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A new stable intermediary mode between η^3-2-aminoallyl complexes and metallacyclobutanimines. Synthesis and structural characteristic of η^3-azatrimethylenemethane and *N*-protonated, *N*-alkylated, *N*-arylated η^3-azatrimethylenemethane complexes of Pt and Pd[1]

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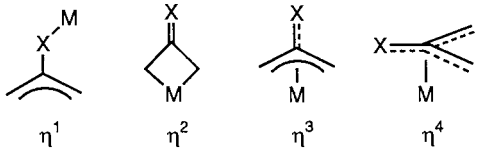
Abstract

Regioselective addition of ammonia, primary or secondary amines, aniline, or amino derivatives either to a neutral (η^1-allenyl)platinum complex *trans*-Pt(Br)(PPh_3)$_2$(η^1-$CHCCH_2$) (**1**) or to a cationic η^3-allenyl/propargyl platinum complex [Pt(PPh_3)$_2$(η^3-C_3H_3)](BF_4) (**2**) provide the synthesis of cationic *N*-protonated, *N*-alkylated, and *N*-arylated η^3-azatrimethylenemethane complexes {Pt(PPh_3)$_2$(η^3-$CH_2C(NRR')CH_2$]}(X) (R = H R′ = H (**3a**), Me (**3b**), Et (**3c**), ^{i}Pr (**3d**), ^{t}Bu (**3e**), c-C_6H_{11} (**3f**), Ph (**3g**), CH_2CH_2OH (**3h**), R = R′ = Et (**3i**), c-C_3H_6 (from azetidine **3j**), Ph (**3k**), R = Me R′ = Ph (**3l**); X = Br, BF_4), respectively. Addition of amides to **1** gave a neutral η^3-azatrimethylenemethane complex Pt(PPh_3)$_2$[η^3-$CH_2C(NSO_2Ph)CH_2$] (**4m**). Similar reactions using palladium complexes yield {Pd(PPh_3)$_2$[η^3-$CH_2C(NRR')CH_2$]}(X) (R = H R′ = ^{i}Pr (**7d**), Ph (**7g**), R = R′ = Et (**7i**); X = Br, BF_4, OTf), Pd(Br)(PPh_3)[η^3-$CH_2C(NEt_2)CH_2$] (**8i**) and Pd(PPh_3)$_2$[η^3-$CH_2C(NR)CH_2$] (R = SO_2Ph (**9m**), *p*-$SO_2C_6H_4Me$ (**9n**)). Synthesis of three complexes, {M(PPh_3)$_2$[η^3-$CH_2C(NHR)CH_2$]}$^+$ (M = Pt R = SO_2Ph (**3m**); M = Pd R = SO_2Ph (**7m**), *p*-$SO_2C_6H_4Me$ (**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 metallacyclobutanimine complexes.[2]

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

1. Introduction

There has been increasing research interest in transition metal complexes of heteronuclear trimethylenemethanes in the form of M[$CH_2C(X)CH_2$]. 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-$CH_2C(=O)CH_2$]; η^3-*N*-TMM to stand for the η^3-azatrimethylenemethane complexes M[η^3-$CH_2C(=NR)CH_2$]. Accordingly, *N*-protonated η^3-*N*-TMM complexes are referred to M[η^3-$CH_2C(NH_2)CH_2$]; and *N*-alkylated or *N*-arylated η^3-*N*-TMM complexes are referred to M[η^3-$CH_2C(NHR)CH_2$] or M[η^3-$CH_2C(NRR')CH_2$] (R, R′ = alkyl or aryl).

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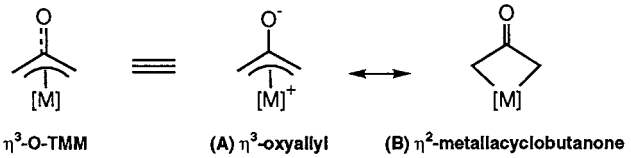
The TMM species of the η^3-form are relatively less investigated, although some have been found useful in organic synthesis [5]. Among them, the η^3-O-TMM complexes of palladium and platinum are the most extensively studied heterotrimethylene methane species [6]. Both experimental and theoretical data 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**).

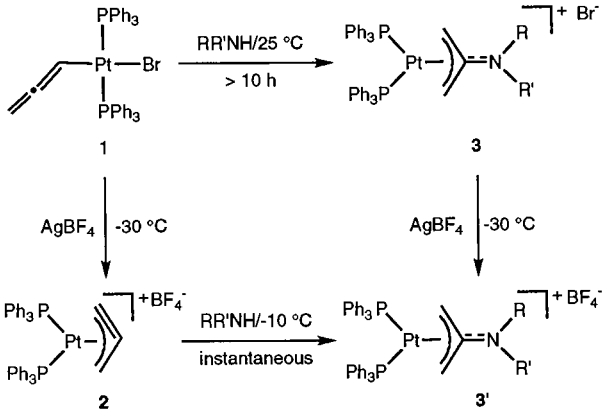


The isoelectronic species of η^3-O-TMM, η^3-*N*-TMM complexes, were virtually unexplored until we reported the first isolable cationic *N*-alkylated η^3-*N*-TMM complexes of platinum in prior preliminary communications [7]. Later on, the *N*-protonated and alkylated η^3-*N*-TMM complexes of iridium were 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

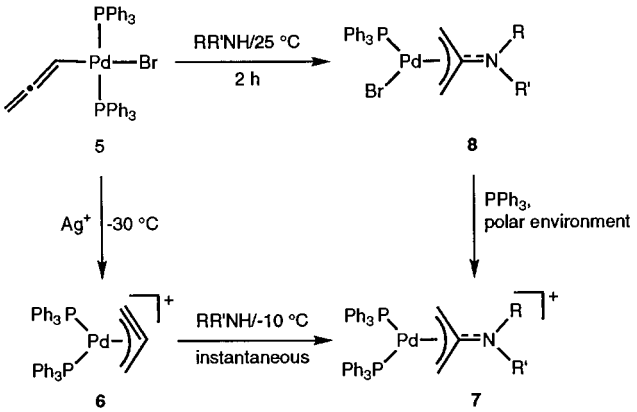
2.1. Synthesis of η^3-N-TMM platinum and palladium complexes

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*-$Pt(Br)(PPh_3)_2(\eta^1\text{-}CHCCH_2)$ (**1**) and equimolar amounts of ammonia, primary or secondary amines, aniline, and other amino derivatives produce $\{Pt(PPh_3)_2(\eta^3\text{-}CH_2C(NRR')CH_2]\}(Br)$ (R = H R′ = H (**3a**), Me (**3b**), Et (**3c**), ^{i}Pr (**3d**), ^{t}Bu (**3e**), c-C_6H_{11} (**3f**), Ph (**3g**), CH_2CH_2OH (**3h**), R = R′ = Et (**3i**), c-C_3H_6 (from azetidine, **3j**), Ph (**3k**), R = Me R′ = Ph (**3l**)). The yields are generally excellent. The BF_4 salts of **3** (**3a**′ and **3g**′) can be obtained either by anionic exchange using $AgBF_4$, or alternatively by the reactions of a cationic η^3-allenyl/propargyl complex $[Pt(PPh_3)_2(\eta^3\text{-}C_3H_3)](BF_4)$ (**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 CH_2Cl_2 (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.

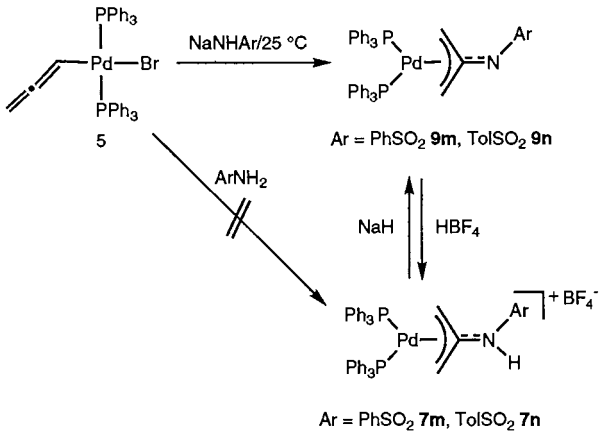


Scheme 1.

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*-$Pd(Br)(PPh_3)_2(\eta^1\text{-}CHCCH_2)$ (**5**) and Et_2NH were allowed to react in CH_2Cl_2 (15 ml) at 25°C for 2 h. A neutral *N*-alkylated η^3-*N*-TMM complex $Pd(Br)(PPh_3)[\eta^3\text{-}CH_2C(NEt_2)CH_2]$ (**8i**) was obtained in 70% isolated yields. Treating **8i** with PPh_3 gave an ionic species as a bromide salt $\{Pd(PPh_3)_2[\eta^3\text{-}CH_2C(NEt_2)CH_2]\}(Br)$ (**7i**). The cation of **7i** with other counter-anions could be prepared by more facile reactions of $[Pd(PPh_3)_2(\eta^3\text{-}C_3H_3)](X)$ (X = PF_6 (**6**), BF_4 (**6**′), OTf (**6**″)) and Et_2NH. Hydroamination of **5** or **6** with NH_3 or $MeNH_2$ could be achieved below 0°C, but the resulting *N*-TMM products decomposed when the temperature was raised to 25°C. Addition of ^{i}PrNH$_2$ or $PhNH_2$ to **5** was successful, when reactions were carried out with the presence of large excess amines. The products are cationic complexes $\{Pd(PPh_3)_2[\eta^3\text{-}CH_2C(NHR)CH_2]\}(Br)$ (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 $Pt(PPh_3)_2[\eta^3\text{-}CH_2C(NR)CHPh]$, prepared from deprotonation of $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(NHR)CHPh]\}^+$. 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*-$Pd(Br)(PPh_3)_2[\eta^1\text{-}CHCCH_2)$ (**5**) with Na(NHAr) in CH_2Cl_2 at 25°C produce $Pd(PPh_3)_2[\eta^3\text{-}CH_2C(NR)CH_2]$ (R = SO_2Ph (**9m**), *p*-$SO_2C_6H_4Me$ (**9n**)) in good yields. The NMR studies show that protonation of **9m** and **9n** instantaneously gives $\{Pd(PPh_3)_2(\eta^3\text{-}CH_2C(NHR)CH_2]\}(BF_4)$ (R = SO_2Ph (**7m**), *p*-$SO_2C_6H_4Me$ (**7n**)). Treating **7m** and **7n** with NaH recovers **9m** and **9n** respectively. Weak amine like $PhSO_2NH_2$ or *p*-MeC_6H_4–SO_2NH_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*-$Pt(PPh_3)_2(OAc)(\eta^1\text{-}CHCCH_2)$ (**10**). Treatment of **10** with $Na(NHSO_2Ph)$ gave another η^1-allenyl complex *trans*-$Pt(PPh_3)_2(NHSO_2Ph)(\eta^1\text{-}CHCCH_2)$ (**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 $Pt(PPh_3)_2(\eta^3\text{-}CH_2C(NSO_2Ph)CH_2]$ (**4m**) (Scheme 4). Protonation of **4m** gives $\{Pt(PPh_3)_2(\eta^3\text{-}CH_2C(NHSO_2Ph)CH_2]\}(BF_4)$ (**3m**).

Hydroamination of a cis η^1-allenylplatinum complex has also been studied. *cis*-Pt(dppe)(Cl)(η^1-$CHCCH_2$) (**12**) was prepared by treating *trans*-$Pt(PPh_3)_2(Cl)(\eta^1\text{-}CHCCH_2)$ with diphenylphosphinoethane (dppe) in benzene. The reaction of $Na(NHSO_2Ph)$ and **12** first yields a cis η^1-allenyl(amido) complex *cis*-$Pt(dppe)(NHSO_2Ph)(\eta^1\text{-}CHCCH_2)$ (**13**) which then transforms into *cis*-Pt(dppe)$[\eta^3\text{-}CH_2C(NSO_2Ph)CH_2]$ (**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, tranformation 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 $MeNH_2$:$EtNH_2$:^{i}PrNH$_2$:c-$C_6H_{11}NH_2$:^{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-$C_6H_{11}NH_2$ and $PhNH_2$ is 2:1, and the qualitative observations showed $EtNH_2 < Et_2NH$ and ^{i}PrNH$_2 < ^n$Pr$_2$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 $MeC_6H_4SO_2NH_2$ 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}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}C-NMR resonances of the cener-carbon of η^3-*N*-TMM complexes appear at δ150 which are down-field compared those of the common η^3-allyl complexes. In addition, the values of J_{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 $CH_2C(N)CH_2$ 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 $60 \pm 4°$ which are smaller than those of the η^3-allyl complexes but much larger than those of metallacyclobutanes. The values of D(C–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**).

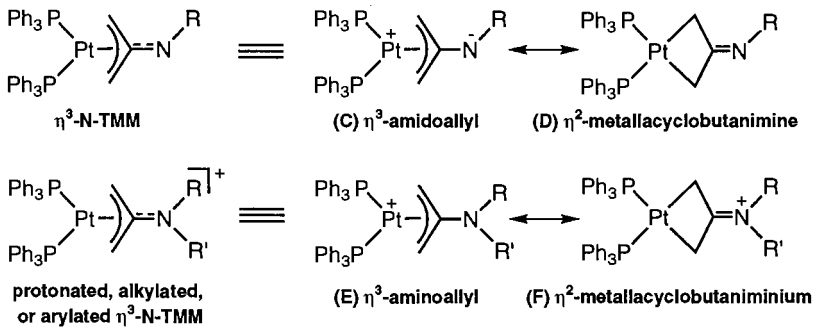
2.4. Base-catalyzed hydrolysis of η^3-*N*-TMM complexes

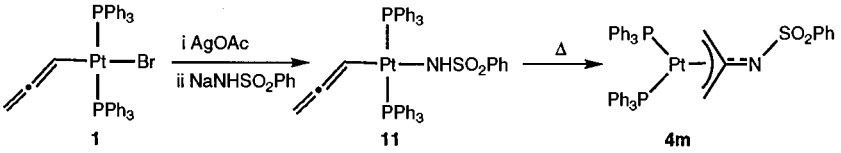
Unlike the deprotonation of $\{Pt(PPh_3)_2[\eta^3$-$CH_2C(NHSO_2Ph)CH_2]\}^+$, which gives $Pt(PPh_3)_2[\eta^3$-$CH_2C(NSO_2Ph)CH_2]$, reaction of $\{Pt(PPh_3)_2(\eta^3$-$CH_2C(NH_2)CH_2]\}^+$ (**3a**) with a methanol solution of KOH yields a new dicationic complex of 1,5-diplatinacycloocta-3,7-diimine $\{cis$-$Pt(PPh_3)_2(\mu$-$CH_2CMeNH)_2\}(Br)_2$ (**15**). The molecular structure of **15** has been confirmed unequivocally by X-ray crystallography. Its ORTEP drawing in Fig. 3 shows that two $-CH_2C(Me)=NH-$ 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 $HOCH_2CH_2NH_2$, *cis*-$\{(Ph_3P)_2Pt[NH_2CH_2CH_2O]\}(Br)$ (**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 $M[\eta^3$-$CH_2C(NR)CH_2]$, *N*-protonated η^3-*N*-TMM $M[\eta^3$-$CH_2C(NH_2)CH_2]$, and *N*-alkylated (or *N*-arylated) η^3-*N*-TMM $M[\eta^3$-$CH_2C(NRR')CH_2]$ 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-$CH_2C(N)CH_2$ 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 Brucker ACE-300 spectrometer. For the ^{31}P-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% H_3PO_4 in $CDCl_3$. 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.

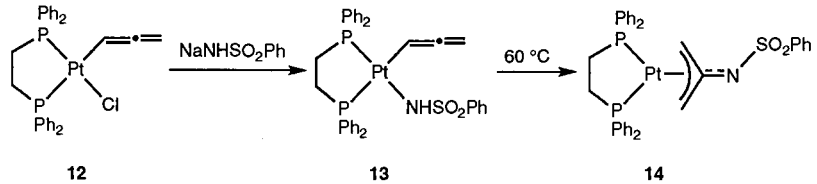
4.2. Synthesis and characterization

4.2.1. *{Pt(PPh$_3$)$_2$[η^3-CH$_2$C(NH$_2$)CH$_2$]}(X) (X = Br **3a**, BF$_4$ **3a′**)*

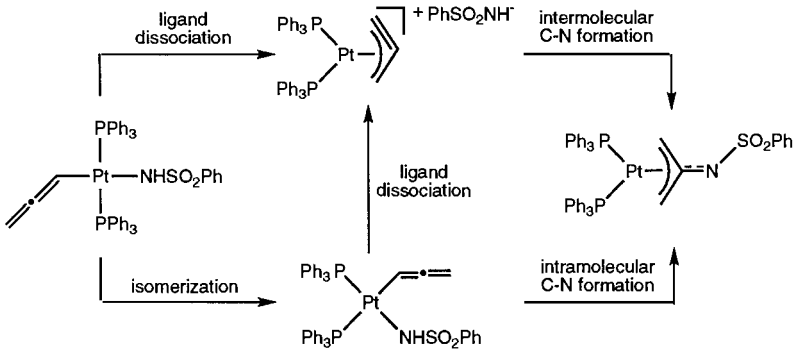
To a two-necked round-bottom flask, was charged with *trans*-Pt(Br)(PPh$_3$)$_2$(η^1-CHCCH$_2$) (**1**) (165 mg, 0.2 mmol) and aqueous ammonia (17 μl of 25% aqueous solution) in CH_2Cl_2 (20 ml). The solution was strred for 1 day and was then concentrated. Addition of diethyl ether to the solution resulted in the precipitation of the white product. The yield was 89%. Alternatively, the reaction of equimolar amounts of [Pt(PPh$_3$)$_2$(η^3-C_3H_3)](BF$_4$) (**2**) (0.2 mmol) and ammonia (0.5 M in dioxane) in chloroform instantaneously resulted in the BF_4 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}; ^{31}P-NMR ($CDCl_3$, 81.015 MHz) δ 19.0 (J_{P-Pt} = 3356 Hz); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.93 (2H, dd with ^{195}Pt 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 ^{195}Pt satellites, J_{H-Pt} = 18.0 Hz, NH); ^{13}C-NMR ($CDCl_3$, 50.32 MHz) δ 44.8 (dd with ^{195}Pt satellites, J_{C-P} = 4.6, 47.6 Hz, J_{C-Pt} = 169.2 Hz, C_t), 127.6–134.9 (phenyl C), 153.1 (td with ^{195}Pt satellites, J_{C-P} = 4.2 Hz, J_{C-Pt} = 88.5 Hz, C_c). Anal. Calc. for $PtC_{39}H_{36}NP_2Br$: C, 54.74; H, 4.24; N, 1.64. Found: C, 54.02; H, 4.32; N, 1.61.

4.2.2. *{Pt(PPh$_3$)$_2$[η^3-CH$_2$C(NHMe)CH$_2$]}(Br) (**3b**)*

Complex **1** (360 mg, 0.43 mmol) and $MeNH_2$ (40 μl 40% aqueous solution, 0.52 mmol) were allowed to react in CH_2Cl_2 (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}; ^{31}P-NMR ($CDCl_3$, 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); ^{1}H-NMR ($CDCl_3$, 300 MHz, 275 K) δ 1.65 (1H, dd with ^{195}Pt 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 ^{195}Pt 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 ^{195}Pt satellites, J_{H-H} = 4.7 Hz, J_{H-Pt} = 22.8 Hz, CH$_3$), 3.23 (1H, br, H_{syn}), 7.1–7.5 (30H, phenyl H), 8.57 (1H, d, J_{H-P} = 4.9 Hz, NH); ^{13}C-NMR ($CDCl_3$, 50.3 MHz) δ 28.8 (d with ^{195}Pt satellites, J_{C-P} = 6.2 Hz, J_{C-Pt} = 11.6 Hz, CH$_3$), 40.1 (dd with ^{195}Pt satellites, J_{C-P} = 4.8, 44.9 Hz, J_{C-Pt} = 176.4 Hz, C_t), 41.5 (d with ^{195}Pt satellites, J_{C-P} = 49.7 Hz, J_{C-Pt} = 201 Hz, C_t), 127–135 (phenyl C), 156.5 (dd with ^{195}Pt satellites, J_{C-P} = 4.6, 9.9 Hz, J_{C-Pt} = 110.7 Hz, C_c); Anal. Calc. for $PtC_{40}H_{38}NP_2Br{\cdot}H_2O$ 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$_3$)$_2$[η^3-CH$_2$C(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 EtNH$_2$ (16.5 μl 70% aqueous solution, 2.1 mmol) gave white solid **3c** in 91% yield (151 mg). ^{31}P-NMR (CDCl$_3$, 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); ^{1}H-NMR (CDCl$_3$, 300 MHz, 273 K) δ 1.04 (3H, t, $J_{H-H}=6.7$ Hz, CH$_2$CH$_3$), 1.60 (1H, dd with ^{195}Pt 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 ^{195}Pt 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, CH$_2$CH$_3$), 3.21 (1H, br, H$_{syn}$), 7.0-7.3 (30H, phenyl H), 8.48 (1H, br, $J_{H-P}=4.9$ Hz, NH); ^{13}C-NMR (CDCl$_3$, 50.32 MHz) δ 15.0 (t, $J_{C-P}=5.3$ Hz, CH$_2$CH$_3$), 37.3 (t, $J_{C-P}=6.4$ Hz, CH$_2$CH$_3$), 39.6 (d with ^{195}Pt satellites, $J_{C-P}=46.8$ Hz, $J_{C-Pt}=178$ Hz, C$_t$), 41.1 (dd with ^{195}Pt satellites, $J_{C-P}=4.4$, 45.3 Hz, $J_{C-Pt}=197$ Hz, C$_t$), 128–134 (phenyl C), 156.1 (t with ^{195}Pt satellites, $J_{C-P}=4.3$ Hz, $J_{C-Pt}=110.3$ Hz, C$_c$).

*4.2.4. {Pt(PPh$_3$)$_2$[η^3-CH$_2$C(NH^{i}Pr)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 ^{i}PrNH$_2$ (18 μl) gave **3d** in 92% yield (148 mg). IR (KBr) $\nu_{C=N}$ 1585 cm^{-1}; ^{31}P-NMR (CDCl$_3$, 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); ^{1}H-NMR (CDCl$_3$, 300 MHz) δ 1.24 (6H, d, $J_{H-H}=6.3$ Hz, CH$_3$), 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 ^{195}Pt satellites, $J_{H-H}=8.2$ Hz, $J_{H-Pt}=27.1$ Hz, NH); ^{13}C-NMR (CDCl$_3$, 75.469 MHz) δ 22.6 (s, CH$_3$), 39.6 (d with ^{195}Pt satellites, $J_{C-P}=46.9$ Hz, $J_{C-Pt}=187$ Hz, C$_t$), 41.0 (d with ^{195}Pt satellites, $J_{C-P}=48.9$ Hz, $J_{C-Pt}=198$ Hz, C$_t$), 45.2 (dd, $J_{C-P}=5.8$, 14.2 Hz, CH), 128–133 (phenyl C), 155.6 (dd, $J_{C-Pt}=101$ Hz, C$_c$); Anal. Calc. for PtC$_{42}$H$_{42}$NP$_2$Br·H$_2$O C, 55.09; H, 4.84; N. 1.53. Found: C, 54.44; H, 4.84; N, 1.53.

Table 1
Relative yields of the *N*-alkylated η^3-*N*-TMM complexes formed from reactions of *trans*-Pt(Br)(PPh$_3$)$_2$(η^1-CHCCH$_2$) (**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$_2$/^{t}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 CDCl$_3$. The relative yields of the products were measured using NMR spectroscopy.

*4.2.5. {Pt(PPh$_3$)$_2$[η^3-CH$_2$C(NH^{t}Bu)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 ^{t}BuNH$_2$ (25 μl, 0.24 mmol) for 2 days gave **3e** in 86% yield (184 mg). IR (KBr) $\nu_{C=N}$ 1585 cm^{-1}; ^{31}P-NMR (CDCl$_3$, 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); ^{1}H-NMR (CDCl$_3$, 300 MHz, 283 K) δ 1.24 (9H, s, CH$_3$), 1.64 (1H, dd with ^{195}Pt 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 ^{195}Pt satellites, $J_{H-Pt}=27$ Hz, NH); ^{13}C-NMR (CDCl$_3$, 50.32 MHz) δ 29.2 (s, CH$_3$), 42.5 (d with ^{195}Pt satellites, $J_{C-P}=45$ Hz, $J_{C-Pt}=190$ Hz, C$_t$), 52.1 (t, $J_{C-P}=5.7$ Hz, Me$_3$C), 127–134 (phenyl C), 156.8 (t with ^{195}Pt satellites, $J_{C-P}=4$ Hz, $J_{C-Pt}=105.6$ Hz, C$_c$); Anal. Calc. for C$_{43}$H$_{44}$NP$_2$PtBr C, 56.65; H, 4.86; N. 1.54. Found: C, 56.65; H, 4.70; N, 1.45.

*4.2.6. {Pt(PPh$_3$)$_2$[η^3-CH$_2$C(NHC$_6$H$_{12}$)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-C$_6$H$_{12}$NH$_2$ (31 μl, 0.25 mmol) gave **3f** in 87% yield (196 mg). IR (KBr) $\nu_{C=N}$ 1577 cm^{-1}; ^{31}P-NMR (CDCl$_3$, 81.015 MHz) δ 19.3 (d, $J_{P-P}=8.9$ Hz, $J_{P-Pt}=$

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}	$C_t(J_{C-Pt})$	$C_c(J_{C-Pt})$
$\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(NRR')CH_2]\}^+$				
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, c-C_6H_{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_2H_4OH (**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_3H_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_2Ph (**3m**)	2.26(42.3)	3.49	52.6(103.4)	138.3
$\{Pd(PPh_3)_2[\eta^3\text{-}CH_2C(NRR')CH_2]\}^+$				
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_2Ph (**7m**)	2.79	3.63		
H, $SO_2C_6H_4Me$ (**7n**)	2.82	3.59		
$Pd(PPh_3)(Br)[\eta^3\text{-}CH_2C(NRR')CH_2]$				
Et, Et (**8i**)	2.12	2.50	43.0	148.2
	2.28	3.17	49.1	
$M(PPh_3)_2[\eta^3\text{-}CH_2C(NR)CH_2]$				
M = Pt, R = SO_2Ph (**4m**)	2.05(51.2)	3.23	50.7(174.5)	158.9(88.9)
M = Pd, R = SO_2Ph (**9m**)	2.26	3.31	61.3	154.5
M = Pd, R = $SO_2C_6H_4Me$ (**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); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.88–1.73 (11H, m, C$\underline{H}_2$ and H_{anti}), 1.99 (1H, dd with ^{195}Pt 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 ^{195}Pt satellites, $J_{H-P} = 8.1$ Hz, $J_{H-Pt} = 27$ Hz, N$\underline{H}$); ^{13}C-NMR ($CDCl_3$, 50.32 MHz) δ 4.8, 25.0, 31.8, 33.2 ($\underline{C}H_2$), 40.2 (d with ^{195}Pt 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, $\underline{C}N$), 127–134 (phenyl C), 155.2 (t with ^{195}Pt satellites, $J_{C-P} = 4.2$ Hz, $J_{C-Pt} = 110.4$ Hz, C_c); Anal. Calc. for $PtC_{45}H_{46}NP_2Br$ C, 57.63; H, 4.94; N. 1.49. Found: C, 56.02; H, 4.92; N, 1.36.

4.2.7. *{Pt(PPh$_3$)$_2$[η^3-CH$_2$C(NHPh)CH$_2$]}(Br **3g**, BF$_4$, **3g′**)*

Refer to the paragraph for **3a** for the detailed procedure. The reaction of complex **1** (150 mg, 0.18 mmol) and $PhNH_2$ (18 μl, 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 $AgBF_4$ (58 mg) in situ. After AgBr was removed by filtration, the filtrate was allowed to react with $PhNH_2$ (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}; ^{31}P-NMR ($CDCl_3$, 81.015 MHz) δ 19.0 ($J_{P-Pt} = 3361$ Hz); ^{1}H-NMR ($CDCl_3$, 300 MHz, 283K) δ 2.09 (2H, br with ^{195}Pt 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 ^{195}Pt satellites, $J_{H-Pt} = 19.3$ Hz, N$\underline{H}$); ^{13}C-NMR ($CDCl_3$, 75.469 MHz) δ 44.9 (d, $J_{C-P} = 43.9$ Hz, C_t), 123.5, 124.9 (N$\underline{C}_{ipso}$), 128–138 (phenyl C), 150.8 (s, C_c); Anal. Calc. for $C_{44}H_{40}NP_2PtBr$ C, 57.46; H, 4.38; N. 1.52. Found: C, 58.11; H, 4.29; N, 1.36. For **3g′**: ^{1}H-NMR ($CDCl_3$, 200 MHz, 283K) δ 2.2 (2H, dd with ^{195}Pt 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 ^{195}Pt satellites, $J_{H-Pt} = 20$ Hz, N$\underline{H}$).

4.2.8. *{Pt(PPh$_3$)$_2$[η^3-CH$_2$C(NHCH$_2$CH$_2$OH)CH$_2$]}(Br) (**3h**)*

Refer to the paragraph for **3a** for the detailed procedure. The reaction of complex **1** (200 mg, 0.24 mmol) and $HOCH_2CH_2NH_2$ (14 μL, 0.24 mmol) gave **3h** in 90% yield. IR (KBr) $\nu_{C=N}$ 1539 cm^{-1}; ^{31}P-NMR ($CDCl_3$, 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); ^{1}H-NMR ($CDCl_3$, 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, $NCH_2C\underline{H}_2OH$), 3.70 (2H, br, $NC\underline{H}_2CH_2OH$), 4.69 (1H, t, $J_{H-H} = 12$ Hz, O$\underline{H}$), 7.1-7.4 (30H, phenyl H), 8.11 (1H, s, $J_{H-P} = 9.7$ Hz, N$\underline{H}$); ^{13}C-NMR ($CDCl_3$, 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, $NCH_2\underline{C}H_2OH$), 59.2 (s, $N\underline{C}H_2CH_2OH$), 128–134 (phenyl C), 154.7 (d with ^{195}Pt satellites, $J_{C-P} = 4.0$ Hz, $J_{C-Pt} = 105.6$ Hz, C_c).

4.2.9. *{Pt(PPh$_3$)$_2$[η^3-CH$_2$C(NEt$_2$)CH$_2$]}(BF$_4$) (**3i′**)*

Refer to the paragraph for **3g′** for the detailed procedure. The reaction of complex **1** (150 mg, 0.18 mmol) and Et_2NH (21 μl) gave **3i′** in 93% yield (151 mg). IR (KBr) $\nu_{C=N}$ 1555 cm^{-1}; ^{31}P-NMR ($CDCl_3$, 81.02 MHz) δ 17.9 ($J_{P-Pt} = 3256$ Hz); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.04 (6H, t, $J_{H-H} = 7.1$ Hz, C$\underline{H}_3CH_2$), 2.33 (4H, br,

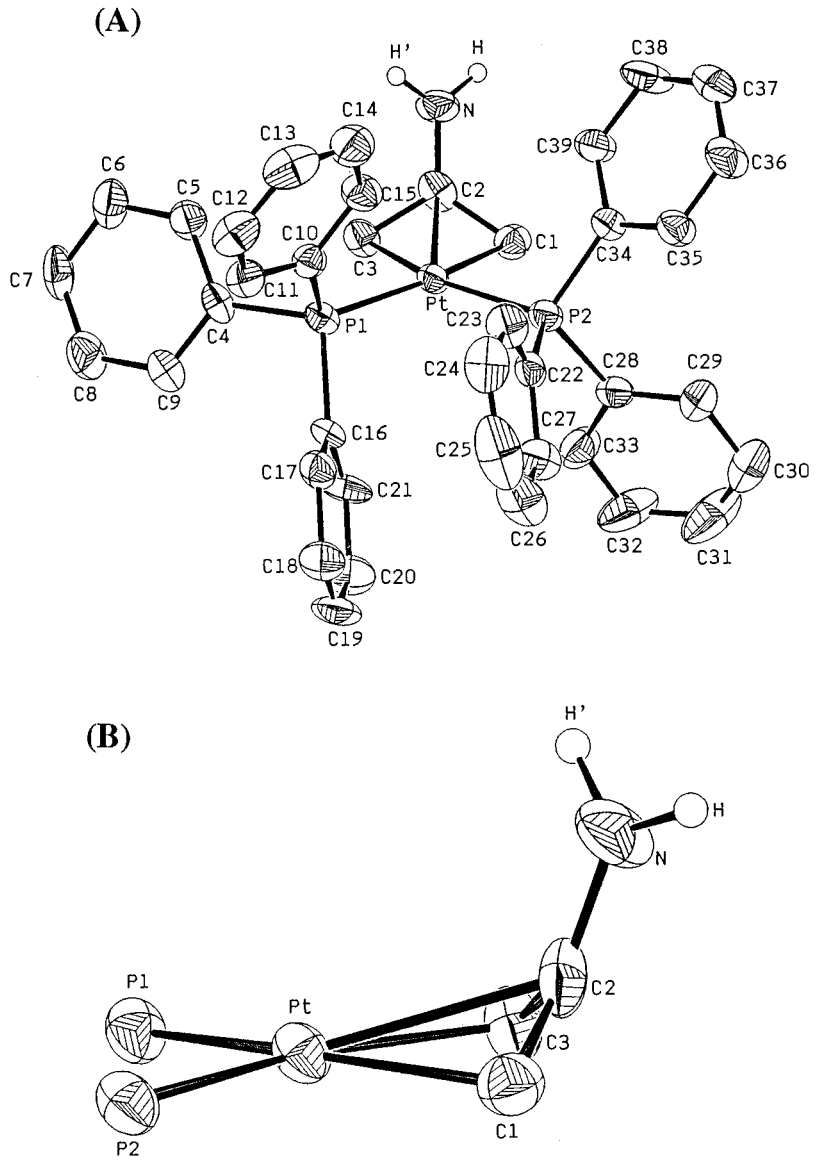


Fig. 1. ORTEP drawings of $\{Pd(PPh_3)_2[\eta^3\text{-}CH_2C(NH_2)CH_2]\}(BF_4)$ (**3a′**) with 50% ellipsoid probability. (a) Top-view, all hydrogen atoms are omitted for clarity. (b) Side-view, phosphino phenyls and all hydrogen atoms (except amino hydrogens) are omitted for clarity.

H_{syn} and H_{anti}), 3.12 (4H, q with ^{195}Pt satellites, $J_{H-H} = 7.1$ Hz, $J_{H-Pt} = 6.6$ Hz, $CH_3C\underline{H}_2$), 7.1–7.8 (30H, phenyl H); ^{13}C-NMR ($CDCl_3$, 50.32 MHz) δ 12.85 (s with ^{195}Pt satellites, $J_{C-Pt} = 9.6$ Hz, $\underline{C}H_3CH_2$), 39.96 (dd with ^{195}Pt satellites, $J_{C-P} = 4.4$, 51.0 Hz, $J_{C-Pt} = 187.8$ Hz, C_t), 43.95 (s with ^{195}Pt satellites, $J_{C-Pt} = 12.0$ Hz, $CH_3\underline{C}H_2$), 128–133 (phenyl C), 157.7 (t with ^{195}Pt satellites, $J_{C-P} = 4.0$ Hz, $J_{C-Pt} = 110.4$ Hz, C_c); Anal. Calc. for $PtC_{43}H_{44}NP_2{-}BrH_2O$ C, 56.65; H, 4.86; N. 1.54. Found: C, 55.90; H, 4.84; N, 1.66.

4.2.10. *{Pt(PPh$_3$)$_2$[η^3-CH$_2$C(NC$_3$H$_6$)CH$_2$]}(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) $\nu_{C=N}$ 1534 cm^{-1}; ^{31}P-NMR ($CDCl_3$, 300 MHz) δ 17.0 ($J_{P-Pt} = 3298$ Hz); ^1H-NMR ($CDCl_3$, 300 MHz, 285 K) δ 2.05 (2H, d with ^{195}Pt satellites, $J_{H-H} = 8.1$ Hz, $J_{H-Pt} = 73.2$ Hz, H_{anti}), 2.23 (2H, br, H_{syn}), 2.35 (2H, $J_{H-H} = 7$ Hz, $NCH_2C\underline{H}_2$), 3.75 (2H, m, $NC\underline{H}_2$-endo), 3.82 (2H, m, $NC\underline{H}_2$-exo), 7.1-7.4 (30H, phenyl H); ^{13}C-NMR ($CDCl_3$, 50.32 MHz) δ 15.6 (s, $NCH_2\underline{C}H_2$), 39.3 (dd with ^{195}Pt satellites, $J_{C-P} = 5.1$, 51 Hz, $J_{C-Pt} = 181.3$ Hz, C_t), 50.2 (s with ^{195}Pt satellites, $J_{C-Pt} = 5.3$ Hz, $N\underline{C}H_2\underline{C}H_2$), 127–134 (phenyl C), 154.3 (t with ^{195}Pt satellites, $J_{C-P} = 4.2$ Hz, $J_{C-Pt} = 106.3$ Hz, C_c).

4.2.11. *{Pt(PPh$_3$)$_2$[η^3-CH$_2$C(NPh$_2$)CH$_2$]}(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,

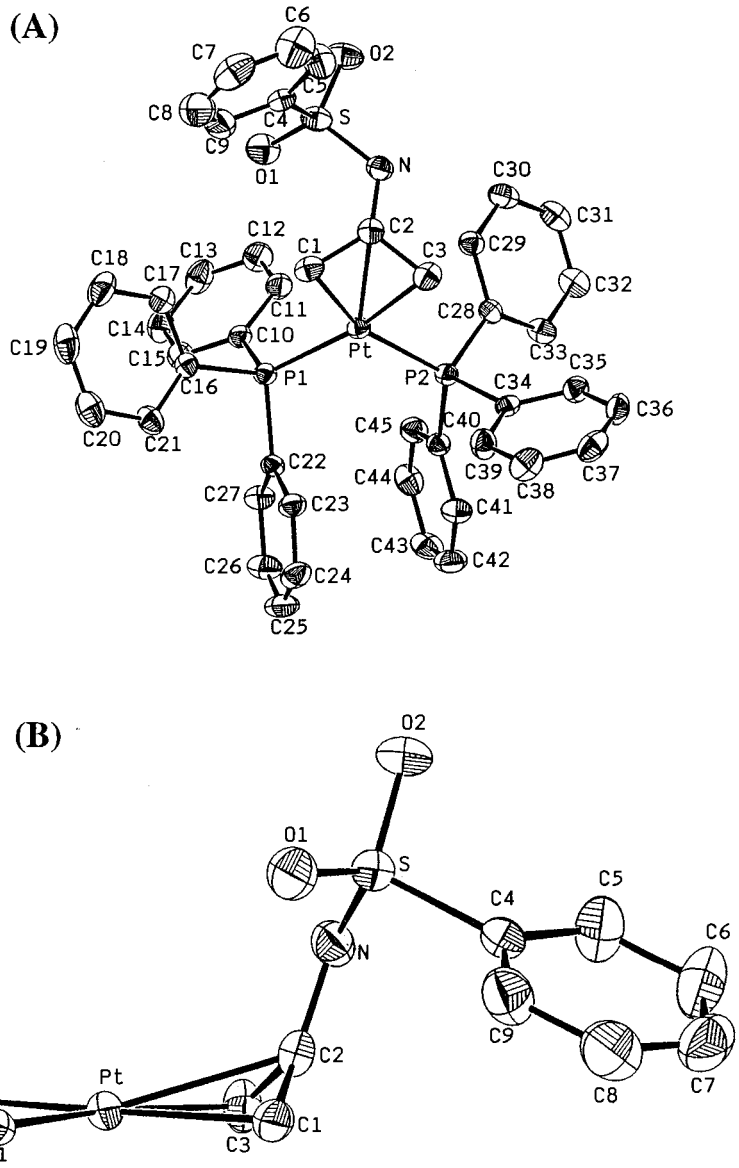


Fig. 2. ORTEP drawings of $Pd(PPh_3)_2[\eta^3\text{-}CH_2C(NSO_2Ph)CH_2]$ (**4m**) with 50% ellipsoid probability. (a) Top-view, all hydrogen atoms are omitted for clarity. (b) Side-view, phosphino phenyls and all hydrogen atoms are omitted for clarity.

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

4.2.12. $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(NMePh)CH_2]\}(BF_4)$ (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) $\nu_{C=N}$ 1598 cm^{-1}; ^{31}P-NMR ($CDCl_3$, 81.015 MHz) δ 17.1 ($J_{P-Pt} = 3384$ Hz); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.34 (2H, br with ^{195}Pt satellites, $J_{H-Pt} = 69.2$ Hz, H_{anti}), 2.51 (2H, br, H_{syn}), 3.07 (3H, s with ^{195}Pt satellites, $J_{H-Pt} = 18.8$ Hz, CH_3), 7.1-7.6 (35H, phenyl H); ^{13}C-NMR ($CDCl_3$, 50.32 MHz) δ 39.6 (s with ^{195}Pt satellites, $J_{C-Pt} = 11.7$ Hz, CH_3), 44.8 (unresolved, C_t), 125.7, 127.6, 128–134, 143.1 (phenyl C), 154.3 (t with ^{195}Pt satellites, $J_{C-P} = 8.5$ Hz, $J_{C-Pt} = 95.3$ Hz, C_c); Anal. Calc. for $PtC_{46}H_{42}NP_2BF_4$ C, 58.00; H, 4.44; N. 1.47. Found: C, 57.55; H, 4.50; N, 1.51.

4.2.13. $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(NHSO_2Ph)CH_2]\}(BF_4)$ (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_t (Å)	M–C_c (Å)	C_t–C_c (Å)	C_c–N (Å)	C_c–C_t–$C_{c'}$ (°)	θ[a] (°)
$\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(NRR')CH_2]\}^+$						
H, H (**3a′**)	2.12(1)	2.329(9)	1.43(1)	1.33(1)	112.8(9)	56(1)
	2.19(3)		1.43(1)			
H, ^{i}Pr (**3d**)	2.17(2)	2.36(1)	1.45(2)	1.47(2)	111(2)	57(2)
	2.19(2)		1.49(3)			
H, Ph (**3g′**)	2.150(8)	2.303(7)	1.41(1)	1.40(1)	113.3(8)	62(1)
	2.176(8)		1.42(1)			
H, C_2H_4OH (**3h**)	2.16(1)	2.30(1)	1.39(2)	1.37(2)	116(1)	58(4)
	2.21(1)		1.44(2)			
Et, Et (**3i′**)	2.11(2)	2.35(2)	1.40(3)	1.34(2)	109(2)	62.6(6)
	2.13(2)		1.42(3)			
C_3H_6 (**3j**)	2.16(1)	2.30(1)	1.39(2)	1.37(2)	116(1)	60(2)
	2.21(1)		1.44(2)			
$Pt(PPh_3)_2[\eta^3\text{-}CH_2C(NR)CH_2]$						
SO_2Ph (**4m**)	2.141(4)	2.333(4)	1.435(6)	1.342(6)	109.9(4)	58.5(4)
	2.147(4)		1.439(6)			
$\{Pd(PPh_3)_2[\eta^3\text{-}CH_2C(NRR')CH_2]\}^+$						
H, ^{i}Pr (**7d**)	2.166(7)	2.326(7)	1.41(1)	1.32(1)	112.6(7)	58.7(7)
	2.168(7)		1.43(1)			
H, Ph (**7g**)	2.14(1)	2.28(1)	1.42(2)	1.38(2)	116(1)	60(1)
	2.20(1)		1.43(2)			
Et, Et (**7i**)	2.156(7)	2.327(7)	1.41(1)	1.35(1)	111.8(6)	58.2(7)
	2.156 (7)		1.43(1)			
$Pd(PPh_3)(Br)[\eta^3\text{-}CH_2C(NRR')CH_2]$						
Et, Et (**8i**)	2.089(3)	2.292(3)	1.409(5)	1.343(5)	110.2(3)	59.2(4)
	2.144(4)		1.414(5)			

[a] The dihedral angle θ is defined by the planes C_t–C_c–$C_{t'}$ and C_t–M–$C_{t'}$.

(85% etherate solution, 0.1 mmol) gave **3m** in 74% yield (75 mg). ^{31}P-NMR ($CDCl_3$, 81.015 MHz) δ 18.1 (J_{P-Pt} = 3729 Hz); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.26 (2H, d with ^{195}Pt satellites, J_{H-P} = 8.8 Hz, J_{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_{H-H} = 7.9 Hz, *o*-H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz) δ 52.6 (dd with ^{195}Pt satellites, J_{C-P} = 4.8, 39.2 Hz, J_{C-Pt} = 103.4 Hz, C_t), 127–134 (phenyl C), 138.3 (t, J_{C-P} = 3.7 Hz, C_c), 138.6 (C_{ipso}).

4.2.14. *Pt(PPh$_3$)$_2$[η^3-CH$_2$C(NSO$_2$Ph)CH$_2$] (**4m**)*

Refer to the paragraph for **9m** for the detailed procedure. IR (KBr) $\nu_{C=N}$ 1479 cm^{-1}, $\nu_{S=O}$ 1137, 1393 cm^{-1}; ^{31}P-NMR ($CDCl_3$, 300 MHz) δ 21.6 (J_{P-Pt} = 3315 Hz); ^{1}H-NMR ($CDCl_3$, 81.015 MHz) δ 2.05 (2H, d with ^{195}Pt satellites, J_{H-P} = 7.7 Hz, J_{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_{H-H} = 6.0 Hz, *o*-H); ^{13}C-NMR ($CDCl_3$, 50.32 MHz) δ 50.7 (dd with ^{195}Pt satellites, J_{C-P} = 4.0, 46.3 Hz, J_{C-Pt} = 174.5 Hz, C_t), 127–134 (phenyl C), 145.0 (C_{ipso}), 158.9 (t with ^{195}Pt satellites, J_{C-P} = 4.1 Hz, J_{C-Pt} = 88.9 Hz, C_c); Anal. Calc. for $PtC_{45}H_{39}NO_2SP_2$ 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)(PPh$_3$)$_2$[η^1-CHCCH$_2$) (**5**)*

To a 30 ml of THF solution that contained 2.5 g of $Pd(PPh_3)_4$, was added 0.24 ml (1.1 equivalents) of propargyl bromide under dry N_2. 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 Et_2O. IR (KBr pellet) $\nu_{C=C=C}$ 1915 cm^{-1}; ^{31}P-NMR ($CDCl_3$, 81.015 MHz) δ 24.2 (s); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.12 (2H, dt, J_{H-H} = 6.1 HZ, J_{H-P} = 1.3 HZ, CHCCH$_2$), 4.67 (1H, tt, J_{H-H} = 6.1 HZ, J_{H-P} = 6.4 HZ, CHCCH$_2$), 7.7–7.2 (30H, m, phenyl H); ^{13}C-NMR ($CDCl_3$, 50.32 MHz, 273 K) δ 66.9 (s, CHCCH$_2$), 87.4 (t, J_{C-P} = 5.1 HZ, CHCCH$_2$), 128–135 (phenyl C), 199.8 (t, J_{C-P} = 3.5 HZ, CHCCH$_2$); FAB MS (*m*/*z*) 750 ($M^+ + 1$); Anal. Calc. for $PdC_{39}H_{33}P_2Br$: C, 62.46; H, 4.44. Found: C, 62.53; H, 4.50.

4.2.16. *[Pd(PPh$_3$)$_2$[η^3-C$_3$H$_3$)](X) (X = PF$_6$ **6**, BF$_4$ **6′**, OTf **6″**)*

To a mixture containing **5** (208 mg, 0.28 mmol) and $AgPF_6$ (75 mg, 0.3 mmol) was added N_2-degassed CH_2Cl_2 (20 ml) at −75°C. The reaction solution was stirred for 40 min to allow the complete precipitation of

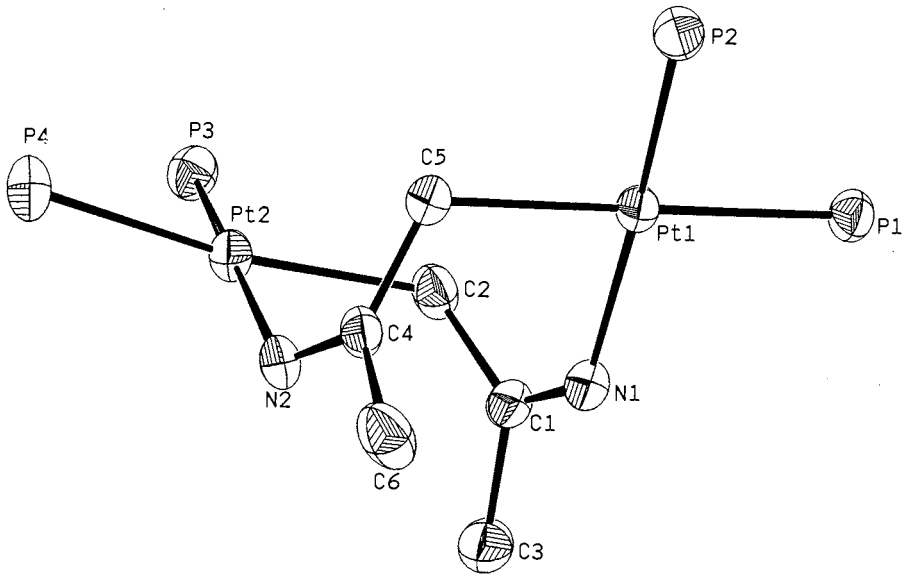


Fig. 3. ORTEP drawing of $\{[cis\text{-}Pt(PPh_3)_2(\mu\text{-}CH_2CMeNH)]_2\}(Br)_2$ (**15**) with 50% ellipsoid probability. All hydrogen atoms and phosphino phenyls are omitted for clarity.

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_{P-P} = 41.5 Hz); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.40 (ddd, 2H, J_{H-H} = 2.1 Hz, J_{P-H} = 1.7, 7.7 Hz, C$\underline{H}_2$), 4.65 (tdd, 1H, J_{H-H} = 2.1 Hz, J_{P-H} = 1.6, 9.0 Hz, C$\underline{H}$), 7.15–7.38 (30 H, m, phenyl H); ^{13}C-NMR ($CDCl_3$, 50.32 MHz, 198 K) δ 57.6 (d, J_{C-P} = 38.7 Hz, $\underline{C}H_2CCH$), 91.3 (d, J_{C-P} = 48.8 Hz, $CH_2\underline{C}CH$), 100.6 (dd, J_{C-P} = 5.8, 8.0 Hz, $CH_2\underline{C}CH$), 128–134 (phenyl C).

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

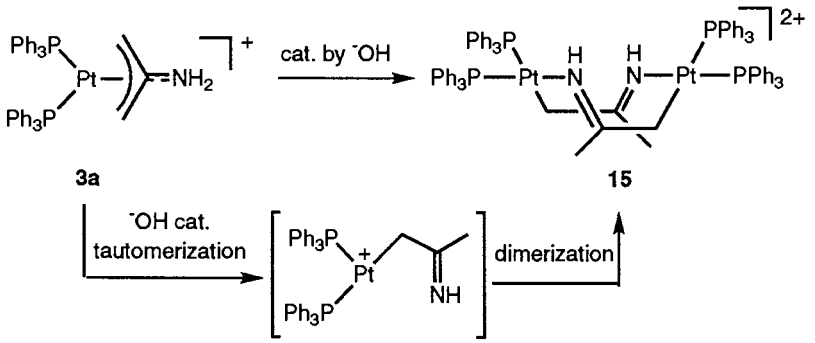
Refer to the paragraph for **7i** for the detailed procedure. The reaction of **5** (150 mg, 0.20 mmol) and AgOTf (51.4 mg, 0.2 mmol) in situ with ^{i}PrNH$_2$ (17 μl) gave **7d**. The isolated yield was 114 mg (65%). The single crystals were grown from $CHCl_3/Et_2O$ cosolvent at 0°C. IR (KBr pellet) $\nu_{C=N}$ 1555 cm^{-1}; ^{31}P-NMR ($CDCl_3$, 300 MHz, 253K) δ 25.1, 26.5 (J_{P-P} = 29.0 Hz); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.13 (6H, d, J_{H-H} = 6.3 Hz, C$\underline{H}_3$), 2.23 (2H, br, H_{anti}), 2.72 (2H, br, H_{syn}), 3.01 (1H, m, J_{H-H} = 6.3, 7.8 Hz, C$\underline{H}$), 6.41 (1H, d, J_{H-H} = 7.1 Hz, N$\underline{H}$), 7.15-7.38 (30H, m, phenyl H); ^{13}C-NMR ($CDCl_3$, 50.32 MHz) δ 22.5 (s, $\underline{C}H_3$), 44.8 (s, $\underline{C}HMe_2$), 50.6 (m, J_{C-P} = 47.4 Hz, C_t), 128–134 (phenyl C), 152.1 (t, J_{C-P} = 5.5 Hz, C_c); MS (FAB) 728 ($M^+ - OTf$).

4.2.18. *{Pd(PPh$_3$)$_2$[η^3-CH$_2$C(NHPh)CH$_2$]}(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 $CHCl_3/Et_2O$ cosolvent at 0°C. IR (KBr pellet) $\nu_{C=N}$ 1550 cm^{-1}; ^{31}P-NMR ($CDCl_3$, 81.015 MHz) δ 26.1; ^{1}H-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, N$\underline{H}$); ^{13}C-NMR ($CDCl_3$, 50.32 MHz) δ 55.2 (m, C_t), 122–139 (phenyl C), 148.5 (t, J_{C-P} = 5.4 Hz, C_c).

4.2.19. *{Pd(PPh$_3$)$_2$[η^3-CH$_2$C(NEt$_2$)CH$_2$]}(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 $CHCl_3/Et_2O$ cosolvent at 0 °C. IR (KBr pellet) $\nu_{C=N}$ 1550 cm^{-1}; ^{31}P-NMR ($CDCl_3$, 81.015 MHz) δ 24.9; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.94 (6H, t, J_{H-H} = 7.1 Hz, $CH_2C\underline{H}_3$), 2.51 (2H, m, H_{anti}), 2.62 (2H, br, H_{syn}), 2.95 (4H, q, J_{H-H} = 7.1 Hz, C$\underline{H}_2$CH$_3$), 7.15–7.38 (30H, m, phenyl H); ^{13}C-NMR ($CDCl_3$, 50.32 MHz) δ 12.8 (s, $CH_2\underline{C}H_3$), 43.9 (s, $\underline{C}H_2CH_3$), 50.0 (m, C_t), 128.8, 130.9, 133.4 (phenyl C), 154.0 (t, J_{C-P} = 4.9 Hz, C_c).



Scheme 7.

*4.2.20. {Pd(PPh$_3$)$_2$[η^3-CH$_2$C(NHSO$_2$Ph)CH$_2$]}(BF$_4$) (**7m**)*

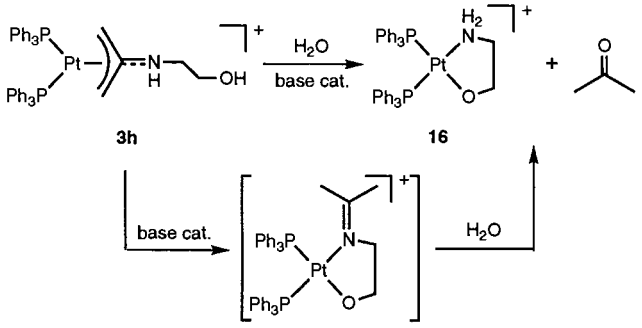
The reaction of **9m** (150 mg, 0.18 mmol) and HBF_4 (85% etherate solution, 33 μl) in CH_2Cl_2 at 25°C gave **7m** in 98% yield (161 mg). IR (KBr pellet) $\nu_{C=N}$ 1500 cm^{-1}; ^{31}P-NMR ($CDCl_3$, 81.015 MHz) δ 25.8; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.79 (2H, br, H_{anti}), 3.63 (2H, s, H_{syn}), 7.18–7.68 (34H, phenyl H), 8.38 (1H, s, NH).

*4.2.21. {Pd(PPh$_3$)$_2$[η^3-CH$_2$C(p-NHSO$_2$C$_6$H$_4$Me)CH$_2$]}(BF$_4$) (**7n**)*

The reaction of **9n** (150 mg, 0.18 mmol) and HBF_4 (85% etherate solution, 30 μl) 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; ^{1}H-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$_3$)[η^3-CH$_2$C(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; ^{1}H-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 $PdC_{25}H_{29}NPBr\cdot0.5\ CH_2Cl_2$: C, 50.77; H, 5.01; N. 2.32. Found: C, 51.16; H, 4.94; N, 2.35.



Scheme 8.

*4.2.23. Pd(PPh$_3$)$_2$[η^3-CH$_2$C(NSO$_2$Ph)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; ^{1}H-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^+).

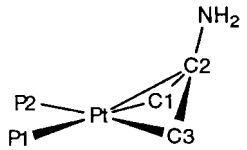
*4.2.24. Pd(PPh$_3$)$_2$[η^3-CH$_2$C(p-NSO$_2$C$_6$H$_4$Me)CH$_2$] (**9n**)*

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; ^{1}H-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^+).

Table 4
X-ray crystal parameters and data collection

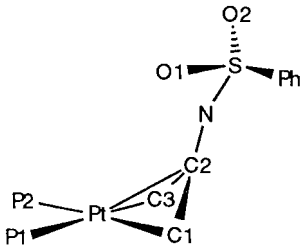
	3a′	3d	3g′	3h	3i′	3j	4m	7d	7g	7i	8i	15	16
Formula	$PtC_{39}H_{36}NP_2BF_4$	$PtC_{42}H_{42}NP_2BrH_2O\cdot CH_2Cl_2$	$PtC_{45}H_{40}NP_2BF_4\cdot 1.5CHCl_3$	$PtC_{41}H_{40}NOP_2Br$	$PtC_{43}H_{44}NP_2BF_4\cdot C_2H_5OH$	$PtC_{42}H_{40}NP_2Br$	$PtC_{45}H_{39}NOP_2P_2S\cdot 2C_6H_6$	$PdC_{42}H_{42}NP_2Br\cdot 2CHCl_3$	$PdC_{46}H_{40}NP_2SO_3F_3\cdot 1.5CH_2Cl_2$	$PdC_{44}H_{44}NP_2SO_3F_3$	$PdC_{25}H_{29}NPBr\cdot 3CH_2Cl_2\cdot C_4H_{10}O$	$Pt_2C_{78}H_{72}N_2P_4Br_2$	$PtC_{38}H_{36}NOP_2Br$
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 × 0.4	0.3 × 0.4 × 0.4	0.15 × 0.25 × 0.45	0.1 × 0.15 × 0.2	0.4 × 0.4 × 0.3	0.35 × 0.5 × 0.5	0.25 × 0.35 × 0.45	0.4 × 0.4 × 0.5	0.2 × 0.3 × 0.5	0.17 × 0.3 × 0.45	0.3 × 0.35 × 0.4	0.35 × 0.45 × 0.45	0.3 × 0.35 × 0.45
Space group	$C2/c$	$P2_12_12_1$	$C2/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$		$P2_1/n$	$C2/c$	$P2_1/n$			$P2_1/n$
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	
ρ (calc.) (mg m^{-3})	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
F(000)	3563	3247	4404	776	1788	1760	1077	2112	3728	1832	564	2020	1688
Radiation, λ (Å)	Mo–K_α, 0.7107	Cu–K_α, 1.54056	Mo–K_α, 0.7107	Mo–K_α, 0.7107	Mo–K_α, 0.7107	Mo–K_α, 0.7107	Mo–K_α, 0.7107	Mo–K_α, 0.7107	Mo–K_α, 0.7107	Mo–K_α, 0.7107	Mo–K_α, 0.7107	Mo–K_α, 0.7107	Mo–K_α, 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	±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 observed	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
$(\Delta/\sigma)_{max}$	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**



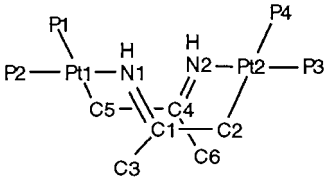
$\{(PPh_3)_2Pt[\eta^3\text{-}CH_2C(NH_2)CH_2]\}(BF_4)$ (**3a**)

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)



$(PPh_3)_2Pt[\eta^3\text{-}CH_2C(NSO_2Ph)CH_2]$ (**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)				



$\{[cis\text{-}Pt(PPh_3)_2(\mu\text{-}CH_2CmeNH)]_2\}(Br)_2$ (**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(PPh$_3$)$_2$(O$_2$CMe)(η^1-CHCCH$_2$) (**10**)*

The reaction of *trans*-Pt(Br)(PPh$_3$)$_2$(η^3-CHCCH$_2$) (**1**) (50 mg, 0.063 mmol) and equimolar AgOAc gave the product quantitatively based on NMR measurements. ^{31}P-NMR (CDCl$_3$, 81.015 MHz) δ 23.2 (J_{P-Pt} = 3165 Hz); ^{1}H-NMR (CDCl$_3$, 300 MHz) δ 0.85 (s, C$\underline{H}_3$), 2.71 (2H, dt with ^{195}Pt satellites, J_{H-H} = 6.5 Hz, J_{H-P} = 3.9 Hz, J_{H-Pt} = 52.0 Hz, C$\underline{H}$), 4.96 (1H, tt, with ^{195}Pt satellites, J_{H-H} = 6.5 Hz, J_{H-P} = 2.5 Hz, J_{H-Pt} = 123.6 Hz, C$\underline{H}_2$), 7.1–7.5 (phenyl H); ^{13}C-NMR (CDCl$_3$, 50.32 MHz) δ 23.1 (s with ^{195}Pt satellites, J_{C-Pt} = 17.7 Hz, $\underline{C}H_3$), 59.7 (t with ^{195}Pt satellites, J_{C-P} = 10.6 Hz, J_{C-Pt} = 848.9 Hz, $\underline{C}H$), 65.9 (s with ^{195}Pt satellites, J_{C-Pt} = 58.6 Hz, $\underline{C}H_2$), 128–134 (phenyl C), 175.6 (s with ^{195}Pt satellites, J_{C-Pt} = 22.1 Hz, $\underline{C}O$), 206.1 (t, J_{C-P} = 3.9 Hz, =$\underline{C}$=).

*4.2.26. trans-Pt(PPh$_3$)$_2$(NHSO$_2$Ph)(η^1-CHCCH$_2$) (**11**)*

To the CDCl$_3$ solution of **10** from above, was added equimolar NaNHSO$_2$Ph. The NMR spectra were then taken. ^{31}P-NMR (CDCl$_3$, 81.015 MHz) δ 21.3 (J_{P-Pt} = 3064 Hz); ^{1}H-NMR (CDCl$_3$, 300 MHz) δ 2.74 (2H, dt with ^{195}Pt satellites, J_{H-H} = 6.0 Hz, J_{H-P} = 2.0 Hz, J_{H-Pt} = 48.4 Hz, C$\underline{H}$), 4.63 (1H, tt, with ^{195}Pt satellites, J_{H-H} = 6.0 Hz, J_{H-P} = 3.8 Hz, J_{H-Pt} = 96.1 Hz, C$\underline{H}_2$), 7.1–7.5 (phenyl H).

*4.2.27. cis-Pt(Cl)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)(η^1-CHCCH$_2$) (**12**)*

To a round-bottom flask containing *trans*-Pt(Cl)(PPh$_3$)$_2$(η^3-CHCCH$_2$) (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). ^{31}P-NMR (CDCl$_3$, 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); ^{1}H-NMR (CDCl$_3$, 300 MHz) δ 2.0-2.5 (4H, m, C$_2$H$_4$), 3.33 (2H, t with ^{195}Pt satellites, J_{H-H} = 6.7 Hz, J_{H-P} = 1.7, 5.3 Hz, J_{H-Pt} = 33.3 Hz, C$\underline{H}_2$), 5.67 (1H, dtd with ^{195}Pt satellites, J_{H-H} = 6.7 Hz, J_{H-P} = 5.3, 6.6 Hz, J_{H-Pt} = 116.5 Hz, C$\underline{H}$), 7.1-7.5 (phenyl H)

*4.2.28. cis-Pt(Ph$_2$PCH$_2$CH$_2$PPh$_2$)(NHSO$_2$Ph)(η^1-CHCCH$_2$) (**13**)*

To a CDCl$_3$ solution containing **12** (30 mg), was added equimolar NaNHSO$_2$Ph. The NMR spectra were then taken. ^{31}P-NMR (CDCl$_3$, 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); ^{1}H–NMR (CDCl$_3$, 50.32 MHz) δ 2.0–2.5 (4H, m, C$_2$H$_4$), 3.76 (2H, t with ^{195}Pt satellites, J_{H-H} = 6.6 Hz, J_{H-Pt} = 36.8 Hz, C$\underline{H}_2$), 4.29 (1H, s with ^{195}Pt satellites, J_{H-Pt} = 23.0 Hz, N$\underline{H}$), 5.37 (1H, dtd, with ^{195}Pt satellites, J_{H-H} = 6.6 Hz, J_{H-P} = 1.5, 6.2 Hz, J_{H-Pt} = 81 Hz, C$\underline{H}$), 7.1–7.5 (phenyl H)

*4.2.29. Pt(Ph$_2$PCH$_2$CH$_2$PPh$_2$)[η^3-CH$_2$C(NSO$_2$Ph)CH$_2$] (**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. ^{31}P-NMR (CDCl$_3$, 81.015 MHz) δ 46.7 (J_{P-Pt} = 3160 Hz); ^{1}H-NMR (CDCl$_3$, 50.32 MHz) δ 2.33 (6H, m, C$_2$H$_4$ and H$_{anti}$), 4.30 (2H, br, H$_{syn}$), 7.1–7.5 (phenyl H).

*4.2.30. {[cis-Pt(PPh$_3$)$_2$(μ-CH$_2$CMeNH)]$_2$}(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 CH$_2$Cl$_2$/acetone. ^{31}P-NMR (CDCl$_3$, 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); ^{1}H-NMR (CDCl$_3$, 300 MHz) δ 1.73 (6H, s, C$\underline{H}_3$), 2.42 (4H, dd, J_{H-P} = 9.2 Hz, unresolved $J'_{H-P'}$ C$\underline{H}_2$), 8.74 (2H, br, N$\underline{H}$).

*4.2.31. cis-{$(PPh_3)_2Pt[NH_2CH_2CH_2O]$}(Br) (**16**)*

Complex **1** (20 mg, 0.024 mmol) reacts with $H_2NCH_2CH_2OH$ (30 μl, 0.048 mmol) in CH_2Cl_2 for 96 h to yield **16** quantitatively. ^{31}P-NMR ($CDCl_3$, 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); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.7 (2H, br, $OC\underline{H}_2$), 3.99 (2H, tt, $NC\underline{H}_2$), 4.9 (2H, br, $N\underline{H}_2$), 7.2–7.6 (30H, phenyl H); ^{13}C-NMR ($CDCl_3$, 50.32 MHz) δ 50.4 ($O\underline{C}H_2$), 73.1 ($N\underline{C}H_2$), 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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