem becomes worse as the metal becomes heavier (more electrons) and the number of transition metal atoms near a hydrogen atom increase.

The structure of the molecule shows that there are two phosphorus atoms bound to Pt. One is P(1) of tricyclohexylphosphine, and the other is P(2) of the *ortho*-substituted triphenylphosphine species. The bond length of Pt–P(1) (2.33 Å) is about 0.05 Å longer than that of Pt–P(1) (2.28 Å). This small difference may be associated with small differences in the characteristics of the bonding of the phosphorus atoms to the platinum, but this may not be a major part of the bonding picture. The structure of the carbonyl-containing ligand probably is more important, because it limits the closest approaches that P(2) and the carbonyl carbon, C(37), can have simultaneously.

The C–O bond length C(37)–O(1) is 1.27 Å. This is longer than C=O bond lengths in typical aldehydes, ketones, carboxylic acids and organic esters, which usually are 1.23 ± 0.01 Å. It is closer to the carbon–oxygen lengths of zwitterion forms, such as in DL-serine, of 1.26 ± 0.01 Å. The longer C=O bond is consistent with the lower ν(C=O) stretching frequency observed for the compound. While it is not clear why it is longer when coordinated to Pt, the possibility of C(37)–O(1) π-bonding does not depend on the C–C(37)–Pt bond angle. Thus, it must depend on the donation or removal of electron density in this bond. Since Pt(d) to CO(π^*) donation could cause this effect, it appears feasible that there is some degree of π-bonding to the interaction of the carbonyl with Pt.

Conclusion

The platinum metal-acyl hydrides were isolated through the reaction between a strongly basic platinum compound and a corresponding aldehyde which is able to form a five-membered chelate ring. In order to achieve the activation of C–H bond we propose that the metal center should be basic, have easily displaceable ligands, and the coordinatively unsaturated. We have succeeded in determining the X-ray crystal structure of a stable platinum acyl hydride which was obtained by oxidative addition of an aromatic aldehyde to a soluble platinum(0) complex. The use of this homogeneous Pt metal complex represents the mildest and perhaps the most selective procedure known for C–H bond activation. In further studies, we are investigating the possibility of carbon–carbon bond cleavage under the same conditions.

Acknowledgements

Funds for the purchase of the Nicolet crystallographic system were provided by the NSF through grant CHE-8206423. We are grateful to Prof. J.W. Suggs for helpful discussions in the course of this work.

References

1 G.W. Parshall, J. Mol. Catal., 4 (1978) 243.
2 Chem. Eng. News., 54 (1976) 25.
3 M.I., Bruce, Angew. Chem., Int. Ed. Eng., 16 (1977) 73.
4 J.W. Suggs, J. Am. Chem. Soc., 100 (1978) 640.
5 J.W. Suggs, J. Am. Chem. Soc., 101 (1979) 489.
6 D. Milstein, Acc. Chem. Res., 17 (1984) 221.
7 T.B. Rauchfuss, J. Am. Chem. Soc., 101 (1979) 1045.
8 E.F. Landvatter and T.B. Rauchfuss, Organometallics, 1 (1982) 506.
9 J.L. Spencer, Inorg. Synth., 19 (1979) 213.
10 (a) C.G. Anklin and P.S. Pregosin, J. Organomet. Chem., 243 (1983) 101; (b) C.G. Anklin, P.S. Pregosin, F. Bachechi, P. Mura and L. Zambonelli, ibid., 222 (1981) 175; (c) H. Motschi, P.S. Pregosin and H. Ruegger, ibid., 193 (1980) 397.
11 G.P. Schiemenz and H. Kaack, Liebigs Ann. Chem., (1973) 1480.
12 L. Abis, A. Sen, and J. Halpern, J. Am. Chem. Soc., 100 (1978) 2916.
13 (a) M. Green, J.A.K. Howard, J. Proud, J.L. Spencer, and F.G.A. Stone, J. Chem. Soc. Chem. Comm., (1976) 671. (b) M. Ciriano, M. Green, J.A.K. Howard, J. Proud, J.L. Spencer, F.G.A. Stone, and C.A. Tsipis, J. Chem. Soc. Dalton, (1978) 801.
14 R. Ros, J. Organomet. Chem., 118 (1976) C53.
15 R. Bau, R.G. Teller, S.W. Kirtley and T.F. Koetzle, Acc. Chem. Res., 12 (1979) 176.
16 R. Bau, W.E. Carrol, D.W. Hart, R.G. Teller and T.F. Koetzle, Adv. Chem. Series, No 167, Amer. Chem. Soc., Washington, D.C. 1978.