

Reaction of *trans*-[Pt(H)₂(PCy₃)₂] with C₆₀ Reductive elimination of H₂ and formation of [Pt(PCy₃)₂(η²-C₆₀)]

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Abstract

Reaction of *trans*-[Pt(H)₂(PCy₃)₂], **1**, with [60]fullerene at room temperature affords [Pt(PCy₃)₂(η²-C₆₀)], **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 η¹ 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 η¹ metal–alkyl and η² metal–olefin derivatives. If tetrachloroethylene is used as 2π component, *trans*-[PtCl(H)(PCy₃)₂] forms exclusively. © 1997 Elsevier Science S.A.

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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 C₆₀ derivatives with interesting magnetic, electronic and photo-physical properties [1].

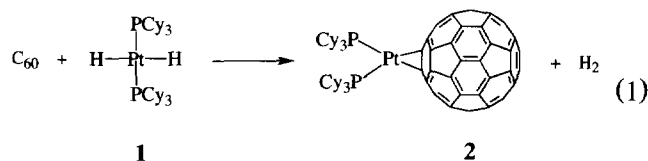
The chemical reactivity of C₆₀ is typical of an electron-poor olefin. C₆₀, in fact, reacts readily with neutral and charged nucleophiles, radical species, carbenes and is a reactive 2π component in thermal and photochemical cycloadditions [1,2]. C₆₀ forms η² complexes with several electron-rich transition metals, such as Pt, Pd, Ni, Rh and Ir,¹ and undergoes hydroboration and hydrozirconation reactions [10,11].

The addition of [Zr(η⁵-C₅H₅)₂Cl(H)] to C₆₀ [11], followed by hydrolysis, leads to a mixture of hydrofullerenes C₆₀H_{2n} (n = 1, 2, 3). Although insertion of C₆₀ into the Zr–H bond could be reasonably supposed,

η¹ alkyl intermediates have never been isolated. Attempts to obtain η¹ derivatives were unsuccessful also with the hydrogenation catalyst [RhH(CO)(PPh₃)₃] that, in presence of C₆₀, eliminates PPh₃ to give η² derivative [Rh(H)CO(PPh₃)₂(η²-C₆₀)] [8] (Scheme 1).

Transition metal hydrides can undergo insertion reaction by unsaturated compounds giving η¹ metal derivatives. In particular, *trans*-[Pt(H)₂(PCy₃)₂], **1**, reacts readily with CO₂ [12], CS₂ [13], C₃O₂ [14,15], F₂C=CF₂ [16] and RC≡CR' [17] to afford stable *trans*-[Pt(η¹-UnsH)(H)(PCy₃)₂] complexes (Uns indicates the unsaturated compound used).

We report here on the unusual behavior of *trans*-dihydride **1** which in presence of C₆₀ gives exclusively the Pt(0) complex [Pt(PCy₃)₂(η²-C₆₀)], **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.



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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(PCy₃)₂], **1**, was synthesized according to Ref. [18]. C₆₀ (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.

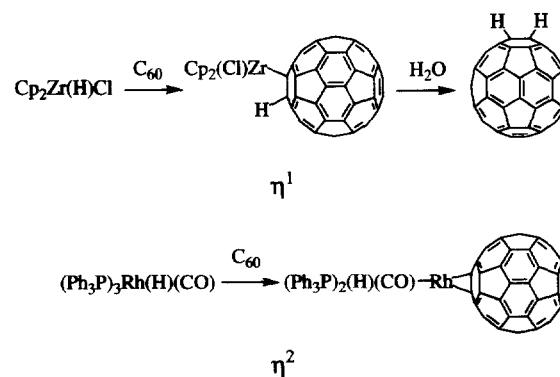
UV-vis absorption spectra were taken on a Perkin-Elmer Lambda 6 spectrophotometer. ¹H, ³¹P and ¹³C NMR spectra were recorded on Bruker AC 200 and AC 250 spectrometers. Chemical shifts are given in parts per million (δ) relative to tetramethylsilane (¹H, ¹³C) and to external 85% H₃PO₄ (³¹P). Positive 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(PCy₃)₂], **1**, with C₆₀. Synthesis of **2**

A solution of 53 mg (0.07 mmol) of **1**, [18] and 50 mg (0.07 mmol) of C₆₀ 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, C₆D₆) δ 1.22–2.51 (m, C₆H₁₁); ¹³C NMR (62.5 MHz, C₆D₆) 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 C₆H₁₁ are not reported). ³¹P{¹H} NMR (200 MHz, C₆D₆) δ 31.23 (s, ¹J_{P-Pt} = 3776 Hz). FAB-MS C₉₆H₆₆P₂Pt (MW = 1475) *m/z* (%) 1475 (M⁺, 1), 755 (Pt(PCy₃)₂⁺, 100), 720 (C₆₀⁺, 52). Anal. Calcd. for C₉₆H₆₆P₂Pt: C, 78.08; H, 4.51. Found: C, 77.26; H, 4.23.

The course of the reaction was also monitored by ¹H and ³¹P{¹H} NMR. To 5 mg of **1** (6.6 × 10⁻³ mmol) dissolved in 1 ml of C₆D₆, 4.8 mg of C₆₀ (6.6 × 10⁻³ mmol) was added. The reaction took place after sonication, giving a deep green solution. ¹H and ³¹P{¹H} NMR spectra were registered before the addition of C₆₀, after 30 min and after 24 h. The results are reported in Table 1.

2.2.2. Reaction of *trans*-[Pt(H)₂(PCy₃)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 C₆D₆ was sealed in an NMR tube and heated to 50 °C. The course of the reactions was monitored by ³¹P{¹H} NMR, following the decreasing of the signal at 53.06 ppm (**1**) and

Table 1
¹H and ³¹P{¹H} NMR data for the reaction of **1** with C₆₀ ^a

	¹ H ^b			³¹ P	
	H-Pt-H	Pt-(¹ C ₆₀ H)	P-Pt-P	P'-Pt-P''	P ₂ Pt(² -C ₆₀)
1	-3.06 (t) ² J _{H-P} = 16.4 ¹ J _{H-Pt} = 798.7		53.06 (s) ¹ J _{P-Pt} = 2866		
1 + C ₆₀ Solution after 30 min	-3.06 (t) ² J _{H-P} = 16.4 ¹ J _{H-Pt} = 798.7	5.74–6.14 ^c	53.06 (s) ¹ J _{P-Pt} = 2866	28.96–32.25 ^c	31.23 (s) ¹ J _{P-Pt} = 3776
1 + C ₆₀ Solution after 24 h					31.23 (s) ¹ J _{P-Pt} = 3776

^a Solvent C₆D₆, r.t., chemical shifts in ppm, *J* in Hz.

^b Signals due to C₆H₁₁ are not reported.

^c Complex unresolved pattern.

Table 2

³¹P{¹H} 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) $^1J_{\text{P-Pt}} = 2866$	32.54 (s) $^1J_{\text{P-Pt}} = 2812$	30.96 (s) $^1J_{\text{P-Pt}} = 3713$
1 + 4	53.06 (s) $^1J_{\text{P-Pt}} = 2866$	32.61 (s) $^1J_{\text{P-Pt}} = 2851$	31.08 (s) $^1J_{\text{P-Pt}} = 3715$

^a Solvent C₆D₆, 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, ($^1J_{\text{P-Pt}} = 2814$ Hz) attributed to *trans*-[PtCl(H)(PCy₃)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 C₆₀ 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 -C₆₀ derivatives obtained by addition of C₆₀ 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 C₆₀. 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(PPh₃)₂(η^2 -C₆₀)] [19] and [Pd(PPh₃)₂(η^2 -C₆₀)] [7] respectively.

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

The ¹H NMR spectrum of compound 2 exhibits a set of resonances due to PCy₃ 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 ³¹P{¹H} NMR spectrum displays a singlet at 31.23 ppm flanked by Pt satellites ($^1J_{\text{P-Pt}} = 3776$ Hz). The value of the $^1J_{\text{P-Pt}}$ coupling constant falls in the range reported for *cis*-Pt(0)(η^2 -olefin) complexes such as [Pt(PPh₃)₂(η^2 -C₆₀)] [4], [Pt(PPh₃)₂(η^2 -C₂H₄)] [21] and [Pt(PCy₃)₂(η^2 -C₂H₄)] [22], and largely differs from the values reported for 1 and other *trans*-

[PtX(H)(PCy₃)₂] compounds, such as *trans*-[Pt(η^1 -C(CHO)CO)(H)(PCy₃)₂] [14], *trans*-[Pt(η^1 -F₂C–CF₂H)(H)(PCy₃)₂] [16], *trans*-[PtCl(H)(PCy₃)₂] [18] and *trans*-[Pt(Br)₂(PCy₃)₂] [23] (Table 3).

The ¹³C NMR spectrum of 2 shows 16 signals between 134 and 165 ppm. A similar set of resonances has been reported for [Pt(PEt₃)₂(η^2 -C₆₀)] [24].

These spectral results are compatible with η^2 coordination of a 6,6 junction of C₆₀ 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(PCy₃)₂]⁺ and *m/z* 720 [C₆₀]⁺.

The formation of the η^2 derivative 2 poses a question on the mechanism of the reaction between 1 and C₆₀, that reasonably involves reductive elimination of H₂. Although reductive elimination is a known process with platinum and other transition metals complexes, elimination of H₂ 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(PCy₃)CO]₃ [25] by hydrogen extrusion. If the reaction is carried out at −60°C, *cis*-[Pt(PCy₃)₂(CO)₂] can be detected in solution [16]. Hydrogen evolution has also been observed either by thermal decomposition of 1 to [Pt(PCy₃)₂] or by treatment of 1 with oxygen [16]. An interesting example, that might be related to the reaction of 1 with C₆₀, has been reported by Clark et al. [17]. They have found that *trans*-[Pt(H)₂(PCy₃)₂] reacts with dimethyl acetylenedicarboxylate to afford the insertion product *trans*-[Pt(η^1 -RC=CRH)(H)(PCy₃)₂], (R = CO₂Me), along with traces of *cis*-[Pt(PCy₃)₂(η^2 -RC≡CR)]. However, mechanistic details have not been presented.

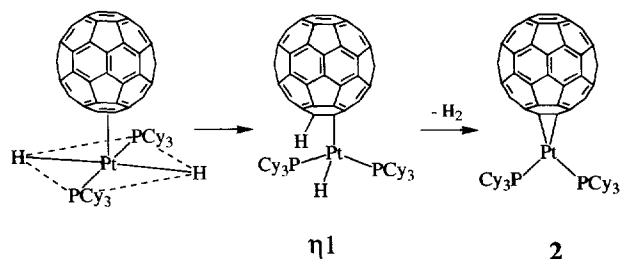
From a mechanistic viewpoint, two possible reaction pathways, leading to metal complex 2, can be distinguished. One pathway based on spontaneous elimination of hydrogen from 1 and one based on a C₆₀–Pt

Table 3

Comparison between ³¹P{¹H} NMR data of 2 and some related compounds

Compound	δ (ppm)	$^1J_{\text{P-Pt}}$ (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 ₂ H ₄)]	34.8	3738	[21]
[Pt(PCy ₃) ₂ (η^2 -C ₂ H ₄)]	42.0	3614	[22]
<i>trans</i> -[Pt(H) ₂ (PCy ₃) ₂], (1)	53.06	2866	This work ^a
<i>trans</i> -[Pt(η^1 -C(CHO)CO)(H)(PCy ₃) ₂]	36.9	2740	[14]
<i>trans</i> -[Pt(η^1 -CF ₂ –CF ₂ H)(H)(PCy ₃) ₂]	36.9	2905	[16]
<i>trans</i> -[PtCl(H)(PCy ₃) ₂]	38.05	2814	This work ^a
<i>trans</i> -[Pt(Br) ₂ (PCy ₃) ₂]	13.4	2320	[23]
<i>cis</i> -[Pt(Br) ₂ (PCy ₃) ₂]	16.9	3585	[23]

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



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 $[Pt(PCy_3)_2(\eta^2-C_{60})]$, **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 $[Zr(\eta^5-C_5H_5)_2Cl(H)]$, which has been attributed to fullerene hydrogen atoms in $[(Zr(\eta^5-C_5H_5)_2Cl)(\eta^1-C_{60}H_n)]$ 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*- $[Pt(\eta^1-CF_2-CF_2(H))(H)(PCy_3)_2]$, whereas, at $-60^\circ C$, the latter inserts onto a Pt–H bond to give *trans*- $[Pt(\eta^1-C(CN)_2-C(CN)_2H)(H)(PCy_3)_2]$ which, upon heating, eliminates HCN affording *trans*- $[Pt(\eta^1-C(CN)=C(CN)_2)(H)(PCy_3)_2]$.

The reaction of complex **1** with dimethyl maleate has been carried out at $50^\circ C$ 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*- $[Pt(\eta^1-CH(R)-CH_2R)(H)(PCy_3)_2]$, ($R = CO_2Me$) and to $[Pt(PCy_3)_2(\eta^2-CH(R)=CHR)]$ 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 $[Pt(PCy_3)_2(\eta^2-C_{60})]$, **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.

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

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