Reaction of trans-[Pt(H)$_2$(PCy$_3$)$_2$] with C$_{60}$
Reductive elimination of H$_2$ and formation of [Pt(PCy$_3$)$_2$(η^2-C$_{60}$)]

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Abstract

Reaction of trans-[Pt(H)$_2$(PCy$_3$)$_2$], 1, with [60]fullerene at room temperature affords [Pt(PCy$_3$)$_2$(η^2-C$_{60}$)], 2, in nearly quantitative yield. The most probable reaction pattern is the insertion of a fullerene 6,6 junction onto a Pt–H bond yielding an η^1 alkyl derivative which, after hydrogen extrusion, gives 2. On the other hand, addition of 1 to different electron-deficient olefins, such as dimethyl maleate and fumarate, furnishes mixtures of both η^1 metal–alkyl and η^2 metal–olefin derivatives. If tetrachloroethylene is used as 2π component, trans-[PtCl(H)(PCy$_3$)$_2$] forms exclusively. © 1997 Elsevier Science S.A.

Keywords: Reductive elimination; Tetrachloroethylene

1. Introduction

The chemistry of the fullerenes has developed into a fascinating field over the past six years. Much of the synthetic work has been performed on [60]fullerene, the most abundant representative of the fullerene family, and synthetic methodologies have been developed that allow the preparation of a wide variety of C$_{60}$ derivatives with interesting magnetic, electronic and photophysical properties [1].
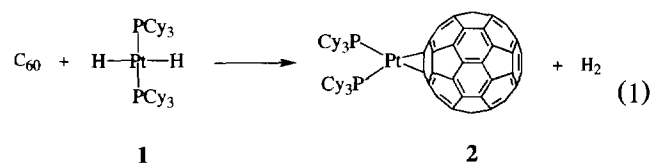
The chemical reactivity of C$_{60}$ is typical of an electron-poor olefin. C$_{60}$, in fact, reacts readily with neutral and charged nucleophiles, radical species, carbenes and is a reactive 2π component in thermal and photochemical cycloadditions [1,2]. C$_{60}$ forms η^2 complexes with several electron-rich transition metals, such as Pt, Pd, Ni, Rh and Ir, [1] and undergoes hydroboration and hydrozirconation reactions [10,11].

The addition of [Zr(η^5-C$_5$H$_5$)$_2$Cl(H)] to C$_{60}$ [11], followed by hydrolysis, leads to a mixture of hydrofullerenes C$_{60}$H$_{2n}$ ($n = 1, 2, 3$). Although insertion of C$_{60}$ into the Zr–H bond could be reasonably supposed,

η^1 alkyl intermediates have never been isolated. Attempts to obtain η^1 derivatives were unsuccessful also with the hydrogenation catalyst [RhH(CO)(PPh$_3$)$_3$] that, in presence of C$_{60}$, eliminates PPh$_3$ to give η^2 derivative [Rh(H)CO(PPh$_3$)$_2$(η^2-C$_{60}$)] [8] (Scheme 1).

Transition metal hydrides can undergo insertion reaction by unsaturated compounds giving η^1 metal derivatives. In particular, trans-[Pt(H)$_2$(PCy$_3$)$_2$], 1, reacts readily with CO$_2$ [12], CS$_2$ [13], C$_3$O$_2$ [14,15], F$_2$C=CF$_2$ [16] and RC≡CR' [17] to afford stable trans-[Pt(η^1-UnsH)(H)(PCy$_3$)$_2$] complexes (Uns indicates the unsaturated compound used).

We report here on the unusual behavior of trans-dihydride 1 which in presence of C$_{60}$ gives exclusively the Pt(0) complex [Pt(PCy$_3$)$_2$(η^2-C$_{60}$)], 2, (Eq. (1)). The study of the reactivity of dihydride 1 has also been extended to other electron-deficient olefins, such as dimethyl maleate, dimethyl fumarate and tetrachloroethylene.

$$\text{C}_{60} + \text{H}-\underset{\overset{|}{\text{PCy}_3}}{\overset{\overset{\text{PCy}_3}{|}}{\text{Pt}}}-\text{H} \longrightarrow \underset{\text{Cy}_3\text{P}}{\overset{\text{Cy}_3\text{P}}{}}\text{Pt}(\text{C}_{60}) + \text{H}_2 \quad (1)$$

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[1] For a recent review see Ref. [3]; see also Refs. [4–9].

2. Experimental section

2.1. Instrumentation and materials

All reactions and manipulations were carried out under an atmosphere of dry argon with standard Schlenk techniques. trans-$[Pt(H)_2(PCy_3)_2]$, **1**, was synthesized according to Ref. [18]. C_{60} (99.5%) was purchased from Bucky-USA. Dimethyl maleate, dimethyl fumarate and tetrachloroethylene were purchased from Aldrich and used without further purification. Solvents were distilled before use.

UV–vis absorption spectra were taken on a Perkin–Elmer Lambda 6 spectrophotometer. ^1H, ^{31}P and ^{13}C NMR spectra were recorded on Bruker AC 200 and AC 250 spectrometers. Chemical shifts are given in parts per million (δ) relative to tetramethylsilane (^1H, ^{13}C) and to external 85% H_3PO_4 (^{31}P). Positive ion FAB mass spectrum of **2** was obtained on a VG ZAB2F instrument by bombarding a mull of **2** in m-nitrobenzylalcohol with 8 keV Xe atoms. Elemental analyses were provided by the Microanalysis Laboratory of the CIMA Department of the University of Padova.

2.2. Synthesis

2.2.1. Reaction of trans-$[Pt(H)_2(PCy_3)_2]$, **1**, with C_{60}. Synthesis of **2**

A solution of 53 mg (0.07 mmol) of **1**, [18] and 50 mg (0.07 mmol) of C_{60} in 40 ml of toluene was sonicated for 10 min and then stirred at room temperature for 3 h. The deep green mixture was filtered with suction over a pad of silica gel and the solvent removed under reduced pressure affording 84 mg (81%) of **2**. Crystallization from diethyl ether gave 75 mg (72%) of greenish, microcrystalline material.

2: m.p. > 200 °C (dec). ^1H NMR (200 MHz, C_6D_6) δ 1.22–2.51 (m, C_6H_{11}); ^{13}C NMR (62.5 MHz, C_6D_6) δ 135.3, 141.9, 142.5, 142.9, 143.1, 143.2, 143.8, 143.9,
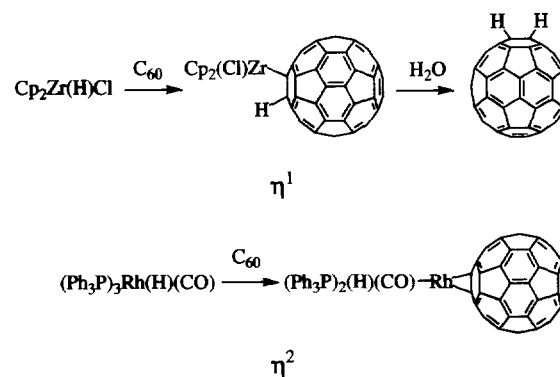
Scheme 1.

144.7, 144.9, 145.1, 145.3, 145.6, 147.3, 148.2, 160.4 (resonances due to C_6H_{11} are not reported). $^{31}P\{^1H\}$ NMR (200 MHz, C_6D_6) δ 31.23 (s, $^1J_{P-Pt} = 3776$ Hz). FAB-MS $C_{96}H_{66}P_2Pt$ (MW = 1475) m/z (%) 1475 ($M^{+\cdot}$, 1), 755 ($Pt(PCy_3)_2^{+\cdot}$, 100), 720 ($C_{60}^{+\cdot}$, 52). Anal. Calcd. for $C_{96}H_{66}P_2Pt$: C, 78.08; H, 4.51. Found: C, 77.26; H, 4.23.

The course of the reaction was also monitored by ^1H and $^{31}P\{^1H\}$ NMR. To 5 mg of **1** (6.6×10^{-3} mmol) dissolved in 1 ml of C_6D_6, 4.8 mg of C_{60} (6.6×10^{-3} mmol) was added. The reaction took place after sonication, giving a deep green solution. ^1H and $^{31}P\{^1H\}$ NMR spectra were registered before the addition of C_{60}, after 30 min and after 24 h. The results are reported in Table 1.

2.2.2. Reaction of trans-$[Pt(H)_2(PCy_3)_2]$, **1**, with dimethyl maleate, **3**, dimethyl fumarate, **4**, and tetrachloroethylene, **5**. General procedure

A solution of 15 mg (0.02 mmol) of **1** and one equivalent of the appropriate alkene in 1 ml of C_6D_6 was sealed in an NMR tube and heated to 50 °C. The course of the reactions was monitored by $^{31}P\{^1H\}$ NMR, following the decreasing of the signal at 53.06 ppm (**1**) and

Table 1
^1H and $^{31}P\{^1H\}$ NMR data for the reaction of **1** with C_{60} [a]

	^1H [b]			^{31}P	
	H–Pt–H	Pt–(η^1-$C_{60}H$)	P–Pt–P	P'–Pt–P''	$P_2Pt(\eta^2$-$C_{60})$
1	−3.06 (t) $^2J_{H-P} = 16.4$ $^1J_{H-Pt} = 798.7$		53.06 (s) $^1J_{P-Pt} = 2866$		
1 + C_{60} Solution after 30 min	−3.06 (t) $^2J_{H-P} = 16.4$ $^1J_{H-Pt} = 798.7$	5.74–6.14 [c]	53.06 (s) $^1J_{P-Pt} = 2866$	28.96–32.25 [c]	31.23 (s) $^1J_{P-Pt} = 3776$
1 + C_{60} Solution after 24 h					31.23 (s) $^1J_{P-Pt} = 3776$

[a] Solvent C_6D_6, r.t., chemical shifts in ppm, J in Hz.
[b] Signals due to C_6H_{11} are not reported.
[c] Complex unresolved pattern.

Table 2
^{31}P{^{1}H} NMR data for the reactions of **1** with **3** and **4**

	P–Pt (1)	P–Pt (η^1-insertion. deriv.)	P–Pt (η^2-olefin deriv.)
1 + 3	53.06 (s) $^1J_{P-Pt} = 2866$	32.54 (s) $^1J_{P-Pt} = 2812$	30.96 (s) $^1J_{P-Pt} = 3713$
1 + 4	53.06 (s) $^1J_{P-Pt} = 2866$	32.61 (s) $^1J_{P-Pt} = 2851$	31.08 (s) $^1J_{P-Pt} = 3715$

^{a} Solvent C_6D_6, r.t., chemical shifts in ppm, J in Hz.

the appearance of new signals. In the reaction of **1** with **5** at 50 °C, compound **1** was consumed almost quantitatively with formation of an intense singlet at 38.05 ppm, ($^1J_{P-Pt} = 2814$ Hz) attributed to *trans*-[PtCl(H)(PCy$_3$)$_2$] by comparison with an authentic sample [18]. In the reaction with **3** and **4** two new resonances were detected along with that due to some unreacted **1**. Raising the reaction temperature to 60 °C caused only decomposition and formation of Pt metal. Data are reported in Table 2.

3. Results and discussion

Addition of one equivalent of C_{60} to a benzene solution of **1** produces a greenish solution, that darkens with time. A deep green color has been observed also for different, 1:1, η^2-C_{60} derivatives obtained by addition of C_{60} to Pt(0) [4,6], Pd(0) [7], Rh(I) [8], and Ir(I) [9] complexes.

Filtration of the raw material through a pad of silica gel followed by concentration of the filtrate, gave compound **2** in almost quantitative yield.

The UV–vis spectrum of **2** presents small changes with respect to that of pristine C_{60}. In particular, there is a difference in the relative intensity of the main electronic transitions, a splitting of that at 330 nm and a new transition around 430 nm. Transitions at 445 nm and 439 nm have been reported for [Pt(PPh$_3$)$_2$(η^2-C_{60})] [19] and [Pd(PPh$_3$)$_2$(η^2-C_{60})] [7] respectively.

The IR spectrum shows the absence of any distinctive Pt–H stretching signals in the range 2400–1600 cm^{-1} [18].

The ^{1}H NMR spectrum of compound **2** exhibits a set of resonances due to PCy$_3$ and no signals attributable to H–Pt, in the typical range of platinum(II) mono hydrides having a trans η^1-carbon (−6 to −11 ppm) [14,17,20].

The ^{31}P{^{1}H} NMR spectrum displays a singlet at 31.23 ppm flanked by Pt satellites ($^1J_{P-Pt} = 3776$ Hz). The value of the $^1J_{P-Pt}$ coupling constant falls in the range reported for *cis*-Pt(0)(η^2-olefin) complexes such as [Pt(PPh$_3$)$_2$(η^2-C_{60})] [4], [Pt(PPh$_3$)$_2$(η^2-C_2H_4)] [21] and [Pt(PCy$_3$)$_2$(η^2-C_2H_4)] [22], and largely differs from the values reported for **1** and other *trans*-

[PtX(H)(PCy$_3$)$_2$] compounds, such as *trans*-[Pt{η^1-C(CHO)CO}(H)(PCy$_3$)$_2$] [14], *trans*-[Pt(η^1-F$_2$C–CF$_2$H)(H)(PCy$_3$)$_2$] [16], *trans*-[PtCl(H)(PCy$_3$)$_2$] [18] and *trans*-[Pt(Br)$_2$(PCy$_3$)$_2$] [23] (Table 3).

The ^{13}C NMR spectrum of **2** shows 16 signals between 134 and 165 ppm. A similar set of resonances has been reported for [Pt(PEt$_3$)$_2$(η^2-C_{60})] [24].

These spectral results are compatible with η^2 coordination of a 6,6 junction of C_{60} to platinum. The proposed structure is further supported by the FAB mass spectrum of **2** showing a weak molecular ion signal at m/z 1475, along with strong signals at m/z 755 [Pt(PCy$_3$)$_2$]$^+$ and m/z 720 [C_{60}]$^{+·}$.

The formation of the η^2 derivative **2** poses a question on the mechanism of the reaction between **1** and C_{60}, that reasonably involves reductive elimination of H$_2$. Although reductive elimination is a known process with platinum and other transition metals complexes, elimination of H$_2$ from compound **1** has been reported only in a few cases. As a matter of fact, compound **1** reacts with CO yielding the trinuclear platinum complex [Pt(PCy$_3$)CO]$_3$ [25] by hydrogen extrusion. If the reaction is carried out at −60 °C, *cis*-[Pt(PCy$_3$)$_2$(CO)$_2$] can be detected in solution [16]. Hydrogen evolution has also been observed either by thermal decomposition of **1** to [Pt(PCy$_3$)$_2$] or by treatment of **1** with oxygen [16]. An interesting example, that might be related to the reaction of **1** with C_{60}, has been reported by Clark et al. [17]. They have found that *trans*-[Pt(H)$_2$(PCy$_3$)$_2$] reacts with dimethyl acetylenedicarboxylate to afford the insertion product *trans*-[Pt(η^1-RC=CRH)(H)(PCy$_3$)$_2$], (R = CO$_2$Me), along with traces of *cis*-[Pt(PCy$_3$)$_2$(η^2-RC≡CR)]. However, mechanistic details have not been presented.

From a mechanistic viewpoint, two possible reaction pathways, leading to metal complex **2**, can be distinguished. One pathway based on spontaneous elimination of hydrogen from **1** and one based on a C_{60}–Pt

Table 3
Comparison betweeen ^{31}P{^{1}H} NMR data of **2** and some related compounds

Compound	δ (ppm)	$^1J_{P-Pt}$ (Hz)	Ref.
2	31.23	3776	This work
[Pt(PPh$_3$)$_2$(η^2-C_{60})]	27.0	3936	[4]
[Pt(PPh$_3$)$_2$(η^2-C_2H_4)]	34.8	3738	[21]
[Pt(PCy$_3$)$_2$(η^2-C_2H_4)]	42.0	3614	[22]
trans-[Pt(H)$_2$(PCy$_3$)$_2$], (**1**)	53.06	2866	This work ^{a}
trans-[Pt(η^1-C(CHO)CO)(H)(PCy$_3$)$_2$]	36.9	2740	[14]
trans-[Pt(η^1-CF$_2$–CF$_2$H)(H)(PCy$_3$)$_2$]	36.9	2905	[16]
trans-[PtCl(H)(PCy$_3$)$_2$]	38.05	2814	This work ^{a}
trans-[Pt(Br)$_2$(PCy$_3$)$_2$]	13.4	2320	[23]
cis-[Pt(Br)$_2$(PCy$_3$)$_2$]	16.9	3585	[23]

^{a} Slightly different values are reported in literature, mainly depending on the solvents used.

$\eta 1$ **2**
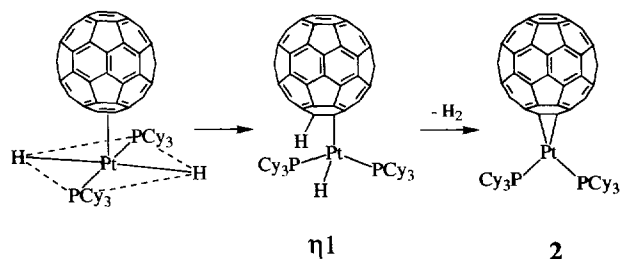
Scheme 2.

pentacoordinated intermediate which may undergo further transformations.

Derivative **1** is quite stable in aromatic solvents at room temperature. Intuitively, spontaneous elimination of H_2 from **1**, followed by coordination of C_{60} to the rather stable $[Pt(PCy_3)_2]$ fragment [26] to yield compound **2**, can be reasonably excluded.

The formation of pentacoordinated platinum adducts has been documented under certain circumstances [16]. [2] Although the metal center in **1** is sterically crowded, C_{60} might approach Pt perpendicularly to the coordination plane to give a pentacoordinated Pt(II) intermediate. This may undergo H_2 reductive elimination to yield **2**, owing to steric encumbrances of fullerene and tricyclohexylphosphines. This route has been suggested in the reaction of C_{60} with mercury–platinum compounds [19]. Alternatively, the coordinated C_{60} may insert on a Pt–H bond, followed by H_2 elimination to yield $[Pt(PCy_3)_2(\eta^2\text{-}C_{60})]$, **2** (Scheme 2). This pattern would be consistent with the acidic character of hydrogen atoms in hydrofullerenes. [28]

In order to clarify the formation pathway of **2**, the course of the reaction has been monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (see Section 2 and Table 1). The ^1H NMR spectrum, recorded 30 min after mixing **1** and C_{60}, shows a complex cluster of weak resonances between 5.74 and 6.14 ppm; the expected resonances due to PCy_3, and a signal at -3.06 ppm due to *trans*-dihydride **1**, which decreases with time.

The resonances around 6 ppm compare well with those recorded at 6.06 and 6.09 ppm for a solution of C_{60} and $[Zr(\eta^5\text{-}C_5H_5)_2Cl(H)]$, which has been attributed to fullerene hydrogen atoms in $[\{Zr(\eta^5\text{-}C_5H_5)_2Cl\}_n(\eta^1\text{-}C_{60}H_n)]$ intermediate [11].

The $^{31}P\{^1H\}$ NMR spectrum, taken after 30 min as well, shows two singlets, at 53.06 ppm ($^1J_{P-Pt} = 2866\,Hz$, *trans*-dihydride **1**) and at 31.23 ppm ($^1J_{P-Pt} = 3776\,Hz$, compound **2**), along with a complex pattern between 28.96 and 32.25 ppm.

After 24 h, NMR spectra show only resonances due

to PCy_3 of compound **2** as a complex set of signals around 1.5 ppm (^1H) and the singlet at 31.23 ppm (^{31}P).

These spectral findings would favour the pathway shown in Scheme 2.

The study of the reactivity of dihydride **1** has been extended to dimethyl maleate **3**, dimethyl fumarate **4** and tetrachloroethylene **5** and the results compared with those obtained earlier with different electron-deficient olefins such as tetrafluoroethylene and tetracyanoethylene [16]. The former gives exclusively the η^1 insertion derivative *trans*-$[Pt\{\eta^1\text{-}CF_2\text{-}CF_2(H)\}(H)(PCy_3)_2]$, whereas, at $-60\,°C$, the latter inserts onto a Pt–H bond to give *trans*-$[Pt\{\eta^1\text{-}C(CN)_2\text{-}C(CN)_2H\}(H)(PCy_3)_2]$ which, upon heating, eliminates HCN affording *trans*-$[Pt\{\eta^1\text{-}C(CN)=C(CN)_2\}(H)(PCy_3)_2]$.

The reaction of complex **1** with dimethyl maleate has been carried out at 50 °C and monitored by $^{31}P\{^1H\}$ NMR spectroscopy (see Section 2 and Table 2). The resonances at 32.54 ppm ($^1J_{P-Pt} = 2812\,Hz$) and at 30.96 ppm ($^1J_{P-Pt} = 3713\,Hz$) have been attributed to *trans*-$[Pt\{\eta^1\text{-}CH(R)\text{-}CH_2R\}(H)(PCy_3)_2]$, $(R = CO_2Me)$ and to $[Pt(PCy_3)_2(\eta^2\text{-}CH(R)=CHR)]$ respectively, mainly on the basis of P–Pt coupling constant values [29]. The η^1/η^2 ratio, which 30 min after mixing **1** and **3** was 1.5, decreased with time. This would support the hypothesis that the η^2 derivative originates from the corresponding η^1 metal complex via H_2 reductive elimination. With dimethyl fumarate, only 20% conversion of dihydride **1** to the η^1/η^2 mixture has been obtained.

With tetrachloroethylene, on the other hand, almost quantitative formation of *trans*-$[PtCl(H)(PCy_3)_2]$ has been observed, similar to what occurs with different chlorinated compounds such as $CHCl_3$ or CCl_4.

4. Conclusions

trans-$[Pt(H)_2(PCy_3)_2]$, **1**, reacts readily with C_{60} to afford exclusively $[Pt(PCy_3)_2(\eta^2\text{-}C_{60})]$, **2**. ^1H and ^{31}P NMR spectra showed that the η^2 olefin complex most probably forms by reductive elimination of hydrogen from a transient η^1 monoinsertion intermediate. The unique C_{60} nature and geometry is probably responsible of the peculiar behavior of **1** which, in the presence of other electron-deficient olefins such as dimethyl maleate or fumarate, furnishes mixtures of both η^1 and η^2 derivatives. These findings contrast to the known reactivity of *trans*-$[Pt(H)_2(PCy_3)_2]$, that gives only η^1 insertion complexes with CO_2, CS_2, C_3O_2 and other olefins such as tetrafluoro- and tetracyanoethylene.

Acknowledgements

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[2] For a recent review on five-coordinated alkene complexes of Pt see Ref. [27].

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