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Journal of Organometallic Chemistry 520 (1996) 85–96

Journal of Organometallic Chemistry

Regioselective addition of chalcogenol to an η^3-propargyl/allenyl complex via formation of the carbon–chalcogen bond leading to new chalcogenoxyallyl species [1]

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Received 30 January 1996

Abstract

Regioselective addition of chalcogenol to an η^3-propargyl complex $[Pt(PPh_3)_2(\eta^3\text{-}C_3H_3)](BF_4)$ (**2**) via the formation of the C–O, C–S, or C–Se bond generates new cationic chalcogenoxyallyl species $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(ER)CH_2]\}(BF_4)$ (E = O, R = Me (**4a**), Et (**4b**), ^{i}Pr (**4c**), ^{t}Bu (**4d**), Ph (**4e**); E = S, R = Et (**5b**), ^{i}Pr (**5c**), ^{t}Bu (**5d**), Ph (**5e**); E = Se, R = Ph (**6e**)) respectively in good yields. Thiol and selenol react with complex **2** much faster than alcohol; and **2** reacts with p-$(HO)C_6H_4(SH)$ to exclusively yield the thioxyallyl product $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(SC_6H_4OH)CH_2]\}(BF_4)$ (**5f**). Among the alcohols and phenol, the reactivity follows the order MeOH > EtOH > ^{i}PrOH > ^{t}BuOH > PhOH. A mechanism comprising a preceding coordination step is postulated. The X-ray structures of **4b**, **4e**, **5b**, **5e** and **6e** are provided.

Keywords: Platinum; Regioselective addition reactions; X-ray structure analysis; Allenyl; Propargyl; Carbon–chalcogen bond formation

1. Introduction

The chemistry of transition metal complexes with the propargyl or allenyl ligand of η^3-mold has recently attracted much attention [1–6]. These new organometallic species have been found to exhibit a remarkable bond-forming ability. Through facile regioselective nucleophilic addition at the central carbon of the ligand, the propargyl/allenyl complexes can be readily transformed into other organometallic species such as substituted allyl or trimethylenemethane derivatives. In typical cases, the cationic η^3-propargyl/allenyl complexes have been found to react with water and methanol to generate hydroxyallyl and methoxyallyl species via the construction of a C–O bond [7–10]. In this article, we report our continued studies of the reactions of an η^3-propargyl/allenyl complex of platinum with a variety of chalcogenols. Such reactions lead to the synthesis of new η^3-chalcogenoxyallyl complexes by undergoing C–O, C–S, and C–Se bond-forming routes. The reaction mechanism has been investigated.

2. Results and discussion

2.1. Synthesis and spectral characterization of η^3-chalcogenoxyallyl complexes

The cationic η^3-propargyl/allenyl complex of platinum $[Pt(PPh_3)_2(\eta^3\text{-}C_3H_3)](BF_4)$ (**2**) was prepared by reaction of *trans*-$Pt(Br)(PPh_3)_2(\eta^1\text{-}CHCCH_2)$ (**1**) with $AgBF_4$ and was often used in situ for the ensuing reactions [7]. The reaction of **2** with equimolar amounts of absolute ethanol in predried chloroform at −20 °C yielded $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(OEt)CH_2]\}(BF_4)$ (**4b**). Using a large excess of ethanol it is possible to avoid the concurrent formation of $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(OH)\text{-}CH_2]\}(BF_4)$ (**3**) resulting from the reaction of **2** with water. The isolated yield of **4b** was 65%. In the ^{31}P NMR spectrum of **4b**, a singlet at δ 17.5 (J_{P-Pt} = 3678 Hz) indicated that its two PPh_3 are magnetically equivalent. The *syn*- and *anti*-hydrogens of **4b** were located at δ 3.05 and 2.81 respectively in the ^1H NMR spectrum;

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[1] This paper is dedicated to the late Professor Hidemasa Takaya of Kyoto University.

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PII S002-328X(96)06269-9

and its ^{13}C data of the terminal and allyl central carbons were found at δ 52.7 and 155.7. In such a reaction, the C–O bond was established exclusively at the central carbon of the η^3-propargyl/allenyl ligand. Analogous regioselective addition of another alcohol to **2** yielded the corresponding alkoxyallyl derivatives $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(OR)CH_2]\}(BF_4)$ (R = Me (**4a**), ^iPr (**4c**), ^tBu (**4d**)) also in good yields. Intriguingly, the poor nucleophile as phenol could also react with **2**, resulting in $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(OPh)CH_2]\}(BF_4)$ (**4e**). When 20 equivalents of phenol was used, **4e** was obtained in 74% yield. The allyl hydrogens of **4e** overlapped at δ 3.05. The ^{13}C data of the two allyl carbons of **4e** (at δ 55.0 and 152.7) are comparable with those of **4b**.

As for the synthesis of alkoxy- and phenoxyallyl via the formation of the C–O bond, the build-up of the C–S and C–Se bonds leading to the new thioxy- and selenoxyallyl complexes $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(ER)CH_2]\}(BF_4)$ (E = S, R = Et (**5b**), ^iPr (**5c**), ^tBu (**5d**), Ph (**5e**); E = Se, R = Ph (**6e**)) could be achieved by adding thiol, thiophenol, or selenophenol respectively to complex **2** (Scheme 1). The use of excess RSH or RSeH would result in the formation of bis-chalcogenolato complexes *cis*-$Pt(ER)_2(PPh_3)_2$ (E = S, Se) which had been dissolved well in benzene and thus could be easily removed from the desired chalcogenoxyallyl products. The NMR data of the thioxyallyl complexes are generally comparable with those of the alkoxyallyl complexes. The *syn*- and *anti*-hydrogens of **5e** were found at δ 3.26 and 3.13, and its terminal and central carbons of allyl were at δ 63.0 and 142.3. The corresponding ^1H NMR data of **6e** were at δ 3.34; and ^{13}C data were at δ 66.2 and 124.0. The substantial high-field shift of the allyl central carbon in **4e**, **5e**, and **6e** is consistent with the decreasing order of the electron-withdrawing ability of the chalcogenoxy substituent.

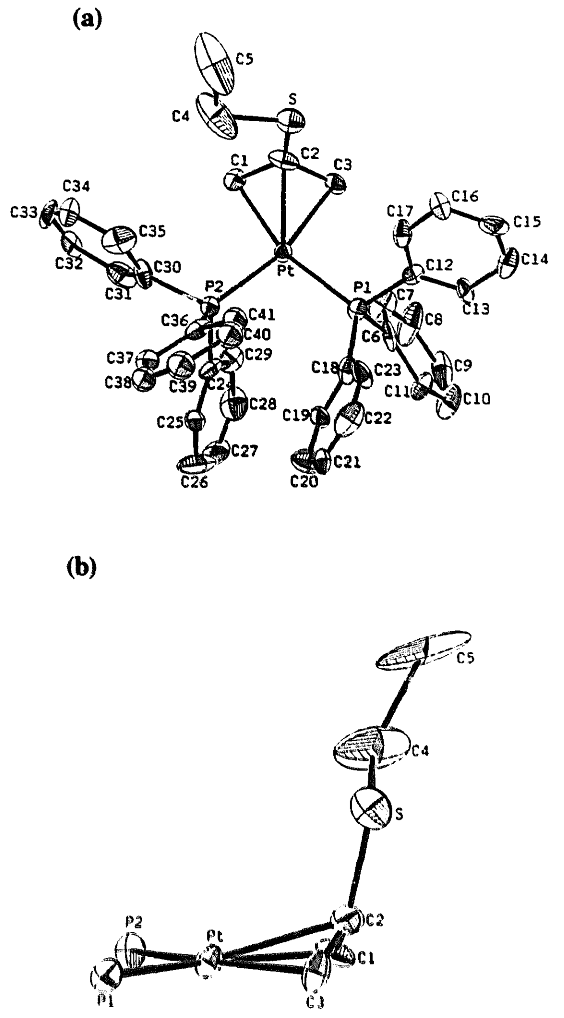
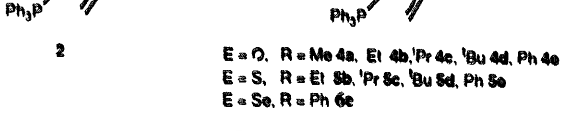


Fig. 1. ORTEP drawings of $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(SEt)CH_2]\}(BF_4)$ (**5b**). (a) Top view, all hydrogen atoms omitted for clarity. (b) Side view, phosphino phenyls and all hydrogen atoms omitted for clarity.



Scheme 1.

2.2. X-ray structures of η^3-chalcogenoxyallyl complexes

The molecular structures of **4b**, **4e**, **5b**, **5e**, and **6e** as single crystals have been determined by X-ray diffraction. They are all similar in a general sense. Figs. 1 and 2 show both the top and side views of the ORTEP drawings of **5b** and **6e** respectively as representatives. The two phosphorus atoms, two allyl terminal carbon atoms, and the platinum atom of such complexes are in the molecular plane, and are disposed in a distorted square-planar geometry. The angles P–Pt–P′ are about 103° and C_t–Pt–C_t' about 67°. The chalcogenoxyallyl moieties are in η^3-mold. Table 1 displays some important structural features of these chalcogenoxyallyl fragments. For the purpose of comparison, the data of unsubstituted allyl, hydroxyallyl and O–TMM ligands in analogous systems are also listed. The chalcogenoxyallyl central carbon inclines away from the metal, so that the Pt–C_c bond is slightly longer than two Pt–C_t bonds. The angles C_t–C_c–C_t' are about 118°. The dihedral angles between the planes C_t–C_c–C_t' and C_t–Pt–C_t' are about 63–67°. Based on such data, and comparing with other relevant results [7,10], the p_π–p_π interaction of all C_c–ER (E = O, S, Se) bonds is significant, but substantially weaker than that of the C_c–O double bond in the O–TMM complex, although the distances of the C_c–E bonds fall in the single bond range.

Table 1
Important structural features of $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(ER)CH_2]\}^+$

X	$M–C_t$ (Å)	$M–C_c$ (Å)	$C_t–C_c$ (Å)	$C_c–C_t–C_c$ (deg)	C–E (Å)	θ [b] (deg)	Ref.
H	2.16(2) 2.17(2)	2.07(2)	1.17(2) 1.26(2)	149(2)	1.0	95	[7]
O	2.12(1) 2.15(1)	2.42(1)	1.47(2) 1.50(2)	108(1)	1.26(2)	56.7	[11]
OH(3)	2.16(2) 2.18(2)	2.16(2)	1.21(3) 1.41(3)	127(2)	1.52(3)	61(3)	[7]
OEt(4b)	2.17(1) 2.19(1)	2.21(1)	1.37(2) 1.36(2)	120(1)	1.42(2)	64(2)	[a]
OPh(4e)	2.176(7) 2.186(6)	2.246(6)	1.38(1) 1.43(1)	117.3(7)	1.361(9)	63.3(8)	[a]
SEt(5b)	2.18(2) 2.20(2)	2.24(2)	1.39(3) 1.45(3)	118(2)	1.76(2)	63.3(2)	[a]
SPh(5e)	2.177(6) 2.177(6)	2.204(6)	1.377(8) 1.413(9)	118.6(6)	1.743(6)	66.1(7)	[3]
SePh(6e)	2.181(6) 2.183(7)	2.205(6)	1.41(1) 1.43(1)	117.7(7)	1.881(7)	67.1(8)	[a]

[a] This work.

[b] The dihedral angle θ is defined by the planes $C_t–C_c–C'_t$ and $C_t–P_t–C'_t$.

2.3. *Relative reactivity and mechanism of addition of chalcogenol to η^3-propargyl/allenyl complex*

The relative reactivity of the η^3-propargyl/allenyl complex with respect to various chalcogenols could be estimated by the competitive reactions. For instance, equimolar amounts of MeOH and EtOH were allowed to concurrently react with **2**. The NMR measurement showed that **4a** and **4b** in the ratio 65:35 resulted at the end of the reaction. Other selected rival pairs among the alcohols and phenols were examined in the same manner. The outcome is listed in Table 2. The normalized ratio MeOH:EtOH:^{i}PrOH:^{t}BuOH:PhOH is about 70:40:23:4:1, indicating that the steric effect is more important than the inductive effect. Similar NMR experiments indicated that the reactions of **2** with PhSH or PhSeH under the same conditions were finished within the measurement of the first spectra. Addition of both PhSH and PhSeH to **2** overwhelmingly exceeded methanol, even 20-fold methanol was employed. The reaction of **2** with equimolar amounts of p-$(HO)C_6H_4(SH)$ selectively results in C–S bond-formation, affording the thioxyallyl product $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(SC_6H_4OH)CH_2]\}(BF_4)$ (**5f**) (Scheme 2). This result also indicates that –SH is a more efficient functional group than –OH in reacting with **2**.

Two pathways of nucleophilic addition have been considered. One is that chalcogenol directly attacks the central carbon of the η^3-allenyl/propargyl ligand. The other is that it requires the precoordination of chalcogenol to the metal, so that addition of chalcogenol to the organic ligand may be facilitated. In viewing the aforementioned studies of reactivity, the latter process seems to be more plausible. The better ligands such as RSH, RSeH react with **2** much faster than alcohol. As to the reactions with alcohol, the ligation can be facilitated by a smaller alcohol. Phenol, which is a bulky poor nucleophile, reacts the slowest with **2** among all studied chalcogenol. The coordination of chalcogenol to **2** provides the metal with an opportunity to promote nucleophilic addition to the propargyl/allenyl moiety. There are two possible courses for such metal-mediated construction of the C–E bonds that are worthy of attention. The first is as shown in Scheme 3. Migration of

Table 2
Relative yields of the chalcogenoxyallyl formed from competitive chalcogenols reacting with **2**

1	MeOH/EtOH	**4a** (65%)	**4b** (35%)				
2	MeOH/^{i}PrOH	**4a** (75%)		**4c** (25%)			
3	EtOH/^{i}PrOH		**4b** (65%)	**4c** (35%)			
4	EtOH/^{t}BuOH		**4b** (91%)		**4d** (9%)		
5 [a]	^{t}BuOH/PhOH				**4d** (79%)	**4e** (21%)	
6 [b]	PhSH/MeOH						**5e** (100%)
7	PhSeH/MeOH						**6e** (100%)

[a] In this entry, ^{t}BuOH and PhOH are both used in 20-fold equivalents of **2**; in the remaining entries, each used REH equimolar with **2**.

[b] In this entry, the molar ratio PhSH : MeOH is 1 : 20.

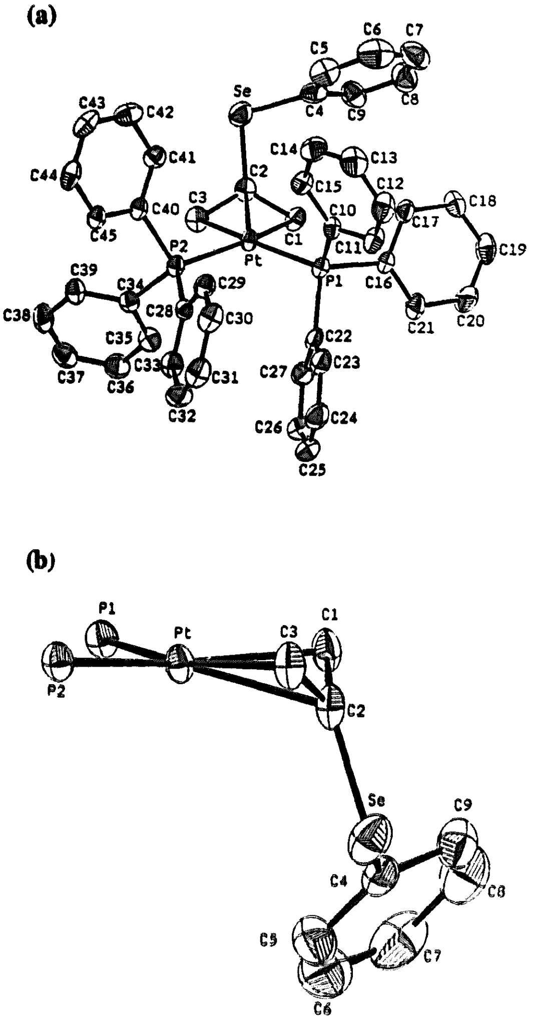
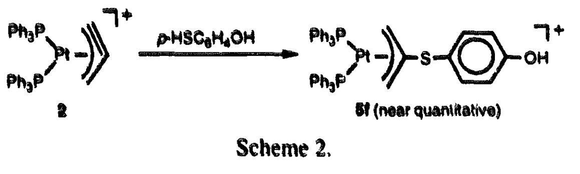
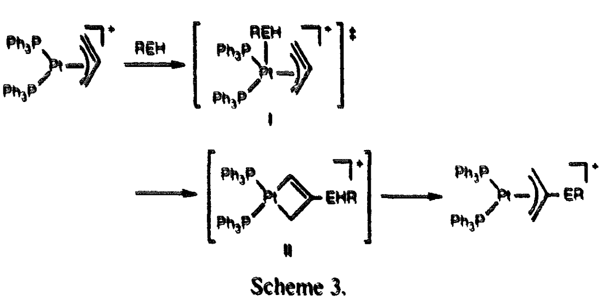


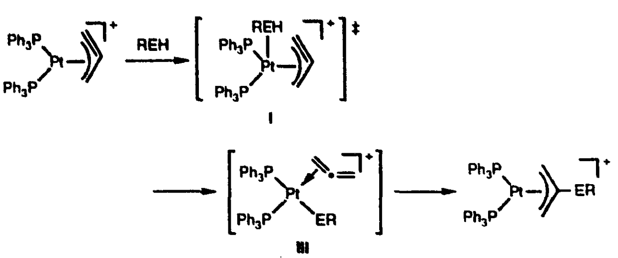
Fig. 2. ORTEP drawings of {Pt(PPh$_3$)$_2$[η^3-CH$_2$C(SePh)CH$_2$]}(BF$_4$) (6e). (a) Top view, all hydrogen atoms omitted for clarity. (b) Side view, phosphino phenyls and all hydrogen atoms omitted for clarity.



Scheme 2.



Scheme 3.



Scheme 4.

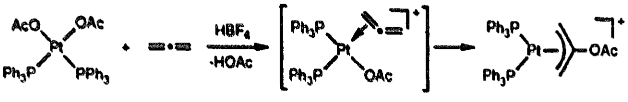
chalcogenol from the metal to the central carbon of the η^3-propargyl/allenyl ligand first yields a metallacyclobutene **II**. The ensuing 1,3-hydrogen shift to the olefinic α-carbon of **II** achieves the chalcogenoxy product. The formation of metallacyclobutene from the η^3-propargyl/allenyl has been observed in a rhenium system [11].

In another pathway, intramolecular hydrogen transfer from coordinated chalcogenol to the η^3-propargyl/allenyl group results in a (π-allene)chalcogenolato intermediate **III**. The reaction is then accomplished by an allene insertion to the chalcogenolato group. This is illustrated in Scheme 4. Migratory insertions of allene into M–C bonds have been known [12–14]. We also found that bubbling allene through *cis*-Pt(PPh$_3$)$_2$(OAc)$_2$ caused no reaction. However, treating this solution with 1 equivalent of HBF$_4$ etherate readily generates the acetyloxyallyl complex {Pt(PPh$_3$)$_2$[η^3-CH$_2$C(OAc)CH$_2$]}(BF$_4$) [3]. Presumably, one of the acetate ligands of *cis*-Pt(PPh$_3$)$_2$(OAc)$_2$ may be deliberated by protonation. The allene coordination follows, resulting in a (π-allene)acetato species **IV** and then the acetyloxyallyl product (Scheme 5). None of the mechanisms of Schemes 3 and 4 should be excluded without further investigation.

3. Experimental section

3.1. General

The IR spectra were recorded on a Bio-Rad FTS-40 spectrophotometer. The NMR spectra were routinely measured on Bruker ACE-200, ACE-300, or Varian Unity + 400 spectrometers. For the ^{31}P NMR spectra, spectrometer frequencies of 81.015 or 121.49 MHz were employed respectively. Chemical shifts are given in ppm (δ) relative to 85% H$_3$PO$_4$ in CDCl$_3$. The corresponding frequencies for ^{13}C NMR spectra were 50.32, 75.47 or 100.64 MHz for the respective spectrometers. Mass spectrometric analyses were collected



Scheme 5.

on a JEOL SX-102A spectrometer. Elemental analyses were carried out on a Perkin-Elmer 2400 CHN analyzer.

3.2. Synthesis and characterization

3.2.1. {Pt(PPh$_3$)$_2$[η^3-CH$_2$C(OMe)CH$_2$]}(BF$_4$) (4a)

Refer to **4b** for the experimental details. ^{31}P NMR (CDCl$_3$) δ 17.3 ($J_{\mathrm{P-Pt}} = 3685$ Hz). ^{1}H NMR (CDCl$_3$) δ 2.80 (2H, dd with ^{195}Pt satellites, $J_{\mathrm{H-H}} = 4.7$ Hz, $J_{\mathrm{P-H}} = 9.1$ Hz, $J_{\mathrm{Pt-H}} = 39.6$ Hz, H$_{anti}$), 3.06 (d, 2H, $J_{\mathrm{H-H}} = 4.7$ Hz, H$_{syn}$), 3.44 (3H, t, $J_{\mathrm{P-H}} = 2.1$ Hz, OCH_3), 7.1–7.5 (m, phenyl H). ^{13}C NMR (CDCl$_3$) δ 52.3 (d with ^{195}Pt satellites, $J_{\mathrm{P-C}} \approx 37$ Hz, $J_{\mathrm{Pt-C}} \approx 100$ Hz, C$_t$), 55.7 (s, OCH$_3$), 127–135 (phenyl carbons), 156.1 ($J_{\mathrm{Pt-C}} \approx 27$ Hz, C$_c$).

3.2.2. {Pt(PPh$_3$)$_2$[η^3-CH$_2$C(OEt)CH$_2$]}(BF$_4$) (4b)

The η^3-propargyl complex **2** was prepared in situ from *trans*-Pt(η^1-CHCCH$_2$)(Br)(PPh$_3$)$_2$ (211 mg, 0.25 mmol) and AgBF$_4$ (50 mg, 0.26 mmol) in predried CH$_2$Cl$_2$ at −20 °C. After filtering off AgBr precipitate, absolute ethanol (20 equiv.) was charged to the filtrate. The solution was stirred at −20 °C for 10 h, and then was concentrated. Addition of Et$_2$O resulted in precipitation of the product in 65% yield (145 mg). ^{31}P NMR (CDCl$_3$) δ 17.5 ($J_{\mathrm{P-Pt}} = 3678$ Hz). ^{1}H NMR (CDCl$_3$) δ 1.28 (3H, t, $J_{\mathrm{H-H}} = 7.0$ Hz, CH$_2$CH_3), 2.81 (2H, dd with ^{195}Pt satellites, $J_{\mathrm{H-H}} = 3.4$ Hz, $J_{\mathrm{P-H}} = 9.1$ Hz, $J_{\mathrm{Pt-H}} = 39.2$ Hz, H$_{anti}$), 3.05 (2H, d, $J_{\mathrm{H-H}} = 3.4$ Hz, H$_{syn}$), 3.62 (2H, q, $J_{\mathrm{H-H}} = 7.0$ Hz, CH_2CH$_3$), δ 7.1–7.5 (m, phenyl H). ^{13}C NMR (CDCl$_3$) δ 14.5 (s, CH$_2$$CH_3$), 52.7 (dd with ^{195}Pt satellites, $J_{\mathrm{P-C}} = 5.3$, 40.4 Hz, $J_{\mathrm{Pt-C}} = 111.4$ Hz, C$_t$), 64.7 (s, CH$_2$CH$_3$), 127–135 (phenyl C), 155.7 (t with ^{195}Pt satellites, $J_{\mathrm{P-C}} = 3.0$ Hz, $J_{\mathrm{Pt-C}} = 30.5$ Hz, C$_c$). Anal. Found: C, 55.31; H, 4.64. $C_{41}H_{39}OP_2PtBF_4$ Calc.: C, 55.23; H, 4.41%.

3.2.3. {Pt(PPh$_3$)$_2$[η^3-CH$_2$C(O^{i}Pr)CH$_2$]}(BF$_4$) (4c)

The yield of **2c** was 77% (130 mg) from 156 mg (0.19 mmol) of **1**. ^{31}P NMR (CDCl$_3$) δ 17.8 ($J_{\mathrm{P-Pt}} =$ 3662 Hz). ^{1}H NMR (CDCl$_3$) δ 1.21 (6H, d, $J_{\mathrm{H-H}} = 6.0$ Hz, CH_3), 2.79 (2H, dd with ^{195}Pt satellites, $J_{\mathrm{H-H}} = 3.5$ Hz, $J_{\mathrm{P-H}} = 9.2$ Hz, $J_{\mathrm{Pt-H}} = 41.5$ Hz, H$_{anti}$), 3.02 (2H, d, $J_{\mathrm{H-H}} = 3.5$ Hz, H$_{syn}$), 4.00 (1H, hep, $J_{\mathrm{H-H}} = 6.0$ Hz, CH), 7.1–7.5 (m, phenyl H). ^{13}C NMR (CDCl$_3$) δ 21.7 (s, CH$_3$), 52.0 (dd with ^{195}Pt satellites, $J_{\mathrm{P-C}} = 36.5$ Hz, $J_{\mathrm{Pt-C}} = 93.6$ Hz, C$_t$), 72.2 (s, CH), 127–135

Table 3
X-ray crystal parameters and data collection

	4b	**4e**	**5b**	**5e**	**6e**
Formula	$PtC_{41}H_{38}OP_2$ BF_4	$PtC_{45}H_{39}OP_2$ $BF_4 \cdot CH_2Cl_2$	$PtC_{41}H_{39}SP_2$ $BF_4 \cdot 1.5CHCl_3$	$PtC_{45}H_{39}SP_2$ $BF_4 \cdot CHCl_3$	$PtC_{45}H_{39}SeP_2$ $BF_4 \cdot CHCl_3$
Formula weight	890.58	1089.58	1086.74	1070.36	1121.99
Crystal dimensions (mm^3)	0.25 × 0.3 × 0.4	0.25 × 0.25 × 0.5	0.13 × 0.28 × 0.4	0.15 × 0.4 × 0.45	0.3 × 0.4 × 0.4
Space group	$P2_1/n$	$P\bar{1}$	$Fdd2$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.560(4)	11.256(2)	38.856(4)	12.842(3)	11.188(4)
b (Å)	21.027(7)	11.605(1)	39.112(3)	12.989(3)	11.901(4)
c (Å)	15.591(7)	17.820(3)	10.584(1)	13.589(5)	18.292(3)
α (deg)	90	106.76(1)	90	89.85(2)	107.78(2)
β (deg)	96.12(4)	91.29(2)	90	92.98(3)	90.69(2)
γ (deg)	90	107.05(1)	90	106.66(2)	106.24(2)
V (Å^3)	3768(3)	2116.2(5)	16085(3)	2168(1)	2214(1)
Z	4	2	16	2	2
ρ (calc) (mg m^{-3})	1.570	1.608	1.646	1.639	1.683
F(000)	1758	1013	7865	976	1097
Radiation, λ (Å)	Mo Kα, 0.7107	Mo Kα, 0.7107	Mo Kα, 0.7107	Mo Kα, 0.7107	Mo, Kα, 0.7107
T (K)	298	298	298	298	298
μ (mm^{-1})	3.895	3.472	3.99	3.30	4.317
Transmission	0.557–1.0	0.778–1.0	0.673–1.0	0.75–1.0	0.752–1.0
Max 2θ (deg)	45	50	50	50	45
h, k, l	± 12, 22, 16	± 12, 13, ± 20	46, 46, 12	± 15, 15, ± 16	± 12, 12, ± 19
No. of reflections measured	4915	7455	3735	7632	5779
No. of reflections observed	3358 (> 2.0σ)	5777 (> 2.0σ)	2945 (> 2.0σ)	6446 (> 2.0σ)	4856 (> 2.0σ)
No. of variables	406	515	395	539	524
$R(F)$	0.045	0.037	0.055	0.031	0.033
$Rw(F)$	0.046	0.037	0.047	0.026	0.034
S	2.11	1.39	2.60	1.95	1.96
$(\Delta/\sigma)_{\max}$	0.0312	0.0031	0.0242	0.042	0.0077

(phenyl C), 155.0 (with ^{195}Pt satellites, $J_{Pt-C} = 34.0$ Hz, C$_c$). Anal. Found: C, 55.89; H, 4.32. $C_{42}H_{41}OP_2PtBF_4$ Calc.: C, 55.70; H, 4.56%.

3.2.4. {Pt(PPh$_3$)$_2$[η^3-CH$_2$C(O^{t}Bu)CH$_2$]}(BF$_4$) (4d)

The yield of **4d** was 58% (127 mg) from 200 mg (0.24 mmol) of **1**. ^{31}P NMR (CDCl$_3$) δ 18.4 ($J_{P-Pt} = 3663$ Hz). ^{1}H NMR (CDCl$_3$) δ 1.31 (9H, s, CH_3), 2.75 (2H, dd with ^{195}Pt satellites, $J_{H-H} = 4.1$ Hz, $J_{P-H} = 9.3$ Hz, $J_{Pt-H} = 39.6$ Hz, H$_{anti}$), 3.09 (2H, d, $J_{H-H} = 4.1$ Hz, H$_{syn}$), 7.1–7.5 (m, phenyl H). ^{13}C NMR (CDCl$_3$) δ 28.7 (s, CH$_3$), 55.0 (dd with ^{195}Pt satellites, $J_{P-C} = 4.5$, 40.2 Hz, $J_{Pt-C} = 115.4$ Hz, C$_t$), 82.9 (s, OCMe$_3$), 127–135 (phenyl C), 155.7 (t with ^{195}Pt satellites, $J_{P-C} = 3.5$ Hz, $J_{Pt-C} = 31.7$ Hz, C$_c$). Anal. Found: C, 55.71; H, 4.54. $C_{43}H_{43}OP_2PtBF_4$ Calc.: C, 56.16; H, 4.71%.

Table 4
Coordinates and isothermal data of non-hydrogen atoms for **4b** with e.s.d.s in parentheses

Atom	x	y	z	B_{eq}
Pt	0.05105(4)	0.636042(25)	0.18395(3)	3.432(2[illegible])
P1	0.0470(3)	0.74450(16)	0.20111(21)	3.62(16)
P2	0.04479(25)	0.59632(16)	0.32030(20)	3.43(15)
O1	−0.1151(11)	0.5742(7)	0.0312(8)	12.5(9)
C1	0.0558(12)	0.6388(7)	0.0449(8)	6.5(8)
C2	0.0039(13)	0.5823(8)	0.0632(9)	7.7(10)
C3	0.0571(13)	0.5425(8)	0.1235(8)	7.0(9)
C4	−0.199(3)	0.5376(22)	0.0553(19)	34.1(40)
C5	−0.3080(16)	0.5278(15)	0.0098(18)	20.5(24)
C6	0.1810(9)	0.7831(6)	0.2477(7)	3.9(6)
C7	0.2810(9)	0.7463(6)	0.2700(8)	4.3(7)
C8	0.3830(9)	0.7773(7)	0.2995(9)	6.1(8)
C9	0.3880(11)	0.8417(7)	0.3074(10)	7.0(8)
C10	0.2923(11)	0.8772(7)	0.2840(10)	7.0(8)
C11	0.1883(11)	0.8481(6)	0.2549(10)	6.3(8)
C12	0.0258(9)	0.7877(5)	0.0972(7)	3.2(6)
C13	0.1175(9)	0.7887(6)	0.0476(7)	4.5(6)
C14	0.1078(10)	0.8206(6)	−0.0292(7)	4.7(7)
C15	0.0059(10)	0.8513(6)	−0.0596(7)	4.7(7)
C16	−0.0856(10)	0.8501(6)	−0.0109(8)	4.9(6)
C17	−0.0776(9)	0.8191(6)	0.0680(7)	4.2(6)
C18	−0.0721(9)	0.7690(6)	0.2612(7)	3.6(6)
C19	−0.1815(9)	0.7434(6)	0.2340(8)	4.2(7)
C20	−0.2763(10)	0.7592(7)	0.2770(9)	5.8(8)
C21	−0.2606(12)	0.7977(8)	0.3486(9)	7.0(9)
C22	−0.1518(12)	0.8240(8)	0.3764(9)	6.7(8)
C23	−0.0609(10)	0.8083(7)	0.3329(8)	5.2(7)
C24	0.1733(8)	0.5502(5)	0.3590(6)	2.9(5)
C25	0.2648(9)	0.5446(6)	0.3080(7)	3.8(6)
C26	0.3639(9)	0.5090(6)	0.3355(8)	4.2(6)
C27	0.3715(10)	0.4803(6)	0.4152(8)	4.9(7)
C28	0.2828(10)	0.4867(6)	0.4674(8)	5.2(7)
C29	0.1844(9)	0.5221(6)	0.4387(8)	4.2(6)
C30	−0.0766(8)	0.5400(6)	0.3146(7)	3.6(6)
C31	−0.0637(10)	0.4754(6)	0.3287(8)	4.8(7)
C32	−0.1589(12)	0.4348(7)	0.3181(10)	6.9(8)
C33	−0.2668(11)	0.4580(8)	0.2932(9)	7.0(9)
C34	−0.2837(10)	0.5228(8)	0.2795(9)	6.3(8)
C35	−0.1878(10)	0.5637(7)	0.2893(8)	5.2(7)
C36	0.0248(8)	0.6442(6)	0.4146(7)	3.5(6)
C37	−0.0608(9)	0.6337(7)	0.4684(8)	5.0(7)
C38	−0.0680(11)	0.6693(7)	0.5426(9)	6.2(8)
C39	0.0095(12)	0.7175(7)	0.5629(8)	6.2(8)
C40	0.0952(11)	0.7296(7)	0.5092(9)	5.9(8)
C41	0.1031(10)	0.6931(7)	0.4372(7)	4.6(6)
B	0.45226	0.61440	0.14441	20.3(14)
F1	0.48415	0.64121	0.21943	14.7(4)
F2	0.34431	0.63450	0.11211	16.0(4)
F3	0.50987	0.62740	0.07464	18.1(5)
F4	0.45692	0.54835	0.15546	13.0(4)

3.2.5. $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(OPh)CH_2]\}(BF_4)$ (4e)

The yield of **4e** was 74% (171 mg) from 208 mg (0.25 mmol) of **1**. ^{31}P NMR (CDCl$_3$) δ 17.3 (J_{P-Pt} = 3736 Hz). ^{1}H NMR (CDCl$_3$) δ 3.04 (2H, dd with ^{195}Pt satellites, J_{H-H} = 4.5 Hz, J_{P-H} = 8.3 Hz, J_{Pt-H} = 39.2 Hz, H_{anti}), 3.05 (2H, H_{syn}), 7.1–7.5 (m, phenyl H). ^{13}C

Table 5
Coordinates and isothermal data of non-hydrogen atoms for **4e** with e.s.d. in parentheses

Atom	*x*	*y*	*z*	B_{eq}
Pt	0.12941(3)	0.24456(3)	0.230831(16)	2.494(10)
P1	0.25831(15)	0.21857(16)	0.13360(10)	2.71(8)
P2	0.26958(16)	0.33002(16)	0.34217(10)	2.64(8)
O	−0.1375(4)	0.0482(5)	0.2222(3)	4.5(3)
C1	0.0391(6)	0.1791(7)	0.1481(4)	4.3(4)
C2	−0.0803(6)	0.1670(7)	0.2185(4)	3.9(4)
C3	−0.0342(6)	0.2749(6)	0.2871(4)	3.4(3)
C4	−0.1442(7)	0.0280(7)	0.2968(4)	4.2(4)
C5	−0.0782(7)	−0.0447(8)	0.3133(5)	5.3(5)
C6	−0.0841(9)	−0.0711(8)	0.3830(6)	6.8(6)
C7	−0.1597(9)	−0.0256(9)	0.4354(6)	6.8(6)
C8	−0.2301(8)	0.0446(9)	0.4189(5)	6.1(5)
C9	−0.2233(7)	0.0700(8)	0.3473(5)	4.8(5)
C10	0.2455(6)	0.0559(6)	0.0816(4)	2.9(3)
C11	0.3276(6)	0.0293(6)	0.0250(4)	3.6(3)
C12	0.3180(7)	−0.0956(7)	−0.0148(4)	4.3(4)
C13	0.2302(7)	−0.1928(7)	0.0012(5)	4.9(4)
C14	0.1503(7)	−0.1687(7)	0.0563(5)	4.7(4)
C15	0.1567(6)	−0.0450(7)	0.0948(4)	3.7(4)
C16	0.4280(6)	0.2917(6)	0.1587(4)	3.1(3)
C17	0.4906(7)	0.4058(7)	0.1472(4)	4.2(4)
C18	0.6207(7)	0.4588(8)	0.1681(5)	5.5(4)
C19	0.6862(7)	0.3973(8)	0.1970(5)	5.7(5)
C20	0.6251(7)	0.2854(8)	0.2090(5)	5.3(5)
C21	0.4965(6)	0.2314(7)	0.1899(4)	3.7(4)
C22	0.2163(6)	0.2881(6)	0.0617(4)	3.0(3)
C23	0.1898(7)	0.4016(7)	0.0898(4)	4.0(4)
C24	0.1568(7)	0.4585(7)	0.0388(5)	4.5(4)
C25	0.1498(7)	0.4042(7)	−0.0418(5)	4.7(4)
C26	0.1751(7)	0.2918(8)	−0.0704(4)	4.7(4)
C27	0.2082(6)	0.2336(7)	−0.0199(4)	3.8(4)
C28	0.3913(6)	0.4716(6)	0.3396(3)	3.1(3)
C29	0.3501(7)	0.5616(7)	0.3195(4)	4.0(4)
C30	0.4346(7)	0.6737(7)	0.3181(5)	4.7(4)
C31	0.5590(8)	0.6979(7)	0.3379(5)	5.5(5)
C32	0.6015(7)	0.6101(8)	0.3573(5)	5.0(4)
C33	0.5185(6)	0.4971(7)	0.3592(4)	3.7(4)
C34	0.2032(6)	0.3818(6)	0.4343(4)	3.0(3)
C35	0.1158(7)	0.2931(7)	0.4582(4)	3.9(4)
C36	0.0618(7)	0.3261(7)	0.5262(4)	4.4(4)
C37	0.0945(8)	0.4496(8)	0.5708(4)	5.1(5)
C38	0.1818(8)	0.5411(7)	0.5493(5)	5.7(5)
C39	0.2358(7)	0.5073(7)	0.4804(4)	4.2(4)
C40	0.3389(6)	0.2185(6)	0.3644(4)	2.8(3)
C41	0.2989(7)	0.0929(6)	0.3171(4)	3.8(4)
C42	0.3414(8)	0.0034(7)	0.3362(5)	4.9(4)
C43	0.4252(8)	0.0391(8)	0.4018(5)	5.4(5)
C44	0.4645(8)	0.1624(8)	0.4492(5)	5.1(4)
C45	0.4217(7)	0.2529(7)	0.4326(4)	4.0(4)
B	0.0725(10)	0.6609(10)	0.2487(6)	5.5(6)
F1	−0.0088(9)	0.7049(8)	0.2286(5)	16.7(8)
F2	0.1786(6)	0.6858(6)	0.2124(4)	10.8(4)
F3	0.1093(6)	0.7173(7)	0.3282(3)	10.6(5)
F4	0.0285(6)	0.5355(6)	0.2323(5)	12.0(5)
C46	0.4406(10)	0.7553(13)	0.1350(6)	10.4(8)
Cl1	0.4690(3)	0.6681(3)	0.04705(18)	8.92(18)
Cl2	0.5482(4)	0.8963(4)	0.17603(24)	13.8(3)

NMR ($CDCl_3$) δ 55.0 (dd with ^{195}Pt satellites, J_{P-C} = 4.9, 39 Hz, J_{Pt-C} = 101.3 Hz, C_t), 127–135 (phenyl carbons), 152.7 (t, J_{P-C} = 3.4 Hz, J_{Pt-C} = 17.5 Hz, C_c).

3.2.6. *{Pt(PPh$_3$)$_2$[η^3-CH$_2$C(SEt)CH$_2$]}(BF$_4$) (5b)*

Refer to **4b**. The reaction was complete within 2 h, and the yield of **5b** was 55% (118 mg) from 200 mg (0.24 mmol) of **1**. ^{31}P NMR ($CDCl_3$) δ 18.0 (J_{P-Pt} =

Table 6

Coordinates and isothermal data of non-hydrogen atoms for **5b** with e.s.d. in parentheses

Atom	*x*	*y*	*z*	B_{eq}
Pt	0.105671(18)	0.179010(20)	0.10907	2.87(3)
S	0.07480(15)	0.14723(17)	−0.1757(6)	5.8(4)
P1	0.16394(11)	0.18880(12)	0.1166(8)	3.3(3)
P2	0.08303(13)	0.22739(14)	0.1913(6)	3.3(3)
C1	0.0559(4)	0.1537(5)	0.0777(17)	3.7(11)
C2	0.0784(5)	0.1405(5)	−0.0119(19)	4.4(12)
C3	0.1116(5)	0.1278(4)	0.0310(19)	3.8(11)
C4	0.0352(8)	0.1772(7)	−0.197(3)	12.4(23)
C5	0.0218(14)	0.1757(12)	−0.350(5)	15.3(42)
C5′	−0.0063(18)	0.177(3)	−0.223(12)	26.4(90)
C6	0.1846(5)	0.1661(5)	0.2463(21)	4.7(11)
C7	0.1688(5)	0.1372(6)	0.2933(22)	5.8(13)
C8	0.1859(5)	0.1190(6)	0.383(3)	8.4(17)
C9	0.2177(6)	0.1289(7)	0.4274(20)	7.8(16)
C10	0.2342(5)	0.1598(5)	0.376(3)	6.6(14)
C11	0.2175(4)	0.1772(5)	0.2958(18)	4.2(11)
C12	0.1865(4)	0.1741(5)	−0.0229(18)	3.2(9)
C13	0.2201(5)	0.1640(5)	−0.0168(19)	4.3(11)
C14	0.2373(4)	0.1547(5)	−0.135(3)	5.3(13)
C15	0.2214(5)	0.1578(5)	−0.2428(22)	5.6(13)
C16	0.1866(5)	0.1673(5)	−0.2551(20)	4.5(11)
C17	0.1711(4)	0.1749(5)	−0.1356(22)	4.3(11)
C18	0.1796(4)	0.2321(4)	0.1306(22)	3.9(11)
C19	0.1770(4)	0.2500(5)	0.2465(23)	4.7(12)
C20	0.1855(6)	0.2814(6)	0.2666(21)	5.8(14)
C21	0.1969(5)	0.2986(6)	0.165(3)	7.4(16)
C22	0.2005(5)	0.2843(6)	0.0501(23)	6.8(14)
C23	0.1922(5)	0.2495(5)	0.0422(21)	5.1(12)
C24	0.0985(4)	0.2335(5)	0.3556(23)	4.0(10)
C25	0.1061(5)	0.2647(5)	0.4073(18)	4.6(11)
C26	0.1177(6)	0.2688(7)	0.5228(24)	8.6(17)
C27	0.1213(5)	0.2388(7)	0.5891(24)	7.7(16)
C28	0.1154(5)	0.2069(6)	0.5441(21)	7.0(15)
C29	0.1035(5)	0.2039(5)	0.4241(19)	4.7(11)
C30	0.0352(5)	0.2253(5)	0.2138(19)	4.1(11)
C31	0.0200(5)	0.2109(5)	0.3183(23)	6.3(15)
C32	−0.0169(4)	0.2080(5)	0.3193(23)	5.9(13)
C33	−0.0353(5)	0.2189(5)	0.215(3)	7.4(17)
C34	−0.0210(4)	0.2334(5)	0.110(3)	4.8(12)
C35	0.0148(5)	0.2342(5)	0.109(3)	6.5(15)
C36	0.0880(4)	0.2669(5)	0.1059(21)	4.0(10)
C37	0.0707(5)	0.2985(5)	0.1520(18)	3.9(10)
C38	0.0776(4)	0.3279(5)	0.0854(22)	4.6(5)
C39	0.0969(5)	0.3284(6)	−0.0249(22)	6.1(6)
C40	0.1140(5)	0.2989(5)	−0.0711(21)	5.5(6)
C41	0.1083(5)	0.2685(5)	0.0077(20)	4.5(5)
C42	0	1/2	0.841(22)	38.8(75)
Cl1	0.0330(6)	0.4906(7)	0.795(3)	28.4(12)
Cl2	0	1/2	1.0213(21)	13.0(6)
C43	0.0871(16)	0.1193(16)	0.488(7)	17.7(21)
Cl3	0.0659(5)	0.0765(5)	0.4821(22)	20.9(7)
Cl4	0.0501(7)	0.1241(7)	0.392(3)	28.7(11)
Cl5	0.0979(7)	0.0981(7)	0.329(4)	30.3(11)

3787 Hz). ^{1}H NMR ($CDCl_3$) δ 1.17 (3H, t, $J_{H-H} = 7.3$ Hz, CH_2CH_3), 2.42 (2H, q, $J_{H-H} = 7.3$ Hz, CH_2CH_3), 3.23 (2H, d with ^{195}Pt satellites, $J_{P-H} = 5.2$ Hz, $J_{Pt-H} = 42.5$ Hz, H_{anti}), 3.37 (2H, s, H_{syn}), 7.1–7.5 (m, phenyl H). ^{13}C NMR ($CDCl_3$) δ 13.8 (s, CH_3), 25.0 (s, CH_2), 62.4 (dd with ^{195}Pt satellites, $J_{P-C} = 32.6$ Hz, $J_{Pt-C} = 102.9$ Hz, C_t), 127–135 (phenyl C), 143.6 (s, C_c).

Table 7
Coordinates and isothermal data of non-hydrogen atoms for **5e** with e.s.d. in parentheses

Atom	x	y	z	B_{eq}
Pt	0.132769(24)	0.25476(3)	0.231523(15)	2.711(11)
P1	0.26321(15)	0.23136(15)	0.13605(9)	2.91(8)
P2	0.26933(15)	0.33415(15)	0.34313(9)	2.96(8)
S	−0.15377(18)	0.02631(18)	0.20498(11)	5.92(11)
C1	−0.0281(5)	0.2055(6)	0.1463(4)	4.4(4)
C2	−0.0720(5)	0.1827(6)	0.2153(4)	4.0(4)
C3	−0.0333(5)	0.2785(6)	0.2850(3)	3.6(3)
C4	−0.1579(6)	0.0175(6)	0.3023(4)	4.7(4)
C5	−0.2325(6)	0.0695(6)	0.3525(4)	5.1(4)
C6	−0.2375(7)	0.0575(7)	0.4263(4)	6.3(5)
C7	−0.1710(7)	−0.0101(7)	0.4490(5)	7.9(6)
C8	−0.0981(8)	−0.0622(7)	0.3993(5)	8.4(6)
C9	−0.0892(7)	−0.0489(7)	0.3257(5)	6.5(5)
C10	0.2469(5)	0.0678(5)	0.0819(3)	2.8(3)
C11	0.1594(5)	−0.0298(6)	0.0971(3)	3.7(4)
C12	0.1515(6)	−0.1541(5)	0.0577(4)	4.5(4)
C13	0.2315(6)	−0.1789(6)	0.0032(4)	4.6(4)
C14	0.3171(6)	−0.0825(6)	−0.0129(3)	4.3(4)
C15	0.3278(5)	0.0405(5)	0.0259(3)	3.5(3)
C16	0.4292(5)	0.2973(5)	0.1598(3)	3.1(3)
C17	0.4964(6)	0.4103(6)	0.1484(4)	4.4(4)
C18	0.6246(6)	0.4676(6)	0.1674(4)	5.7(4)
C19	0.6871(6)	0.3942(7)	0.1977(4)	5.8(5)
C20	0.6243(6)	0.2831(6)	0.2096(4)	4.9(4)
C21	0.4968(6)	0.2358(6)	0.1919(3)	4.0(3)
C22	0.2222(5)	0.3040(5)	0.0655(3)	2.9(3)
C23	0.1972(6)	0.4178(6)	0.0943(3)	4.1(4)
C24	0.1601(6)	0.4758(6)	0.0438(4)	5.0(4)
C25	0.1487(6)	0.4193(6)	−0.0355(4)	4.7(4)
C26	0.1731(6)	0.3064(6)	−0.0640(3)	4.7(4)
C27	0.2093(6)	0.2503(6)	−0.0147(3)	3.8(4)
C28	0.3902(5)	0.4738(5)	0.3420(3)	3.2(3)
C29	0.5168(6)	0.4967(6)	0.3598(3)	3.7(4)
C30	0.6004(6)	0.6079(6)	0.3571(4)	5.3(4)
C31	0.5606(7)	0.6971(6)	0.3381(4)	6.0(4)
C32	0.4359(7)	0.6773(6)	0.3209(4)	5.2(4)
C33	0.3504(6)	0.5656(6)	0.3222(3)	4.1(4)
C34	0.2016(5)	0.3847(5)	0.4339(3)	3.2(3)
C35	0.2356(6)	0.5092(5)	0.4813(4)	4.3(4)
C36	0.1838(7)	0.5427(6)	0.5503(4)	5.5(4)
C37	0.0963(6)	0.4509(6)	0.5704(4)	5.2(4)
C38	0.0629(6)	0.3286(6)	0.5247(4)	4.6(4)
C39	0.1150(6)	0.2970(5)	0.4582(3)	3.8(4)
C40	0.3370(5)	0.2206(5)	0.3640(3)	3.1(3)
C41	0.4191(6)	0.2518(6)	0.4316(3)	4.1(4)
C42	0.4613(6)	0.1617(6)	0.4491(4)	5.2(4)
C43	0.4224(7)	0.0404(6)	0.4025(4)	5.3(4)
C44	0.3403(6)	0.0066(6)	0.3380(4)	5.0(4)
C45	0.2978(6)	0.0962(5)	0.3183(3)	4.1(4)
C46	0.4361(9)	0.7458(9)	0.1336(5)	10.7(7)
Cl1	0.4718(3)	0.66937(25)	0.04811(16)	11.08(20)
Cl2	0.5172(3)	0.8916(3)	0.17641(18)	14.34(23)
B	0.0641(9)	0.6638(8)	0.2489(5)	6.5(6)
F1	0.0307(5)	0.5449(4)	0.2356(4)	13.0(5)
F2	0.1740(5)	0.6946(5)	0.2170(3)	12.1(4)
F3	−0.0115(7)	0.7074(6)	0.2271(4)	19.6(7)
F4	0.0986(5)	0.7266(5)	0.3272(3)	11.39(16)

3.2.7. $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(S^iPr)CH_2]\}(BF_4)$ (5c)

The yield of **5c** was 59% (207 mg) from 341 mg (0.41 mmol) of **1**. ${}^{31}P$ NMR ($CDCl_3$) δ 18.2 (J_{P-Pt} = 3792 Hz). ${}^{1}H$ NMR ($CDCl_3$) δ 1.20 (6H, d, J_{H-H} = 6.0 Hz, CH_3), 2.78 (1H, hep, J_{H-H} = 6.3 Hz, CH), 3.20 (2H, d with ${}^{195}Pt$ satellites, J_{P-H} = 5.1 Hz, J_{Pt-H} = 44.4 Hz, H_{anti}), 3.38 (2H, H_{syn}), 7.1–7.5 (m, phenyl H). ${}^{13}C$ NMR ($CDCl_3$) δ 23.2 (s, CH_3), 36.3 (s, $C(Me)_2$), 64.0

Table 8
Coordinates and isothermal data of non-hydrogen atoms for **6e** with e.s.d. in parentheses

Atom	x	y	z	B_{eq}
Pt	0.13373(3)	0.25786(3)	0.234831(5)	2.760(13)
Se	−0.16341(8)	0.02398(9)	0.20007(5)	5.38(5)
P1	0.26766(17)	0.32893(17)	0.34517(10)	3.01(10)
P2	0.26599(17)	0.23635(18)	0.13984(10)	3.03(10)
C1	−0.0330(6)	0.2826(7)	0.2900(4)	3.6(4)
C2	−0.0725(6)	0.1900(7)	0.2159(4)	3.6(4)
C3	−0.0252(6)	0.2200(7)	0.1513(4)	4.1(5)
C4	−0.1611(7)	0.0138(7)	0.3019(5)	4.4(4)
C5	−0.0914(8)	−0.0531(8)	0.3210(5)	6.2(6)
C6	−0.0953(9)	−0.0667(9)	0.3932(7)	8.3(7)
C7	−0.1661(9)	−0.0159(10)	0.4458(6)	7.9(7)
C8	−0.2344(9)	0.0528(9)	0.4275(5)	7.1(6)
C9	−0.2353(7)	0.0651(8)	0.3552(5)	5.3(5)
C10	0.3348(6)	0.2166(6)	0.3637(4)	3.4(4)
C11	0.4168(7)	0.2467(7)	0.4291(4)	4.7(5)
C12	0.4598(8)	0.1573(8)	0.4440(5)	5.9(5)
C13	0.4189(9)	0.0368(8)	0.3962(5)	6.2(6)
C14	0.3359(8)	0.0051(7)	0.3331(5)	5.5(5)
C15	0.2944(7)	0.0954(7)	0.3167(4)	4.1(4)
C16	0.1972(6)	0.3769(6)	0.4352(4)	3.0(4)
C17	0.1095(7)	0.2874(7)	0.4554(4)	4.1(4)
C18	0.0537(7)	0.3173(8)	0.5228(4)	4.8(5)
C19	0.0855(8)	0.4383(8)	0.5698(4)	5.4(5)
C20	0.1714(8)	0.5275(8)	0.5504(5)	5.7(5)
C21	0.2273(7)	0.4980(7)	0.4824(4)	4.5(5)
C22	0.3894(6)	0.4674(6)	0.3470(4)	3.5(4)
C23	0.5166(7)	0.4897(7)	0.3645(4)	4.6(5)
C24	0.5999(7)	0.5989(8)	0.3674(5)	5.5(5)
C25	0.5586(8)	0.6898(8)	0.3534(5)	6.2(5)
C26	0.4338(8)	0.6687(8)	0.3342(5)	5.6(5)
C27	0.3500(7)	0.5581(7)	0.2303(4)	4.3(4)
C28	0.4351(6)	0.2999(6)	0.1641(4)	3.1(3)
C29	0.4979(7)	0.2353(7)	0.1953(4)	3.8(4)
C30	0.6275(7)	0.2794(8)	0.2129(4)	4.9(5)
C31	0.6936(7)	0.3880(8)	0.2014(5)	5.4(5)
C32	0.6338(7)	0.4517(7)	0.1724(5)	5.1(5)
C33	0.5038(7)	0.4085(7)	0.1533(4)	4.3(5)
C34	0.2264(6)	0.3103(6)	0.0732(4)	3.2(4)
C35	0.2063(7)	0.4242(7)	0.1034(4)	4.2(4)
C36	0.1679(7)	0.4815(7)	0.0556(5)	5.0(5)
C37	0.1500(7)	0.4263(8)	−0.0224(5)	4.9(5)
C38	0.1706(7)	0.3144(8)	−0.0535(4)	5.1(5)
C39	0.2089(7)	0.2546(7)	−0.0070(4)	4.1(4)
C40	0.2478(6)	0.0757(6)	0.0836(4)	3.2(4)
C41	0.1590(6)	−0.0186(7)	0.0985(4)	4.0(4)
C42	0.1492(7)	−0.1400(7)	0.0580(5)	5.3(5)
C43	0.2257(7)	−0.1677(7)	0.0011(5)	5.1(5)
C44	0.3137(7)	−0.0735(7)	−0.0138(4)	4.6(4)
C45	0.3269(6)	0.0464(7)	0.0270(4)	3.7(4)
B	0.0760(11)	0.6668(11)	0.2514(7)	6.8(8)
F1	0.0947(7)	0.7382(6)	0.3268(3)	11.9(5)
F2	0.0418(6)	0.5486(5)	0.2438(4)	11.2(5)
F3	0.1935(6)	0.6946(6)	0.2247(4)	11.1(4)
F4	0.0055(9)	0.7013(9)	0.2145(5)	17.5(8)
C46	0.4549(9)	0.7582(10)	0.1332(6)	7.7(7)
Cl1	0.4553(3)	0.6795(3)	0.03631(17)	9.25(18)
Cl2	0.4743(3)	0.9125(3)	0.14977(19)	10.18(21)
Cl3	0.5839(4)	0.7474(3)	0.18473(21)	11.7(3)

(dd with ^{195}Pt satellites, $J_{P-C} = 36.8$ Hz, $J_{Pt-C} = 98.2$ Hz, C$_t$), 127–135 (phenyl C), 143.2 (s, C$_c$). Anal. Found: C, 54.56; H, 4.35. $C_{42}H_{41}SP_2PtBF_4$ Calc.: C, 54.73; H, 4.48%.

3.2.8. *$\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(S^tBu)CH_2]\}(BF_4)$ (5d)*

The yield of **5d** was 78% (156 mg) from 178 mg (0.21 mmol) of **1**. ^{31}P NMR (CDCl$_3$) δ 18.4 ($J_{P-Pt} = 3884$ Hz). ^{1}H NMR (CDCl$_3$) δ 1.33 (9H, s, CH_3), 3.47

Table 9
Selected bond distances (Å) and angles (deg)

$\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(OEt)CH_2]\}(BF_4)$(4b)					
Pt–P1	2.297(3)	Pt–P2	2.292(3)	Pt–C1	2.17(1)
Pt–C2	2.21(1)	Pt–C3	2.19(1)	C1–C2	1.37(2)
C2–C3	1.36(2)	C2–O1	1.42(2)	C4–O1	1.33(3)
C4–C5	1.39(4)				
P1–Pt–P2	104.5(1)	P1–Pt–C1	95.3(4)	P1–Pt–C2	126.9(4)
P1–Pt–C3	161.0(4)	P2–Pt–C1	160.1(4)	P2–Pt–C2	125.0(4)
P2–Pt–C3	94.5(4)	C1–Pt–C2	36.5(6)	C1–Pt–C3	65.7(5)
C2–Pt–C3	35.9(6)	Pt–C1–C2	73.3(8)	Pt–C2–C1	70.2(8)
Pt–C2–C3	71.0(8)	Pt–C3–C2	73.2(9)	Pt–C2–O1	120(1)
C1–C2–C3	120(1)	C1–C2–O1	117(1)	C3–C2–O1	121(2)
C2–O1–C4	133(2)				
$\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(OPh)CH_2]\}(BF_4)$(4e)					
Pt–P1	2.295(2)	Pt–P2	2.284(2)	Pt–C1	2.176(7)
Pt–C2	2.246(6)	Pt–C3	2.186(6)	C1–C2	1.38(1)
C2–C3	1.43(1)	C2–O	1.361(9)	C4–O	1.415(9)
P1–Pt–P2	101.73(6)	P1–Pt–C1	94.0(2)	P1–Pt–C2	127.7(2)
P1–Pt–C3	158.5(2)	P2–Pt–C1	164.0(2)	P2–Pt–C2	129.4(2)
P2–Pt–C3	97.3(2)	C1–Pt–C2	36.3(3)	C1–Pt–C3	66.7(3)
C2–Pt–C3	37.5(3)	Pt–C1–C2	74.6(4)	Pt–C2–C1	69.1(4)
Pt–C2–C3	69.0(3)	Pt–C3–C2	73.5(4)	Pt–C2–O	120.5(4)
C1–C2–C3	117.3(7)	C1–C2–O	118.0(6)	C3–C2–O	122.9(6)
C2–O–C4	119.1(5)				
$\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(SEt)CH_2]\}(BF_4)$(5b)					
P1–P1	2.298(4)	Pt–P2	2.261(5)	Pt–C1	2.20(2)
Pt–C2	2.24(2)	Pt–C3	2.18(2)	C1–C2	1.39(3)
C2–C3	1.45(3)	C2–S	1.76(2)	C4–S	1.95(3)
P1–Pt–P2	103.3(2)	P1–Pt–C1	161.3(5)	P1–Pt–C2	126.7(6)
P1–Pt–C3	93.6(5)	P2–Pt–C1	95.3(5)	P2–Pt–C2	126.7(6)
P2–Pt–C3	163.0(5)	C1–Pt–C2	36.4(7)	C1–Pt–C3	67.7(7)
C2–PtC3	38.4(7)	Pt–C1–C2	74(1)	Pt–C2–C1	70(1)
Pt–C2–C3	69(1)	Pt–C3–C2	73(1)	Pt–C2–S	120(1)
C1–C2–C3	118(2)	C1–C2–S	125(2)	C3–C2–S	115(2)
$\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(SPh)CH_2]\}(BF_4)$(5e)					
Pt–P1	2.294(2)	Pt–P2	2.286(2)	Pt–C1	2.177(6)
Pt–C2	2.204(6)	Pt–C3	2.177(6)	C1–C2	1.413(9)
C2–C3	1.377(8)	C2-S	1.743(6)	C4–S	1.779(7)
P1–Pt–P2	101.90(6)	P1–Pt–C1	92.5(2)	P1–Pt–C2	126.7(2)
P1–Pt–C3	158.4(2)	P2–Pt–C1	164.2(2)	P2–Pt–C2	130.4(2)
P2–Pt–C3	98.0(2)	C1–Pt–C2	37.6(2)	C1–Pt–C3	66.9(2)
C2–Pt–C3	36.6(2)	Pt–C1–C2	72.2(3)	Pt–C2–C1	70.1(3)
Pt–C2–C3	70.6(3)	Pt–C3–C2	72.7(3)	Pt–C2–S	123.0(3)
C1–C2–C3	118.6(6)	C1–C2–S	115.0(5)	C3–C2–S	125.8(3)
C2–S–C4	104.8(3)				
$\{Pt[\eta^3\text{-}CH_2C(SePh)CH_2](PPh_3)_2\}(BF_4)$(6e)					
Pt–P1	2.283(2)	Pt–P2	2.297(2)	Pt–C1	2.181(6)
P–C2	2.205(6)	Pt–C3	2.183(7)	C1–C2	1.43(1)
C2–C3	1.41(1)	C2–Se	1.881(7)	C4–Se	1.904(8)
P1–Pt–P2	102.64(7)	P1–Pt–C1	97.0(2)	P1–Pt–C2	131.0(2)
P1–Pt–C3	163.5(2)	P2–Pt–C1	158.7(2)	P2–Pt–C2	125.4(2)
P2–Pt–C3	91.9(2)	C1–Pt–C2	38.1(3)	C1–Pt–C3	67.6(3)
C2–Pt–C3	37.4(3)	Pt–C1–C2	71.9(4)	Pt–C2–C1	70.0(4)
Pt–C2–C3	70.5(4)	Pt–C3–C2	72.2(4)	Pt–C2–Se	122.8(3)
C1–C2–C3	117.7(7)	C1–C2–Se	124.6(5)	C3–C2–Se	117.0(5)
C2–Se–C4	102.7(3)				

(2H, d with ^{195}Pt satellites, $J_{P-H} = 7.6$ Hz, $J_{Pt-H} = 40.0$ Hz, H_{anti}), 3.63 (2H, H_{syn}), 7.1–7.5 (m, phenyl H). ^{13}C NMR ($CDCl_3$) δ 31.4 (s, CH_3), 48.7 (s, $J_{P-C} = 11.2$ Hz, SCMe$_3$), 70.7 (dd with ^{195}Pt satellites, $J_{P-C} = 3.4$, 33.8 Hz, $J_{Pt-C} = 92.2$ Hz, C_t), 127–135 (phenyl C), 136.1 (s, $J_{Pt-C} = 20$ Hz, C_c).

3.2.9. $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(SPh)CH_2]\}(BF_4)$ (5e)

The yield of **5e** was 68% (351 mg) from 452 mg (0.54 mmol) of **1**. ^{31}P NMR ($CDCl_3$) δ 18.2 ($J_{P-Pt} = 3801$ Hz). ^{1}H NMR ($CDCl_3$) δ 3.13 (2H, dd with ^{195}Pt satellites, $J_{H-H} = 3.4$ Hz, $J_{P-H} = 8.4$ Hz, $J_{Pt-H} = 42.5$ Hz, H_{anti}), δ 3.26 (2H, d with ^{195}Pt satellites, $J_{H-H} = 3.4$ Hz, H_{syn}), δ 7.1–7.5 (m, phenyl H). ^{13}C NMR ($CDCl_3$) δ 63.0 (dd with ^{195}Pt satellites, $J_{P-C} = 4.8$, 36.5 Hz, $J_{Pt-C} = 97.8$ Hz, C_t), 127–135 (phenyl C), 142.3 (t, $J_{P-C} = 2.9$ Hz, C_c). Anal. Found: C, 52.20; H, 3.95. $C_{45}H_{39}SP_2PtBF_4 \cdot CH_2Cl_2 \cdot H_2O$ Calc.: C, 52.19; H, 4.09%.

3.2.10. $\{Pt(Ph_3P)_2[\eta^3\text{-}CH_2C(p\text{-}SC_6H_4OH)CH_2]\}(BF_4)_2$ (5f)

To a $CDCl_3$ solution containing **2** (35 mg) was injected equimolar amounts of p-HSC_6H_4OH. The NMR spectra were taken at 298 K. ^{31}P NMR ($CDCl_3$) δ 18.4 ($J_{P-Pt} = 3765$ Hz). ^{1}H NMR ($CDCl_3$) δ 2.80 (2H, d with ^{195}Pt satellites, $J_{P-H} = 8.5$ Hz, $J_{Pt-H} = 45.5$ Hz, H_{anti}), 3.26 (2H, s, H_{syn}), 7.1–7.5 (m, phenyl H), 7.97 (1H, s, OH). ^{13}C NMR ($CDCl_3$) δ 62.1 (dd with ^{195}Pt satellites, $J_{P-C} = 3.3$, 37.4 Hz, $J_{Pt-C} = 100.7$ Hz, C_t), 127–135 (phenyl C), 144.4 (C_c).

3.2.11. $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(SePh)CH_2]\}(BF_4)$ (6e)

The yield of **6e** was 83% (316 mg) from 318 mg (0.38 mmol) of **1**. ^{31}P NMR ($CDCl_3$) δ 18.2 ($J_{P-Pt} = 3841$ Hz). ^{1}H NMR ($CDCl_3$) δ 3.34 (2H, s, H_{syn}), 3.34 (2H, d with ^{195}Pt satellites, $J_{P-H} = 7.8$ Hz, $J_{Pt-H} = 40.4$ Hz, H_{anti}), 7.1–7.5 (m, phenyl H). ^{13}C NMR ($CDCl_3$) δ 66.2 (dd with ^{195}Pt satellites, $J_{P-C} = 4.7$, 35.5 Hz, $J_{Pt-C} = 95.5$ Hz, C_t), 124.0 (s, C_c), 127–135 (phenyl C). Anal. Found: C, 53.45; H, 4.14. $C_{45}H_{39}SeP_2PtBF_4$ Calc.: C, 53.91; H, 3.92%.

3.2.12. X-ray crystallographic analysis

Diffraction data were measured on a Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. The cell parameters were determined by a least-squares fit on 25 reflections. Intensity data were corrected for absorption on the basis of an experimental ψ rotation curve. The refinement procedure was by a full-matrix least-squares method including all the non-hydrogen atoms anisotropically. Hydrogen atoms were fixed at the ideal geometry and C–H distance 1.0 Å; their isotopic thermal parameters were fixed to the values of the attached carbon atoms at the convergence of the isotropic refinement. Atomic scattering factors were taken from the *International Tables of Crystallographic Data*, Vol. IV [15]. Computing programs are from the NRC VAX package [16]. Crystallographic data and selected atomic coordinates and bond parameters are collected in Tables 3–9. The rest of the data are supplied as supplementary material.

Acknowledgements

We thank the National Science Council, Taiwan for financial support.

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