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Slippage of η^3-allenyl/propargyl to an η^1 structure and tautomerization of η^1-propargyl to η^1-allenyl in ligand addition and substitution reactions of platinum(II) complexes

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Abstract

Reactions of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]OTf$ with each of PMe_3, CO and Br^- result in the addition of these species to the metal and a change in hapticity of the $\eta^3\text{-}CH_2CCPh$ to $\eta^1\text{-}CH_2C{\equiv}CPh$ or $\eta^1\text{-}C(Ph){=}C{=}CH_2$. Thus, PMe_3 affords $[(PMe_3)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]^+$, CO gives both $[trans\text{-}(PPh_3)_2Pt(CO)(\eta^1\text{-}CH_2C{\equiv}CPh)]^+$ and $[trans\text{-}(PPh_3)_2Pt(CO)(\eta^1\text{-}C(Ph){=}C{=}CH_2)]^+$, and LiBr yields $cis\text{-}(PPh_3)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$, which undergoes isomerization to $trans\text{-}(PPh_3)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$. Substitution reactions of *cis*- and $trans\text{-}(PPh_3)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$ each lead to tautomerization of $\eta^1\text{-}CH_2C{\equiv}CPh$ to $\eta^1\text{-}C(Ph){=}C{=}CH_2$, with $trans\text{-}(PPh_3)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$ affording $[(PMe_3)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]^+$ at ambient temperature and the slower reacting *cis* isomer giving $[trans\text{-}(PPh_3)(PMe_3)_2Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]^+$ at 54 °C . All new complexes were characterized by a combination of elemental analysis, FAB mas spectrometry and IR and NMR (^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$) spectroscopy. The structure of $[(PMe_3)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]BPh_4{\cdot}0.5MeOH$ was determined by single-crystal X-ray diffraction analysis. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Platinum complexes; Allenyl complexes; Propargyl complexes; Crystal structure

1. Introduction

In recent years a number of papers have dealt with transition-metal η^1-propargyl–η^1-allenyl tautomerism [1–8]. These processes are thought to proceed by intermediacy of a metal η^3-allenyl/propargyl, and in some cases evidence exists for such a pathway.

η^3-Allenyl/propargyl complexes of transition metals have attracted considerable attention because of their unusual chemical behavior toward nucleophilic reagents which add to the central carbon atom of the hydrocarbyl ligand [1,7a,b,9–11]. However, reactions are also known which result in addition of nucleophile/ligand to the metal center with rearrangement of the η^3-allenyl/propargyl to η^1-allenyl or η^1-propargyl [1,7a,12]. Transformations of this type are important, since they can provide insight into η^1-propargyl–η^1-allenyl tautomerism in transition-metal complexes. In this paper we report on such reactions of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]^+$ as well as on η^1-propargyl to η^1-allenyl tautomerization in the course of ligand substitution reactions of *cis*- and $trans\text{-}(PPh_3)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$. An X-ray structural study of $[(PMe_3)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]BPh_4$ is described. Some aspects of our investigation (but not the structure) have already been communicated [7a].

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2. Experimental

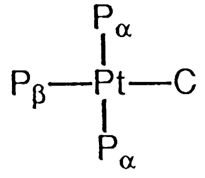
2.1. General procedures, measurements and materials

Reactions and sample manipulations were generally conducted under an atmosphere of argon by use of standard procedures [13]. Solvents were dried [14], distilled under argon and degassed before use. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. IR, NMR (^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H}) and FAB mass spectra were obtained as previously described [7].

Reagents were procured from various commercial sources and used as received. The complexes *cis*- and *trans*-$(PPh_3)_2PtBr(\eta^1$-$CH_2{\equiv}CPh)$ and $[(PPh_3)_2Pt(\eta^3$-$CH_2CCPh)]OTf$ (OTf = O_3SCF_3) were prepared by our published procedures [7b].

2.2. Reaction of *trans*-$(PPh_3)_2PtBr(\eta^1$-$CH_2C{\equiv}CPh)$ with PMe_3

A solution of PMe_3 in toluene (3.0 ml, 1.0 M, 3.0 mmol) was added to *trans*-$(PPh_3)_2PtBr(\eta^1$-$CH_2C{\equiv}CPh)$ (0.654 g, 0.715 mmol) dissolved in 40 ml of THF at room temperature. The resulting yellow solution began to cloud after several minutes and was stirred vigorously for 18 h. The white precipitate that formed during this time was collected on a filter frit and washed with 20 ml of hexane, and the yellow–orange filtrate was discarded. The precipitate was dissolved in 2 ml of MeOH in air, and the solution was filtered into a flask containing $NaBPh_4$ (0.300 g, 0.877 mmol) in 1.5 ml of MeOH. The voluminous ivory precipitate was collected on a filter frit, washed with 60 ml of hexane and dried briefly. This product was found to contain some salt impurities which were removed by addition of 100 ml of CH_2Cl_2 and filtration of the cloudy solution through a 2 × 2 cm column of wet Celite. The filtrate was concentrated to 10 ml under vacuum, and hexane (100 ml) was introduced with stirring to induce the precipitation of the ivory product. After reducing the mixture volume to 50 ml, the solid was collected on a filter frit, washed with 20 ml of hexane and dried under vacuum overnight. Yield of $[(PMe_3)_3Pt(\eta^1$-$C(Ph){=}C{=}CH_2)]BPh_4$, 0.475 g (78%). IR (Nujol): ν(C=C=C) 1908 cm^{-1} (m). ^{1}H NMR ($CD_3C(O)CD_3$): δ 7.62–6.75 (m, 25H, Ph), 4.26 (q, $^5J_{PH} = 5.4$ Hz, $^4J_{PtH} = 38.0$ Hz, 2H, CH_2), 1.85 (d, $^2J_{PH} = 9.3$ Hz, $^3J_{PtH} = 21.7$ Hz, 9H, $P_\beta Me_3$), 1.60 (t, $^2J_{PH} = 3.8$ Hz, $^3J_{PtH} = 28.9$ Hz, 18H, $P_\alpha Me_3$). ^{13}C{^{1}H} NMR ($CD_3C(O)CD_3$): δ 202.4 (t, $^3J_{PC} = 4$ Hz, unresolved $^2J_{PtC}$, =C=), 164.9 (qsept, $^1J_{C11B} = 49.6$ Hz, $^1J_{C10B} = 14.4$ Hz, *ipso*-PhB), 142.7 (t, $^3J_{P\alpha C} = 1.6$ Hz, $^2J_{PtC} = 16$ Hz, *ipso*-*Ph*C), 137.0 (m, *m*-PhB), 129.9 (s, *o*-*Ph*C), 127.3 (s, *p*-*Ph*C), 126.0 (m, *o*-PhB), 122.2 (s, *p*-PhB), 101.6 (dt, $^2J_{P\beta C} = 90$ Hz, $^2J_{P\alpha C} = 12$ Hz, $^1J_{PtC} = 603$ Hz, Ph*C*), 69.9 (dt, $^4J_{P\beta C} = 6.4$ Hz, $^4J_{P\alpha C} = 2.0$ Hz, $^3J_{PtC} = 45$ Hz, $^1J_{CH} = 167$ Hz, CH_2), 18.1 (dt, $^1J_{P\beta C} = 33.5$ Hz, $^3J_{P\alpha C} = 2.1$ Hz, $^2J_{PtC} = 25.8$ Hz, $P_\beta Me_3$), 16.0 (td, $^1J_{P\alpha C} = 19.9$ Hz, $^3J_{P\beta C} = 2.3$ Hz, $^2J_{PtC} = 35.1$ Hz, $P_\alpha Me_3$). ^{31}P{^{1}H} NMR ($CD_3C(O)CD_3$): δ −21.2 (d, $^2J_{PP} = 23.7$ Hz, $^1J_{PtP} = 2488$ Hz, $P_\alpha Me_3$), −28.3 (t, $^2J_{PP} = 23.7$ Hz, $^1J_{PtP} = 1991$ Hz, $P_\beta Me_3$). FAB MS: ^{195}Pt, *m*/*z* 538 (M^+), 423 ($M^+ - C_3H_2Ph$), 347 ($M^+ - C_3H_2Ph{-}PMe_3$). *Anal.* Found: C, 58.63; H, 6.38. Calc. for $C_{42}H_{54}BP_3Pt$: C, 58.81; H, 6.35%.



2.3. Reaction of *cis*-$(PPh_3)_2PtBr(\eta^1$-$CH_2C{\equiv}CPh)$ with PMe_3

A stirred solution of *cis*-$(PPh_3)_2PtBr(\eta^1$-$CH_2C{\equiv}CPh)$ (0.330 g, 0.361 mmol) in 50 ml of THF at 54 °C was treated with PMe_3 in toluene (10.0 ml, 1.0 M, 10 mmol). The resulting solution was stirred for 10 h, and the white precipitate that had formed was collected on a filter frit and converted to the BPh_4^- salt in a manner analogous to that described above for $[(PMe_3)_3Pt(\eta^1$-$C(Ph){=}C{=}CH_2)]BPh_4$. Yield of [*trans*-$(PPh_3)(PMe_3)_2Pt$-$(\eta^1$-$C(Ph){=}C{=}CH_2)]BPh_4$, 0.183 g (49%). IR (Nujol): ν(C=C=C) 1908 cm^{-1} (m). ^{1}H NMR ($CD_3C(O)CD_3$): δ 8.00–6.75 (m, 40H, Ph), 4.44 (q, $^5J_{PH} = 1.8$ Hz, $^4J_{PtH} = 13.7$ Hz, 2H, CH_2), 1.11 (t, $^2J_{PH} = 3.9$ Hz, $^3J_{PtH} = 28.2$ Hz, 18H, PMe_3). ^{31}P{^{1}H} NMR ($CD_3C(O)CD_3$): δ 15.1 (t, $^2J_{PP} = 23.5$ Hz, $^1J_{PtP} = 2153$ Hz, PPh_3), −21.9 (d, $^2J_{PP} = 23.5$ Hz, $^1J_{PtP} = 2486$ Hz, PMe_3).

2.4. Reaction of $[(PPh_3)_2Pt(\eta^3$-$CH_2CCPh)]OTf$ with PMe_3

To a stirred solution of $[(PPh_3)_2Pt(\eta^3$-$CH_2CCPh)]$-OTf (0.090 g, 0.092 mmol) in 30 ml of THF at 0 °C was added dropwise a solution of PMe_3 in toluene (1.2 ml, 1.0 M, 1.2 mmol). After 20 h of reaction time, during which the temperature was allowed to rise to 25 °C , solvent was removed, the residue was treated with 40 ml of hexane and the resulting mixture was stirred for 2 h. The contents were filtered, and the filtrate was discarded. The collected solid was extracted into 10 ml of acetone, and the extract was filtered and evaporated to dryness under vacuum. The remaining solid was dissolved in MeOH, and the resulting solution was treated with ca. 0.1 g (0.3 mmol) of $NaBPh_4$. The rest of the work-up closely followed that given in Section 2.2. Yield of $[(PMe_3)_3Pt(\eta^1$-$C(Ph){=}C{=}CH_2)]$-BPh_4, 0.048 g (62%). Spectroscopic properties of the product matched those of the sample prepared from *trans*-$(PPh_3)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$ and PMe_3.

2.5. Reaction of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]OTf$ with CO

Carbon monoxide was passed into a stirred solution of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]OTf$ (0.208 g, 0.211 mmol) in 4 ml of CH_2Cl_2 at room temperature. After 2 h, hexane (20 ml) was added, and the resulting solution was concentrated to 15 ml to induce the precipitation of a bright yellow solid. The solid was collected on a filter frit and dried under vacuum overnight. Yield of a ca. 1:1 mixture of [*trans*-$(PPh_3)_2Pt(CO)(\eta^1\text{-}CH_2C{\equiv}CPh)$]OTF (A) and [*trans*-$(PPh_3)_2Pt(CO)(\eta^1\text{-}C(Ph){=}C{=}CH_2)$]OTf (B), 0.174 g (81%). ^{1}H NMR (CD_2Cl_2): δ 8.0–6.6 (m, Ph), 3.65 (t, $^5J_{PH} = 4.7$ Hz, $^4J_{PtH} = 38$ Hz, CH_2 of B), 1.98 (t, $^3J_{PH} = 9.7$ Hz, $^2J_{PtH} = 83$ Hz, CH_2 of A). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 203.1 (t, $^3J_{PC} = 4.8$ Hz, =C= of B), 175.2 (t, $^2J_{PC} = 9.0$ Hz, CO), 174.5 (t, $^2J_{PC} = 10.1$ Hz, CO), 138–123 (m, Ph), 101.5 (t, $^2J_{PC} = 8.9$ Hz, Ph*C* of B), 92.2 (s, $^3J_{PtC} = 78$ Hz, Ph*C* of A), 72.9 (s, $^3J_{PtC} = 40$ Hz, CH_2 of B), 7.1 (t, $^2J_{PC} = 3$ Hz, $^1J_{PtC} = 484$ Hz, CH_2 of A). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 17.6 (s, $^1J_{PtP} = 2677$ Hz), 14.3 (s, $^1J_{PtP} = 2573$ Hz).

Table 1
Summary of crystal data, data collection and structure refinement parameters for $[(PMe_3)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]BPh_4\cdot 0.5MeOH$

Empirical formula	$C_{42}H_{54}BP_3Pt\cdot 0.5CH_4O$
Formula weight	873.73
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	9.770(2)
b (Å)	20.965(4)
c (Å)	21.459(4)
α (°)	104.13(1)
β (°)	96.68(1)
γ (°)	98.54(1)
V (Å^3)	4161(1)
Z	4
D_{calc} (g cm^{-3})	1.39
Crystal size (mm)	$0.4 \times 0.4 \times 0.6$
Diffractometer	Enraf–Nonius CAD4
λ (Å)	0.71069 (graphite-monochromated Mo Kα)
Temperature (K)	294 ± 1
μ (cm^{-1})	35.50
F(000)	1808
Scan type	$\omega/2\theta$
ω Scan rate (° min^{-1})	1–7
θ Range (°)	2.0–24.0
Scan angle (°) [a]	$0.95 + 0.35\tan\theta$
Aperture width	$1 + \tan\theta$
Intensity monitors	3
Transmission factors	0.882–1.000
Data collected [b]	13409
Unique data with $I > 3\sigma(I)$	10067
R [c]	0.030
R_w [d]	0.036
w	1
GOF [e]	2.697
Residuals in final map (e Å^{-3})	-0.12, 0.71

[a] Extended by 25% on both sides for background measurements.

[b] Measured after each 4000 s.

[c] $R = \Sigma|F_o - F_c|/\Sigma|F_o|$.

[d] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

[e] $\mathrm{GOF} = [\Sigma w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$; m = number of observables, n = number of variables.

2.6. Reaction of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]OTf$ with LiBr

A solution of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]OTf$ (ca. 30 mg) in 15 ml of 2:1 THF–CH_2Cl_2 was treated with LiBr (ca. 10 mg), and the contents were stirred for 1 h at room temperature. The reaction solution was then concentrated to 3 ml, and its $^{31}P\{^1H\}$ NMR spectrum was recorded. The spectrum showed signals which were assigned to *cis*- and *trans*-$(PPh_3)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$ in ca. 9:1 ratio on the basis of published data for authentic samples [7b].

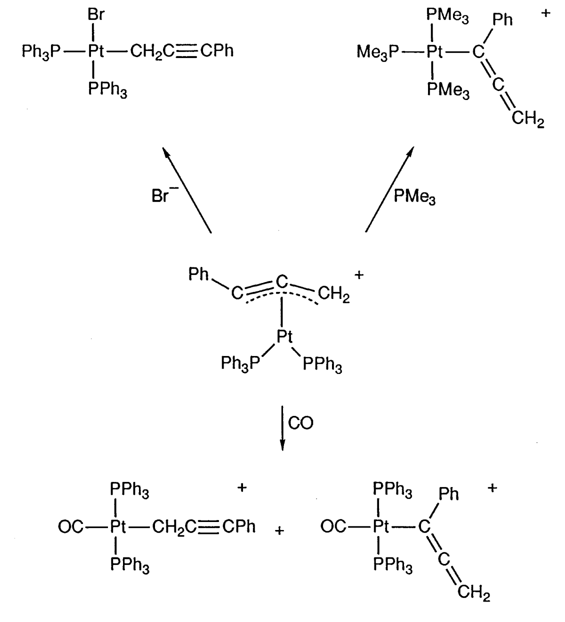
2.7. Crystallographic analysis of $[(PMe_3)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]BPh_4\cdot 0.5MeOH$

Crystals of $[(PMe_3)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]BPh_4\cdot 0.5MeOH$ were grown from acetone–methanol solution by slow evaporation of the solvent. Lattice constants were determined by a least-squares refinement of 25 reflections, accurately centered on an Enraf–Nonius CAD4 diffractometer. A summary of the crystal data and the details of the intensity data collection and refinement are provided in Table 1. No significant change in intensities of control reflections was observed over the course of data collection. The data were corrected for Lorentz polarization effects, as well as for absorption, through an empirical correction based on the Ψ scans of four close-to-axial reflections. The structure was solved by conventional Fourier methods. Final full-matrix least-squares refinement, with the fixed contribution of the hydrogen atoms ($B = 1.3B_{eq}$ Å^2), converged to the R and R_w values given in Table 1. Scattering factors, anomalous dispersion terms, and programs were taken from the Enraf–Nonius SDP library [15].

3. Results and discussion

3.1. Reactions of platinum(II) complexes with PMe_3

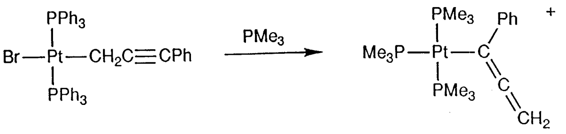
Reaction of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]OTf$ with a large excess PMe_3 in THF first at 0 °C and then at



Scheme 1. Ligand addition reactions of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]^+$.

25 °C for a total of 40 h afforded $[(PMe_3)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]^+$, which was isolated as $[(PMe_3)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]BPh_4$ in 62% yield (Scheme 1).

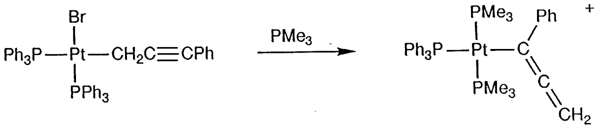
The η^1-allenyl product can be prepared more conveniently and in a higher yield by treatment of *trans*-$(PPh_3)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$ with ca. 4 equiv. of PMe_3 in THF at room temperature for 18 h. Work-up and addition of $NaBPh_4$ in MeOH, as detailed in Section 2.4, gave $[(PMe_3)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2]BPh_4$ as an ivory solid in 78% yield (Eq. (1)).



(1)

Use of *cis*-$(PPh_3)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$ in conjunction with PMe_3 in THF also furnished $[(PMe_3)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]^+$, but the reaction was slower than that of *trans*-$(PPh_3)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$. The corresponding chloride *cis*-$(PPh_3)_2PtCl(\eta^1\text{-}CH_2C{\equiv}CPh)$ can be employed as well; however, it has a lower solubility in THF and does not react as cleanly as the *cis* and *trans* bromides. This general synthetic methodology is applicable also to complexes $[(PR_3)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]^+$ containing some other phosphines; e.g. $[(PMe_2Ph)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]^+$ was prepared by a similar treatment of *trans*-$(PPh_3)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$ with an excess of PMe_2Ph in THF.

The reaction of *cis*-$(PPh_3)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$ with an excess of PMe_3 in THF at room temperature was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. A number of intermediate platinum(II) phosphine complexes had been observed in 18 h, after which time the starting material was still incompletely consumed. Identification of these transients was not possible but, based on the chemical shifts, they appear to be the result of successive substitutions of PMe_3 for PPh_3 at platinum. In contrast, when the reaction was conducted at 40 °C for 4 h, only one major product was observed by $^{31}P\{^1H\}$ NMR spectroscopy. This product was prepared on a larger scale by reacting *cis*-$(PPh_3)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$ with an excess of PMe_3 in THF at 54 °C , and was isolated as the white $BPh_4{}^-$ salt [*trans*-$(PPh_3)(PMe_3)_2Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]BPh_4$ in 49% yield (Eq. (2)).



(2)

The remaining PPh_3 in the product undergoes gradual substitution by PMe_3 at ambient temperature to afford $[(PMe_3)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]BPh_4$.

The product $[(PMe_3)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]BPh_4$ was characterized by IR and NMR (^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$) spectroscopy, FAB mass spectrometry and elemental analysis. Its structure was determined by X-ray diffraction analysis. The mixed-phosphine complex [*trans*-$(PPh_3)(PMe_3)_2Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2]BPh_4$ was assigned structure on the basis of IR and ^1H and $^{31}P\{^1H\}$ spectroscopic evidence. Each complex shows an IR $\nu(C{=}C{=}C)$ absorption at 1908 cm^{-1} and a ^1H NMR signal of the CH_2 at δ 4.44–4.26 as a quartet ($^5J_{PH} = 1.8–5.4$ Hz) with platinum-195 satellites, which implicates η^1-allenyl bonding of the hydrocarbyl group [1–7,16–20]. The former complex contains inequivalent PMe_3 ligands as evidenced by two Me proton resonances, a doublet ($^2J_{PH} = 9.3$ Hz) at δ 1.85 and a triplet ($^2J_{PH} = 3.8$ Hz) at δ 1.60, each with platinum-195 satellites, in a 1:2 intensity ratio, and two $^{31}P\{^1H\}$ resonances, a doublet at δ −21.2 and a triplet at δ −28.3, with $^2J_{PP} = 23.7$ Hz and $^1J_{PtP} = 2488$ and 1991 Hz, respectively. The PPh_3–PMe_3 complex shows only one kind of PMe_3 ligand by the appearance of a ^1H resonance at δ 1.11 as a triplet ($^2J_{PH} = 3.9$ Hz) with platinum-195 satellites. Its $^{31}P\{^1H\}$ NMR spectrum consists of two signals, a triplet at δ 15.1, assigned to PPh_3, and a doublet at δ −21.9, assigned to PMe_3, with $^2J_{PP} = 23.5$ Hz and $^1J_{PtP} = 2153$ and 2486 Hz, respectively, to indicate a *trans* structure for the cation $[(PPh_3)(PMe_3)_2Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]^+$. The $^{13}C\{^1H\}$ NMR spectrum of $[(PMe_3)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]BPh_4$ is in complete accord with the assigned structure [2,4–6,16,18–20]. Resonances of the hydrocarbyl ligand occur at δ 202.4 for =C=, δ 101.6 with two different coupling constants $^2J_{PC}$, 90 (*trans*) and 12 Hz (*cis*), and a very large $^1J_{PtC}$ of 603 Hz for Ph*C*, and δ 69.9 with

$^2J_{PC}$ = 6.4 and 2.0 Hz, $^3J_{PtC}$ = 45 Hz, and $^1J_{CH}$ = 167 Hz (^{1}H-coupled spectrum) for CH_2. There are also separate resonances of the PMe_3 carbons for P_α and P_β (cf. Section 2.4 for α, β designations) at δ 18.1 and 16.0, respectively, with appropriate coupling constants $^1J_{PC}$, $^3J_{PC}$ and $^1J_{PtC}$. The FAB mass spectrum shows peaks of the complex cation (M^+) and fragments derived by loss of C_3H_2Ph and of C_3H_2Ph plus PMe_3.

Since there are few published structures of mononuclear transition-metal η^1-allenyl complexes [18b,19–21], especially if the phosphoniumallenylidene analogs [22] are excluded, we carried out an X-ray diffraction analysis on the $[(PMe_3)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]BPh_4$ obtained from acetone–methanol as the 0.5MeOH solvate. The crystals were found to contain two crystallographically independent molecules, A and B; the structure of complex cation A is shown in Fig. 1. Selected bond distances and angles are listed in Table 2.

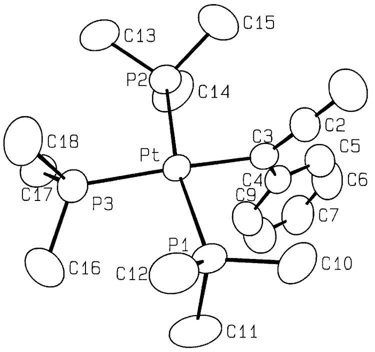


Fig. 1. Molecular structure of $[(PMe_3)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]^+$ with 50% probability ellipsoids. Hydrogen atoms have been omitted.

Table 2
Selected bond distances (Å), bond angles (°) and torsion angles (°) for $[(PMe_3)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]BPh_4{\cdot}0.5MeOH$

	Molecule A	Molecule B
Pt–P(1)	2.319(2)	2.316(2)
Pt–P(2)	2.326(2)	2.313(2)
Pt–P(3)	2.314(3)	2.320(3)
Pt–C(3)	2.084(9)	2.090(9)
C(1)–C(2)	1.34(1)	1.31(2)
C(2)–C(3)	1.31(1)	1.30(1)
C(3)–C(4)	1.48(1)	1.47(1)
P(1)–Pt–P(2)	168.26(9)	170.6(1)
P(1)–Pt–P(3)	95.00(8)	94.80(8)
P(1)–Pt–C(3)	87.1(2)	86.2(2)
P(2)–Pt–P(3)	94.99(9)	93.97(9)
P(2)–Pt–C(3)	83.8(2)	85.2(2)
P(3)–Pt–C(3)	172.3(2)	176.3(3)
Pt–C(3)–C(2)	121.2(7)	118.4(7)
Pt–C(3)–C(4)	118.4(6)	119.8(6)
C(1)–C(2)–C(3)	178(1)	178(1)
C(2)–C(3)–C(4)	120.4(8)	121.8(9)
P(1)–Pt–C(3)–C(2)	−86.6(7)	−90.1(8)
P(1)–Pt–C(3)–C(4)	95.5(6)	92.0(7)
P(2)–Pt–C(3)–C(2)	86.0(7)	85.9(8)
P(2)–Pt–C(3)–C(4)	−92.0(6)	−92.1(7)
P(3)–Pt–C(3)–C(2)	168(1)	164(3)
P(3)–Pt–C(3)–C(4)	−11(2)	−14(4)
Pt–C(3)–C(4)–C(5)	159.2(7)	163.9(7)
C(2)–C(3)–C(4)–C(5)	−19(1)	−14(1)

The platinum is bonded to one η^1-(1-phenylallenyl) and three PMe_3 ligands whose donor atoms adopt approximately square planar geometry around the metal. The bond angles around the Pt center vary from 83.8(2)–87.1(2)° between phosphorus and carbon, i.e. for P(1)–Pt–C(3) and P(2)–Pt–C(3), to 93.97(9)–95.00(8)° between two phosphorus atoms, i.e. for P(1)–Pt–P(3) and P(2)–Pt–P(3). The sum of these bond angles is 360.9 and 360.2° in molecules A and B, respectively, and the deviations from the least-squares plane defined by Pt and the four donor atoms are: Pt 0.003, P(1) 0.136, P(2) 0.140, P(3) −0.119 and C(3) −0.159 Å for molecule A; and Pt 0.003, P(1) −0.072, P(2) −0.073, P(3) 0.063 and C(3) 0.081 Å for molecule B. The Pt–P bond distances of 2.313(2)–2.326(2) Å are similar to those reported for a number of platinum(II) bromo α,β-unsaturated hydrocarbyl phosphine complexes [19,20]. There is no difference in the Pt–P bond distance for the two *trans* phosphines and the phosphine *trans* to carbon. The Pt–C bond of 2.084(9) Å for molecule A and 2.090(9) Å for molecule B is longer than a normal Pt–C_{sp2} bond of 1.98 Å [23]. However, it is very similar to that reported for another platinum(II) η^1-allenyl complex, *trans*-$(PPh_3)_2PtBr(\eta^1\text{-}CH{=}C{=}CMe_2)$, which measures 2.10(3) Å [19], and close to that found in *trans*-$(PPh_3)_2PtBr(\eta^1\text{-}CH{=}C{=}CH_2)$, i.e. 2.040(5) Å [20].

The η^1-allenyl fragment C(1)C(2)C(3) is linear (178(1)°), and the bond distances C(1)–C(2) (1.34(1) Å for molecule A and 1.31(2) Å for molecule B) and C(2)–C(3) (1.31(1) Å for molecule A and 1.30(1) Å for molecule B) are normal [18b,19–21]. The average angles Pt–C(3)–C(2), Pt–C(3)–C(4) and C(2)–C(3)–C(4) are very close to 120°, summing up, as expected, to 360.0° for both molecules A and B. The PtC(3)C(2) plane is perpendicular to the least-squares plane PtP(1)P(2)P(3)C(3), with the dihedral angle being 89.9° for molecule A and 92.2° for molecule B.

3.2. Other reactions of platinum(II) complexes

The complex $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]OTf$ reacts with CO in CH_2Cl_2 solution at room temperature to afford a ca. 1:1 mixture of [*trans*-$(PPh_3)_2Pt(CO)(\eta^1\text{-}CH_2C{\equiv}CPh)]OTf$ and [*trans*-$(PPh_3)_2Pt(CO)(\eta^1\text{-}C(Ph){=}C{=}CH_2)]OTf$ in 81% yield (Scheme 1). Efforts to separate these two complexes, or to convert the mixture to one isomer by heating, repeatedly were thwarted by accompanying decomposition.

The presence of both the η^1-propargyl [*trans*-$(PPh_3)_2Pt(CO)(\eta^1\text{-}CH_2C{\equiv}CPh)]^+$ and the η^1-allenyl [*trans*-$(PPh_3)_2Pt(CO)(\eta^1\text{-}C(Ph){=}C{=}CH_2]^+$ in the isolated solid is indicated by its ^{1}H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra. Thus, the ^{1}H NMR spectrum shows two CH_2 triplets (owing to J_{PH} coupling), that of the $PtC(Ph){=}C{=}CH_2$ at δ 3.65 and that of the $PtCH_2C{\equiv}CPh$ at δ 1.98. These chemical shifts are characteristic of the two tautomeric structures [1–6,16–20], and the magnitude of J_{PtH} coupling for the allenyl (38 Hz) is smaller than that for the propargyl (83 Hz), as expected [1–3,6–8,18–20]. The $^{13}C\{^1H\}$ NMR spectrum shows characteristic signals of the allenyl =C= at δ 203.1 [1,4–8,16,18–20] and of the propargyl CH_2 at δ 7.1 [1,6–8,16,18], the latter with a large $^1J_{PtC}$ constant of 484 Hz to indicate Pt–CH_2 bonding. There are two CO resonances at δ 175.2 and 174.5. The remaining signals also are readily assignable to the allenyl and propargyl species (Section 2.5). The occurrence of two $^{31}P\{^1H\}$ resonances at δ 17.6 and 14.3 as singlets with slightly different $^1J_{PtP}$ coupling constants of 2677 and 2573 Hz, respectively, accords with the presence of the two tautomeric species and their *trans* structures.

The foregoing products of the reaction of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]OTf$ with CO are analogous to those of the corresponding reaction with the isonitrile $CNCMe_3$ [24]. The latter also gives the η^1-propargyl and η^1-allenyl, [*trans*-$(PPh_3)_2Pt(CNCMe_3)$-$(\eta^1\text{-}CH_2C{\equiv}CPh)]OTf$ and [*trans*-$(PPh_3)_2Pt(CNCMe_3)$-$(\eta^1\text{-}C(Ph){=}C{=}CH_2)]OTf$, respectively, but in the ratio > 6:1.

In contrast to the aforementioned reactions of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]OTf$ with CO and $CNCMe_3$, treatment of the η^3-allenyl/propargyl complex with LiBr in THF–CH_2Cl_2 affords only η^1-propargyl products. Thus, after 1 h at room temperature a ca. 9:1 mixture of *cis*- and *trans*-$(PPh_3)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$ was obtained (Scheme 1) which was characterized in situ by $^{31}P\{^1H\}$ NMR spectroscopy. Since *cis*-$(PPh_3)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$ undergoes isomerization to *trans*-$(PPh_3)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$ under these conditions, it is likely that the initial product of Br^- addition is exclusively the *cis* isomer. In a related study, Kurosawa and co-workers recently reported [12b] that $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]OTf$ readily adds Cl^- in CD_2Cl_2 at −78 °C to room temperature to give only *cis*-$(PPh_3)_2PtCl(\eta^1\text{-}CH_2C{\equiv}CPh)$.

Thus, there appear to be two patterns for ligand addition reactions at metal of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]^+$. The neutral ligands CO and $CNCMe_3$ (L) yield the *trans* isomer of each tautomeric form of allenyl/propargyl, i.e. [*trans*-$(PPh_3)_2PtL(\eta^1\text{-}C(Ph){=}C{=}CH_2)]^+$ and [*trans*-$(PPh_3)_2PtL(\eta^1\text{-}CH_2C{\equiv}CPh)]^+$. However, the halides Br^- and Cl^- (X^-) afford exclusively (or almost exclusively) the η^1-propargyl tautomer as the *cis* isomer of $(PPh_3)_2PtX(\eta^1\text{-}CH_2C{\equiv}CPh)$. These results suggest that the anionic and the neutral adding species interact differently with the substrate complex $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]^+$. Whereas the anions because of their charge probably approach the metal in the vicinity of the η^3-CH_2CCPh group to give a cis product, a point also made by Kurosawa [12b], neutral species may enter in between the two PPh_3 ligands. Of course, such a proposal assumes that there is no *cis* addition followed by rapid *cis*-to-*trans* product isomerization for the latter group of incoming ligands, i.e. CO and $CNCMe_3$, and this point has not been demonstrated. The formation of η^1-allenyl and/or η^1-propargyl adducts may be due to several factors which include a preference for ligand addition to platinum at the CH_2 or the CPh side of the η^3-CH_2CCPh group and optimization of the overall (σ and π) bonding in the product. Clearly, additional studies on an expanded range of reacting ligands must be conducted before some of these points are resolved.

4. Supplementary material

Crystallographic data for the structure of $[(PMe_3)_3Pt(\eta^1\text{-}C(Ph){=}C{=}CH_2)]BPh_4\cdot 0.5MeOH$ have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 159531. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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