

A new stable intermediary mode between η^3 -2-aminoallyl complexes and metallacyclobutanimes. Synthesis and structural characteristic of η^3 -azatrimethylenemethane and *N*-protonated, *N*-alkylated, *N*-arylated η^3 -azatrimethylenemethane complexes of Pt and Pd¹

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Abstract

Regioselective addition of ammonia, primary or secondary amines, aniline, or amino derivatives either to a neutral (η^1 -allyl)platinum complex *trans*-Pt(Br)(PPh₃)₂(η^1 -CHCCH₂) (**1**) or to a cationic η^3 -allenyl/propargyl platinum complex [Pt(PPh₃)₂(η^3 -C₃H₃)](BF₄) (**2**) provide the synthesis of cationic *N*-protonated, *N*-alkylated, and *N*-arylated η^3 -azatrimethylenemethane complexes {Pt(PPh₃)₂(η^3 -CH₂C(NRR')CH₂)}(X) (R = H R' = H (**3a**), Me (**3b**), Et (**3c**), ^{*i*}Pr (**3d**), ^{*t*}Bu (**3e**), *c*-C₆H₁₁ (**3f**), Ph (**3g**), CH₂CH₂OH (**3h**), R = R' = Et (**3i**), *c*-C₃H₆ (from azetidine **3j**), Ph (**3k**), R = Me R' = Ph (**3l**); X = Br, BF₄), respectively. Addition of amides to **1** gave a neutral η^3 -azatrimethylenemethane complex Pt(PPh₃)₂[η^3 -CH₂C(NSO₂Ph)CH₂] (**4m**). Similar reactions using palladium complexes yield {Pd(PPh₃)₂[η^3 -CH₂C(NRR')CH₂]}(X) (R = H R' = ^{*i*}Pr (**7d**), Ph (**7g**), R = R' = Et (**7i**); X = Br, BF₄, OTf), Pd(Br)(PPh₃)₂[η^3 -CH₂C(NEt₂)CH₂] (**8i**) and Pd(PPh₃)₂[η^3 -CH₂C(NR)CH₂] (R = SO₂Ph (**9m**), *p*-SO₂C₆H₄Me (**9n**)). Synthesis of three complexes, {M(PPh₃)₂[η^3 -CH₂C(NHR)CH₂]}⁺ (M = Pt R = SO₂Ph (**3m**); M = Pd R = SO₂Ph (**7m**), *p*-SO₂C₆H₄Me (**7n**)), can not be done by hydroamination reactions, but has been successful using protonation of η^3 -*N*-TMM complexes **4m**, **9m**, and **9n**, respectively. Spectroscopic and crystallographic characterizations indicate that these *N*-TMM complexes exhibit intermediary structural features between η^3 -2-aminoallyl and metallacyclobutanime complexes.² © 1998 Elsevier Science S.A. All rights reserved.

Keywords: η^3 -Azatrimethylenemethane complexes; Pt; Pd; Structural characteristic

1. Introduction

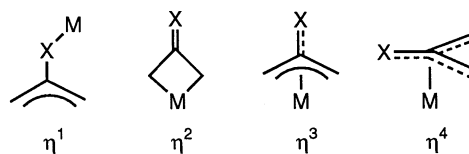
There has been increasing research interest in transition metal complexes of heteronuclear trimethylen-

emethanes in the form of M[CH₂C(X)CH₂]. The hetero-TMM compounds which contain the heteroatoms X as O, S, or Si have been examined [1–3]. Four types of mononuclear bonding modes in η^1 -, η^2 -, η^3 - or η^4 -form have been structurally characterized [4].

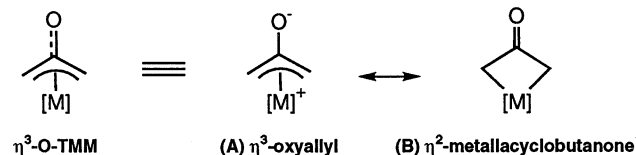
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¹ JTC dedicates this article to Professor Akira Nakamura of Osaka University on his retirement.

² We designate η^3 -O-TMM to stand for the η^3 -oxatrimethylenemethane complexes M[η^3 -CH₂C(=O)CH₂]; η^3 -*N*-TMM to stand for the η^3 -azatrimethylenemethane complexes M[η^3 -CH₂C(=NR)CH₂]. Accordingly, *N*-protonated η^3 -*N*-TMM complexes are referred to M[η^3 -CH₂C(NH₂)CH₂]; and *N*-alkylated or *N*-arylated η^3 -*N*-TMM complexes are referred to M[η^3 -CH₂C(NHR)CH₂] or M[η^3 -CH₂C(NRR')CH₂] (R, R' = alkyl or aryl).



The TMM species of the η^3 -form are relatively less investigated, although some have been found useful in organic synthesis [5]. Among them, the η^3 -O-TMM complexes of palladium and platinum are the most extensively studied heterotrimethylene methane species [6]. Both experimental and theoretical data indicate that the η^3 -O-TMM complexes have the resonance structure between a zwitterionic η^3 -2-oxyallyl form (A) and a metallacyclobutanone form (B).

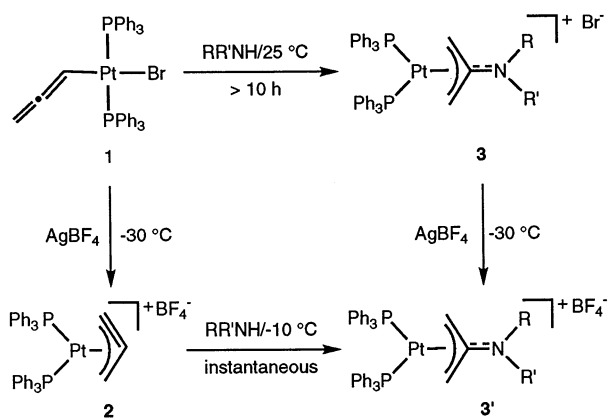


The isoelectronic species of η^3 -O-TMM, η^3 -*N*-TMM complexes, were virtually unexplored until we reported the first isolable cationic *N*-alkylated η^3 -*N*-TMM complexes of platinum in prior preliminary communications [7]. Later on, the *N*-protonated and alkylated η^3 -*N*-TMM complexes of iridium were also prepared [8]. In the mean time, Wojcicki and Murai published their independent work on the neutral η^3 -*N*-TMM complexes [9]. These *N*-TMM complexes constitute a class of new heterotrimethylenemethane species. We report here our complete studies of the title complexes including synthesis, characterization, structure, and reaction scope.

2. Results and discussion

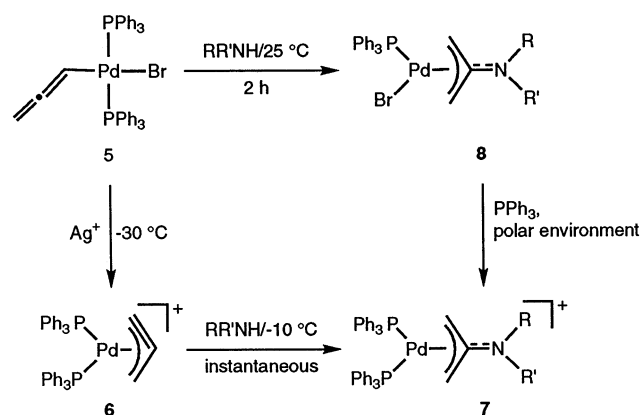
2.1. Synthesis of η^3 -*N*-TMM platinum and palladium complexes

Synthesis of *N*-protonated, *N*-alkylated and *N*-arylated η^3 -*N*-TMM complexes is established by regioselective hydroamination of metal allenyl or metal propargyl complexes. The reactions of *trans*-Pt(Br)(PPh₃)₂(η^1 -CHCCH₂) (1) and equimolar amounts of ammonia, primary or secondary amines, aniline, and other amino derivatives produce {Pt(PPh₃)₂(η^3 -CH₂C(NRR')CH₂)}(Br) (R = H R' = H (3a), Me (3b), Et (3c), ^{*i*}Pr (3d), ^{*t*}Bu (3e), *c*-C₆H₁₁ (3f), Ph (3g), CH₂CH₂OH (3h), R = R' = Et (3i), *c*-C₃H₆ (from azetidine, 3j), Ph (3k), R = Me R' = Ph (3l)). The yields are generally excellent. The BF₄ salts of 3 (3a' and 3g') can be obtained either by anionic exchange using AgBF₄, or alternatively by the reactions of a cationic η^3 -allenyl/propargyl complex [Pt(PPh₃)₂(η^3 -C₃H₃)](BF₄) (2) with the corresponding amino compounds (Scheme 1). In a typical case, the reaction of 1 and aqueous ammonia (0.2 mmol for each) in CH₂Cl₂ (20 ml) at 25°C would take over a day to completion. The hydroamination reactions of the cationic 2 with similar molar mass are accomplished instantaneously at -10°C.

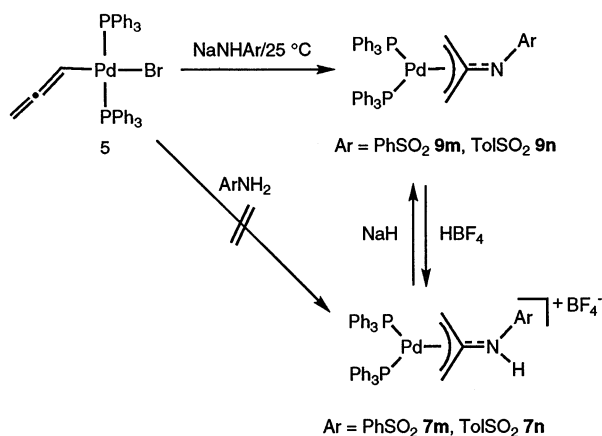


Scheme 1.

The *N*-alkylated and *N*-arylated η^3 -*N*-TMM complexes of palladium are prepared using the same methodology as for preparing the platinum analogs, but the lability of the palladium system makes somewhat distinct reactivity. Equimolar amounts (0.27 mmol) *trans*-Pd(Br)(PPh₃)₂(η^1 -CHCCH₂) (5) and Et₂NH were allowed to react in CH₂Cl₂ (15 ml) at 25°C for 2 h. A neutral *N*-alkylated η^3 -*N*-TMM complex Pd(Br)(PPh₃)₂[η^3 -CH₂C(NEt₂)CH₂] (8i) was obtained in 70% isolated yields. Treating 8i with PPh₃ gave an ionic species as a bromide salt {Pd(PPh₃)₂[η^3 -CH₂C(NEt₂)CH₂]}(Br) (7i). The cation of 7i with other counter-anions could be prepared by more facile reactions of [Pd(PPh₃)₂(η^3 -C₃H₃)](X) (X = PF₆ (6), BF₄ (6'), OTf (6'')) and Et₂NH. Hydroamination of 5 or 6 with NH₃ or MeNH₂ could be achieved below 0°C, but the resulting *N*-TMM products decomposed when the temperature was raised to 25°C. Addition of ^{*i*}PrNH₂ or PhNH₂ to 5 was successful, when reactions were carried out with the presence of large excess amines. The products are cationic complexes {Pd(PPh₃)₂[η^3 -CH₂C(NHR)CH₂]}(Br) (R = ^{*i*}Pr (7d), Ph (7g)) instead of the neutral species, presumably the polar environment favors the ionic species (Scheme 2).



Scheme 2.



Scheme 3.

The isoelectronic nitrogen derivatives of η^3 -O-TMM are η^3 -N-TMM complexes. Wojcicki reported the first structurally characterized η^3 -N-TMM complexes $\text{Pt}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NR})\text{CHPh}]$, prepared from deprotonation of $\{\text{Pt}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NHR})\text{CHPh}]\}^+$. We found that addition of amide to the allenyl complexes can also generate the neutral η^3 -N-TMM complexes readily. The reactions of *trans*- $\text{Pd}(\text{Br})(\text{PPh}_3)_2[\eta^1\text{-CHCCH}_2]$ (**5**) with $\text{Na}(\text{NHAr})$ in CH_2Cl_2 at 25°C produce $\text{Pd}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NR})\text{CH}_2]$ ($\text{R} = \text{SO}_2\text{Ph}$ (**9m**), *p*- $\text{SO}_2\text{C}_6\text{H}_4\text{Me}$ (**9n**)) in good yields. The NMR studies show that protonation of **9m** and **9n** instantaneously gives $\{\text{Pd}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NHR})\text{CH}_2]\}(\text{BF}_4)$ ($\text{R} = \text{SO}_2\text{Ph}$ (**7m**), *p*- $\text{SO}_2\text{C}_6\text{H}_4\text{Me}$ (**7n**)). Treating **7m** and **7n** with NaH recovers **9m** and **9n** respectively. Weak amine like PhSO_2NH_2 or *p*- $\text{MeC}_6\text{H}_4\text{-SO}_2\text{NH}_2$ fails to add to **5** (Scheme 3).

2.2. Reaction mechanism of hydroamination of η^1 -allenyl complexes

We have further examined the reactions of η^1 -allenyl complexes with amide. Adding AgOAc to **1** resulted in ligand substitution, giving *trans*- $\text{Pt}(\text{PPh}_3)_2(\text{OAc})(\eta^1\text{-CHCCH}_2)$ (**10**). Treatment of **10** with $\text{Na}(\text{NHSO}_2\text{Ph})$ gave another η^1 -allenyl complex *trans*- $\text{Pt}(\text{PPh}_3)_2(\text{NHSO}_2\text{Ph})(\eta^1\text{-CHCCH}_2)$ (**11**). The NMR studies suggest that the two phosphine ligands in **11** are in *trans* arrangement, and the acetate ligand is displaced presumably by amide. The identification of **11** is evidenced by its transformation into $\text{Pt}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NSO}_2\text{Ph})\text{CH}_2]$ (**4m**) (Scheme 4). Protonation of **4m** gives $\{\text{Pt}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NHSO}_2\text{Ph})\text{CH}_2]\}(\text{BF}_4)$ (**3m**).

Hydroamination of a *cis* η^1 -allenylplatinum complex has also been studied. *cis*- $\text{Pt}(\text{dppe})(\text{Cl})(\eta^1\text{-CHCCH}_2)$ (**12**) was prepared by treating *trans*- $\text{Pt}(\text{PPh}_3)_2(\text{Cl})(\eta^1\text{-CHCCH}_2)$ with diphenylphosphinoethane (dppe) in benzene. The reaction of $\text{Na}(\text{NHSO}_2\text{Ph})$ and **12** first yields a *cis* η^1 -allenyl(amido) complex *cis*- $\text{Pt}(\text{dppe})(\text{NHSO}_2\text{Ph})(\eta^1\text{-CHCCH}_2)$ (**13**) which then transforms into *cis*- $\text{Pt}(-$

$\text{dppe})[\eta^3\text{-CH}_2\text{C}(\text{NSO}_2\text{Ph})\text{CH}_2]$ (**14**) by heating at 60°C (Scheme 5).

The formation of amido complexes **11** and **13** strongly supports that the mechanism of hydroamination of the η^1 -allenyl complexes likely involves a preceding coordination step of amide [10]. In another word, the metal center plays a crucial role to mediate the addition of the N–H bond across the allenyl C=C bond [11]. From the mechanistic viewpoint, transformation of the allenyl(amido) complexes into η^3 -N-TMM complexes may have two possible pathways. The amination step may be achieved via intramolecular C–N bond formation. Alternatively, amide dissociation will give rise to an η^3 -allenyl/propargyl intermediate which then undergoes intermolecular C–N bond formation (Scheme 6).

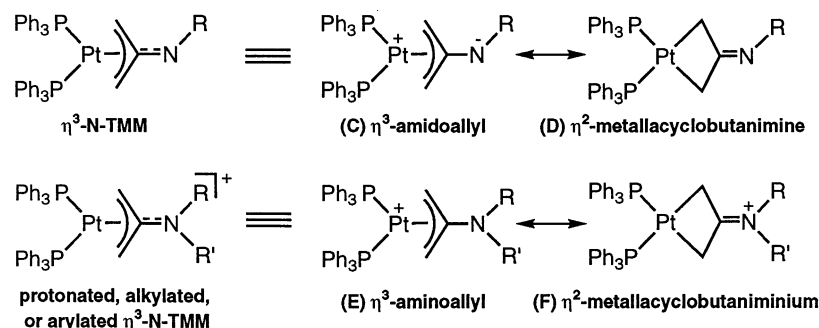
More evidences are obtained from the competitive kinetic experiments which afford relative reactivity of hydroamination of **1** toward different amines. In a typical case, to a CDCl_3 solution (0.5 ml) containing **1** (20 mg) was injected a mixture of MeNH_2 and EtNH_2 with each having 10-fold equivalents. At the end of the reaction, the NMR integration gave the relative yields of **3b** and **3c** as 1.7:1. Table 1 collects the results measured for a series primary amines and aniline. The relative reactivity is estimated as $\text{MeNH}_2:\text{EtNH}_2:\text{PrNH}_2:\text{c-C}_6\text{H}_{11}\text{NH}_2:\text{t-BuNH}_2 = 24:14:8:8:1$. These data indicate the importance of the steric effect and show consistency with the mechanism involving amine coordination. On the other hand, the relative reactivity between *c*- $\text{C}_6\text{H}_{11}\text{NH}_2$ and PhNH_2 is 2:1, and the qualitative observations showed $\text{EtNH}_2 < \text{Et}_2\text{NH}$ and $\text{PrNH}_2 < \text{Pr}_2\text{NH}$ in reaction rates, suggesting that the electronic factor should not be negligible. This is also reasonable since better nucleophilicity would facilitate coordination and the addition as well. Amines with poor coordinating ability and nucleophilicity such as PhSO_2NH_2 or $\text{MeC}_6\text{H}_4\text{SO}_2\text{NH}_2$ indeed fail hydroamination to **1** and **5**.

2.3. Spectroscopic and structural characteristic of η^3 -N-TMM complexes

The spectral characteristic of η^3 -N-TMM complexes resemble those of central-carbon-substituted η^3 -allyl complexes [12]. As collected in Table 2, the $^1\text{H-NMR}$ resonances of *syn*- and *anti*-hydrogens of η^3 -N-TMM complexes are diastereotopic. The *anti*-protons are at high field and usually better resolved. The *syn*-protons appear as a broadened singlet. In the cases of alkylated η^3 -N-TMM complexes such as **3b**, **3c**, **3e**, **3f**, and **3h**, four allyl hydrogens well split. These data evidence the C–N double bond in these η^3 -N-TMM complexes. The $^{13}\text{C-NMR}$ resonances of the center-carbon of η^3 -N-TMM complexes appear at $\delta 150$ which are down-field compared those of the common η^3 -allyl complexes. In addition, the values of $J_{\text{C-Pt}}$ of η^3 -N-TMM complexes, which are in the region of 100–110 Hz, are distinctly larger than those of η^3 -allyl complexes (20–40 Hz), and are useful parameters for characterization.

The ^{31}P -NMR spectra of complexes **3** show two magnetically non-equivalent phosphines and support a η^3 -*N*-TMM rather than a η^3 -allyl structure. We examined ^{31}P -NMR coalescence for **3d** and **3e**, which occurred at 318 and 305 K, respectively. The coalescence temperature (T_c) allows to estimate the rotational energy barrier (ΔG) along the C–N bond. The calculated ΔG is 15.9 kcal mol $^{-1}$ for **3d** and 14.6 kcal mol $^{-1}$ for **3e** [13]. The palladium analog **7d** shows relatively lower T_c at 283 K which affords $\Delta G = 13.4$ kcal mol $^{-1}$. These thermodynamic data also support the C–N double bond character.

The X-ray diffractions for single crystals provide structural understanding for these η^3 -*N*-TMM complexes. Crystallographic analysis for **3a'**, **3d**, **3g'**, **3h**, **3i**, **3j**, **4m**, **7d**, **7g**, **7i**, and **8i** have been done and the ORTEP drawings of **3a'** and **4m** are shown in Figs. 1 and 2, respectively, as the representatives. Complex **4m** which is a neutral η^3 -*N*-TMM complex and **3a'** which is the prototype of cationic *N*-protonated η^3 -*N*-TMM complex are generally alike. Both show that $\text{CH}_2\text{C}(\text{N})\text{CH}_2$ moieties use three carbon atoms to bond with the metal. The C_3N atoms are nearly coplanar. The central carbon is only slightly out of plane to the opposite side of the metal. As a result, the distance of Pt– C_c is longer than the Pt– C_t distances. The important bond parameters are listed in Table 3. One of the most characteristic features of a η^3 -*N*-TMM complex is that the lengths of two C_t – C_c bond and the C_c –N bond are within the double bond range. It is worth to note that the dihedral angles (θ) defined by the C_t –M– C_t' and C_t – C_c – C_t' planes of these complexes are $60 \pm 4^\circ$ which are smaller than those of the η^3 -allyl complexes but much larger than those of metallacyclobutanes. The values of $\text{D}(\text{C}=\text{N})$ and θ can serve pragmatic characterizing criteria for such η^3 -*N*-TMM complexes. In addition, the angles of C_t – C_c – C_t' are 110° which are smaller than those of η^3 -allyl complexes (115 – 120°) [12]. In similarity to the isoelectronic η^3 -*O*-TMM complexes, the neutral η^3 -*N*-TMM complexes have the resonance structures of η^3 -2-amidoallyl (C) and metallacyclobutanimine (D); and the protonated, alkylated, and arylated η^3 -*N*-TMM cations have the resonance structures of η^3 -2-aminoallyl (E) and metallacyclobutaniminium (F).



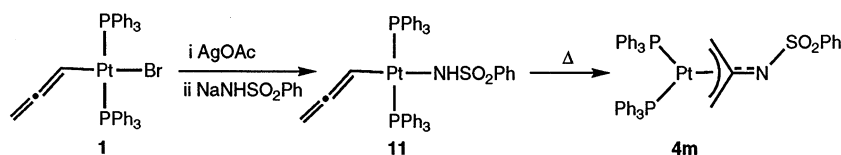
2.4. Base-catalyzed hydrolysis of η^3 -*N*-TMM complexes

Unlike the deprotonation of $\{\text{Pt}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NHSO}_2\text{Ph})\text{CH}_2]\}^+$, which gives $\text{Pt}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NSO}_2\text{Ph})\text{CH}_2]$, reaction of $\{\text{Pt}(\text{PPh}_3)_2(\eta^3\text{-CH}_2\text{C}(\text{NH}_2)\text{CH}_2)\}^+$ (**3a**) with a methanol solution of KOH yields a new dicationic complex of 1,5-diplatinacycloocta-3,7-diimine $\{\text{cis-Pt}(\text{PPh}_3)_2(\mu\text{-CH}_2\text{CMeNH})_2\}$ (**Br**) $_2$ (**15**). The molecular structure of **15** has been confirmed unequivocally by X-ray crystallography. Its ORTEP drawing in Fig. 3 shows that two $-\text{CH}_2\text{C}(\text{Me})=\text{NH}-$ bridging ligands link the two platinum centers to form an eight-member metallacycle. The cyclic framework is in a boat form and the two C–N double bonds are nearly parallel. Complex **15** is the first example of diplatina metallacycle containing bridging imines [14].

The usage of alkaline appears to be essential to the dimerization of **3a**, since adding NaOPh to **3a** fails to generate **15**. The transformation of **3a** into **15** is similar to enamine–imine tautomerization via a course of deprotonation–protonation as illustrated in Scheme 7. In another reaction treating **1** with excess $\text{HOCH}_2\text{CH}_2\text{NH}_2$, *cis*- $\{(\text{Ph}_3\text{P})_2\text{Pt}[\text{NH}_2\text{CH}_2\text{CH}_2\text{O}]\}$ (**Br**) (**16**) and acetone were recovered. The same products were acquired from the reaction with equimolar amounts of **3h** and Et_3N . We propose that **1** first undergoes hydroamination to give **3h**. The following step is similar to the formation of **15** from **3a**. The *N*-alkylated η^3 -*N*-TMM complex **3h** proceeds base-catalyzed enamine–imine tautomerization followed by hydrolysis of imine moiety. Complex **16** is thus formed along with acetone (Scheme 8).

3. Concluding remarks

Platinum and palladium complexes of η^3 -*N*-TMM $\text{M}[\eta^3\text{-CH}_2\text{C}(\text{NR})\text{CH}_2]$, *N*-protonated η^3 -*N*-TMM $\text{M}[\eta^3\text{-CH}_2\text{C}(\text{NH}_2)\text{CH}_2]$, and *N*-alkylated (or *N*-arylated) η^3 -*N*-TMM $\text{M}[\eta^3\text{-CH}_2\text{C}(\text{NRR}')\text{CH}_2]$ are successfully prepared by regioselective addition of amides, ammonia, amines, or amino derivatives to the η^1 -allenyl or η^3 -allenyl/propargyl complexes. Spectroscopic



Scheme 4.

and X-ray crystallographic analyses provide the instrumentation for characterization. The η^3 -*N*-TMM metal complexes make a class of new organometallic species with intermediary structural characteristic between η^3 -aminoallyl and metallacyclobutanimine complexes. The common moiety of η^3 -CH₂C(N)CH₂ is subjected to base-catalyzed enamine–imine tautomerization.

4. Experimental section

4.1. General

Solvents were dried by standard procedures. IR spectra were recorded on a Bio-Rad FTS-40 spectrophotometer. The NMR spectra were recorded on either a Bruker AC-E200 or a Bruker ACE-300 spectrometer. For the ³¹P-NMR spectra, the spectrometer frequency at 81.015 or 121.49 MHz was employed, and chemical shifts are given in ppm (δ) relative to 85% H₃PO₄ in CDCl₃. Values upfield of the standard are defined as negative. Mass spectrometric analyses were collected on a JEOL SX-102A spectrometer. Elemental analyses were done on a Perkin-Elmer 2400 CHN analyzer.

4.2. Synthesis and characterization

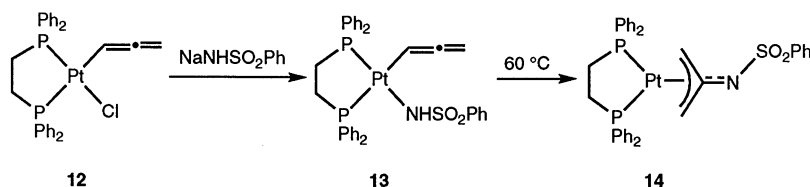
4.2.1. $\{Pt(PPh_3)_2[\eta^3-CH_2C(NH_2)CH_2]\}(X)$ ($X = Br$ **3a**, BF_4 **3a'**)

To a two-necked round-bottom flask, was charged with *trans*-Pt(Br)(PPh₃)₂(η^3 -CHCCH₂) (**1**) (165 mg, 0.2 mmol) and aqueous ammonia (17 μ l of 25% aqueous solution) in CH₂Cl₂ (20 ml). The solution was stirred for 1 day and was then concentrated. Addition of diethyl ether to the solution resulted in the precipitation of the white product. The yield was 89%. Alternatively, the reaction of equimolar amounts of [Pt(PPh₃)₂(η^3 -

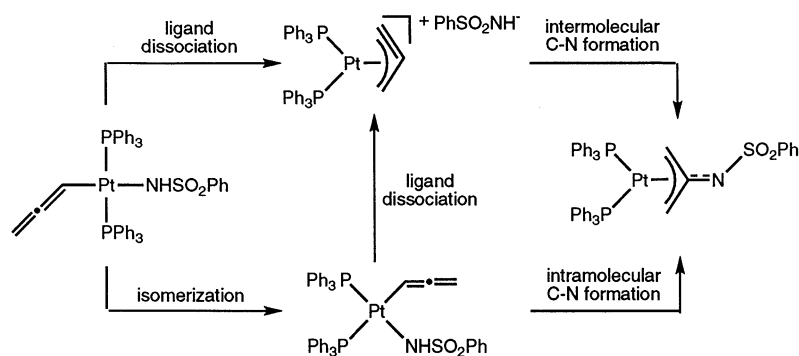
C₃H₃)](BF₄) (**2**) (0.2 mmol) and ammonia (0.5 M in dioxane) in chloroform instantaneously resulted in the BF₄ salt of **3a'** over 90% yield. Selected spectral data: IR (KBr pallet) $\nu_{C=N}$ 1513 cm⁻¹, ν_{N-H} 3446, 3359, 3255 cm⁻¹; ³¹P-NMR (CDCl₃, 81.015 MHz) δ 19.0 ($J_{P-Pt} = 3356$ Hz); ¹H-NMR (CDCl₃, 300 MHz) δ 1.93 (2H, dd with ¹⁹⁵Pt satellites, $J_{H-P} = 4.7, 10.3$ Hz, $J_{H-Pt} = 62.8$ Hz, H_{anti}), 2.83 (2H, br, H_{syn}), 6.50 (2H, s with ¹⁹⁵Pt satellites, $J_{H-Pt} = 18.0$ Hz, NH); ¹³C-NMR (CDCl₃, 50.32 MHz) δ 44.8 (dd with ¹⁹⁵Pt satellites, $J_{C-P} = 4.6, 47.6$ Hz, $J_{C-Pt} = 169.2$ Hz, C₁), 127.6–134.9 (phenyl C), 153.1 (td with ¹⁹⁵Pt satellites, $J_{C-P} = 4.2$ Hz, $J_{C-Pt} = 88.5$ Hz, C₂). Anal. Calc. for PtC₃₉H₃₆NP₂Br: C, 54.74; H, 4.24; N, 1.64. Found: C, 54.02; H, 4.32; N, 1.61.

4.2.2. $\{Pt(PPh_3)_2[\eta^3-CH_2C(NHMe)CH_2]\}(Br)$ (**3b**)

Complex **1** (360 mg, 0.43 mmol) and MeNH₂ (40 μ l 40% aqueous solution, 0.52 mmol) were allowed to react in CH₂Cl₂ (20 ml) at 25°C for 4 h. The yield of white **3b** was 92% (344 mg). IR (KBr pallet) $\nu_{C=N}$ 1579 cm⁻¹; ³¹P-NMR (CDCl₃, 81.0 MHz) δ 18.4 (d, $J_{P-P} = 8.7$ Hz, $J_{P-Pt} = 3196$ Hz), 19.7 (d, $J_{P-P} = 8.7$ Hz, $J_{P-Pt} = 3317$ Hz); ¹H-NMR (CDCl₃, 300 MHz, 275 K) δ 1.65 (1H, dd with ¹⁹⁵Pt satellites, $J_{H-H} = 6.7$ Hz, $J_{H-P} = 11.2$ Hz, $J_{H-Pt} = 67$ Hz, H_{anti}), 1.97 (1H, dd with ¹⁹⁵Pt satellites, $J_{H-H} = 6.7$ Hz, $J_{H-P} = 11.2$ Hz, $J_{H-Pt} = 67$ Hz, H_{anti}), 2.31 (1H, br, H_{syn}), 2.64 (3H, d with ¹⁹⁵Pt satellites, $J_{H-H} = 4.7$ Hz, $J_{H-Pt} = 22.8$ Hz, CH₃), 3.23 (1H, br, H_{syn}), 7.1–7.5 (30H, phenyl H), 8.57 (1H, d, $J_{H-P} = 4.9$ Hz, NH); ¹³C-NMR (CDCl₃, 50.3 MHz) δ 28.8 (d with ¹⁹⁵Pt satellites, $J_{C-P} = 6.2$ Hz, $J_{C-Pt} = 11.6$ Hz, CH₃), 40.1 (dd with ¹⁹⁵Pt satellites, $J_{C-P} = 4.8, 44.9$ Hz, $J_{C-Pt} = 176.4$ Hz, C₁), 41.5 (d with ¹⁹⁵Pt satellites, $J_{C-P} = 49.7$ Hz, $J_{C-Pt} = 201$ Hz, C₁), 127–135 (phenyl C), 156.5 (dd with ¹⁹⁵Pt satellites, $J_{C-P} = 4.6, 9.9$ Hz, $J_{C-Pt} = 110.7$ Hz, C₂); Anal. Calc. for PtC₄₀H₃₈NP₂Br·H₂O C, 54.12; H, 4.54; N, 1.58. Found: C, 53.47; H, 4.58; N, 1.56.



Scheme 5.



Scheme 6.

4.2.3. $\{Pt(PPh_3)_2[\eta^3-CH_2C(NHEt)CH_2]\}(Br)$ (**3c**)

Refer to the paragraph for **3a** for the detailed procedure. The reaction of complex **1** (156 mg, 0.19 mmol) and EtNH₂ (16.5 μl 70% aqueous solution, 2.1 mmol) gave white solid **3c** in 91% yield (151 mg). ³¹P-NMR (CDCl₃, 81.015 MHz) δ 19.0 (d, $J_{P-P} = 8.4$ Hz, $J_{P-Pt} = 3224$ Hz), 19.7 (d, $J_{P-P} = 8.4$ Hz, $J_{P-Pt} = 3275$ Hz); ¹H-NMR (CDCl₃, 300 MHz, 273 K) δ 1.04 (3H, t, $J_{H-H} = 6.7$ Hz, CH₂CH₃), 1.60 (1H, dd with ¹⁹⁵Pt satellites, $J_{H-H} = 6.6$ Hz, $J_{H-P} = 10.9$ Hz, $J_{H-Pt} = 68$ Hz, H_{anti}), 1.96 (1H, dd with ¹⁹⁵Pt satellites, $J_{H-H} = 6.6$ Hz, $J_{H-P} = 10.9$ Hz, $J_{H-Pt} = 68$ Hz, H_{anti}), 2.24 (1H, br, H_{syn}), 2.91, 3.10 (1H, 1H, q, q, $J_{H-H} = 6.7$ Hz, CH₂CH₃), 3.21 (1H, br, H_{syn}), 7.0–7.3 (30H, phenyl H), 8.48 (1H, br, $J_{H-P} = 4.9$ Hz, NH); ¹³C-NMR (CDCl₃, 50.32 MHz) δ 15.0 (t, $J_{C-P} = 5.3$ Hz, CH₂CH₃), 37.3 (t, $J_{C-P} = 6.4$ Hz, CH₂CH₃), 39.6 (d with ¹⁹⁵Pt satellites, $J_{C-P} = 46.8$ Hz, $J_{C-Pt} = 178$ Hz, C₁), 41.1 (dd with ¹⁹⁵Pt satellites, $J_{C-P} = 4.4$, 45.3 Hz, $J_{C-Pt} = 197$ Hz, C₁), 128–134 (phenyl C), 156.1 (t with ¹⁹⁵Pt satellites, $J_{C-P} = 4.3$ Hz, $J_{C-Pt} = 110.3$ Hz, C₀).

4.2.4. $\{Pt(PPh_3)_2[\eta^3-CH_2C(NH^iPr)CH_2]\}(Br)$ (**3d**)

Refer to the paragraph for **3a** for the detailed procedure. The reaction of complex **1** (150 mg, 0.18 mmol) and ⁱPrNH₂ (18 μl) gave **3d** in 92% yield (148 mg). IR

(KBr) $\nu_{C=N}$ 1585 cm⁻¹; ³¹P-NMR (CDCl₃, 81.015 MHz) δ 19.0 (d, $J_{P-P} = 8.4$ Hz, $J_{P-Pt} = 3256$ Hz), 19.6 (d, $J_{P-P} = 8.4$ Hz, $J_{P-Pt} = 3215$ Hz); ¹H-NMR (CDCl₃, 300 MHz) δ 1.24 (6H, d, $J_{H-H} = 6.3$ Hz, CH₃), 2.2 (4H, br, H_{syn} and H_{anti}), 3.27 (1H, m, $J_{H-H} = 6.3$, 8.2 Hz, $J_{H-P} = 4$ Hz, CH), 7.1–7.4 (30H, phenyl H), 8.75 (1H, d with ¹⁹⁵Pt satellites, $J_{H-H} = 8.2$ Hz, $J_{H-Pt} = 27.1$ Hz, NH); ¹³C-NMR (CDCl₃, 75.469 MHz) δ 22.6 (s, CH₃), 39.6 (d with ¹⁹⁵Pt satellites, $J_{C-P} = 46.9$ Hz, $J_{C-Pt} = 187$ Hz, C₁), 41.0 (d with ¹⁹⁵Pt satellites, $J_{C-P} = 48.9$ Hz, $J_{C-Pt} = 198$ Hz, C₁), 45.2 (dd, $J_{C-P} = 5.8$, 14.2 Hz, CH), 128–133 (phenyl C), 155.6 (dd, $J_{C-Pt} = 101$ Hz, C₀); Anal. Calc. for PtC₄₂H₄₂NP₂Br·H₂O C, 55.09; H, 4.84; N, 1.53. Found: C, 54.44; H, 4.84; N, 1.53.

4.2.5. $\{Pt(PPh_3)_2[\eta^3-CH_2C(NH^iBu)CH_2]\}(Br)$ (**3e**)

Refer to the paragraph for **3a** for the detailed procedure. The reaction of complex **1** (201 mg, 0.24 mmol) and ⁱBuNH₂ (25 μl, 0.24 mmol) for 2 days gave **3e** in 86% yield (184 mg). IR (KBr) $\nu_{C=N}$ 1585 cm⁻¹; ³¹P-NMR (CDCl₃, 81.015 MHz, 283 K) δ 19.6 (d, $J_{P-P} = 8.2$ Hz, $J_{P-Pt} = 3264$ Hz), 20.4 (d, $J_{P-P} = 8.2$ Hz, $J_{P-Pt} = 3235$ Hz); ¹H-NMR (CDCl₃, 300 MHz, 283 K) δ 1.24 (9H, s, CH₃), 1.64 (1H, dd with ¹⁹⁵Pt satellites, $J_{H-H} = 6.5$ Hz, $J_{H-P} = 10.7$ Hz, $J_{H-Pt} = 61$ Hz, H_{anti}), 2.20 (1H, dd, $J_{H-H} = 5.5$ Hz, $J_{H-P} = 11.6$ Hz, H_{anti}), 2.36, 3.42 (1H, 1H, br, br, H_{syn}), 7.1–7.3 (30H, phenyl H), 7.76 (1H, s with ¹⁹⁵Pt satellites, $J_{H-Pt} = 27$ Hz, NH); ¹³C-NMR (CDCl₃, 50.32 MHz) δ 29.2 (s, CH₃), 42.5 (d with ¹⁹⁵Pt satellites, $J_{C-P} = 45$ Hz, $J_{C-Pt} = 190$ Hz, C₁), 52.1 (t, $J_{C-P} = 5.7$ Hz, Me₃C), 127–134 (phenyl C), 156.8 (t with ¹⁹⁵Pt satellites, $J_{C-P} = 4$ Hz, $J_{C-Pt} = 105.6$ Hz, C₀); Anal. Calc. for C₄₃H₄₄NP₂PtBr C, 56.65; H, 4.86; N, 1.54. Found: C, 56.65; H, 4.70; N, 1.45.

4.2.6. $\{Pt(PPh_3)_2[\eta^3-CH_2C(NHC_6H_{12})CH_2]\}(Br)$ (**3f**)

Refer to the paragraph for **3a** for the detailed procedure. The reaction of complex **1** (200 mg, 0.24 mmol) and c-C₆H₁₂NH₂ (31 μl, 0.25 mmol) gave **3f** in 87% yield (196 mg). IR (KBr) $\nu_{C=N}$ 1577 cm⁻¹; ³¹P-NMR (CDCl₃, 81.015 MHz) δ 19.3 (d, $J_{P-P} = 8.9$ Hz, $J_{P-Pt} =$

Table 1

Relative yields of the *N*-alkylated η^3 -*N*-TMM complexes formed from reactions of *trans*-Pt(Br)(PPh₃)₂(η^1 -CHCCH₂) (**1**) with amines

Amines	Relative yields of the products (%)					
	3b	3c	3d	3e	3f	3g
MeNH ₂ /EtNH ₂	63	37				
EtNH ₂ / ⁱ PrNH ₂		64	36			
ⁱ PrNH ₂ / ⁱ BuNH ₂			89	11		
ⁱ PrNH ₂ /PhNH ₂				67		33
c-C ₆ H ₁₁ NH ₂ /PhNH ₂					67	33

In a typical case, **1** (20 mg) and a mixture of amines (or aniline) with each in 10-fold equivalents were allowed to react in 0.5 ml of CDCl₃. The relative yields of the products were measured using NMR spectroscopy.

Table 2

Selected NMR data of η^3 -*N*-TMM complexes and *N*-protonated, *N*-alkylated, *N*-arylated η^3 -*N*-TMM complexes of Pt and Pd

R, R'	H _{anti} (J_{H-Pt})	H _{syn}	C _t (J_{C-Pt})	C _c (J_{C-Pt})
{Pt(PPh ₃) ₂ [η^3 -CH ₂ C(NRR')CH ₂]} ⁺				
H, H (3a)	1.93(62.8)	2.83	44.8(169.2)	153.1(88.5)
H, Me (3b)	1.65(67)	2.31	40.1(176.4)	156.5(110.7)
	1.97(67)	3.23	41.5(201)	
H, Et (3c)	1.60(68)	2.24	39.6(177.9)	156.1(110.3)
	1.96(68)	3.21	41.1(196.6)	
H, ⁱ Pr (3d)	2.06	2.41	39.6(186.8)	155.6(101)
			41.0(197.6)	
H, ^t Bu (3e)	1.64(61)	2.36	42.5(190)	156.8(105.6)
	2.20	3.42		
H, <i>c</i> -C ₆ H ₁₁ (3f)	—	2.76	40.2(184.2)	155.2(110.4)
	1.99(68.9)	3.44	40.8	
H, Ph (3g)	2.09(62.5)	3.40	44.9(176.4)	150.8
H, C ₂ H ₄ OH (3h)	1.75	2.32	41.8	154.7(105.6)
	2.01	2.99	42.5	
Et, Et (3i)	2.33	2.33	40.0(187.8)	157.7(110.4)
C ₃ H ₆ (3j)	2.05(73.2)	2.23	39.3(181.3)	154.3(106.3)
Ph, Ph (3k)	2.62(60)	2.83	48.9	151.4
Me, Ph (3l)	2.34(69.2)	2.51	44.8	154.3(95.3)
H, SO ₂ Ph (3m)	2.26(42.3)	3.49	52.6(103.4)	138.3
{Pd(PPh ₃) ₂ [η^3 -CH ₂ C(NRR')CH ₂]} ⁺				
H, ⁱ Pr (7d)	2.23	2.72	50.6	152.1
H, Ph (7g)	2.53	3.38	55.2	148.5
Et, Et (7i)	2.51	2.62	50.0	154.0
H, SO ₂ Ph (7m)	2.79	3.63		
H, SO ₂ C ₆ H ₄ Me (7n)	2.82	3.59		
Pd(PPh ₃) ₂ (Br)[η^3 -CH ₂ C(NRR')CH ₂]				
Et, Et (8i)	2.12	2.50	43.0	148.2
	2.28	3.17	49.1	
M(PPh ₃) ₂ [η^3 -CH ₂ C(NR)CH ₂]				
M = Pt, R = SO ₂ Ph (4m)	2.05(51.2)	3.23	50.7(174.5)	158.9(88.9)
M = Pd, R = SO ₂ Ph (9m)	2.26	3.31	61.3	154.5
M = Pd, R = SO ₂ C ₆ H ₄ Me (9n)	2.25	3.31	61.2	154.8

3235 Hz), 19.7 (d, $J_{P-P} = 8.9$ Hz, $J_{P-Pt} = 3251$ Hz); ¹H-NMR (CDCl₃, 300 MHz) δ 0.88–1.73 (11H, m, CH₂ and H_{anti}), 1.99 (1H, dd with ¹⁹⁵Pt satellites, $J_{H-H} = 6.3$ Hz, $J_{H-P} = 10.6$ Hz, $J_{H-Pt} = 68.9$ Hz, H_{anti}), 2.19 (1H, br, Cy), 2.76, 3.44 (1H, 1H, br, br, H_{syn}), 7.0–7.7 (30H, phenyl H), 8.66 (1H, d with ¹⁹⁵Pt satellites, $J_{H-P} = 8.1$ Hz, $J_{H-Pt} = 27$ Hz, NH); ¹³C-NMR (CDCl₃, 50.32 MHz) δ 4.8, 25.0, 31.8, 33.2 (CH₂), 40.2 (d with ¹⁹⁵Pt satellites, $J_{C-P} = 48.7$ Hz, $J_{C-Pt} = 184.2$ Hz, C_t), 40.8 (d, $J_{C-P} = 7.5$, 45.2 Hz, C_t), 52.9 (t, $J_{C-P} = 8$ Hz, CN), 127–134 (phenyl C), 155.2 (t with

¹⁹⁵Pt satellites, $J_{C-P} = 4.2$ Hz, $J_{C-Pt} = 110.4$ Hz, C_c); Anal. Calc. for PtC₄₅H₄₆NP₂Br C, 57.63; H, 4.94; N, 1.49. Found: C, 56.02; H, 4.92; N, 1.36.

4.2.7. {Pt(PPh₃)₂[η^3 -CH₂C(NHPh)CH₂]}(Br **3g**, BF₄, **3g'**)

Refer to the paragraph for **3a** for the detailed procedure. The reaction of complex **1** (150 mg, 0.18 mmol) and PhNH₂ (18 μ L, 0.20 mmol) took 96 h to give **3g** in 78% yields (130 mg). Alternatively, complex **2** was first prepared from **1** (250 mg, 0.30 mmol) and AgBF₄ (58 mg) in situ. After AgBr was removed by filtration, the filtrate was allowed to react with PhNH₂ (0.33 mmol) for 1 h at 25°C. The yield of **3g'** was 85% (234 mg). For **3g**: IR (KBr) $\nu_{C=N}$ 1551 cm⁻¹; ³¹P-NMR (CDCl₃, 81.015 MHz) δ 19.0 ($J_{P-Pt} = 3361$ Hz); ¹H-NMR (CDCl₃, 300 MHz, 283K) δ 2.09 (2H, br with ¹⁹⁵Pt satellites, $J_{H-Pt} = 62.5$ Hz, H_{anti}), 3.40 (2H, br, H_{syn}), 7.0–7.5 (35H, phenyl H), 10.1 (1H, s with ¹⁹⁵Pt satellites, $J_{H-Pt} = 19.3$ Hz, NH); ¹³C-NMR (CDCl₃, 75.469 MHz) δ 44.9 (d, $J_{C-P} = 43.9$ Hz, C_t), 123.5, 124.9 (NC_{ipso}), 128–138 (phenyl C), 150.8 (s, C_c); Anal. Calc. for C₄₄H₄₀NP₂PtBr C, 57.46; H, 4.38; N, 1.52. Found: C, 58.11; H, 4.29; N, 1.36. For **3g'**: ¹H-NMR (CDCl₃, 200 MHz, 283K) δ 2.2 (2H, dd with ¹⁹⁵Pt satellites, $J_{H-P} = 4.6$, 8.8 Hz, $J_{H-Pt} = 68$ Hz, H_{anti}), 3.12 (2H, br, H_{syn}), 7.1–7.6 (35H, phenyl H), 8.4 (1H, s with ¹⁹⁵Pt satellites, $J_{H-Pt} = 20$ Hz, NH).

4.2.8. {Pt(PPh₃)₂[η^3 -CH₂C(NHCH₂CH₂OH)CH₂]}(Br) (**3h**)

Refer to the paragraph for **3a** for the detailed procedure. The reaction of complex **1** (200 mg, 0.24 mmol) and HOCH₂CH₂NH₂ (14 μ L, 0.24 mmol) gave **3h** in 90% yield. IR (KBr) $\nu_{C=N}$ 1539 cm⁻¹; ³¹P-NMR (CDCl₃, 81.015 MHz) δ 18.1 (d, $J_{P-P} = 9$ Hz, $J_{P-Pt} = 3270$ Hz), 19.3 (d, $J_{P-P} = 9$ Hz, $J_{P-Pt} = 3348$ Hz); ¹H-NMR (CDCl₃, 300 MHz) δ 1.75, 2.01 (1H, 1H, br, br, H_{anti}), 2.32, 2.99 (1H, 1H, br, br, H_{syn}), 3.14 (2H, br, NCH₂CH₂OH), 3.70 (2H, br, NCH₂CH₂OH), 4.69 (1H, t, $J_{H-H} = 12$ Hz, OH), 7.1–7.4 (30H, phenyl H), 8.11 (1H, s, $J_{H-P} = 9.7$ Hz, NH); ¹³C-NMR (CDCl₃, 50.32 MHz) δ 41.8 (d, $J_{C-P} = 47.3$ Hz, C_t), 42.5 (d $J_{C-P} = 49.5$ Hz, C_t), 45.6 (s, NCH₂CH₂OH), 59.2 (s, NCH₂CH₂OH), 128–134 (phenyl C), 154.7 (d with ¹⁹⁵Pt satellites, $J_{C-P} = 4.0$ Hz, $J_{C-Pt} = 105.6$ Hz, C_c).

4.2.9. {Pt(PPh₃)₂[η^3 -CH₂C(NEt₂)CH₂]}(BF₄) (**3i'**)

Refer to the paragraph for **3g'** for the detailed procedure. The reaction of complex **1** (150 mg, 0.18 mmol) and Et₂NH (21 μ L) gave **3i'** in 93% yield (151 mg). IR (KBr) $\nu_{C=N}$ 1555 cm⁻¹; ³¹P-NMR (CDCl₃, 81.02 MHz) δ 17.9 ($J_{P-Pt} = 3256$ Hz); ¹H-NMR (CDCl₃, 300 MHz) δ 1.04 (6H, t, $J_{H-H} = 7.1$ Hz, CH₃CH₂), 2.33 (4H, br,

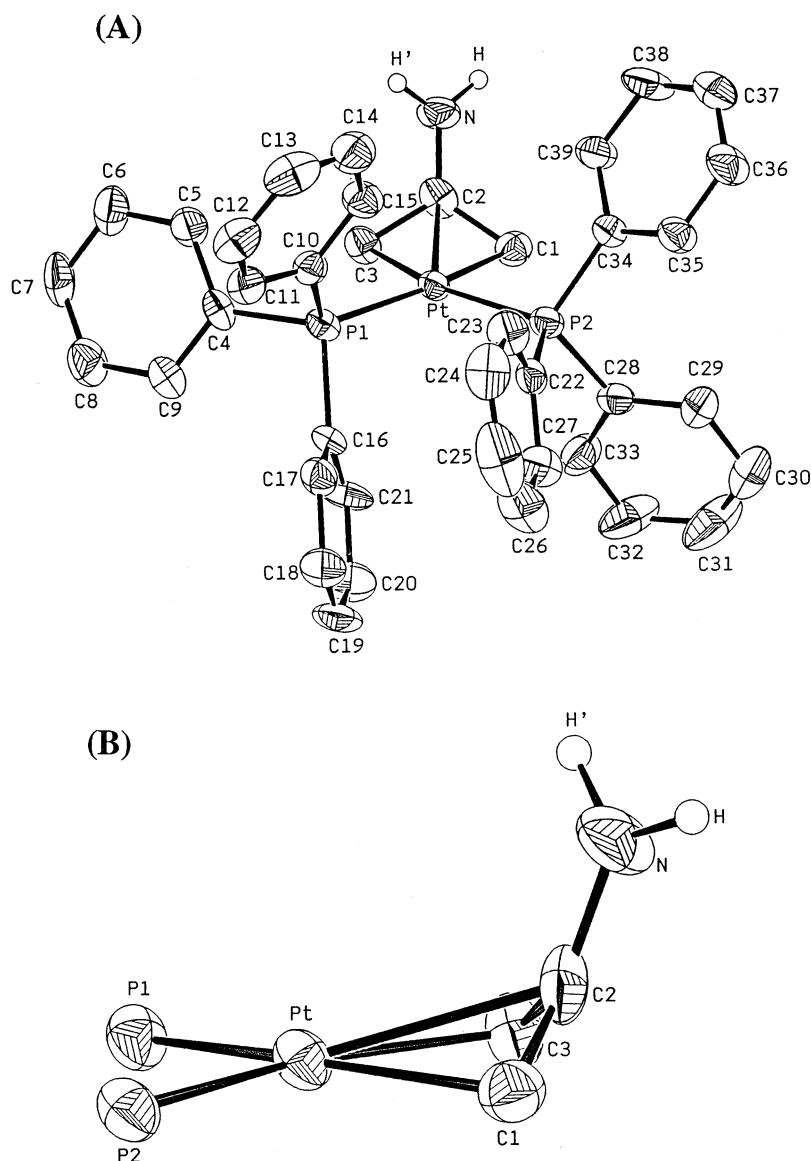


Fig. 1. ORTEP drawings of $\{\text{Pt}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NH}_2)\text{CH}_2]\}(\text{BF}_4)$ (**3a**) with 50% ellipsoid probability. (a) Top-view, all hydrogen atoms are omitted for clarity. (b) Side-view, phosphino phenyls and all hydrogen atoms (except amino hydrogens) are omitted for clarity.

H_{syn} and H_{anti}), 3.12 (4H, q with ^{195}Pt satellites, $J_{\text{H-H}} = 7.1$ Hz, $J_{\text{H-Pt}} = 6.6$ Hz, CH_3CH_2), 7.1–7.8 (30H, phenyl H); $^{13}\text{C-NMR}$ (CDCl_3 , 50.32 MHz) δ 12.85 (s with ^{195}Pt satellites, $J_{\text{C-Pt}} = 9.6$ Hz, CH_3CH_2), 39.96 (dd with ^{195}Pt satellites, $J_{\text{C-P}} = 4.4$, 51.0 Hz, $J_{\text{C-Pt}} = 187.8$ Hz, C_i), 43.95 (s with ^{195}Pt satellites, $J_{\text{C-Pt}} = 12.0$ Hz, CH_3CH_2), 128–133 (phenyl C), 157.7 (t with ^{195}Pt satellites, $J_{\text{C-P}} = 4.0$ Hz, $J_{\text{C-Pt}} = 110.4$ Hz, C_o); Anal. Calc. for $\text{PtC}_{43}\text{H}_{44}\text{NP}_2\text{-BrH}_2\text{O}$ C, 56.65; H, 4.86; N, 1.54. Found: C, 55.90; H, 4.84; N, 1.66.

4.2.10. $\{\text{Pt}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NC}_3\text{H}_6)\text{CH}_2]\}(\text{Br})$ (**3j**)

Refer to the paragraph for **3a** for the detailed procedure. The reaction of complex **1** (305 mg, 0.364 mmol) and azetidine (25 μl , 0.37 mmol) gave **3j** in 91% yield (297 mg). IR (KBr) $\nu_{\text{C-N}}$ 1534 cm^{-1} ; $^{31}\text{P-NMR}$

(CDCl_3 , 300 MHz) δ 17.0 ($J_{\text{P-Pt}} = 3298$ Hz); $^1\text{H-NMR}$ (CDCl_3 , 300 MHz, 285 K) δ 2.05 (2H, d with ^{195}Pt satellites, $J_{\text{H-H}} = 8.1$ Hz, $J_{\text{H-Pt}} = 73.2$ Hz, H_{anti}), 2.23 (2H, br, H_{syn}), 2.35 (2H, $J_{\text{H-H}} = 7$ Hz, NCH_2CH_2), 3.75 (2H, m, $\text{NCH}_2\text{-endo}$), 3.82 (2H, m, $\text{NCH}_2\text{-exo}$), 7.1–7.4 (30H, phenyl H); $^{13}\text{C-NMR}$ (CDCl_3 , 50.32 MHz) δ 15.6 (s, NCH_2CH_2), 39.3 (dd with ^{195}Pt satellites, $J_{\text{C-P}} = 5.1$, 51 Hz, $J_{\text{C-Pt}} = 181.3$ Hz, C_i), 50.2 (s with ^{195}Pt satellites, $J_{\text{C-Pt}} = 5.3$ Hz, NCH_2CH_2), 127–134 (phenyl C), 154.3 (t with ^{195}Pt satellites, $J_{\text{C-P}} = 4.2$ Hz, $J_{\text{C-Pt}} = 106.3$ Hz, C_o).

4.2.11. $\{\text{Pt}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NPh}_2)\text{CH}_2]\}(\text{BF}_4)$ (**3k**)

Refer to the paragraph for **3g** for the detailed procedure. The reaction of **2** prepared from **1** (210 mg, 0.25 mmol) and AgBF_4 (48 mg) in situ, with Ph_2NH (45 mg,

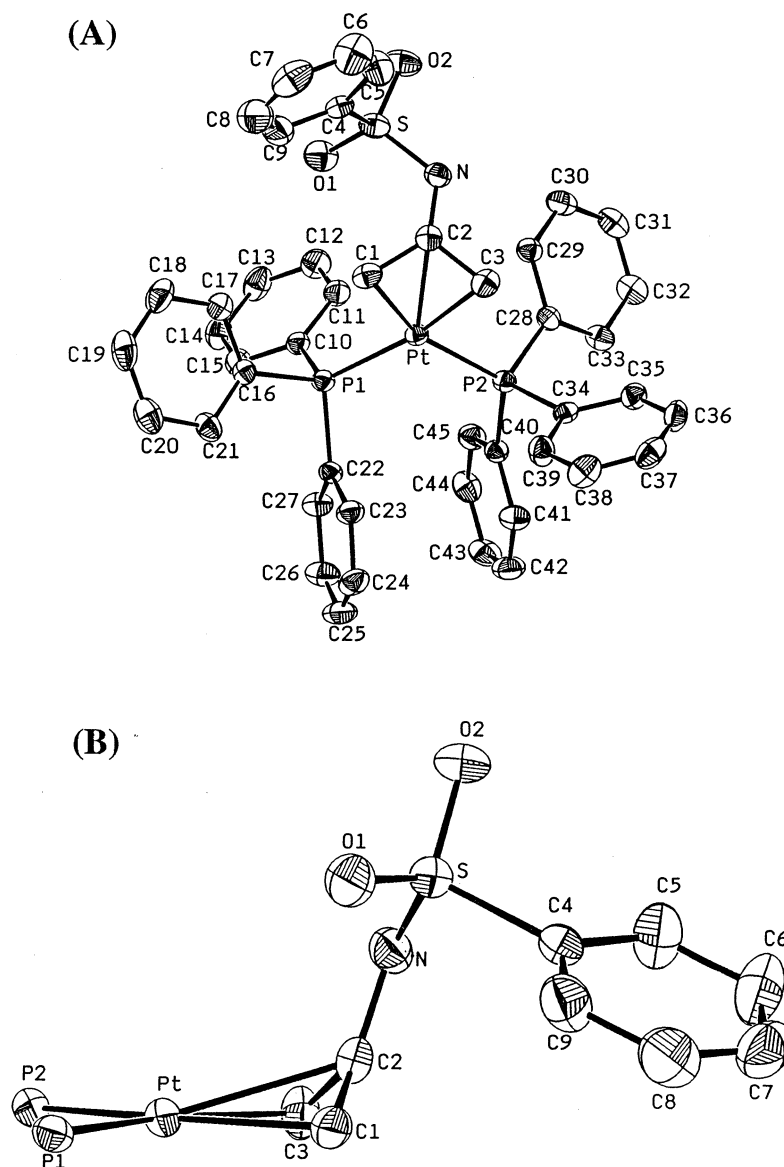


Fig. 2. ORTEP drawings of $\text{Pd}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NSO}_2\text{Ph})\text{CH}_2]$ (**4m**) with 50% ellipsoid probability. (a) Top-view, all hydrogen atoms are omitted for clarity. (b) Side-view, phosphino phenyls and all hydrogen atoms are omitted for clarity.

0.28 mmol) gave **3k** in 73% yield (185 mg). IR (KBr) $\nu_{\text{C-N}}$ 1590 cm^{-1} ; $^{31}\text{P-NMR}$ (CDCl_3 , 81.015 MHz) δ 17.6 ($J_{\text{P-Pt}} = 3464$ Hz); $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ 2.62 (2H, dd with ^{195}Pt satellites, $J_{\text{H-H}} = 4.6$, $J_{\text{H-P}} = 9.4$ Hz, $J_{\text{H-P}} = 60$ Hz, H_{anti}), 2.83 (2H, br, H_{syn}), 7.0–7.6 (40H, phenyl H); $^{13}\text{C-NMR}$ (CDCl_3 , 50.32 MHz) δ 48.93 (dd, $J_{\text{C-Pcis}} = 15$ Hz, $J_{\text{C-Ptrans}} = 32$ Hz, C_1), 117.8, 120.9, 126–134, 142.6, 143.1 (phenyl C), 151.3 (s with ^{195}Pt satellites, $J_{\text{C-Pt}} = 58$ Hz, C_c).

4.2.12. $\{\text{Pt}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NMePh})\text{CH}_2]\}(\text{BF}_4)$ (**3l**)

Refer to the paragraph for **3g'** for the detailed procedure. The reaction of **2** prepared from **1** (250 mg, 0.30 mmol) and AgBF_4 (58 mg) in situ, with MePhNH (33 μl) gave **3l** in 78% yield (223 mg). IR (KBr) $\nu_{\text{C-N}}$ 1598

cm^{-1} ; $^{31}\text{P-NMR}$ (CDCl_3 , 81.015 MHz) δ 17.1 ($J_{\text{P-Pt}} = 3384$ Hz); $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ 2.34 (2H, br with ^{195}Pt satellites, $J_{\text{H-Pt}} = 69.2$ Hz, H_{anti}), 2.51 (2H, br, H_{syn}), 3.07 (3H, s with ^{195}Pt satellites, $J_{\text{H-Pt}} = 18.8$ Hz, C_H_3), 7.1–7.6 (35H, phenyl H); $^{13}\text{C-NMR}$ (CDCl_3 , 50.32 MHz) δ 39.6 (s with ^{195}Pt satellites, $J_{\text{C-Pt}} = 11.7$ Hz, C_H_3), 44.8 (unresolved, C_1), 125.7, 127.6, 128–134, 143.1 (phenyl C), 154.3 (t with ^{195}Pt satellites, $J_{\text{C-P}} = 8.5$ Hz, $J_{\text{C-Pt}} = 95.3$ Hz, C_c); Anal. Calc. for $\text{PtC}_{46}\text{H}_{42}\text{NP}_2\text{BF}_4$ C, 58.00; H, 4.44; N, 1.47. Found: C, 57.55; H, 4.50; N, 1.51.

4.2.13. $\{\text{Pt}(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NHSO}_2\text{Ph})\text{CH}_2]\}(\text{BF}_4)$ (**3m**)

The reaction of **4m** (92 mg, 0.1 mmol) and HBF_4

Table 3

Selected bond parameters of η^3 -*N*-TMM complexes, *N*-protonated, *N*-alkylated, *N*-arylated η^3 -*N*-TMM complexes of Pt and Pd

R, R'	M–C ₁ (Å)	M–C _c (Å)	C ₁ –C _c (Å)	C _c –N (Å)	C _c –C ₁ –C _{c'} (°)	θ^a (°)
{Pt(PPh ₃) ₂ [η^3 -CH ₂ C(NRR')CH ₂]} ⁺						
H, H (3a')	2.12(1) 2.19(3)	2.329(9)	1.43(1) 1.43(1)	1.33(1)	112.8(9)	56(1)
H, 'Pr (3d)	2.17(2) 2.19(2)	2.36(1)	1.45(2) 1.49(3)	1.47(2)	111(2)	57(2)
H, Ph (3g')	2.150(8) 2.176(8)	2.303(7)	1.41(1) 1.42(1)	1.40(1)	113.3(8)	62(1)
H, C ₂ H ₄ OH (3h)	2.16(1) 2.21(1)	2.30(1)	1.39(2) 1.44(2)	1.37(2)	116(1)	58(4)
Et, Et (3i')	2.11(2) 2.13(2)	2.35(2)	1.40(3) 1.42(3)	1.34(2)	109(2)	62.6(6)
C ₃ H ₆ (3j)	2.16(1) 2.21(1)	2.30(1)	1.39(2) 1.44(2)	1.37(2)	116(1)	60(2)
Pt(PPh ₃) ₂ [η^3 -CH ₂ C(NR)CH ₂]						
SO ₂ Ph (4m)	2.141(4) 2.147(4)	2.333(4)	1.435(6) 1.439(6)	1.342(6)	109.9(4)	58.5(4)
{Pd(PPh ₃) ₂ [η^3 -CH ₂ C(NRR')CH ₂]} ⁺						
H, 'Pr (7d)	2.166(7) 2.168(7)	2.326(7)	1.41(1) 1.43(1)	1.32(1)	112.6(7)	58.7(7)
H, Ph (7g)	2.14(1) 2.20(1)	2.28(1)	1.42(2) 1.43(2)	1.38(2)	116(1)	60(1)
Et, Et (7i)	2.156(7) 2.156 (7)	2.327(7)	1.41(1) 1.43(1)	1.35(1)	111.8(6)	58.2(7)
Pd(PPh ₃)(Br)[η^3 -CH ₂ C(NRR')CH ₂]						
Et, Et (8i)	2.089(3) 2.144(4)	2.292(3)	1.409(5) 1.414(5)	1.343(5)	110.2(3)	59.2(4)

^a The dihedral angle θ is defined by the planes C₁–C_c–C_{c'} and C₁–M–C_c.

(85% etherate solution, 0.1 mmol) gave **3m** in 74% yield (75 mg). ³¹P-NMR (CDCl₃, 81.015 MHz) δ 18.1 ($J_{\text{P-Pt}} = 3729$ Hz); ¹H-NMR (CDCl₃, 300 MHz) δ 2.26 (2H, d with ¹⁹⁵Pt satellites, $J_{\text{H-P}} = 8.8$ Hz, $J_{\text{H-Pt}} = 42.3$ Hz, H_{anti}), 3.49 (2H, br, H_{syn}), 6.64 (1H, br, NH), 7.2–7.5 (33H, phenyl H), 7.72 (2H, d, $J_{\text{H-H}} = 7.9$ Hz, *o*-H); ¹³C-NMR (CDCl₃, 50.3 MHz) δ 52.6 (dd with ¹⁹⁵Pt satellites, $J_{\text{C-P}} = 4.8$, 39.2 Hz, $J_{\text{C-Pt}} = 103.4$ Hz, C₁), 127–134 (phenyl C), 138.3 (t, $J_{\text{C-P}} = 3.7$ Hz, C_c), 138.6 (C_{ipso}).

4.2.14. Pt(PPh₃)₂[η^3 -CH₂C(NSO₂Ph)CH₂] (**4m**)

Refer to the paragraph for **9m** for the detailed procedure. IR (KBr) $\nu_{\text{C=N}} 1479$ cm⁻¹, $\nu_{\text{S=O}} 1137$, 1393 cm⁻¹; ³¹P-NMR (CDCl₃, 300 MHz) δ 21.6 ($J_{\text{P-Pt}} = 3315$ Hz); ¹H-NMR (CDCl₃, 81.015 MHz) δ 2.05 (2H, d with ¹⁹⁵Pt satellites, $J_{\text{H-P}} = 7.7$ Hz, $J_{\text{H-Pt}} = 51.2$ Hz, H_{anti}), 3.23 (2H, br, H_{syn}), 7.18–7.28 (33H, phenyl H), 7.73 (2H, d, $J_{\text{H-H}} = 6.0$ Hz, *o*-H); ¹³C-NMR (CDCl₃, 50.32 MHz) δ 50.7 (dd with ¹⁹⁵Pt satellites, $J_{\text{C-P}} = 4.0$, 46.3 Hz, $J_{\text{C-Pt}} = 174.5$ Hz, C₁), 127–134 (phenyl C), 145.0 (C_{ipso}), 158.9 (t with ¹⁹⁵Pt satellites, $J_{\text{C-P}} = 4.1$ Hz, $J_{\text{C-Pt}} = 88.9$ Hz, C_c); Anal. Calc. for PtC₄₅H₃₉NO₂SP₂ C, 59.08; H, 4.30; N, 1.53. Found: C, 59.11; H, 4.40; N, 1.55.

4.2.15. trans-Pd(Br)(PPh₃)₂[η^1 -CHCCH₂] (**5**)

To a 30 ml of THF solution that contained 2.5 g of Pd(PPh₃)₄, was added 0.24 ml (1.1 equivalents) of propargyl bromide under dry N₂. The yellow reaction solution turned to colorless after 20 min. Further stirring for 30 min caused a whitish yellow precipitate of **5**. The solution was then concentrated to 15 ml and was filtered. Solid product in 90% yield (1.46 g) was recovered after being washed by Et₂O. IR (KBr pellet) $\nu_{\text{C=C}} 1915$ cm⁻¹; ³¹P-NMR (CDCl₃, 81.015 MHz) δ 24.2 (s); ¹H-NMR (CDCl₃, 300 MHz) δ 3.12 (2H, dt, $J_{\text{H-H}} = 6.1$ Hz, $J_{\text{H-P}} = 1.3$ Hz, CHCCH₂), 4.67 (1H, tt, $J_{\text{H-H}} = 6.1$ Hz, $J_{\text{H-P}} = 6.4$ Hz, CHCCH₂), 7.7–7.2 (30H, m, phenyl H); ¹³C-NMR (CDCl₃, 50.32 MHz, 273 K) δ 66.9 (s, CHCCH₂), 87.4 (t, $J_{\text{C-P}} = 5.1$ Hz, CHCCH₂), 128–135 (phenyl C), 199.8 (t, $J_{\text{C-P}} = 3.5$ Hz, CHCCH₂); FAB MS (m/z) 750 (M⁺ + 1); Anal. Calc. for PdC₃₉H₃₃P₂Br: C, 62.46; H, 4.44. Found: C, 62.53; H, 4.50.

4.2.16. [Pd(PPh₃)₂][η^3 -C₃H₃](X) (X = PF₆ **6**, BF₄ **6'**, OTf **6''**)

To a mixture containing **5** (208 mg, 0.28 mmol) and AgPF₆ (75 mg, 0.3 mmol) was added N₂-degassed CH₂Cl₂ (20 ml) at –75°C. The reaction solution was stirred for 40 min to allow the complete precipitation of

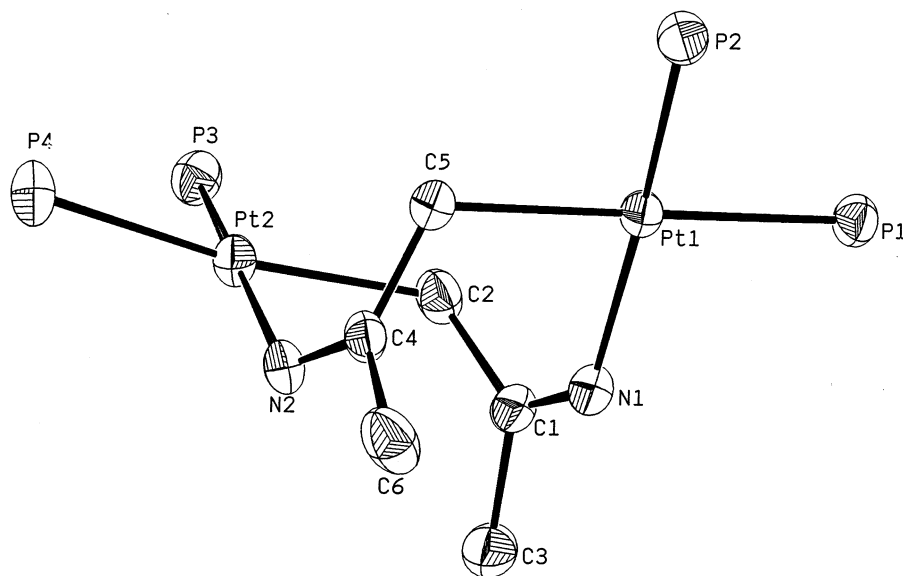


Fig. 3. ORTEP drawing of $\{[cis\text{-Pt}(\text{PPh}_3)_2(\mu\text{-CH}_2\text{CMeNH})_2](\text{Br})_2\}$ (**15**) with 50% ellipsoid probability. All hydrogen atoms and phosphino phenyls are omitted for clarity.

AgBr. After AgBr was removed by filtration, the solution was concentrated and addition of degassed Et_2O to the solution resulted in whitish yellow solids. The product contains small amounts of silver salts. The purification would cause the decomposition of the desired compound. Analogous reactions of **5** with AgBF_4 or AgOTf at -50°C generate the η^3 -allenyl/propargyl palladium cation as well. The products are identified with NMR because the isolation of **6'** and **6''** is difficult. For further synthetic purpose, complex **6** are usually prepared in situ. Selected spectral data for **6**: ^{31}P -NMR (CDCl_3 , 81.015 MHz, 198 K) δ 26.7, 28.0 (d, $J_{\text{P-P}} = 41.5$ Hz); ^1H -NMR (CDCl_3 , 300 MHz) δ 3.40 (ddd, 2H, $J_{\text{H-H}} = 2.1$ Hz, $J_{\text{P-H}} = 1.7, 7.7$ Hz, CH_2), 4.65 (tdd, 1H, $J_{\text{H-H}} = 2.1$ Hz, $J_{\text{P-H}} = 1.6, 9.0$ Hz, CH), 7.15–7.38 (30 H, m, phenyl H); ^{13}C -NMR (CDCl_3 , 50.32 MHz, 198 K) δ 57.6 (d, $J_{\text{C-P}} = 38.7$ Hz, CH_2CCH), 91.3 (d, $J_{\text{C-P}} = 48.8$ Hz, CH_2CCH), 100.6 (dd, $J_{\text{C-P}} = 5.8, 8.0$ Hz, CH_2CCH), 128–134 (phenyl C).

4.2.17. $\{Pd(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NH}^i\text{Pr})\text{CH}_2]\}(\text{Br})$ (**7d**)

Refer to the paragraph for **7i** for the detailed procedure. The reaction of **5** (150 mg, 0.20 mmol) and AgOTf (51.4 mg, 0.2 mmol) in situ with $^i\text{PrNH}_2$ (17 μl) gave **7d**. The isolated yield was 114 mg (65%). The single crystals were grown from $\text{CHCl}_3/\text{Et}_2\text{O}$ cosolvent at 0°C . IR (KBr pellet) $\nu_{\text{C=N}}$ 1555 cm^{-1} ; ^{31}P -NMR (CDCl_3 , 300 MHz, 253K) δ 25.1, 26.5 ($J_{\text{P-P}} = 29.0$ Hz); ^1H -NMR (CDCl_3 , 300 MHz) δ 1.13 (6H, d, $J_{\text{H-H}} = 6.3$ Hz, CH_3), 2.23 (2H, br, H_{anti}), 2.72 (2H, br, H_{syn}), 3.01 (1H, m, $J_{\text{H-H}} = 6.3, 7.8$ Hz, CH), 6.41 (1H, d, $J_{\text{H-H}} = 7.1$ Hz, NH), 7.15–7.38 (30H, m, phenyl H); ^{13}C -NMR (CDCl_3 , 50.32 MHz) δ 22.5 (s, CH_3), 44.8 (s, CHMe_2),

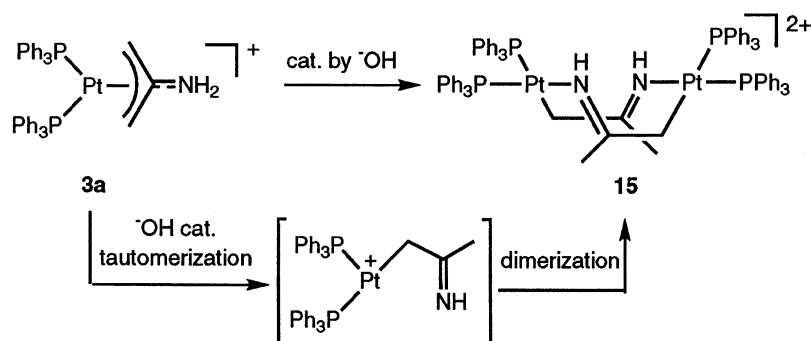
50.6 (m, $J_{\text{C-P}} = 47.4$ Hz, C_1), 128–134 (phenyl C), 152.1 (t, $J_{\text{C-P}} = 5.5$ Hz, C_α); MS (FAB) 728 ($\text{M}^+ - \text{OTf}$).

4.2.18. $\{Pd(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NHPh})\text{CH}_2]\}(\text{OTf})$ (**7g**)

Refer to the paragraph for **7i** for the detailed procedure. The reaction of **6''** prepared from **5** (155 mg, 0.21 mmol) and AgOTf (53.1 mg, 0.21 mmol) in situ with PhNH_2 (19 μl) gave **7g**. The isolated yield was 96 mg (50%). The single crystals were grown from $\text{CHCl}_3/\text{Et}_2\text{O}$ cosolvent at 0°C . IR (KBr pellet) $\nu_{\text{C=N}}$ 1550 cm^{-1} ; ^{31}P -NMR (CDCl_3 , 81.015 MHz) δ 26.1; ^1H -NMR (CDCl_3 , 300 MHz) δ 2.53 (2H, m, H_{anti}), 3.38 (2H, br, H_{syn}), 7.14–7.41 (30H, m, phenyl H), 8.60 (1H, s, NH); ^{13}C -NMR (CDCl_3 , 50.32 MHz) δ 55.2 (m, C_1), 122–139 (phenyl C), 148.5 (t, $J_{\text{C-P}} = 5.4$ Hz, C_α).

4.2.19. $\{Pd(\text{PPh}_3)_2[\eta^3\text{-CH}_2\text{C}(\text{NEt}_2)\text{CH}_2]\}(\text{OTf})$ (**7i**)

To a two-neck round bottle which contained **5** (150 mg, 0.2 mmol) and AgOTf (51.4 mg, 0.2 mmol), was charged dried N_2 -degassed CH_2Cl_2 (15 ml) at -40°C . After 40 min, white AgBr precipitate was removed by filtration. Diethyl amine (21 μl) was injected. The solution was stirred for another 30 min, and then was concentrated to 5 ml by vacuo. Addition of diethyl ether (25 ml) resulted in a light yellow product in 80% yield. The single crystals were grown from $\text{CHCl}_3/\text{Et}_2\text{O}$ cosolvent at 0°C . IR (KBr pellet) $\nu_{\text{C=N}}$ 1550 cm^{-1} ; ^{31}P -NMR (CDCl_3 , 81.015 MHz) δ 24.9; ^1H -NMR (CDCl_3 , 300 MHz) δ 0.94 (6H, t, $J_{\text{H-H}} = 7.1$ Hz, CH_2CH_3), 2.51 (2H, m, H_{anti}), 2.62 (2H, br, H_{syn}), 2.95 (4H, q, $J_{\text{H-H}} = 7.1$ Hz, CH_2CH_3), 7.15–7.38 (30H, m, phenyl H); ^{13}C -NMR (CDCl_3 , 50.32 MHz) δ 12.8 (s, CH_2CH_3), 43.9 (s, CH_2CH_3), 50.0 (m, C_1), 128.8, 130.9, 133.4 (phenyl C), 154.0 (t, $J_{\text{C-P}} = 4.9$ Hz, C_α).



Scheme 7.

4.2.20. $\{Pd(PPh_3)_2[\eta^3-CH_2C(NHSO_2Ph)CH_2]\}(BF_4)$ (**7m**)

The reaction of **9m** (150 mg, 0.18 mmol) and HBf_4 (85% etherate solution, 33 μ l) in CH_2Cl_2 at 25°C gave **7m** in 98% yield (161 mg). IR (KBr pellet) $\nu_{C=N}$ 1500 cm^{-1} ; ^{31}P -NMR ($CDCl_3$, 81.015 MHz) δ 25.8; 1H -NMR ($CDCl_3$, 300 MHz) δ 2.79 (2H, br, H_{anti}), 3.63 (2H, s, H_{syn}), 7.18–7.68 (34H, phenyl H), 8.38 (1H, s, NH).

4.2.21. $\{Pd(PPh_3)_2[\eta^3-CH_2C(p-NHSO_2C_6H_4Me)CH_2]\}(BF_4)$ (**7n**)

The reaction of **9n** (150 mg, 0.18 mmol) and HBf_4 (85% etherate solution, 30 μ l) in CH_2Cl_2 at 25 °C gave **7n** in 98% yield (164 mg). IR (KBr pellet) $\nu_{C=N}$ 1520 cm^{-1} ; ^{31}P -NMR ($CDCl_3$, 81.015 MHz) δ 25.8; 1H -NMR ($CDCl_3$, 300 MHz) δ 2.15 (3H, s, CH_3), 2.82 (2H, br, H_{anti}), 3.59 (2H, s, H_{syn}), 7.18–7.68 (35H, phenyl H), 8.32 (1H, s, NH).

4.2.22. $Pd(Br)(PPh_3)_2[\eta^3-CH_2C(NEt_2)CH_2]$ (**8i**)

To a round-bottom flask containing **5** (200 mg, 0.27 mmol), was charged dried N_2 -degassed CH_2Cl_2 (15 ml) at 25°C, followed by the injection of diethylamine (two equivalents). The solution was vigorously stirred for 2 h, and then was concentrated to 5 ml by vacuo. Addition of diethyl ether (15 ml) resulted in a white product

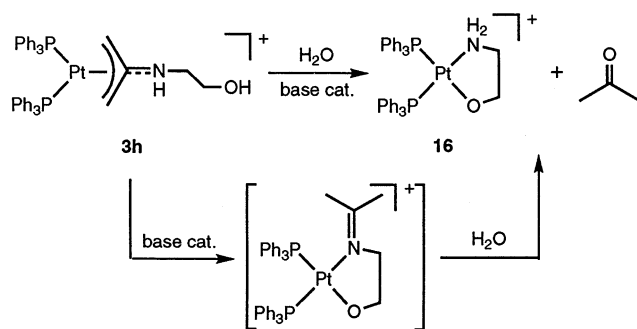
in 70% yield (105 mg). The single crystals were grown from $CHCl_3/Et_2O$ cosolvent at 0°C. IR (KBr pellet) $\nu_{C=N}$ 1527 cm^{-1} ; ^{31}P -NMR ($CDCl_3$, 81.015 MHz) δ 22.9; 1H -NMR ($CDCl_3$, 300 MHz) δ 1.03 (6H, t, $J_{H-H} = 7.0$ Hz, CH_2CH_3), 2.12 (1H, d, $J_{H-H} = 4.2$ Hz, H_{anti}), 2.28 (1H, ddd, $J_{H-H} = 4.2, 5.1$ Hz, $J_{H-P} = 4.2$ Hz, H_{anti}), 2.50 (1H, dd, $J_{H-H} = 3.3$ Hz, $J_{H-P} = 11.2$ Hz, H_{syn}), 3.02 (4H, q, $J_{H-H} = 7.1$ Hz, CH_2CH_3), 3.17 (1H, ddd, $J_{H-H} = 3.3, 5.1$ Hz, $J_{H-P} = 5.9$ Hz, H_{syn}), 7.35–7.69 (15H, m, phenyl H); ^{13}C -NMR ($CDCl_3$, 50.32 MHz) δ 13.0 (s, CH_2CH_3), 43.0 (s, C_t trans to Br), 44.2 (s, CH_2CH_3), 49.1 (d, $J_{C-P} = 47.4$ Hz, C_t trans to PPh_3), 128.1, 128.3, 130.0, 134.1 (phenyl C), 148.2 (s, C_c); MS (FAB) 560 (M^+); Anal. Calc. for $PdC_{25}H_{29}NPBr \cdot 0.5 CH_2Cl_2$: C, 50.77; H, 5.01; N, 2.32. Found: C, 51.16; H, 4.94; N, 2.35.

4.2.23. $Pd(PPh_3)_2[\eta^3-CH_2C(NSO_2Ph)CH_2]$ (**9m**)

Refer to the paragraph for **7i** for the detailed procedure. The reaction of **5** (250 mg, 0.33 mmol) and $NaNHSO_2Ph$ (80% mineral oil, 90 mg, 0.40 mmol) in CH_2Cl_2 at 25°C gave **9m** in 70% yield (190 mg). IR (KBr pellet) $\nu_{C=N}$ 1480 cm^{-1} , $\nu_{S=O}$ 1161, 1382 cm^{-1} ; ^{31}P -NMR ($CDCl_3$, 81.015 MHz) δ 27.0; 1H -NMR ($CDCl_3$, 300 MHz) δ 2.26 (2H, m, H_{anti}), 3.31 (2H, s, H_{syn}), 7.18–7.68 (35H, phenyl H); ^{13}C -NMR ($CDCl_3$, 50.32 MHz) δ 61.3 (m, C_t), 126–134 (phenyl C), 154.5 (s, C_c); MS (FAB) 825 (M^+).

4.2.24. $Pd(PPh_3)_2[\eta^3-CH_2C(p-NSO_2C_6H_4Me)CH_2]$ (**9n**)

Refer to the paragraph for **7i** for the detailed procedure. The reaction of **5** (250 mg, 0.33 mmol) and $NaNHSO_2C_6H_4Me$ (97 mg, 0.40 mmol) gave **9n** in 72% yield (200 mg). IR (KBr pellet) $\nu_{C=N}$ 1480 cm^{-1} , $\nu_{S=O}$ 1161, 1382 cm^{-1} ; ^{31}P -NMR ($CDCl_3$, 81.015 MHz) δ 27.0; 1H -NMR ($CDCl_3$, 300 MHz) δ 2.25 (5H, m, CH_3 and H_{anti}), 3.31 (2H, s, H_{syn}), 7.15–7.65 (34H, phenyl H); ^{13}C -NMR ($CDCl_3$, 50.32 MHz) δ 21.3 (s, CH_3), 61.2 (m, C_t), 128–134 (phenyl C), 154.8 (s, C_c); MS (FAB) 839 (M^+).

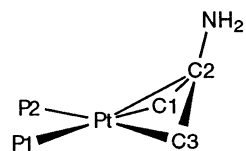


Scheme 8.

Table 4
X-ray crystal parameters and data collection

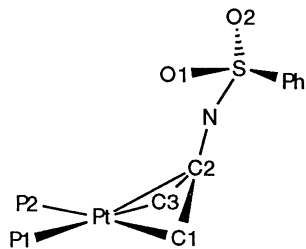
	3a'	3d	3g'	3h	3i'	3j	4m	7d	7g	7i	8i	15	16
Formula	PtC ₃₉ H ₃₆ NP ₂ BF ₄	PtC ₄₂ H ₄₂ NP ₂ BrH ₂ O·CH ₂ Cl ₂	PtC ₄₅ H ₄₀ NP BF ₄ ·1.5CH Cl ₃	PtC ₄₁ H ₄₀ NO P ₂ Br	PtC ₄₃ H ₄₄ NP BF ₄ ·C ₂ H ₅ O H	PtC ₄₂ H ₄₀ NP ₂ Br	PtC ₄₅ H ₃₉ NO P ₂ S ₂ ·2C ₆ H ₆	PdC ₄₂ H ₄₂ NP 2Br·2CHCl ₃ H ₂ Cl ₂	PdC ₄₆ H ₄₀ NP SO ₃ F ₃ ·1.5C 2SO ₃ F ₃	PdC ₄₄ H ₄₄ NP SO ₃ F ₃	PdC ₂₅ H ₂₀ NP Br·3CH ₂ Cl ₂ ·C ₄ H ₁₀ O	Pt ₅ C ₇₈ H ₇₂ N ₂ P ₄ Br ₂	PtC ₃₈ H ₃₆ NO P ₂ Br
Formula weight	901.61	1000.70	1116.91	899.72	964.75	895.74	1071.12	1047.81	1039.63	892.25	560.79	2040.26	859.60
Crystal size (mm)	0.05 × 0.2	0.3 × 0.4	0.15 × 0.25	0.1 × 0.15	0.4 × 0.4	0.35 × 0.5	0.25 × 0.35	0.4 × 0.4	0.2 × 0.3	0.17 × 0.3	0.3 × 0.35	0.35 × 0.45	0.3 × 0.35
Space group	× 0.4 C2/c	× 0.4 P2 ₁ -2 ₁	× 0.45 C2/c	× 0.2 P2 ₁ /n	× 0.3 P2 ₁ /n	× 0.5 P2 ₁ /n	× 0.45 P2 ₁ /n	× 0.5 P2 ₁ /n	× 0.5 C2/c	× 0.45 P2 ₁ /n	× 0.4 P2 ₁ /n	× 0.45 P2 ₁ /n	× 0.45 P2 ₁ /n
a (Å)	20.733(3)	14.416(3)	34.775(3)	11.601(2)	11.219(3)	11.519(2)	10.708(4)	10.947(3)	35.278(6)	11.366(6)	9.054(2)	14.361(2)	14.780(3)
b (Å)	17.708(3)	40.203(3)	14.283(2)	20.893(5)	22.252(4)	20.690(5)	11.009(2)	10.990(4)	14.438(6)	21.747(8)	10.641(3)	14.785(4)	11.342(3)
c (Å)	23.740(4)	13.827(2)	21.183(2)	15.331(4)	16.827(5)	15.778(6)	21.663(6)	40.16(1)	21.364(4)	17.091(6)	14.111(7)	22.545(7)	20.336(7)
α (°)	90	90	90	90	90	90	94.40(2)	90	90	90	73.48(3)	92.71(2)	90
β (°)	117.87(3)	90	117.229(8)	95.05(2)	92.71(2)	93.80(3)	101.22(3)	96.61(2)	115.33(1)	91.76(4)	72.10(3)	91.03(2)	(92.917(3))
γ (°)	90	90	90	90	90	90	100.53(3)	90	90	90	73.56(2)	117.23(2)	90
V (Å ³)	7705(2)	8014(2)	9356(2)	3702(2)	4196(2)	3752(2)	2446(1)	4799(3)	9836(5)	4222(3)	1211.4(7)	4248(2)	3405(2)
Z	8	8	8	4	4	4	2	4	8	4	22	4	4
ρ (calc.)	1.554	1.549	1.585	1.614	1.505	1.586	1.454	1.450	1.404	1.348	1.537	1.594	1.673
(mg m ⁻³)													
F(000)	3563	3247	4404	776	1788	1760	1077	2112	3728	1832	564	2020	1688
Radiation,	Mo-K _α	Cu-K _α	Mo-K _α	Mo-K _α	Mo-K _α	Mo-K _α	Mo-K _α	Mo-K _α	Mo-K _α	Mo-K _α	Mo-K _α	Mo-K _α	Mo-K _α
λ (Å)	0.7107	1.54056	0.7107	0.7107	0.7107	0.7107	0.7107	0.7107	0.7107	0.7107	0.7107	0.7107	0.7107
T (K)	298	300	298	298	300	298	298	298	298	298	298	298	298
μ (mm ⁻¹)	3.80	7.58	3.14	5.02	3.50	4.946	3.03	1.639	5.215	6.056	2.465	4.56	5.449
Transmission	0.705–1.0	0.548–1.0	0.770–1.0	0.550–1.0	0.699–1.0	0.788–1.0	0.929–1.0	0.940–1.0	0.931–1.0	0.915–1.0	0.762–1.0	0.87–1.0	0.854–1.0
Max 2θ (°)	50	120	50	45	50	50	50	45	45	45	45	45	45
h, k, l	±21, 21, 28	16, 45, 15 25	±36, 16, 25	±12, 22, 16	+13, 26, 19	±13, 24, 18	±12, 13, ±25	±11, 11, 43	±34, 15, 22	±12, 23, ±18	±9, 11, ± 14	±15–13, 15, ±24	±15, 12, 21
No. of reflections measured	6956	6607	8226	4837	7778	6658	8623	6412	6416	5513	3176	11548	4432
No. of reflections served	3773 (> 2.0σ)	6398 (> 2.5σ)	4953 (> 2.0σ)	2727 (> 2.0σ)	4123 (> 2.5σ)	4083 (> 2.0σ)	6825 (> 2.0σ)	3727 (> 2.0σ)	3857 (> 2.0σ)	3728 (> 2.0σ)	2666 (> 2.0σ)	7712 (> 2.0σ)	3208 (> 2.0σ)
No. of variables	461	863	523	374	425	433	577	496	514	496	279	893	398
R(F)	0.044	0.059	0.058	0.079	0.055	0.045	0.030	0.047	0.068	0.048	0.023	0.050	0.047
R _w (F)	0.041	0.081	0.059	0.080	0.062	0.046	0.026	0.046	0.083	0.050	0.018	0.051	0.049
S	1.40	3.37	2.98	3.40	2.98	2.50	1.17	1.84	1.27	2.02	1.88	2.13	2.81
(Δ/σ) _{max}	0.0122	0.499	0.0152	0.0305	0.894	0.1542	0.0088	0.0392	0.0239	0.0417	0.0599	0.0339	0.0107

Table 5
Selected bond distances (Å) and angles (°) of **3a**, **4m**, and **15**



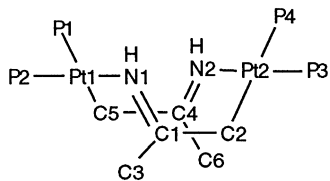
$\{(\text{PPh}_3)_2\text{Pt}[\eta^3\text{-CH}_2\text{C}(\text{NH}_2)\text{CH}_2]\}(\text{BF}_4)$ (**3a**)

Pt–P1	2.272(3)	Pt–P2	2.300(3)	Pt–C1	2.19(3)
Pt–C2	2.329(9)	Pt–C3	2.12(1)	C1–C2	1.43(1)
C2–C3	1.43(1)	C2–N	1.33(1)		
P1–Pt–P2	101.4(1)	P1–Pt–C1	163.3(3)	P1–Pt–C2	130.2(3)
P1–Pt–C3	96.9(3)	P2–Pt–C1	94.5(3)	P2–Pt–C2	126.5(3)
P2–Pt–C3	161.5(3)	C1–Pt–C2	36.8(4)	C1–Pt–C3	67.1(4)
C2–Pt–C3	37.1(4)	Pt–C1–C2	76.9(6)	Pt–C2–C1	66.3(6)
Pt–C2–C3	63.5(5)	Pt–C3–C2	79.4(6)	Pt–C2–N	126.0(7)
C1–C2–C3	112.8(9)	C1–C2–N	123.3(9)	C3–C2–N	122(1)



$(\text{PPh}_3)_2\text{Pt}[\eta^3\text{-CH}_2\text{C}(\text{NSO}_2\text{Ph})\text{CH}_2]$ (**4m**)

Pt–P1	2.286(1)	Pt–P2	2.274(1)	Pt–C1	2.141(4)
Pt–C2	2.333(4)	Pt–C3	2.147(4)	C1–C2	1.439(6)
C2–C3	1.435(6)	C2–N	1.342(6)	S–N	1.599(4)
S–O1	1.441(3)	S–O2	1.439(3)	S–C4	1.782(5)
P1–Pt–P2	104.10(5)	P1–Pt–C1	99.3(1)	P1–Pt–C2	131.1(1)
P1–Pt–C3	165.7(1)	P2–Pt–C1	156.5(1)	P2–Pt–C2	121.8(1)
P2–Pt–C3	90.0(1)	C1–Pt–C2	37.2(2)	C1–Pt–C3	66.5(2)
C3–Pt–C2	37.1(2)	Pt–C1–C2	78.7(2)	Pt–C2–C1	64.1(2)
Pt–C3–C2	78.5(3)	Pt–C2–C3	64.4(2)	Pt–C2–N	125.6(3)
C1–C2–C3	109.9(4)	C1–C2–N	130.0(4)	C3–C2–N	117.9(4)
C2–N–S	120.6(3)	N–S–O1	114.2(2)	N–S–O2	105.9(2)
N–S–C4	106.4(2)	O2–S–O1	116.5(2)	O1–S–C4	106.9(2)
O2–S–C4	106.3(2)				



$\{[\text{cis-Pt}(\text{PPh}_3)_2(\mu\text{-CH}_2\text{CmeNH})_2]\}(\text{Br})_2$ (**15**)

Table 5 (continued)

Pt1–P1	2.310(3)	Pt1–P2	2.266(4)	Pt1–N1	2.052(9)
Pt1–C5	2.15(1)	Pt2–P3	2.260(4)	Pt2–P4	2.313(4)
Pt2–N2	2.04(1)	Pt2–C2	2.13(1)	N1–C1	1.28(2)
N2–C4	1.30(2)	C1–C2	1.47(2)	C1–C3	1.48(2)
C4–C5	1.43(2)	C4–C6	1.49(2)		
P1–Pt1–P2	98.3(1)	P1–Pt1–N1	88.2(3)	P1–Pt1–C5	173.1(3)
P2–Pt1–N1	170.1(3)	P2–Pt1–C5	85.9(3)	N1–Pt1–C5	88.4(4)
Pt1–N1–C1	131.0(8)	N1–C1–C2	124(1)	N1–C1–C3	120(1)
C2–C1–C3	116(1)	Pt1–C5–C4	112.6(8)	P3–Pt2–P4	99.5(1)
P3–Pt2–N2	169.1(3)	P3–Pt2–C2	84.9(3)	P4–Pt2–N2	88.8(3)
P4–Pt2–C2	169.5(3)	N2–Pt2–C2	88.1(4)	Pt2–N2–C4	131.7(8)
N2–C4–C5	120(1)	N2–C4–C6	120(1)	C5–C4–C6	120(1)
Pt2–C2–C1	115.4(8)				

4.2.25. *trans*-Pt(PPh₃)₂(O₂CMe)(η¹-CHCCH₂) (**10**)

The reaction of *trans*-Pt(Br)(PPh₃)₂(η³-CHCCH₂) (**1**) (50 mg, 0.063 mmol) and equimolar AgOAc gave the product quantitatively based on NMR measurements. ³¹P-NMR (CDCl₃, 81.015 MHz) δ 23.2 (*J*_{P–Pt} = 3165 Hz); ¹H-NMR (CDCl₃, 300 MHz) δ 0.85 (s, CH₃), 2.71 (2H, dt with ¹⁹⁵Pt satellites, *J*_{H–H} = 6.5 Hz, *J*_{H–P} = 3.9 Hz, *J*_{H–Pt} = 52.0 Hz, CH), 4.96 (1H, tt, with ¹⁹⁵Pt satellites, *J*_{H–H} = 6.5 Hz, *J*_{H–P} = 2.5 Hz, *J*_{H–Pt} = 123.6 Hz, CH₂), 7.1–7.5 (phenyl H); ¹³C-NMR (CDCl₃, 50.32 MHz) δ 23.1 (s with ¹⁹⁵Pt satellites, *J*_{C–Pt} = 17.7 Hz, C=CH₃), 59.7 (t with ¹⁹⁵Pt satellites, *J*_{C–P} = 10.6 Hz, *J*_{C–Pt} = 848.9 Hz, CH), 65.9 (s with ¹⁹⁵Pt satellites, *J*_{C–Pt} = 58.6 Hz, CH₂), 128–134 (phenyl C), 175.6 (s with ¹⁹⁵Pt satellites, *J*_{C–Pt} = 22.1 Hz, C=O), 206.1 (t, *J*_{C–P} = 3.9 Hz, C=).

4.2.26. *trans*-Pt(PPh₃)₂(NHSO₂Ph)(η¹-CHCCH₂) (**11**)

To the CDCl₃ solution of **10** from above, was added equimolar NaNHSO₂Ph. The NMR spectra were then taken. ³¹P-NMR (CDCl₃, 81.015 MHz) δ 21.3 (*J*_{P–Pt} = 3064 Hz); ¹H-NMR (CDCl₃, 300 MHz) δ 2.74 (2H, dt with ¹⁹⁵Pt satellites, *J*_{H–H} = 6.0 Hz, *J*_{H–P} = 2.0 Hz, *J*_{H–Pt} = 48.4 Hz, CH), 4.63 (1H, tt, with ¹⁹⁵Pt satellites, *J*_{H–H} = 6.0 Hz, *J*_{H–P} = 3.8 Hz, *J*_{H–Pt} = 96.1 Hz, CH₂), 7.1–7.5 (phenyl H).

4.2.27. *cis*-Pt(Cl)(Ph₂PCH₂CH₂PPh₂)(η¹-CHCCH₂) (**12**)

To a round-bottom flask containing *trans*-Pt(Cl)(PPh₃)₂(η³-CHCCH₂) (262 mg, 0.33 mmol), was introduced a benzene solution containing equimolar dppe dropwise into 15 ml benzene. The reaction solution was vigorously stirred for 20 min. Adding hexane resulted in the product in 91% yield (200 mg). ³¹P-NMR (CDCl₃, 300 MHz) δ 41.8 (d, *J*_{P–P} unresolved, *J*_{P–Pt} = 4087 Hz), 43.0 (d, *J*_{P–P} unresolved, *J*_{P–Pt} = 1994 Hz); ¹H-NMR (CDCl₃, 300 MHz) δ 2.0–2.5 (4H, m, C₂H₄), 3.33 (2H, t with ¹⁹⁵Pt satellites, *J*_{H–H} = 6.7 Hz, *J*_{H–P} = 1.7, 5.3 Hz, *J*_{H–Pt} = 33.3 Hz, CH₂), 5.67 (1H,

dtd with ¹⁹⁵Pt satellites, *J*_{H–H} = 6.7 Hz, *J*_{H–P} = 5.3, 6.6 Hz, *J*_{H–Pt} = 116.5 Hz, CH), 7.1–7.5 (phenyl H)

4.2.28. *cis*-Pt(Ph₂PCH₂CH₂PPh₂)(NHSO₂Ph)(η¹-CHCCH₂) (**13**)

To a CDCl₃ solution containing **12** (30 mg), was added equimolar NaNHSO₂Ph. The NMR spectra were then taken. ³¹P-NMR (CDCl₃, 81.015 MHz) δ 39.5 (d, *J*_{P–P} unresolved, *J*_{P–Pt} = 3521 Hz), 45.5 (d, *J*_{P–P} unresolved, *J*_{P–Pt} = 2205 Hz); ¹H-NMR (CDCl₃, 50.32 MHz) δ 2.0–2.5 (4H, m, C₂H₄), 3.76 (2H, t with ¹⁹⁵Pt satellites, *J*_{H–H} = 6.6 Hz, *J*_{H–Pt} = 36.8 Hz, CH₂), 4.29 (1H, s with ¹⁹⁵Pt satellites, *J*_{H–Pt} = 23.0 Hz, NH), 5.37 (1H, dtd, with ¹⁹⁵Pt satellites, *J*_{H–H} = 6.6 Hz, *J*_{H–P} = 1.5, 6.2 Hz, *J*_{H–Pt} = 81 Hz, CH), 7.1–7.5 (phenyl H)

4.2.29. Pt(Ph₂PCH₂CH₂PPh₂)[η³-CH₂C(NSO₂Ph)CH₂] (**14**)

The solution of **13** from above was heated at 60°C for 12 h to give complex **14** as the only noticeable product based on the NMR measurements. ³¹P-NMR (CDCl₃, 81.015 MHz) δ 46.7 (*J*_{P–Pt} = 3160 Hz); ¹H-NMR (CDCl₃, 50.32 MHz) δ 2.33 (6H, m, C₂H₄ and H_{anti}), 4.30 (2H, br, H_{syn}), 7.1–7.5 (phenyl H).

4.2.30. {[*cis*-Pt(PPh₃)₂(μ-CH₂CMeNH)]₂}(Br)₂ (**15**)

Complex **1** (0.18 mmol) and ammonia (0.2 mmol) were allowed to react in chloroform for 1 day, followed with methanolated KOH (14mg KOH in 1 ml MeOH) to the reaction solution. The solution was dried by vacuo after 5 min. Dichloromethane was added and the potassium salt was filtered off. A white product was precipitated and was washed by acetone. The yield was 64%. Single crystals were grown from CH₂Cl₂/acetone. ³¹P-NMR (CDCl₃, 81.015 MHz) δ 12.9 (d, *J*_{P–P} = 16.5 Hz, *J*_{P–Pt} = 3420 Hz), 22.9 (d, *J*_{P–P} = 16.5 Hz, *J*_{P–Pt} = 2243 Hz); ¹H-NMR (CDCl₃, 300 MHz) δ 1.73 (6H, s, CH₃), 2.42 (4H, dd, *J*_{H–P} = 9.2 Hz, unresolved *J*_{H–P} CH₂), 8.74 (2H, br, NH).

4.2.31. *cis*-{(PPh₃)₂Pt[NH₂CH₂CH₂O]}(Br) (**16**)

Complex **1** (20 mg, 0.024 mmol) reacts with H₂NCH₂CH₂OH (30 μl, 0.048 mmol) in CH₂Cl₂ for 96 h to yield **16** quantitatively. ³¹P-NMR (CDCl₃, 81.015 MHz) δ 8.4 (d, *J*_{P-P} = 22.2 Hz, *J*_{P-Pt} = 3674 Hz), 11.5 (d, *J*_{P-P} = 22.2 Hz, *J*_{P-Pt} = 3132 Hz); ¹H-NMR (CDCl₃, 300 MHz) δ 2.7 (2H, br, OCH₂), 3.99 (2H, tt, NCH₂), 4.9 (2H, br, NH₂), 7.2–7.6 (30H, phenyl H); ¹³C-NMR (CDCl₃, 50.32 MHz) δ 50.4 (OCH₂), 73.1 (NCH₂), 128–133 (phenyl C).

4.3. X-ray crystallographic analysis

Diffraction data were measured at 300 K on a Nonius CAD-4 diffractometer with graphite-monochromatized Mo-K_α radiation. 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 the C–H distance of 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 Ref. [15]. Computing programs are from the NRCC SDP VAX package [16]. Crystallographic data of **3a'**, **3d**, **3g'**, **3h**, **3i**, **3j**, **4m**, **7d**, **7g**, **7i**, **8i**, **15**, and **16** are listed in Table 4. The selected bond parameters of **3a**, **4m**, and **15** are listed in Table 5. Other detailed data are supplied in Section 5.

5. Supplementary material

Fully labeled ORTEP drawing and tables giving complete crystal data, complete bond lengths and angles, atomic coordinates, and thermal parameters for **3a'**, **3d**, **3g'**, **3h**, **3i'**, **3j**, **4m**, **7d**, **7g**, **7i**, **8i**, **15**, and **16** (115 pages). Ordering information is given on any current masthead page.

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