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Formation of platinum allyl and propargyl complexes from protonation of platinum enyne and diyne complexes

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Abstract

Protonation of $(Ph_3P)_2Pt[\eta^2\text{-}HC{\equiv}CC(CH_3){=}CH_2]$ (**2a**) with excess $HBF_4{\cdot}Et_2O$ produced the π-allyl complex $(Ph_3P)_2Pt[\eta^3\text{-}H_2C{=}CC(CH_3){=}CH_2]^+BF_4^-$ (**3a-BF$_4$**) instead of a π-propargyl complex. Reaction of excess CF_3CO_2H with **2a** initially produced the analogous π-allyl complex **3a-CF$_3$CO$_2$** which then added CF_3CO_2H across the vinylidene unit of **3a-CF$_3$CO$_2$** to give the π-allyl complex $(Ph_3P)_2Pt[\eta^3\text{-}CH_3C(CF_3CO_2)C(CH_3)CH_2]^+CF_3CO_2^-$ (**5a**). Protonation of the platinum diyne complex $[(p\text{-}CH_3\text{–}C_6H_4)_3P]_2Pt(\eta^2\text{-}CH_3C{\equiv}CC{\equiv}CCH_3)$ (**7b**) with $HBF_4{\cdot}Et_2O$ at $-73°C$ initially produced the platinum hydride complex *trans*-$[(p\text{-}CH_3\text{–}C_6H_4)_3P]_2PtH(\eta^2\text{-}CH_3C{\equiv}CC{\equiv}CCH_3)^+BF_4^-$ (**9**), which rearranged to the platinum π-propargyl complex $[(p\text{-}CH_3\text{–}C_6H_4)_3P]_2Pt[\eta^3\text{-}(CH_3CH{=})\text{-}CC{\equiv}CCH_3]^+BF_4^-$ (**11**) at $-28°C$. © 1997 Elsevier Science S.A.

Keywords: Crystal structures; Platinum complexes; Allyl complexes; Propargyl complexes

1. Introduction

π-Propargyl metal complexes [1] are the triple bond analogs of π-allyl metal complexes, which have been used extensively in organic synthesis. π-Propargyl complexes have been proposed as transient intermediates in catalytic cycles [2] and recently a number of stable π-propargyl complexes have been synthesized [3–6]. Because of their similarity, synthetic routes to π-propargyl and π-allyl complexes are often analogous. Examples include protonation of η^2-propargyl or η^2-allyl alcohol complexes [3a,7], hydride abstraction from η^2-alkyne or η^2-alkene complexes [3,8] and reaction of propargyl or allyl Grignard reagents with metal halides [4,9] (Scheme 1).

We set out to explore protonation of platinum enyne and diyne complexes as a new route to π-propargyl complexes. Similar routes to π-allyl complexes from protonation of metal η^4-diene complexes [7] have been reported, and we recently observed the formation of the π-allyl complex $Cp^*(CO)_2Re[\eta^3\text{-}CH_2{=}CHC(CH_3)_2]^+BF_4^-$ upon protonation of the η^2-diene complex $Cp^*(CO)_2Re[\eta^2\text{-}CH_2{=}CHC(CH_3){=}CH_2]$ with $HBF_4{\cdot}Et_2O$ [10]. Hill and co-workers successfully employed the protonation of a ruthenium diyne complex to synthesize a ruthenium π-propargyl complex [6a].

Here we report that protonation of a platinum enyne complex produced a cationic π-allyl platinum complex at room temperature instead of a π-propargyl complex. However, protonation of platinum diyne complexes led to the corresponding π-propargyl platinum complexes which were observable at low temperature. These π-propargyl platinum complexes are similar to compounds previously synthesized [5].

2. Results and discussion

2.1. Synthesis of platinum enyne complexes

The known complex $(Ph_3P)_2Pt[\eta^2\text{-}HC{\equiv}CC(CH_3){=}CH_2]$ (**2a**) needed as a starting material for these protonation studies was prepared in 60% yield by reaction of $(Ph_3P)_2Pt(\eta^2\text{-}H_2C{=}CH_2)$ (**1a**) with the conjugated enyne $HC{\equiv}CC(CH_3){=}CH_2$. Previously, **2a** had been prepared by reaction of *cis*-$(PPh_3)_2PtCl_2$ with $HC{\equiv}CC(CH_3){=}CH_2$ and N_2H_4 [11]. A characteristically high frequency ^1H NMR resonance for the alkyne hydrogen at δ 7.14 (J_{PtH} = 23 Hz) and two vinyl hydrogen resonances at δ 4.97 and 4.85 for the uncoordinated isopropenyl group established coordination of the alkyne in **2a**. If the alkene had been coordinated to Pt, then both the vinyl and acetylenic resonances would have appeared at substantially lower frequency. The observation

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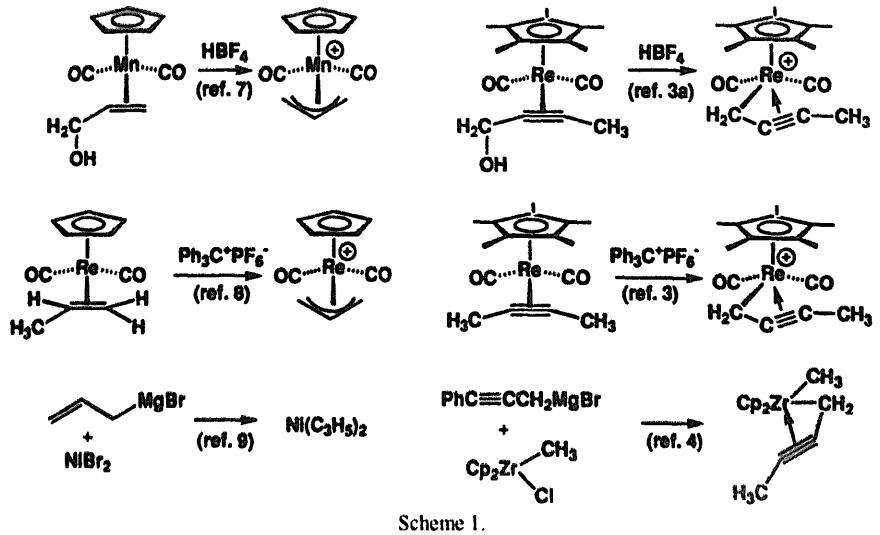


Scheme 1.

of two ^{31}P NMR resonances at δ 31 (d, J_{PP} = 35 Hz, J_{PtP} = 3080 Hz) and 27 (d, J_{PP} = 35 Hz, J_{PtP} = 3440 Hz) is consistent with in-plane coordination of the alkyne in **2a** and slow rotation about the platinum alkyne bond. The analogous compound $[(p\text{-}CH_3\text{-}C_6H_4)_3P]_2Pt[\eta^2\text{-}HC{\equiv}CC(CH_3){=}CH_2]$ (**2b**) was made by a similar route in 57% yield.

2.2. π-Allyl complex formation from HBF_4 addition to a platinum enyne complex

Protonation of $(Ph_3P)_2Pt[\eta^2\text{-}HC{\equiv}CC(CH_3){=}CH_2]$ (**2a**) with excess $HBF_4 \cdot Et_2O$ produced the π-allyl complex $(Ph_3P)_2Pt[\eta^3\text{-}H_2C{=}CC(CH_3){=}CH_2]^+BF_4^-$ (**3a-BF_4**) (Scheme 2), which was isolated as an orange solid in 69% yield. The spectra of **3a-BF_4** were very similar to those of the analogous PF_6 salt (**3a-PF_6**) previously prepared by Green and co-workers via chloride abstraction from a σ-2-butadienyl platinum complex [12]. Key features of the ^1H NMR spectrum of **3a-BF_4** include resonances for the vinyl hydrogens at δ 5.63 and 4.10 and for the allyl hydrogens at δ 3.71 and 3.35.

The π-allyl complex **3a-BF_4** results from protonation of **2a** at the triple bond and subsequent coordination of the double bond. Protonation at the double bond would have produced a π-propargyl complex whose *gem*-dimethyl group would have been easily detected by NMR spectroscopy.

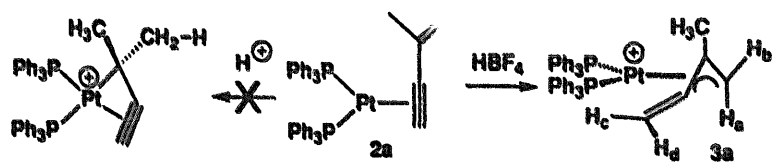
Similarly, addition of excess CF_3CO_2H to **2a** in CD_2Cl_2 gave the unstable π-allyl complex $(Ph_3P)_2Pt[\eta^3\text{-}H_2C{=}CC(CH_3){=}CH_2]^+CF_3CO_2^-$ (**3a-CF_3CO_2**) in 93% yield (NMR internal standard). The analogous tolyl phosphine complex $[(p\text{-}CH_3\text{-}C_6H_4)_3P]_2Pt[\eta^3\text{-}H_2C{=}CC(CH_3){=}CH_2]^+$-$CF_3CO_2^-$ (**3b-CF_3CO_2**) was prepared by a similar procedure in 84% NMR yield.

2.3. σ-2-Butadienyl complex from addition of trifluoroacetic acid

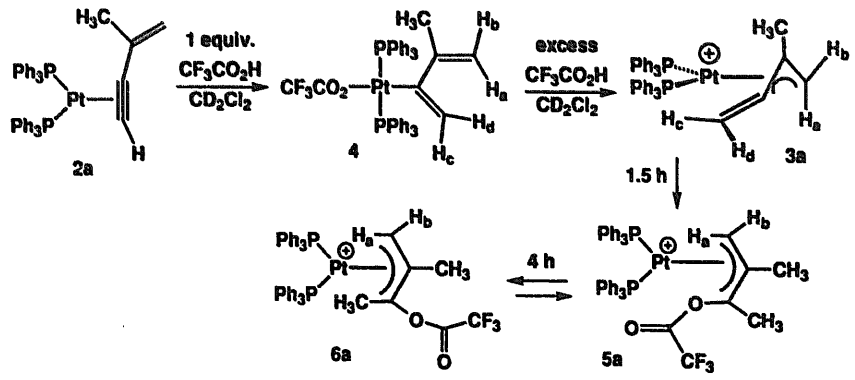
Surprisingly, addition of *only one* equivalent of CF_3CO_2H to a solution of **2a** in CD_2Cl_2 produced the neutral σ-2-butadienyl complex *trans*-$(Ph_3P)_2(CF_3CO_2)Pt[\eta^1\text{-}H_2C{\equiv}CC(CH_3){=}CH_2]$ (**4**) (Scheme 3). Since **4** decomposed upon attempted isolation, it was characterized spectroscopically. Use of an internal NMR standard showed that **4** was formed in 77% yield. The ^1H NMR spectrum of **4** was very similar to that of the corresponding chloride which had been previously synthesized by Villa and co-workers [11] from addition of $HC{\equiv}CC(CH_3){=}CH_2$ to a dilute solution of *cis*-$(PPh_3)_2PtCl_2$ and N_2H_4, and by Green and co-workers [12] from addition of 2-chloro-1,3-butadiene to a solution of **1a**. Key features of the ^1H NMR spectrum of **4** include resonances for four vinyl hydrogens at δ 5.76, 5.24, 4.75 and 4.34. The observation of a single ^{31}P NMR resonance at δ 23 (J_{PtP} = 3280 Hz) provides evidence for the *trans* relationship of the phosphines.

The formation of **4** results from protonation of the coordinated alkyne and coordination of trifluoroacetate to platinum. As in the case of protonation with HBF_4, no evidence for protonation at the uncomplexed alkene was obtained.

Addition of a second equivalent of CF_3CO_2H to σ-2-butadienyl complex **4** led to the formation of the π-allyl complex **3a-CF_3CO_2**. We suggest that hydrogen bonding between excess trifluoroacetic acid and trifluoroacetate anion shifts



Scheme 2.



Scheme 3.

the equilibrium away from the neutral complex **4** and towards the ionic complex **3a**-CF_3CO_2. The observation that excess trifluoroacetic acid reacts with **2a** in THF-d_8 (instead of CD_2Cl_2) to form the neutral σ-2-butadienyl complex **4** in 73% NMR yield is consistent with this hypothesis. Hydrogen bonding between the excess acid and THF frees trifluoroacetate anion for addition to platinum.

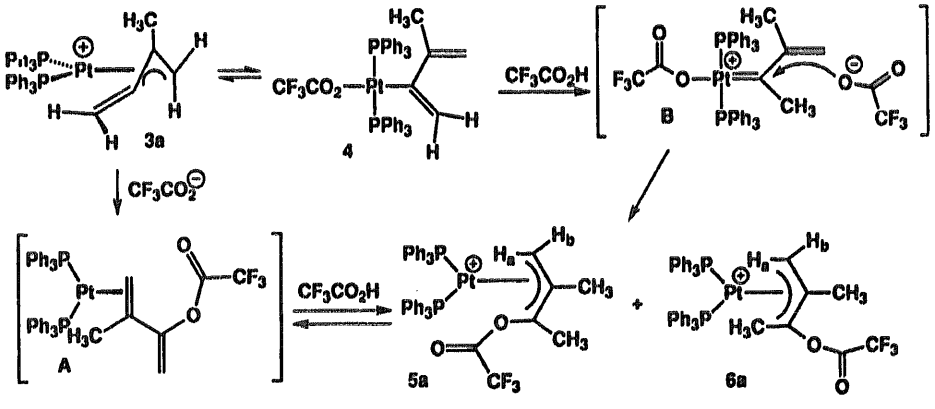
2.4. Addition of CF_3CO_2H across the vinylidene unit of 3a

The π-allyl complex **3a**-CF_3CO_2 reacted with excess CF_3CO_2H slowly at room temperature to add CF_3CO_2H across the vinylidene double bond of **3a** (Scheme 3). After 1.5 h, the resonances for **3a**-CF_3CO_2 began to disappear and a new compound **5a** began to form. After 4 h, a third compound **6a** with a spectrum similar to that of **5a** appeared; the ratio of **5a**:**6a** was 2:1. After 16 h, **3a**-CF_3CO_2 had completely disappeared and the ratio of **5a**:**6a** was 1:1.8. The combined yield of **5a** and **6a** was 62% as determined by ^1H NMR spectroscopy. The tris(*p*-tolyl)phosphine analogs **5b** and **6b** were similarly formed in 77% combined yield.

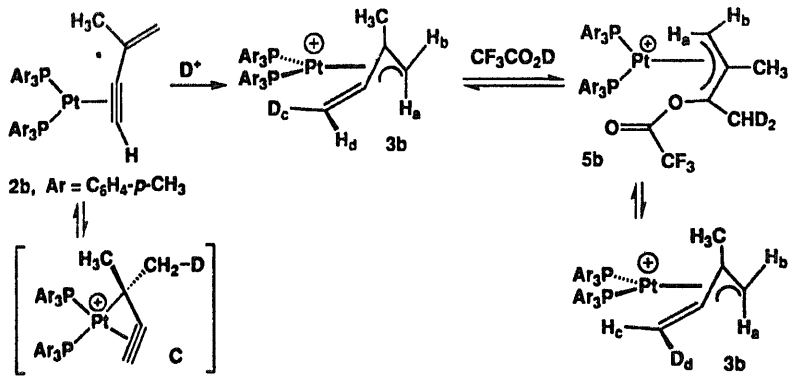
The ^1H and ^{31}P NMR spectra of **5a** and **6a** are consistent with their formulation as the *syn* and *anti* π-allyl isomers of $(Ph_3P)_2Pt[\eta^3\text{-}CH_3C(CF_3CO_2)C(CH_3)CH_2]^+CF_3CO_2^-$. The kinetic isomer **5a** is assigned a structure with a *syn* methyl group on the π-allyl ligand. The appearance of two methyl resonances for **5a** at δ 2.06 (J_{PtH} = 54 Hz, CH_2CCH_3) and 1.22 (J_{PH} = 3, 7.5 Hz, J_{PtH} = 24 Hz, $CH_3C(CF_3CO_2)$) and for **6a** at δ 2.03 (J_{PtH} = 62 Hz, CH_2CCH_3) and 1.12 (J_{PH} = 4.5 Hz, J_{PtH} = 6 Hz, $CH_3C(CF_3CO_2)$) played a key role in the structural assignments. The π-allyl hydrogens of **5a** appeared at δ 3.4 and 2.9, while those of **6a** appeared at δ 3.3 and 2.9. The chemical shifts and coupling patterns for the methyl groups of **5a** and **6a** are similar to those of the methyl groups in Stang's π-allyl complex $(PPh_3)_2Pt[\eta^3\text{-}(CH_3)_2CC(CH_3)CH_2]^+O_3SCF_3^-$ [13]. The *anti* assignment of the $CH_3(CF_3CO_2)C$ methyl group of **6a** is based on the observation of larger J_{MePt} and J_{MeP} coupling constants for **6a** compared with **5a**.

A similar addition across the *exo*-methylene group of an *exo*-methylene π-allyl complex was observed by Green and co-workers [14]. Reaction of $Cp^*(CO)_2Mo(\eta^3\text{-}CH_2CHC{=}CH_2)$ with CF_3SO_3H followed by addition of PPh_3 produced the phosphine substituted allyl complex $Cp^*(CO)_2Mo[\eta^3\text{-}CH_2CHC(Me)PPh_3]^+BF_4^-$.

There are two plausible routes for addition of CF_3CO_2H across the exomethylene unit of **3a**. The first involves nucleophilic attack of trifluoroacetate at the π-allyl unit to give the η^2-diene complex **A** which then undergoes protonation of the uncomplexed alkene to form π-allyl complexes **5a** and **6a**. Alternatively, the σ-2-butadienyl complex **4** which is likely to be in equilibrium with **3a** might undergo protonation to form cationic carbene complex **B**. Addition of trifluoroacetate to the carbene carbon, followed by ionization of the Pt-bound trifluoroacetate could then lead to the formation of **5a** and **6a** (Scheme 4).



Scheme 4.



Scheme 5.

2.5. Reaction of $[(p\text{-}CH_3\text{-}C_6H_4)_3P]_2Pt(\eta^2\text{-}HC{\equiv}CC(CH_3){=}CH_2)$ (2b) with CF_3CO_2D

This reaction was studied to gain information concerning the stereochemistry and mechanism of formation of **3b**. If initial deuteration occurred at platinum followed by deuteride transfer to the alkyne carbon, then deuterium would be found *cis* to Pt in **3b**. Direct deuteration of the alkyne carbon could lead to deuterium *trans* to Pt in **3b**. These deuterium studies also reveal whether reversible π-propargyl cation formation is occurring via protonation at the remote alkene carbon. Reversible formation of π-propargyl complex **C** could lead to deuterium incorporation into the π-allyl group of **3b** (Scheme 5).

The tris(*p*-tolyl)phosphine complex **2b** was used in these studies since the *p*-tolyl methyl group provided a useful internal standard for ^1H NMR integration. After 6 min, ^1H NMR analysis of the reaction of **2b** with excess CF_3CO_2D in CD_2Cl_2 showed 84% conversion to π-allyl cation **3b**; 47% deuterium incorporation into the vinyl site *cis* to platinum was observed and no deuterium was detected ($< 5\%$) at other sites [1]. ^2H NMR also showed exclusive deuterium incorporation at the *cis* vinyl site.

After 1.5 h, 36% of π-allyl cation **3b** and 36% of *endo*-methyl π-allyl complex **5b** were observed by ^1H NMR integration; none of the *exo*-methyl π-allyl complex **6b** was detected. Deuterium was now seen in both vinyl sites of **3b**: 60% deuterium incorporation at the *cis* site and 58% at the *trans* site. The only site of incorporation of deuterium into the trifluoroacetic acid addition product **5b** was the *endo*-methyl group which had 1.6 D per methyl group. ^2H NMR showed deuterium incorporation into both the *cis* and *trans* vinyl sites of **3b** but no deuterium at other sites.

After 4.5 h, only 12% **3b** remained and 19% **5b** and 39% **6b** had formed with 58% deuterium incorporation of the methyl groups on the terminal carbon. The methyl groups on the terminal π-allyl carbon of **5b** and **6b** had 1.6 D per methyl group.

The absence of deuterium in the allyl positions and in the methyl group of **3b** at 0.1 and 1.5 h rules out rapid and reversible formation of π-propargyl complex **C** from **2b** prior to formation of **3b**. The fact that no deuterium gets incorporated into either the π-allyl sites or the methyl group on the central allylic carbon provides evidence that there is no reversible equilibrium between **5b** or **6b** and the π-propargyl complex **C**.

Selective deuterium incorporation into the vinyl site *cis* to Pt in **3b** at short times is consistent with deuteration at Pt followed by transfer of deuteride from Pt to the complexed alkyne. Deuterium incorporation into the vinyl site *trans* to platinum in **3b** at longer times can be explained by the reversible formation of **5b**, which allows deuterium to move between *cis* and *trans* sites of **3b**. At short times, **5b** is the kinetic product of addition of CF_3CO_2H to **3b**. At longer times, the equilibration of **5b** with **3b** allows the eventual buildup of the thermodynamic addition product **6b**.

2.6. Protonation of platinum diyne complexes

Our attempts to prepare π-propargyl platinum compounds by protonation of the uncomplexed double bond of platinum η^2-enyne complexes **2a** and **2b** failed due to competing protonation of the complexed triple bond which produced π-allyl complexes. We initiated studies of platinum η^2-diyne complexes since protonation of either the complexed or uncomplexed triple bond would produce a π-propargyl complex. Previously, Hill and co-workers successfully employed this strategy to synthesize ruthenium π-propargyl complexes [6a].

2.7. Synthesis of platinum diyne complexes

Reaction of $[(p\text{-}CH_3\text{-}C_6H_4)_3P]_2Pt(\eta^2\text{-}H_2C{=}CH_2)$ (**1b**) with the diyne $CH_3C{\equiv}CC{\equiv}CCH_3$ gave $[(p\text{-}CH_3\text{-}C_6H_4)_3P]_2Pt(\eta^2\text{-}CH_3C{\equiv}CC{\equiv}CCH_3)$ (**7b**) as a yellow solid in 68% yield. Similarly, the η^2-diyne complex $[(p\text{-}CH_3\text{-}C_6H_4)_3P]_2Pt[\eta^2\text{-}(CH_3)_3SiC{\equiv}CC{\equiv}CSi(CH_3)_3]$ (**8**) was obtained in 58% yield from reaction of **1b** with the corresponding diyne. Previously, $[(C_6H_5)_3P]_2Pt(\eta^2\text{-}CH_3C{\equiv}CC{\equiv}CCH_3)$ (**7a**) and $[(C_6H_5)_3P]_2Pt(\eta^2\text{-}Me_3SiC{\equiv}CC{\equiv}CSiMe_3)$ were synthesized by similar routes [15].

In the ^1H NMR spectrum of **7b**, a doublet at δ 2.44 ($J_{PH} = 6.4$ Hz, $J_{PtH} = 40$ Hz) was assigned to the methyl

[1] The low deuterium incorporations are attributed to adventitious H sources in these small scale reactions.

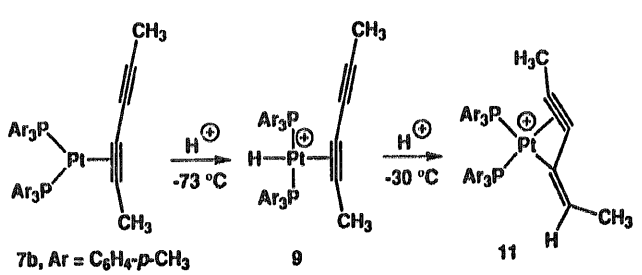
group on the coordinated alkyne due to its higher frequency chemical shift and larger platinum and phosphorus couplings compared with the doublet at δ 1.78 (J_{PH} = 3.4 Hz, J_{PtH} = 20 Hz), which was assigned to the methyl group on the uncoordinated alkyne. In the ^{31}P NMR spectrum of **7b**, the observation of two doublets at δ 28 (d, J_{PP} = 34 Hz, J_{PtP} = 3390 Hz) and 26 (d, J_{PP} = 34 Hz, J_{PtP} = 3610 Hz) requires a significant barrier to alkyne rotation and to migration of Pt between the two alkynes.

2.8. Protonation of platinum diyne complexes with $HBF_4 \cdot Et_2O$

Reaction of the yellow platinum diyne complexes with $HBF_4 \cdot Et_2O$ in CD_2Cl_2 at room temperature produced dark purple mixtures of intractable decomposition products. However, when protonation was carried out at low temperature, ^{1}H and ^{31}P NMR observation at low temperature provided evidence for initial formation of metal hydride intermediates that rearranged to π-propargyl complexes upon slow warming.

When the reaction of [(*p*-CH_3-C_6H_4)$_3$P]$_2$Pt(η^2-$CH_3C{\equiv}CC{\equiv}CCH_3$) (**7b**) with $HBF_4 \cdot Et_2O$ in CD_2Cl_2 at −73°C was monitored by low temperature NMR spectroscopy, evidence was obtained for protonation at platinum to produce the platinum hydride complex *trans*-[(*p*-CH_3-C_6H_4)$_3$P]$_2$PtH(η^2-$CH_3C{\equiv}CC{\equiv}CCH_3$)$^+$ BF_4^- (**9**) (Scheme 6). In the ^{1}H NMR spectrum at −73°C, a metal hydride resonance was observed at δ −9.13 (t, J_{PH} = 9.7 Hz, J_{PtH} = 1390 Hz). The small J_{PH} coupling is that expected for a hydride *cis* to two equivalent phosphines; *cis* J_{PH} couplings are usually less than 10 Hz, while *trans* J_{PH} couplings are normally greater than 100 Hz [16]. The observation of a single *p*-methyl resonance at δ 2.47 provided evidence for equivalent *trans* (*p*-CH_3-C_6H_4)$_3$P ligands. The observation of two methyl singlets at δ 1.65 and 2.30 (s, J_{PH} = 45 Hz) for the alkyne methyl groups provides evidence for an η^2-diyne complex with the alkyne ligand perpendicular to the plane of the platinum complex. Alkynes are known to coordinate perpendicular to the plane of Pt(II) complexes [17]. The observation of a single resonance at δ 30 (J_{PtP} = 2750 Hz) in the ^{31}P NMR spectrum at −73°C also supports the structure assigned to **9**.

Low temperature protonation of diyne complex **8** also produced the platinum hydride complex *trans*-[(*p*-CH_3-C_6H_4)$_3$P]$_2$PtH(η^2-$SiMe_3C{\equiv}CC{\equiv}CSiMe_3$)$^+$ BF_4^- (**10**),



Scheme 6.

which was characterized by low temperature NMR spectroscopy.

When a solution of the platinum hydride complex *trans*-[(*p*-CH_3-C_6H_4)$_3$P]$_2$PtH(η^2-$CH_3C{\equiv}CC{\equiv}CCH_3$)$^+$ BF_4^- (**9**) was warmed to −28°C, conversion to the π-propargyl complex [(*p*-CH_3-C_6H_4)$_3$P]$_2$Pt[η^3-($CH_3CH{=}$)$CC{\equiv}C$-CH_3]$^+$ BF_4^- (**11**) was observed by NMR spectroscopy. Decomposition of **11** occurred slowly over a day at −18°C. In the ^{1}H NMR spectrum of **11**, the appearance of a vinyl multiplet at δ 3.9 coupled to a methyl group at δ 1.7 (d, J = 6.5 Hz) provided evidence for an *exo*-ethylidene group; a broad singlet at δ 1.54 was assigned to the methyl group of the π-propargyl unit and methyl singlets at δ 2.40 and 2.33 were assigned to the inequivalent tris(*p*-tolyl)phosphine ligands. We are uncertain about the stereochemistry of the *exo*-ethylidene group but only a single isomer was seen. In the ^{31}P NMR spectrum, doublets at δ 14 (J_{PP} = 18 Hz, J_{PtP} = 4480 Hz) and δ 13 (J_{PP} = 18 Hz, J_{PtP} = 3330 Hz) were assigned to the inequivalent phosphine ligands. The synthesis of a number of π-propargyl platinum complexes and their reactions with nucleophiles have been reported [5].

Similarly, the platinum hydride complex *trans*-[(*p*-CH_3-C_6H_4)$_3$P]$_2$PtH(η^2-$SiMe_3C{\equiv}CC{\equiv}CSiMe_3$)$^+$ BF_4^- (**10**) rearranged to the π-propargyl complex [(*p*-CH_3-C_6H_4)$_3$P]$_2$-Pt[η^3-($Me_3SiCH{=}$)$CC{\equiv}CSiMe_3$]$^+$ BF_4^- (**12**) at −28°C.

2.9. Protonation of platinum diyne complexes with CF_3CO_2H

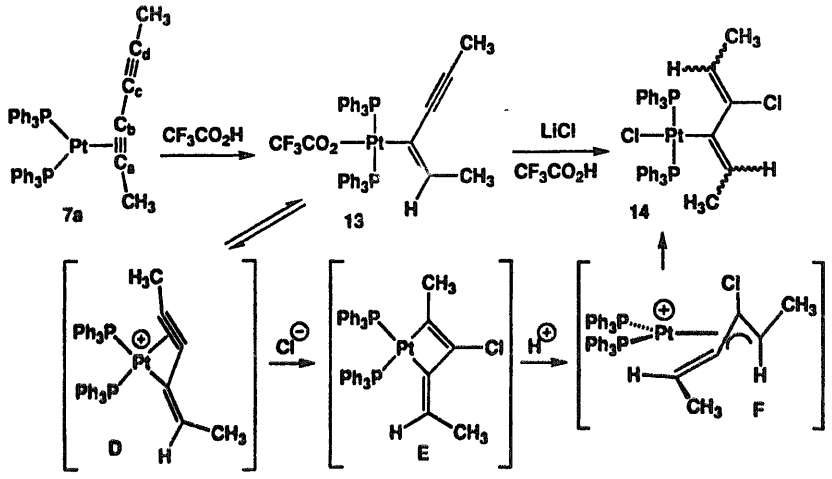
Addition of excess CF_3CO_2H to a yellow solution of diyne complex [(C_6H_5)$_3$P]$_2$Pt(η^2-$CH_3C{\equiv}CC{\equiv}CCH_3$) (**7a**) in CD_2Cl_2 produced an orange solution of the σ-propargyl complex *trans*-(Ph_3P)$_2$(CF_3CO_2)Pt[η^1-(*E*-$CH_3CH{=}$)$CC{\equiv}C$-CH_3] (**13**) (60% yield by NMR internal standard method), which decomposed upon attempted isolation (Scheme 7).

The structure of **13** was assigned spectroscopically. In the ^{31}P NMR spectrum, a single resonance at δ 23.6 (J_{PtP} = 3280 Hz) was assigned to the equivalent *trans* phosphines. In the ^{1}H NMR spectrum, a methyl singlet at δ 1.4 (J_{PtH} = 23 Hz) was assigned to the $\equiv CCH_3$ group and a doublet of triplets at δ 0.9 (dt, J_{HH} = 6.5 Hz, J_{PH} = 2.5 Hz) and a quartet at δ 4.4 (J_{HH} = 6.5, J_{PtH} = 75 Hz) were assigned to the $\equiv CHCH_3$ unit. The 75 Hz Pt–C≡C–H coupling is consistent with a configuration with Pt *cis* to H; typically *trans* couplings are ~135 Hz while *cis* couplings are ~70 Hz [18].

The fact that protonation of the enyne complex **2a** with excess CF_3CO_2H produced the ionic π-allyl complex **3a**, while protonation of diyne complex **7a** produced the neutral σ-propargyl complex **13**, is a reflection of the lower stability of π-propargyl complexes relative to π-allyl complexes.

2.10. In situ trapping of a π-propargyl complex by chloride

Addition of excess LiCl to a solution of σ-propargyl complex **13** containing excess CF_3CO_2H led to the isolation of



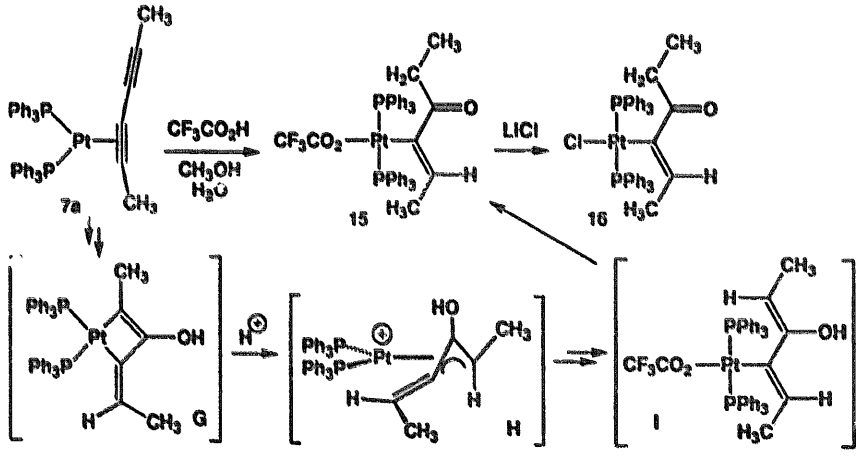
Scheme 7.

trans-$(Ph_3P)_2ClPt[\eta^1$-C(=CHCH$_3$)C(Cl)=CHCH$_3$] (**14**) as a white solid. The isotope pattern of the molecular ion in the mass spectrum provided definitive evidence for the addition of two equivalents of HCl to **7a** in the formation of **14**. The observation of a single resonance in the ^{31}P NMR spectrum of **14** at δ 23.5 (J_{PtP} = 3000 Hz) established the presence of equivalent *trans* phosphines. Evidence for two different =CHCH$_3$ units in **14** was obtained from ^{1}H NMR spectroscopy: one vinyl resonance at δ 6.9 (q, J = 6.5 Hz) was coupled to a methyl resonance at δ 1.41 (d, J = 6.5 Hz) while another vinyl resonance at δ 5.5 (q, J = 6.5 Hz, $J_{Pt,H}$ = 100 Hz) was coupled to a methyl resonance at δ 1.40 (d, J = 6.5 Hz).

While **14** is the formal product of the addition of HCl across the triple bond of **13** and replacement of the platinum bound trifluoroacetate by chloride, it is difficult to explain the regiochemistry of HCl addition across the triple bond by a simple addition to the alkyne. The formation of the σ-2-butadienyl complex **14** can be explained by invoking π-propargyl intermediate **D** as shown in Scheme 7. We suggest that σ-propargyl complex **13** may be in equilibrium with the ionic π-propargyl intermediate **D**. Nucleophilic attack of chloride at the central carbon of the propargyl unit would produce the metallacyclobutene intermediate **E**. We have previously observed addition of soft nucleophiles to the central carbon of rhenium π-propargyl complexes [3b]; more recently, the addition of nucleophiles to the central carbon of π-propargyl palladium and platinum complexes has been observed [5]. Protonation of the metallacycle to produce π-allyl cation **F**, followed by chloride attack at platinum completes the route to σ-2-butadienyl complex **14**.

2.11. *In situ trapping of a π-propargyl complex by water*

When excess CF_3CO_2H was condensed into a yellow CH_2Cl_2 solution of **7a** in the presence of wet methanol, an orange solution of *trans*-$(Ph_3P)_2(CF_3CO_2)Pt[\eta^1$-C(*Z*-=CHCH$_3$)COCH$_2CH_3$] (**15**) was produced (Scheme 8). Since attempts to isolate **15** led to decomposition, only spectral characterization was possible. ^{31}P NMR spectroscopy provided evidence for a single major species with equivalent *trans* phosphines (δ 22.7, J_{PtP} = 3180 Hz). ^{1}H NMR provided evidence for an ethyl group with a CH_2 quartet at δ 1.76 (q, J = 7 Hz) and a CH_3 triplet at δ 0.43 (t, J = 7 Hz) and for an ethylidene group with a vinyl resonance at δ 6.23 (J_{HH} = 7



Scheme 8.

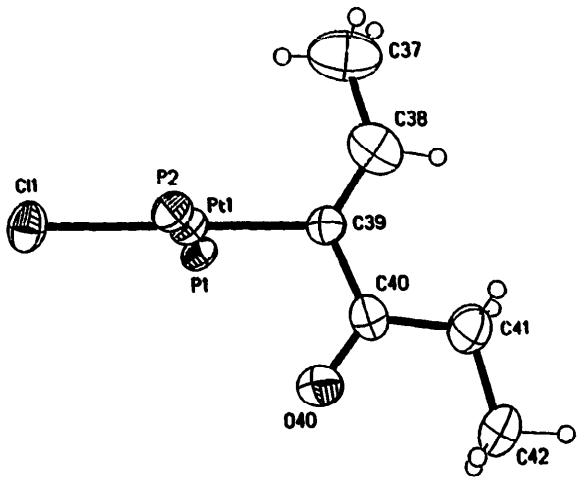


Fig. 1. X-ray crystal structure of *trans*-$(Ph_3P)_2ClPt[\eta^1\text{-}C(Z\text{-}=CHCH_3)\text{-}COCH_2CH_3]$ (**16**). Phenyl groups are omitted for clarity. Selected bond lengths (Å) and angles (°) for **16**: Pt–C(39), 2.038(8); C(38)–C(39), 1.339(13); C(39)–C(40), 1.477(13); C(40)–O, 1.221(11); Pt–C(39)–C(40), 115.1(6); Pt–C(39)–C(38), 123.4(8); C(39)–C(38)–O, 118.4(8).

Hz, $J_{Pt1} = 2$ Hz, $J_{Pt1} = 110$ Hz) and a methyl doublet at δ 1.45 ($J = 7$ Hz).

While protonation of platinum alkyne complexes normally produces *cis* Pt–C=C–H units, the Pt–C=C–H unit of **15** clearly has a *trans* geometry. We suggest that the *cis* isomer may be formed initially and then rearranged to the observed *trans* configuration by reversible protonation of the vinyl group of **H**. A similar reversible protonation was invoked to explain scrambling of deuterium into both the *cis* and *trans* positions of the vinylidene of π-allyl complex **3a** (Scheme 5).

Exchange of chloride with the platinum bound trifluoroacetate of **15** led to the isolation of the platinum chloride complex *trans*-$(Ph_3P)_2ClPt[\eta^1\text{-}C(Z\text{-}=CHCH_3)COCH_2CH_3]$ (**16**) in 10% yield after purification by thin layer chromatography on silica gel. The ^1H and ^{31}P NMR spectra of **16** were similar to those of the trifluoroacetate analog **15**. A ^{13}C NMR resonance at δ 186 and an IR band at 1653 cm^{-1} provided evidence for a ketone carbonyl. The X-ray crystal structure of **16** confirmed the structural assignment (Fig. 1).

The proposed mechanism for formation of **15** starts with nucleophilic attack on the π-propargyl intermediate by residual water to form metallacyclobutene complex **G**, followed by proton transfer to produce hydroxy-allyl complex **H**. It has been shown previously that protic nucleophiles add across platinum π-propargyl complexes to form similar π-allyl complexes [5]. Subsequent attack of trifluoroacetate at platinum would produce the σ-2-butadienyl complex **I**. Finally tautomerization of the enol of **I** to a ketone gives **15**.

3. Conclusions

Attempts to prepare π-propargyl platinum complexes by protonation of platinum(0) enyne complexes led instead to *exo*-vinylidene π-allyl complexes. Unstable π-propargyl complexes were successfully made by protonation of platinum(0) diyne complexes and products resulting from nucleophilic attack at the central carbon of the π-propargyl unit were obtained.

4. Experimental

4.1. General

Manipulations of air-sensitive compounds were performed either in a nitrogen atmosphere glovebox or by standard high-vacuum line techniques. Hexane, THF, THF-d_8, C_6H_6, C_6D_6 and diethyl ether were distilled from sodium and benzophenone. CH_2Cl_2 and CD_2Cl_2 were distilled from calcium hydride. Trifluoroacetic acid was distilled from phosphorus pentoxide.

^1H NMR spectra were obtained on a Bruker WP 200, WP 270, AC 250, AC 300 or AM 500 spectrometer. Yields were determined from ^1H NMR spectra using hexamethylbenzene as an internal standard. $^{13}C\{^1H\}$ NMR spectra were obtained on a Bruker AM 500 spectrometer operating at 126 MHz. $^{31}P\{^1H\}$ spectra were obtained on a Bruker AC 300 spectrometer operating at 121 MHz or a Bruker AM 500 operating at 202.5 MHz. IR spectra were measured on Mattson Genesis or Mattson Polaris FT-IR spectrometers. Mass spectra were determined on a VG AutoSpec M mass spectrometer. Elemental analyses were performed by Desert Analytics.

4.2. $[(p\text{-}CH_3\text{-}C_6H_4)_3P]_2Pt(\eta^2\text{-}H_2C{=}CH_2)$ (**1b**)

This complex was prepared by the procedure reported for the preparation of **1a** [19]. A solution of K_2PtCl_4 (375 mg, 0.90 mmol) in 10 ml of H_2O was added dropwise to a refluxing solution of $P(C_6H_4\ p\text{-}CH_3)_3$ (500 mg, 1.64 mmol) in 15 ml ethanol. After 2 h at reflux, the resulting solid was filtered, washed with H_2O (15 ml), EtOH (25 ml) and Et_2O (10 ml) to give $[(p\text{-}CH_3\text{-}C_6H_4)_3P]_2PtCl_2$ as an off-white solid (650 mg, 90%). The solid was dissolved in CH_2Cl_2 (12 ml) and EtOH (12 ml) at 0°C and ethylene was bubbled through the solution for 30 min. Addition of excess $NaBH_4$ (200 mg, 5.3 mmol) suspended in EtOH (30 ml) resulted in gas evolution and formation of a precipitate. The precipitate was filtered, washed with H_2O (30 ml), EtOH (10 ml) and cold Et_2O (3 ml) to give **1b** (490 mg, 80%) as a gray solid. ^1H NMR (C_6D_6, 200 MHz): δ 7.60 (m, H_o), 6.83 (m, H_m), 2.72 (d, $J_{Pt1} = 3$ Hz, $J_{Pt1} = 60$ Hz, $H_2C{=}CH_2$), 1.98 (s, $p\text{-}CH_3$).

4.3. $(Ph_3P)_2Pt[\eta^2\text{-}HC{\equiv}CC(CH_3){=}CH_2]$ (**2a**)

A solution of $(Ph_3P)_2Pt(\eta^2\text{-}H_2C{=}CH_2)$ (**1a**) (150 mg, 0.2 mmol) and excess 2-methyl-1-buten-3-yne (0.05 ml, 0.5 mmol) in benzene (2 ml) was stirred for 3 h. The solution was concentrated to 0.2 ml under vacuum, and hexane (20 ml) was added. The resulting precipitate was filtered and

washed with hexane (10 ml) to give **2a** (95 mg, 60%) as an off-white solid; m.p. (dec.) 130°C. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.57 (dm, H_o), 7.14 (s, J_{PtH} = 23 Hz, ≡CH), 6.91 (br d, H_m and H_p), 4.97, 4.85 (br s, =CH_2), 2.22 (br s, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202.5 MHz): δ 31 (d, J_{PP} = 35 Hz, J_{PtP} = 3080 Hz), 27 (d, J_{PP} = 35 Hz, J_{PtP} = 3440 Hz). MS (FAB): calc. (obs.) for $C_{41}H_{36}P_2Pt$ 786 (786). *Anal.* Calc. for $C_{41}H_{36}P_2Pt$: C, 62.67; H, 4.62. Found C, 62.28; H, 4.51%.

4.4. [(p-CH_3-C_6H_4)$_3$P]$_2$Pt[η^2-HC≡CC(CH_3)=CH_2] (2b)

Reaction of excess 2-methyl-1-buten-3-yne (1 mmol) with **1b** (210 mg, 0.25 mmol) in 5 ml THF for 3 h followed by evaporation of solvent and washing with 20 ml of hexane gave **2b** as a white solid (126 mg, 57%); m.p. (dec.) 146°C. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.25 (dd, J_{PH} = 5 Hz, J_{HH} = 4 Hz, H_o), 7.15 (dd, J_{PH} = 5 Hz, J_{HH} = 4 Hz, H_o'), 6.96 (d, J = 4 Hz, H_m), 6.91 (d, J = 4 Hz, H_m'), 6.75 (dd, J_{PH} = 11.5, 5 Hz, J_{PtH} = 26 Hz), 4.67 (br s, $\omega_{1/2}$ = 3.5 Hz, =C*H*H), 4.30 (br s, $\omega_{1/2}$ = 3.5 Hz, =CH*H*), 2.30 (s, *p*-CH_3), 2.28 (s, *p*-CH_3'), 1.99 (s, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121 MHz): δ 28.6 (d, J_{PP} = 33 Hz, J_{PtP} = 3540 Hz), 24.7 (d, J_{PP} = 33 Hz, J_{PtP} = 3440 Hz). MS (FAB): calc. (obs.) for $C_{47}H_{48}P_2Pt$ + H 870.3 (870.2).

4.5. (Ph_3P)$_2$Pt(η^2-CH_3C≡CC≡CCH_3) (7a)

2,4-Hexadiyne (200 mg, 2.6 mmol) and **1a** (380 mg, 0.44 mmol) in 10 ml THF were stirred overnight and the solvent was evaporated. The yellow residue was dissolved in 2 ml THF and 20 ml hexane were added to give **7a** (140 mg, 41%) as a yellow solid; m.p. (dec.) 153°C. ^{1}H NMR (C_6D_6, 300 MHz): δ 6.8–7.7 (Ph), 2.4 (d, J_{PH} = 8 Hz, J_{PtH} = 38 Hz, CH_3), 1.8 (d, J_{PH} = 3 Hz, J_{PtH} = 18 Hz, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202.5 MHz): δ 28.6 (d, J_{PP} = 33 Hz, J_{PtP} = 3576 Hz), 27.4 (d, J_{PP} = 33 Hz, J_{PtP} = 3280 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2, 126 MHz): δ 128–135 (m, Ph), 134.8 (d, J_{PC} = 12.5 Hz, C_γ), 125.3 (dd, J_{PC} = 72, 6 Hz, C_b), 100.6 (dd, J_{PC} = 72, 9 Hz, C_a), 95.5 (d, J_{PC} = 5 Hz, J_{PtC} = 25 Hz, C_d), 12.0 (m, J_{PtC} = 37 Hz, C≡CCH_3, bound alkyne), 5.6 (s, C≡CCH_3, free alkyne) (see Scheme 7 for assignments of C_a, etc.). MS (FAB): calc. (obs.) for $C_{41}H_{36}P_2Pt$ 786 (786).

4.6. [(p-CH_3-C_6H_4)$_3$P]$_2$Pt(η^2-CH_3C≡CC≡CCH_3) (7b)

Reaction of **1b** (55 mg, 0.066 mmol) and 2,4-hexadiyne (8 mg, 0.1 mmol) in THF (3 ml) for 3 h, followed by evaporation of solvent, and washing with pentane (10 ml) gave **7b** (40 mg, 68%) as a white–yellow solid. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.8–7.5 (m, H_o), 6.9–6.7 (m, H_m), 2.44 (d, J_{PH} = 6.4 Hz, J_{PtH} = 40 Hz, CH_3), 2.00, 1.97 (s, *p*-CH_3s); 1.78 (d, J_{PH} = 3.4 Hz, J_{PtH} = 20 Hz, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202.5 MHz): δ 28 (d, J_{PP} = 34 Hz, J_{PtP} = 3390 Hz), 26 (d, J_{PP} = 34 Hz, J_{PtP} = 3610 Hz). MS (FAB): calc. (obs.) for $C_{42}H_{36}P_2Pt$ 797.2 (797.1).

4.7. [(p-CH_3-C_6H_4)$_3$P]$_2$Pt[η^2-(CH_3)$_3$SiC≡CC≡CSi(CH_3)$_3$] (8)

Reaction of **1b** (50 mg, 0.06 mmol) and (CH_3)$_3$Si–C≡CC≡CSi(CH_3)$_3$ (15 mg, 0.077 mmol) in THF (2 ml) for 3 h, followed by evaporation of solvent, and washing with hexane (1 ml) gave **8** as a yellow solid (35 mg, 58%). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 7.25 (m, H_o), 6.97 (m, H_m), 2.31 (s, *p* CH_3s), 0.11, −0.15 (s, Si(CH_3)$_3$s). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202.5 MHz): δ 27 (d, J_{PP} = 35 Hz, J_{PtP} = 3670 Hz), 26 (d, J_{PP} = 35 Hz, J_{PtP} = 3720 Hz). MS (FAB): calc. (obs.) for $C_{52}H_{60}P_2PtSi_2$ 998 (998). *Anal.* Calc. for $C_{52}H_{60}P_2PtSi_2$: C, 62.57; H, 6.06. Found: C, 62.92; H, 6.05%.

4.8. (Ph_3P)$_2$Pt[η^3-H_2C=CC(CH_3)=CH_2]$^+$ BF_4^- (3a-BF_4)

Addition of excess HBF_4·Et_2O (0.05 ml, 85%, 0.30 mmol) to a benzene solution of **2a** (20 mg, 0.025 mmol) gave a red–orange solution. Addition of Et_2O gave a pale orange precipitate, which was filtered and washed with Et_2O (10 ml) to give **3a-BF_4** (15 mg, 69%) as a pale yellow solid. ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 7.6–7.0 (m, C_6H_5s), 5.63 (dm, H_d), 4.10 (m, J_{PH} = 11.1 Hz, J_{PtH} = 31.1 Hz, H_c), 3.71 (br s, H_b), 3.35 (m, J_{PH} = 7.8 Hz, J_{PtH} = 33.0 Hz, H_a), 2.18 (s, J_{PtH} = 66.5 Hz, CH_3) (see Scheme 2 for assignments of H_a, etc.). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 23 (d, J_{PP} = 11 Hz, J_{PtP} = 4190 Hz), 15 (d, J_{PP} = 11 Hz, J_{PtP} = 3300 Hz). MS (FAB): calc. (obs.) for $C_{41}H_{37}P_2PtBF_4 - BF_4$ 786 (786). *Anal.* Calc. for $C_{41}H_{37}P_2PtBF_4$: C, 56.37; H, 4.27. Found: C, 56.09; H, 4.04%.

4.9. (Ph_3P)$_2$Pt[η^3-H_2C=CC(CH_3)=CH_2]$^+$ $CF_3CO_2^-$ (3a-CF_3CO_2)

CF_3CO_2H (0.02 mmol) was added to an NMR tube containing a CD_2Cl_2 solution of **2a** (10 mg, 0.013 mmol) and C_6Me_6 (internal NMR integration standard) to give a purple solution of **3a-CF_3CO_2** (93% NMR yield). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.1–7.8 (Ph), 5.61 (ddd, J_{PH} = 17, 7 Hz, J_{HH} = 3 Hz, J_{PtH} = 24 Hz, H_d), 4.10 (dt, J_{PH} = 11, 3 Hz, J_{HH} = 3 Hz, J_{PtH} = 22 Hz, H_c), 3.70 (br s, $\omega_{1/2}$ = 8 Hz, H_b), 3.34 (d, J_{PH} = 8 Hz, J_{PtH} = 34 Hz, H_a), 2.17 (s, J_{PtH} = 66 Hz, CH_3) (see Scheme 3 for assignments of H_a, etc.). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121 MHz): δ 23 (d, J_{PP} = 11 Hz, J_{PtP} = 4140 Hz), 15 (d, J_{PP} = 11 Hz, J_{PtP} = 3270 Hz).

4.10. [(p-CH_3-C_6H_4)$_3$P]$_2$Pt[η^3-H_2C=CC(CH_3)=CH_2]$^+$ $CF_3CO_2^-$ (3b-CF_3CO_2)

CF_3CO_2H (0.02 mmol) was added to an NMR tube containing a CD_2Cl_2 solution of **2b** (10 mg, 0.013 mmol) and C_6Me_6 (internal NMR integration standard) to give a purple solution of **3b-CF_3CO_2** (84% NMR yield). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.0–7.5 (*o*, *m*-tolyl), 5.59 (ddd, J_{PH} = 17, 7 Hz, J_{HH} = 3 Hz, J_{PtH} = 25 Hz, H_d), 4.10 (d,

J_{PH} = 12 Hz, J_{PtH} = 24 Hz, H_c), 3.63 (br s, $\omega_{1/2}$ = 8 Hz, H_b), 3.30 (d, J_{PH} = 8 Hz, J_{PtH} = 34 Hz, H_a), 2.37 (s, *p*-CH_3s), 2.13 (s, J_{PtH} = 66 Hz, CH_3) (see Scheme 5 for assignments of H_a, etc.). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz): δ 21.3 (d, J_{PP} = 11 Hz, J_{PtP} = 4160 Hz), 13.7 (d, J_{PP} = 11 Hz, J_{PtP} = 3290 Hz).

4.11. *Trans*-$(Ph_3P)_2(CF_3CO_2)Pt[\eta^1$-$H_2C{=}CC(CH_3){=}CH_2]$ (4)

CF_3CO_2H (0.06 mmol) was added to an NMR tube containing a THF-d_8 solution of **2a** (20 mg, 0.026 mmol) and C_6Me_6 (internal NMR integration standard) to give a yellow solution of **4** (73% NMR yield). ^1H NMR (THF-d_8, 300 MHz): δ 7.2–7.8 (Ph), 5.77 (d, J_{HH} = 3 Hz, H_a), 5.18 (s, J_{PtH} = 122 Hz, H_d), 4.71 (s, J_{PtH} = 68 Hz, H_c), 4.27 (br s, $\omega_{1/2}$ = 9 Hz, H_b), 1.11 (s, CH_3) (see Scheme 3 for assignments of H_a, etc.). $^{31}P\{^1H\}$ NMR (THF-d_8, 121 MHz): δ 27 (s, J_{PtP} = 3290 Hz). $^{13}C\{^1H\}$ NMR (THF-d_8, 126 MHz): δ 159.6 (q, J_{CF} = 38 Hz, CF_3CO_2), 148.4 (s, CCH_3), 138.0 (t, J_{PC} = 9 Hz, PtC), 135–128 (m, Ph), 120.7 (s, J_{PtC} = 60 Hz, $PtC{=}CH_2$), 118.5 (q, J_{CF} = 195 Hz, J_{PtC} = 44 Hz, CF_3CO_2), 118.0 (s, $C(CH_3){=}CH_2$), 20.2 (s, CH_3).

CF_3CO_2H (0.03 mmol) was added to an NMR tube containing a CD_2Cl_2 solution of **2a** (20 mg, 0.026 mmol) and C_6Me_6 (internal NMR integration standard) to give an orange solution of **4** (77% NMR yield). ^1H NMR (CD_2Cl_2, 300 MHz): δ 7.2–7.8 (Ph), 5.76 (d, J_{HH} = 3 Hz, H_a), 5.24 (s, J_{PtH} = 122 Hz, H_d), 4.75 (s, J_{PtH} = 68 Hz, H_c), 4.34 (br s, $\omega_{1/2}$ = 9 Hz, H_b), 1.12 (s, CH_3) (see Scheme 3 for assignments of H_a, etc.). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz): δ 23 (s, J_{PtP} = 3280 Hz).

4.12. $(Ph_3P)_2Pt[\eta^1$-$CH_3C(CF_3CO_2)C(CH_3)CH_2]^+$ $CF_3CO_2^-$ (5a and 6a)

CF_3CO_2H (0.02 mmol) was added to an NMR tube containing a CD_2Cl_2 solution of **2a** (10 mg, 0.013 mmol) and C_6Me_6 (internal NMR integration standard). After 16 h, a 1:1.8 mixture of **5a** and **6a** (62% combined NMR yield) was observed. *Anti*-CH_3 isomer **5a**: ^1H NMR (CD_2Cl_2, 300 MHz): δ 7.2–7.8 (Ph), 3.4 (m, H_b), 2.9 (d, J_{PH} = 9 Hz, J_{PtH} = 36 Hz, H_a), 2.06 (s, J_{PtH} = 54 Hz, central CH_3), 1.22 (dd, J_{PH} = 7.5, 3 Hz, J_{PtH} = 24 Hz, *anti*-CH_3) (see Scheme 4 for assignments of H_a, etc.). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202.5 MHz): δ 17.5 (d, J_{PP} = 13 Hz, J_{PtP} = 3930 Hz), 14.7 (d, J_{PP} = 13 Hz, J_{PtP} = 3580 Hz). *Syn*-CH_3 isomer **6a**: ^1H NMR (CD_2Cl_2, 300 MHz): δ 7.2–7.8 (Ph), 3.3 (m, H_b), 2.9 (d, J_{PH} = 9 Hz, J_{PtH} = 36 Hz, H_a) 2.03 (s, J_{PtH} = 62 Hz, central CH_3), 1.12 (d, J_{PH} = 4.5 Hz, J_{PtH} = 6 Hz, *syn*-CH_3) (see Scheme 4 for assignments of H_a, etc.). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202.5 MHz): δ 17.6 (d, J_{PP} = 12.1 Hz, J_{PtP} = 3810 Hz), 14.7 (d, J_{PP} = 12.1 Hz, J_{PtP} = 3580 Hz).

4.13. $[(p\text{-}CH_3\text{-}C_6H_4)_3P]_2Pt[\eta^3$-$CH_3C(CF_3CO_2)$-$C(CH_3)CH_2]^+$ $CF_3CO_2^-$ (5b and 6b)

CF_3CO_2H (0.02 mmol) was added to an NMR tube containing a CD_2Cl_2 solution of **2b** (10 mg, 0.013 mmol) and C_6Me_6 (internal NMR integration standard). After 24 h, a 1:2 mixture of **5b** and **6b** (77% combined NMR yield) was observed. *Anti*-CH_3 isomer **5b**: ^1H NMR (CD_2Cl_2, 300 MHz): δ 7.0–7.4 (*m*, *o*-tolyl), 3.30 (m, H_b), 2.90 (dd, J_{PH} = 9, 3 Hz, J_{PtH} = 36 Hz, H_a), 2.380 (s, *p*-tolyl CH_3), 2.375 (s, *p*-tolyl CH_3'), 2.02 (s, J_{PtH} = 57 Hz, central CH_3), 1.20 (dd, J_{PH} = 8, 3 Hz, J_{PtH} = 14 Hz, *anti*-CH_3) (see Scheme 5 for assignments of H_a, etc.). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz): δ 16.5 (d, J_{PP} = 13.5 Hz, J_{PtP} = 3930 Hz), 12.8 (d, J_{PP} = 13.5 Hz, J_{PtP} = 3580 Hz). *Syn*-CH_3 isomer **6b**: ^1H NMR (CD_2Cl_2, 300 MHz): δ 7.0–7.4 (*m*, *o*-tolyl), 3.30 (m, H_b), 2.84 (dd, J_{PH} = 9, 3 Hz, J_{PtH} = 36 Hz, H_a), 2.39 (s, *p*-tolyl CH_3), 2.36 (s, *p*-tolyl CH_3'), 1.98 (s, J_{PtH} = 60 Hz, central CH_3), 1.18 (d, J_{PH} = 4 Hz, J_{PtH} = 7 Hz, *syn*-CH_3) (see Scheme 5 for assignments of H_a, etc.). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz): δ 15.9 (d, J_{PP} = 12.6 Hz, J_{PtP} = 3950 Hz), 12.7 (d, J_{PP} = 12.6 Hz, J_{PtP} = 3610 Hz).

4.14. *Trans*-$[(p\text{-}CH_3\text{-}C_6H_4)_3P]_2PtH$-$(\eta^2$-$CH_3C{\equiv}CC{\equiv}CCH_3)^+$ BF_4^- (9) and $[(p\text{-}CH_3\text{-}C_6H_4)_3P]_2$-$Pt[\eta^3$-$(CH_3CH{=})CC{\equiv}CCH_3]^+$ BF_4^- (11)

$HBF_4 \cdot Et_2O$ (5 μl, 85%, 0.030 mmol) was added by syringe to a concentrated solution of **7b** (20 mg, 0.023 mmol) containing C_6Me_6 (internal NMR integration standard) in CD_2Cl_2 (0.3 ml) at −78°C. The resulting purple solution of **9** was analyzed by ^1H NMR in a probe pre-cooled to −73°C. Upon warming to −28°C in the NMR probe, conversion of **9** to **11** occurred. For **9**: ^1H NMR (CD_2Cl_2, −73°C, 500 MHz): δ 7.5–7.2 (m, H_o and H_m), 2.47 (s, *p*-CH_3), 2.30 (s, J_{PtH} = 45 Hz, CH_3), 1.65 (s, CH_3), −9.13 (t, J_{PH} = 9.7 Hz, J_{PtH} = 1390 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −73°C, 202.5 MHz): δ 30 (br s, J_{PtP} = 2750 Hz). For **11**: ^1H NMR (CD_2Cl_2, −28°C, 500 MHz): δ 7.5–6.9 (m, H_o and H_m), 3.9 (m, $=CHCH_3$), 2.40 (s, *p*-CH_3), 2.33 (s, *p*-CH_3), 1.74 (d, J = 7.6 Hz, $=CHCH_3$), 1.54 (br s, $C{\equiv}CCH_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −33°C, 202.5 MHz): δ 14 (d, J_{PP} = 18 Hz, J_{PtP} = 4480 Hz), 13 (d, J_{PP} = 18 Hz, J_{PtP} = 3330 Hz).

4.15. *Trans*-$[(p\text{-}CH_3\text{-}C_6H_4)_3P]_2PtH$-$(\eta^2$-$SiMe_3C{\equiv}CC{\equiv}SiMe_3)^+$ BF_4^- (10) and $[(p\text{-}CH_3\text{-}C_6H_4)_3P]_2$-$Pt[\eta^3$-$(Me_3SiCH{=})CC{\equiv}CSiMe_3]^+$ BF_4^- (12)

$HBF_4 \cdot Et_2O$ (5 μl, 85%, 0.030 mmol) was added by syringe to a concentrated solution of **8** (20 mg, 0.020 mmol) containing C_6Me_6 (internal NMR integration standard) in CD_2Cl_2 (0.3 ml) at −78°C. The resulting dark brown solution of **10** was analyzed by ^1H NMR in a probe pre-cooled to −73°C. Upon warming to −28°C in the NMR probe, conversion of **10** to **12** occurred. For **10**: ^1H NMR (CD_2Cl_2, −73°C, 500 MHz): δ 7.6–6.9 (m, H_o and H_m), 2.37 (s, *p*-

CH_3), −0.12, −0.41 (s, $Si(CH_3)_3$s), −9.24 (t, J_{PH} = 7.6 Hz, J_{PtH} = 1450 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −73°C, 202.5 MHz): δ 26 (br s, J_{PtP} = 2770 Hz). For **12**: ^1H NMR (CD_2Cl_2, −23°C, 500 MHz): δ 7.4–6.8 (m, H_o and H_m), 4.25 (m, =CH), 2.35, 2.33 (s, *p*-CH_3s), 0.04, −0.31 (s, $Si(CH_3)_3$s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −23°C, 202.5 MHz): δ 16 (d, J_{PP} = 20 Hz, J_{PtP} = 4950 Hz), 12 (d, J_{PP} = 20 Hz, J_{PtP} = 3030 Hz).

4.16. *Trans*-$(Ph_3P)_2(CF_3CO_2)Pt$-[η^1-(*E*-$CH_3CH{=})CC{\equiv}CCH_3$] (13)

CF_3CO_2H (0.04 mmol) was added to an NMR tube containing a CD_2Cl_2 solution of **7a** (10 mg, 0.013 mmol) and C_6Me_6 (internal NMR integration standard) to give an orange solution of **13** (60% NMR yield). ^1H NMR (CD_2Cl_2, 300 MHz): δ 7.0–7.5 (Ph), 4.4 (q, J_{HH} = 6.5 Hz, J_{PtH} = 75 Hz, =CH), 1.4 (s, J_{PtH} = 23 Hz, $\equiv CCH_3$), 0.9 (dt, J_{HH} = 6.5 Hz, J_{PH} = 2.5 Hz, $=CCH_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz): δ 23.6 (s, J_{PtP} = 3280 Hz).

4.17. *Trans*-$(Ph_3P)_2ClPt[\eta^1$-$C(=CHCH_3)C(Cl)=CHCH_3]$ (14)

CF_3CO_2H (0.04 mmol) was added to a yellow solution of **7a** (100 mg, 0.13 mmol) in 5 ml CH_2Cl_2. After 10 min, excess LiCl (100 mg, 2.4 mmol) was added. Solvent was evaporated under vacuum to give a brown residue. Thin layer chromatography (silica gel, CH_2Cl_2) gave **14** (5 mg, 5%) as white crystals. ^1H NMR (CD_2Cl_2, 300 MHz): δ 7.0–7.7 (Ph), 6.9 (q, J_{HH} = 6.5 Hz, CCl=C*H*Me), 5.5 (q, J_{HH} = 6.5 Hz, J_{PtH} = 100 Hz, PtC=C*H*Me), 1.410 (d, *J* = 6.5 Hz, CH_3), 1.402 (d, *J* = 6.5 Hz, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz): δ 23.5 (s, J_{PtP} = 3000 Hz). HRMS (FAB): calc. (obs.) for $C_{42}H_{38}Cl_2P_2Pt$ 870.1474 (870.1467).

4.18. *Trans*-$(Ph_3P)_2(CF_3CO_2)Pt[\eta^1$-$C(Z$-$=CHCH_3)$-$COCH_2CH_3]$ (15)

CF_3CO_2H (1 mmol) was added to a yellow solution of **7a** (100 mg, 0.13 mmol) in 5 ml CH_2Cl_2 and 5 ml MeOH. After 3 h, solvent was evaporated to give **15** as a solid. ^1H NMR (CD_2Cl_2, 300 MHz): δ 7.2–7.8 (Ph), 6.23 (qt, J_{HH} = 7 Hz, J_{PH} = 2 Hz, J_{PtH} = 110 Hz, =C*H*Me), 1.76 (q, *J* = 7 Hz, CH_2Me), 0.43 (t, *J* = 7 Hz, CH_2CH_3), 1.45 (d, *J* = 7 Hz, $=CHCH_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz): δ 22.7 (s, J_{PtP} = 3180 Hz).

4.19. *Trans*-$(Ph_3P)_2ClPt[\eta^1$-$C(Z$-$=CHCH_3)COCH_2CH_3]$ (16)

CF_3CO_2H (1 mmol) was added to a yellow solution of **7a** (100 mg, 0.13 mmol) in 5 ml CH_2Cl_2 and 5 ml MeOH. After 3 h, LiCl (50 mg, 1.2 mmol) was added and solvent was evaporated under vacuum to give a brown residue. Thin layer chromatography (silica gel, 1:1 hexane:ether) gave **16** (10 mg, 10%) as white crystals. ^1H NMR (CD_2Cl_2, 300 MHz): δ 7.2–7.8 (Ph), 6.25 (q, J_{HH} = 7 Hz, J_{PtH} = 112 Hz, =C*H*Me), 1.65 (d, J_{HH} = 7 Hz, J_{PtH} = 12 Hz, $=CHCH_3$), 1.4 (q, *J* = 7 Hz, CH_2CH_3), 0.4 (t, *J* = 7 Hz, CH_2CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz): δ 23.9 (s, J_{PtP} = 3120 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz): δ 186 (C=O), 144 (*C*H=C), 128–135 (Ph), 107 (PtC=*C*), 30.0 (CH_2), 21.4 (C=CCH_3), 8.7 (CH_2CH_3).

Table 1
Crystal data and structure refinement for **16**

Empirical formula	$C_{42}H_{39}ClOP_2Pt$
Crystal color, habit	yellow prism
Crystal size	0.40×0.40×0.10 mm
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	11.9062(2)
b (Å)	18.4314(4)
c (Å)	18.0104(3)
β (°)	107.907(2)
Volume (Å^3)	37.60.88(12)
Peaks to determine cell	8192
θ Range of cell peaks (°)	2.5–26.0
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Z	4
Formula weight	852.21
Density (calc.) (Mg m^{-3})	1.505
Absorption coefficient (mm^{-1})	3.918
F(000)	1696
$R(F)$ [a] (%)	5.15
$wR(F^2)$ [a] (%)	13.81

[a] *R* factors are defined as follows: $R(F) = \{\Sigma F_o - kF_c\}/\Sigma F_o$; $wR(F^2) = (\{\Sigma w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\})^{1/2}$.

4.20. *X-ray crystallography of trans*-$(Ph_3P)_2ClPt$-[η^1-$C(Z$-$=CHCH_3)COCH_2CH_3$] (16)

Crystals of **16** suitable for X-ray analysis were obtained by slow evaporation of a CD_2Cl_2 solution. A yellow prism-shaped crystal of dimensions 0.40×0.40×0.10 mm was selected for structural analysis. The X-ray diffraction study was performed with a Siemens SMART ccd area detector mounted on a Siemens P4 diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). With the sample at χ = 40°, the intensity data were measured as a series of 1210 φ-oscillation frames each of 0.3°/frame for 30 s/frame. The detector was positioned 5.26 cm from the sample. Cell parameters were determined from a non-linear least-squares fit to the settings angles of 8192 peaks in the range 2.5 < θ < 25°. Standard reflections for each data set showed no significant decrease in intensity throughout acquisition. A total of 13672 data was measured to θ_{max} = 26.08°. A semi-empirical absorption correction was applied that gave minimum and maximum transmittances of 0.596 and 0.958, respectively. The data were merged to form a set of 5907 independent data with R_{int} = 0.0510. The space group $P2_1/c$ was determined by systematic absences and statistical tests,

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **16**

	x	y	z	U_{eq} [a]
Pt(1)	422(1)	6084(1)	7585(1)	48(1)
Cl(1)	−259(3)	4915(1)	7028(1)	72(1)
P(1)	2263(2)	5802(1)	7513(1)	47(1)
P(2)	−1365(2)	6288(1)	7782(1)	45(1)
C(1)	2370(8)	5615(4)	6546(5)	49(2)
C(2)	1378(9)	5590(5)	5908(5)	55(2)
C(3)	1436(11)	5452(5)	5160(5)	74(3)
C(4)	2516(12)	5338(5)	5063(6)	73(3)
C(5)	3532(11)	5354(5)	5681(6)	75(3)
C(6)	3463(9)	5506(5)	6429(5)	57(2)
C(7)	2783(9)	4999(5)	8091(5)	58(2)
C(8)	2636(14)	4955(6)	8828(6)	106(5)
C(9)	3006(17)	4346(7)	9288(7)	131(7)
C(10)	3493(16)	3775(6)	9014(8)	112(5)
C(11)	3648(12)	3808(5)	8308(7)	84(3)
C(12)	3287(10)	4419(5)	7841(6)	64(3)
C(13)	3443(8)	6471(5)	7883(5)	52(2)
C(14)	4349(10)	6385(6)	8548(6)	75(3)
C(15)	5221(12)	6931(8)	8813(7)	99(4)
C(16)	5114(13)	7569(8)	8398(8)	99(4)
C(17)	4197(12)	7655(6)	7731(7)	81(3)
C(18)	3347(9)	7110(5)	7463(5)	62(2)
C(19)	−1443(8)	7041(5)	8434(4)	49(2)
C(20)	−1372(9)	6923(5)	9205(5)	65(3)
C(21)	−1318(11)	7511(7)	9691(6)	84(3)
C(22)	−1307(10)	8213(7)	9432(6)	80(3)
C(23)	−1372(10)	8329(6)	8677(7)	77(3)
C(24)	−1453(10)	7745(5)	8173(6)	64(3)
C(25)	−2584(8)	6484(4)	6897(4)	46(2)
C(26)	−3607(9)	6794(4)	6930(5)	53(2)
C(27)	−4512(9)	6915(5)	6268(5)	59(2)
C(28)	−4425(10)	6735(5)	5537(5)	63(2)
C(29)	−3384(9)	6420(5)	5514(5)	65(3)
C(30)	−2452(9)	6289(5)	6178(5)	61(2)
C(31)	−1848(8)	5511(4)	8242(5)	50(2)
C(32)	−2999(11)	5361(6)	8136(7)	82(3)
C(33)	−3324(14)	4812(7)	8564(8)	111(5)
C(34)	−2472(14)	4413(6)	9076(7)	91(4)
C(35)	−1345(13)	4547(6)	9183(6)	84(3)
C(36)	−988(11)	5089(6)	8776(5)	77(3)
C(37)	329(15)	7775(9)	6820(8)	131(6)
C(38)	879(12)	7682(7)	7635(7)	88(4)
C(39)	1012(8)	7071(5)	8055(5)	50(2)
C(40)	1542(10)	7078(5)	8912(6)	64(3)
O(40)	1589(10)	6508(4)	9266(4)	109(3)
C(41)	1937(11)	7754(6)	9345(6)	81(3)
C(42)	2314(15)	7645(6)	10210(7)	116(5)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

and confirmed by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 [20]. A total of 424 parameters was refined against 5906 data to give $wR(F^2) = 0.1381$ and $S = 1.191$ using weights of $w = 1/[\sigma^2(F^2) + (0.0601P)^2 + 7.6831P]$, where $P = [F_o^2 + 2F_c^2]/3$. The final $R(F)$ was 0.0515 for the 4697 observed ($I > 2\sigma(I)$) data. The largest shift/e.s.d. was −0.014 in the final refinement cycle. The final difference map had maxima and minima of 1.416 and −1.021 e $Å^{-1}$, respectively. Crystallographic data are given in Table 1. Atomic coordinates are given in Table 2.

5. Supplementary material

The atomic positional parameters for **16** have been deposited with the Cambridge Crystallographic Data Centre.

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