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Platinum complexes with diamino-substituted phosphorus ligands: Synthesis, characterization, and their reactivity with a Lewis acid

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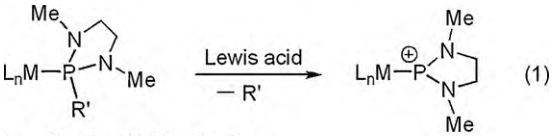
ABSTRACT

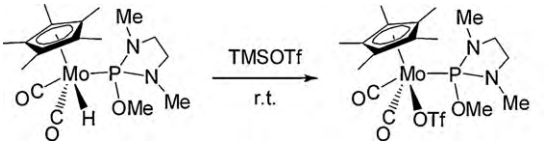
Reaction of dialkyl- or diaryl-platinum complexes $PtR_2(cod)$ (cod = η^2, η^2-1,5-cyclooctadiene, R = Me, *p*-tol) with diamino-substituted phosphorus ligands $P(NMeCH_2)_2(R')$ (R′ = OMe, NEt_2) produced neutral complexes, *cis*-$[Pt(R)_2\{P(NMeCH_2)_2(R')\}_2]$. On the other hand, reaction of dihalogeno platinum complex $PtX_2(cod)$ (X = Cl, I) with $P(NMeCH_2)_2(OMe)$ yielded a cationic complex $[PtX\{P(NMeCH_2)_2(OMe)\}_3]X$. A platinum complex having both methyl and halogeno ligands, PtMeX(cod), reacted with $P(NMeCH_2)_2(OMe)$ to give a cationic methyl complex $[PtMe\{P(NMeCH_2)_2(OMe)\}_3]X$, by contrast, it reacted with $P(NMeCH_2)_2(NEt_2)$ to yield a neutral methyl complex $[PtMeX\{P(NMeCH_2)_2(NEt_2)\}_2]$. Reaction of $[PtMe\{P(NMeCH_2)_2(OMe)\}_3]X$ with $BF_3{\cdot}OEt_2$ and then $NaBPh_4$ afforded $[PtX\{P(NMeCH_2)_2(OMe)\}_3]BPh_4$, showing preferential Me group abstraction on the Pt center rather than the OMe abstraction on the phosphorus atom, followed by the coordination of X to the Pt center. All new complexes were fully characterized using ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR measurements and elemental analyses. In addition, structures of several complexes were determined by single crystal X-ray diffraction studies.

1. Introduction



M = Cr, Mo, W, Mn, Fe, Ru
R' = alkoxy, amino

Diamino-substituted phosphorus compounds have been used as good precursors of transition metal phosphenium complexes [1–9] as well as of metal-free phosphenium compounds [1–4,10]. Transition metal complexes bearing $P(NMeCH_2)_2(R')$ (R′ = alkoxy, amino) have been converted into the corresponding phosphenium complexes for Cr, Mo, W, Mn, Fe, and Ru complexes by the reaction with a Lewis acid, such as $BF_3{\cdot}OEt_2$ or $Me_3SiSO_3CF_3$ (TMSOTf) (Eq. (1)) [3,4]. In these reactions, an R′ group on the phosphorus is abstracted as an anion by a Lewis acid. In contrast, in the reaction of a molybdenum complex having a hydride ligand and $P(NMeCH_2)_2(OMe)$, $[Cp^*Mo(H)(CO)_2\{P(NMeCH_2)_2(OMe)\}]$, with TMSOTf, a preferential H^- abstraction followed by OTf^- coordination on the Mo center takes place to give $[Cp^*Mo(CO)_2(OTf)\{P(NMeCH_2)_2(OMe)\}]$ rather than OMe^- abstraction at the P center (Eq. (2)) [11].



Many complexes bearing a diamino-substituted phosphorus ligand have been synthesized for several kinds of transition metals and have been subjected to the reaction with a Lewis acid. However, a platinum complex with $P(NMeCH_2)_2(R')$ has not been reported to date.

With platinum complexes, it should be noted that: (i) platinum phosphenium complexes have been reported in

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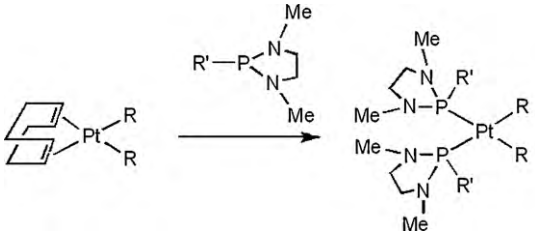
the reaction of a Pt(0) complex with a metal-free phosphenium or with an N-heterocyclic carbene adduct of a phosphenium [12] and (ii) $L_nPt–R$ (R = H [13], Me [14], Ph [15]) shows R/OTf exchange in the reaction with R″OTf (R″ = H, Me, Me_3Si) to give $L_nPt–OTf$ (Eq. (3)).

$$L_nPt{-}R + R''OTf \longrightarrow L_nPt{-}OTf + R{-}R'' \quad (3)$$

Herein, we report the reactions of $PtR_2(cod)$ (R_2 = Me, *p*-tol, Cl, I) with $P(NMeCH_2)_2R'$ (R′ = OMe, NEt_2), crystal structures of Pt complexes with $P(NMeCH_2)_2R'$ thus prepared, and the reactivity of the Pt complexes with a Lewis acid because R abstraction from the Pt and R′ abstraction from the P are conceivable.

2. Results and discussion

A dialkyl- or diaryl-platinum complex, $PtR_2(cod)$ (cod = η^2, n^2-1,5-cyclooctadiene, R = Me, *p*-tol) [16], reacted with a diamino-substituted P ligand, $P(NMeCH_2)_2(R')$ (R′ = OMe [17], NEt_2 [18]), at room temperature to produce a neutral complex, *cis*-$[Pt(R)_2\{P(NMeCH_2)_2(R')\}_2]$ (R′ = OMe, R = Me: **1**, *p*-tol: **2**, R′ = NEt_2, R = Me: **3**, *p*-tol: **4**) in appropriate to excellent yields [Eq. (4)]. The $^{31}P\{^1H\}$ NMR spectra of **1**–**4** showed the singlet flanked by ^{195}Pt satellites at δ 125.07 ($^1J_{PPt}$ = 2860 Hz) for **1**, 118.56 ($^1J_{PPt}$ = 2809 Hz) for **2**, 120.13 ($^1J_{PPt}$ = 2860 Hz) for **3**, and 107.40 ($^1J_{PPt}$ = 2688 Hz) for **4**.

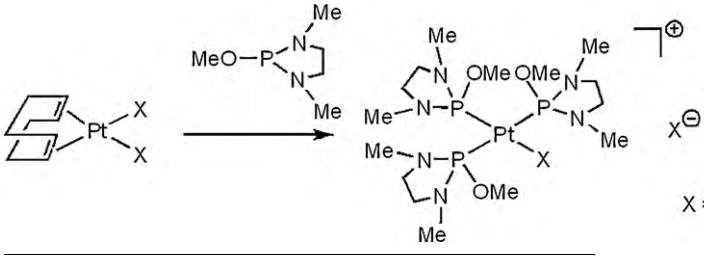


R′ = OMe, R = Me : **1** 98%
R = *p*-tol: **2** 81%
R′ = NEt_2, R = Me : **3** 70%
R = *p*-tol: **4** 90%

(4)

The structures of **1**–**3** were determined by single-crystal X-ray diffraction analyses. The molecular structures of **1**–**3** are shown in Figs. 1–3. Crystal data and the selected bond lengths and angles are listed in Tables 1 and 2. As two independent molecules of **1** and **3** crystallized in the unit cell, only one molecule (Pt1) is shown for **1** and **3** with the atom numbering scheme in Figs. 1 and 3. Complexes **1**–**3** have a typical square-planar configuration: the platinum has two methyl or *p*-tol ligands and two P ligands. These P ligands are situated mutually in a *cis* position. The Pt–P bond distances of **1**–**3** resemble those of previously reported *cis*-$PtMe_2L_2$ (L = monodentate tertiary phosphorus ligand) (2.252–2.344 Å) [14(a),19,20]. The Pt–C bond distances (2.097(7)–2.144(8) Å for **1**, 2.067(5), 2.078(6) Å for **2**, and 2.119(5), 2.122(4) Å for **3**) are similar to those of analogous complexes (2.075–2.132 Å for *cis*-$[Pt(Me)_2(PR_3)_2]$ (R_3 = $Me(C_2F_5)_2$ [14(a)], Et_3, $PhMe_2$, Ph_2Me, $(pyrl)_3$, and Cy_3 [19]) and 2.057(12), 2.057(9) Å for *cis*-$[Pt(p\text{-}tol)_2(PEt_3)_2]$ [20]).

The reaction of the dihalogeno platinum complex, $PtX_2(cod)$, with $P(NMeCH_2)_2(OMe)$ formed a cationic triphosphite platinum complex, $[PtX\{P(NMeCH_2)_2(OMe)\}_3]X$ (X = Cl: **5**, I: **6**) [21], as a white solid in high and excellent yields [Eq. (5)]. Complexes **5** and **6** were formed in high yields when $PtX_2(cod)$ and $P(NMeCH_2)_2(OMe)$ were treated in the 1:3 molar ratio. The same complexes were formed even if they were treated in the 1:2 ratio and $PtX_2\{P(NMeCH_2)_2(OMe)\}_2$ (X = Cl, I) were not obtained. Roulet et al. and Mézailles et al. reported analogous reactions of $PtX_2(PMe_3)_2$ (X = Cl, Br) with PMe_3 to produce $[PtX(PMe_3)_3]X$ [22(a)] and of $PtCl_2(cod)$ with (Mes)P = CH(NMe_2) (Mes = 2,4,6-$Me_3C_6H_2$) to produce $[PtCl\{(Mes)P{=}CH(NMe_2)\}_3]Cl$ [22(b)]. The $^{31}P\{^1H\}$ NMR spectra of **5** and **6** show the two signals with ^{195}Pt satellites at δ 71.24 (t, $^2J_{PP}$ = 13 Hz, $^1J_{PPt}$ = 5375 Hz, *trans* to Cl) and 99.17 (d, $^2J_{PP}$ = 13 Hz, $^1J_{PPt}$ = 3633 Hz, *cis* to Cl) for **5** in the 1:2 peak area ratio, and 70.43 (t, $^2J_{PP}$ = 15 Hz, $^1J_{PPt}$ = 5158 Hz, *trans* to I) and 93.63 (d, $^2J_{PP}$ = 15 Hz, $^1J_{PPt}$ = 3512 Hz, *cis* to I) for **6** in the 1:2 peak area ratio.



X = Cl: **5** 91%
I : **6** 97%

(5)

The analogous cationic complexes **7** and **8** were obtained in high yields in the reactions of a methyl(halogeno) platinum complex, PtMeX(cod) (X = Cl, I), with $P(NMeCH_2)_2(OMe)$ in the 1:3 molar ratio [Eq. (6)]. In this case, $Pt(Me)(X)\{P(N(MeCH_2)_2(OMe))\}_2$ (X = Cl, I) were not obtained as in [Eq. (5)] even in the reaction of PtMeX(cod) with $P(NMeCH_2)_2(OMe)$ in the 1:2 molar ratio. In contrast, the reaction of PtMeX(cod) (X = Cl, I) with a diamino-

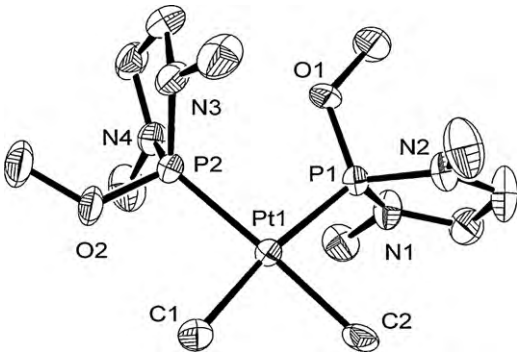


Fig. 1. Crystal structure of Pt1 molecule of **1** at the 50% ellipsoidal level. The hydrogen atoms are omitted for simplicity.

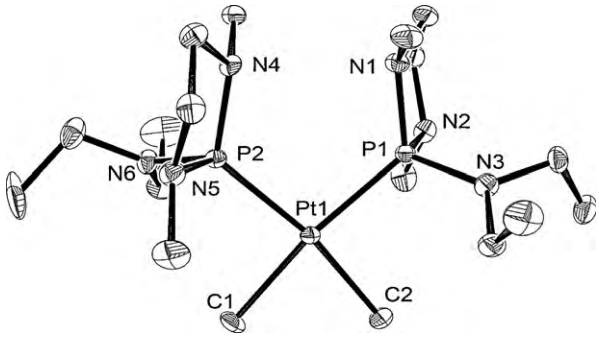


Fig. 3. Crystal structure of Pt1 molecule of **3** at the 50% ellipsoidal level. The hydrogen atoms are omitted for simplicity.

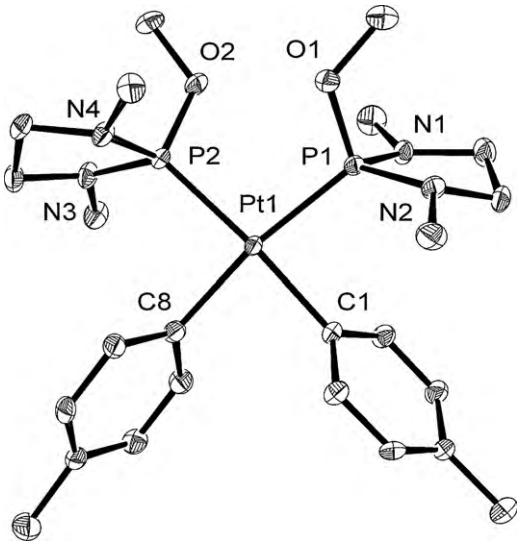
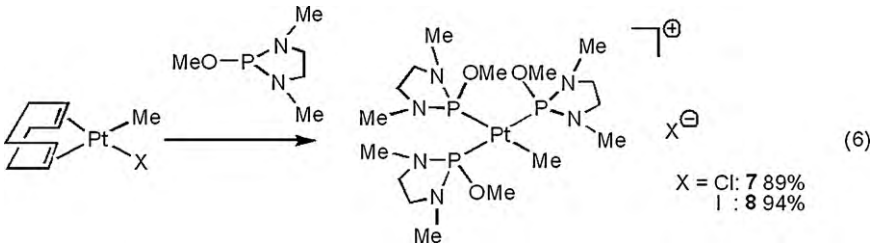


Fig. 2. Crystal structure of **2** at the 50% ellipsoidal level. The hydrogen atoms are omitted for simplicity.

substituted phosphine ligand having NEt_2 group on the P atom, $P(NMeCH_2)_2(NEt_2)$, gave the natural bis(phosphine) platinum complexes **9** and **10** [Eq. (7)]. In the ^1H NMR spectra of **7** and **8**, the methyl group on the Pt center showed a doublet ($^3J_{PH}$ = 8.8 Hz) of triplets ($^3J_{PH}$ = 7.3 Hz) with ^{195}Pt satellites ($^2J_{PtH}$ = 56.0 Hz) at δ 0.31 for **7** and 0.22 for **8**, indicating the presence of three phosphite ligands coordinated to the Pt center. The $^{31}P\{^1H\}$ NMR data of **9** indicate the presence of *trans* and *cis* isomers in *ca.* 2:1 ratio. With *cis*-**9**, the ^{195}Pt satellite value ($^1J_{PPt}$ = 6037 Hz) of the doublet at δ 82.84 (assignable to P *trans* to Cl) was larger than the corresponding value ($^1J_{PPt}$ = 2651 Hz) of the doublet at δ 116.60 (assignable to P *trans* to Me). This tendency is similar to that of analogous *cis*-$PtMeClL_2$ (L = monodentate tertiary phosphorus ligand) [23]. With **10**, the *trans* isomer was observed exclusively. The difference between the *cis*/*trans* ratio in **9** and **10** may derive from the steric bulkiness of a halogeno ligand on the Pt center [20].

Table 1
Crystal data and experimental parameters used for the intensity data collection of **1–3**. Procedure and final results of the structure determination.

Empirical formula	$C_{12}H_{32}N_4O_2P_2Pt$ **1**	$C_{24}H_{40}N_4O_2P_2Pt$ **2**	$C_{18}H_{46}N_6P_2Pt$ **3**
Formula weight	521.45	673.63	603.64
T (K)	203(2)	110(1)	110(1)
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	Pbca	C2/c
a (Å)	9.3500(5)	13.4206(5)	35.942(3)
b (Å)	29.4100(17)	14.4097(5)	9.3194(7)
c (Å)	14.3700(9)	27.8523(11)	23.0164(17)
β (°)	95.000(3)		90.521(4)
Volume (Å^3)	3936.5(4)	5386.3(3)	7709.2(10)
Z	8	8	12
ρ_{calcd} (mg m^{-3})	1.760	1.661	1.560
μ (cm^{-1})	7.300	5.356	5.600
F(000)	2048	2688	3648
Crystal size (mm^3)	0.22 × 0.05 × 0.03	0.20 × 0.18 × 0.06	0.10 × 0.08 × 0.08
Reflections collected	30204	38829	29063
R(int)	5218 (0.032)	6063 (0.0407)	8701 (0.0412)
R ($I > 2\sigma(I)$)	0.056	0.0477	0.0427
w$R2$	0.091	0.1049	0.0745
Goodness of fit	1.085	1.524	1.163



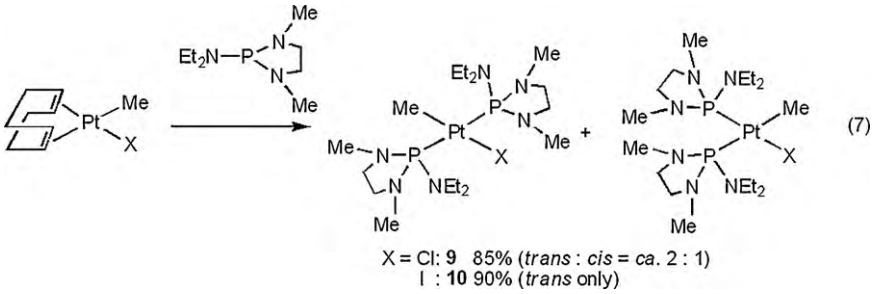


Table 2
Selected bond lengths (Å) and bond angles (°) for **1-3**.

	1	2	3
Pt1–C1	2.109(8)	2.067(5)	2.119(5)
Pt1–C2(C8 for **2**)	2.144(8)	2.078(6)	2.122(4)
Pt1–P1	2.2512(19)	2.2737(13)	2.2781(12)
Pt1–P2	2.2568(19)	2.2627(13)	2.2753(12)
P1–O1(N3 for **3**)	1.615(5)	1.625(4)	1.672(4)
P2–O2(N6 for **3**)	1.619(6)	1.625(4)	1.668(4)
C1–Pt1–C2(C8 for **2**)	86.7(3)	84.8(2)	81.3(2)
P1–Pt1–P2	96.21(7)	98.66(5)	100.56(4)

The molecular structures of **6**, **8**, and **10** are depicted in Figs. 4–6 with the atomic numbering scheme. Table 3 summarizes the crystallographic data. The selected bond lengths and angles are listed in Table 4. The Pt centers of **6**, **8**, and **10** have a distorted square-planar geometry. With **6**, the distance of Pt–P bond *trans* to I (2.2343(11) Å) is shorter than those of *trans* to phosphite ligand (2.3211(12), 2.2987(13) Å) due to weak *trans* influence of an iodo ligand. On the other hand, three Pt–P bond distances of **8** (2.2882(16) Å for *trans* to Me, 2.2864(17), 2.2883(16) Å for *trans* to the phosphite ligand) are almost the same. The difference of Pt–P bond distances between **6** and **8** probably stems from the stronger *trans* influence of methyl ligand than of iodide ligand. Complex **10** has Me and I ligands in a *trans* position. The Pt–P and Pt–C bond distances of **10** (Pt–P = 2.300(3), 2.294(3) Å and Pt–C = 2.072(11) Å) are comparable to those of *cis*-$[Pt(Me)_2\{P(NMeCH_2)_2(NEt_2)\}_2]$ **3** (Pt–P = 2.2781(12), 2.2753(12) Å and Pt–C = 2.119(5), 2.122(4) Å).

As several Pt complexes with diamino-substituted phosphorus compounds were obtained, reactions of **1**–**10** with a Lewis acid were examined. To a CH_2Cl_2 solution of **1**–**10** in an NMR tube was added 2- or 3-fold molar

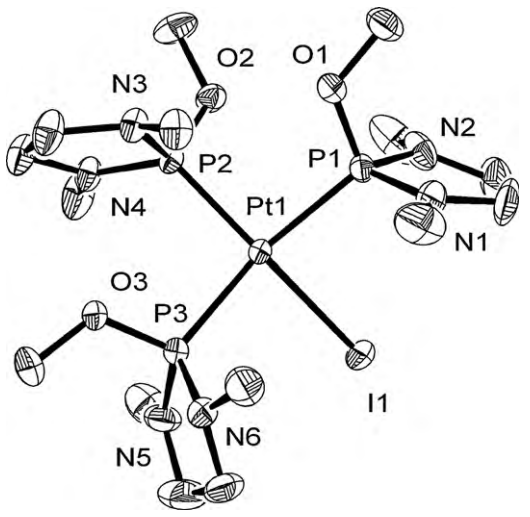


Fig. 4. Crystal structure of a cation part of **6**·CH_2Cl_2 with 50% thermal ellipsoidal plots. An anion part, hydrogen atoms, and CH_2Cl_2 were omitted for simplicity.

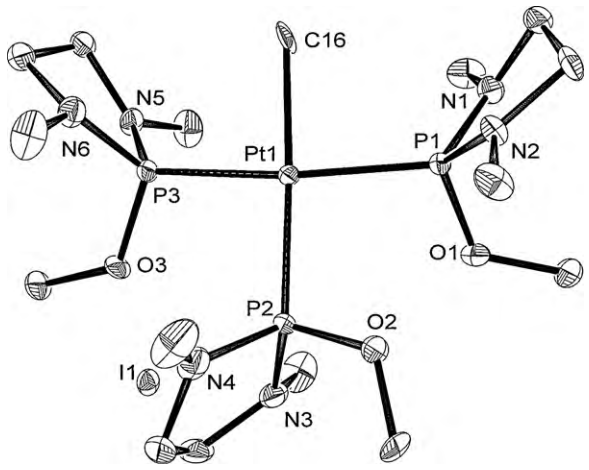


Fig. 5. Crystal structure of **8** at the 50% ellipsoidal level. The hydrogen atoms are omitted for simplicity.

Table 3
Crystal data and experimental parameters used for the intensity data collection of **6**, **8**, and **10**. Procedure and final results of the structure determination.

Empirical formula	$C_{16}H_{41}N_6O_3P_3Cl_2I_2Pt$ **6**	$C_{16}H_{42}N_6O_3P_3IPt$ **8**	$C_{17}H_{43}N_6P_2IPt$ **10**
Formula weight	978.25	781.46	715.50
T (K)	203(2)	110(2)	110(1)
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$P2_1/n$	Pcab
a (Å)	7.3640(2)	11.6851(7)	14.7786(16)
b (Å)	19.2021(8)	9.9735(6)	14.7576(17)
c (Å)	22.5145(9)	24.0650(15)	23.059(2)
β (°)		96.246(3)	
Volume (Å^3)	3183.6(2)	2787.9(3)	5029.0(10)
Z	4	4	8
ρ_{calcd} (mg m^{-3})	2.041	1.862	1.890
μ (cm^{-1})	6.693	6.340	6.950
F(000)	1864	1520	2784
Crystal size (mm^3)	0.38 × 0.08 × 0.05	0.30 × 0.20 × 0.10	0.30 × 0.20 × 0.02
Reflections collected	24980	20607	37063
R(int)	7141 (0.0263)	6185 (0.0281)	5740 (0.0809)
R ($I > 2\sigma(I)$)	0.0253	0.0379	0.0953
w$R2$	0.0598	0.1141	0.1439
Goodness of fit	1.008	1.425	1.545

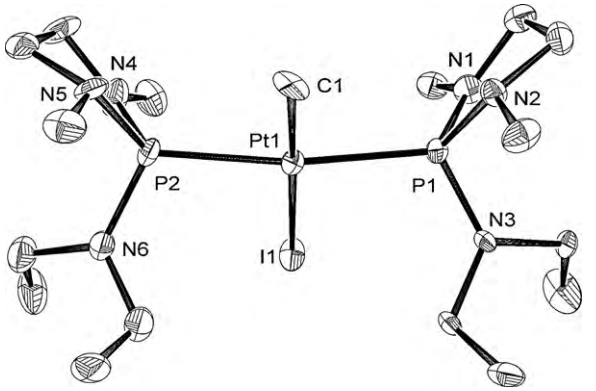


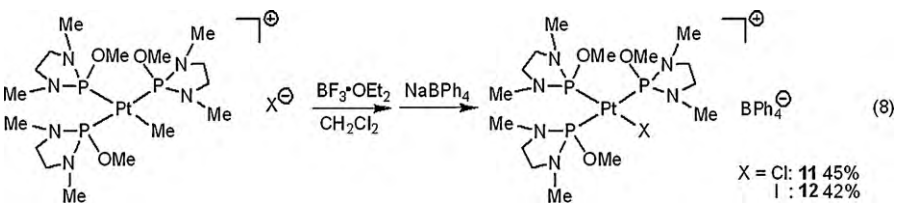
Fig. 6. Crystal structure of **10** at the 50% ellipsoidal level. The hydrogen atoms are omitted for simplicity.

Table 4
Selected bond lengths (Å) and bond angles (°) for **6**, **8**, and **10**.

	6	**8**	**10**
Pt1–P1	2.3211(12)	2.2864(17)	2.300(3)
Pt1–P2	2.2343(11)	2.2882(16)	2.294(3)
Pt1–P3	2.2987(13)	2.2883(16)	
Pt1–I1	2.6586(3)		2.7352(9)
Pt1–C16 (C1 for 10)		2.136(7)	2.072(11)
P1–O1(N3 for 10)	1.589(4)	1.608(5)	1.662(11)
P2–O2(N6 for 10)	1.589(3)	1.596(5)	1.666(11)
P3–O3	1.596(4)	1.593(5)	
P1–Pt1–P2	94.61(5)	94.48(6)	170.37(12)
P2–Pt1–P3	95.42(5)	94.57(6)	

excess amount of HOTf, Me_3SiOTf, MeOTf, or $BF_3{\cdot}OEt_2$ at room temperature, and then the $^{31}P\{^1H\}$ NMR spectra were recorded at 25 °C. In all cases except **7** and **8**, several signals were observed, indicating that some complicated reactions took place. However, there is no signal in the region of a phosphenium ligand [4]. In the reactions of **7** and **8** with $BF_3{\cdot}OEt_2$, a relatively clean reaction took place. Fig. 7 depicts the $^{31}P\{^1H\}$ NMR spectra of **8** and a solution containing **8** and $BF_3{\cdot}OEt_2$. After 2 h, a doublet at 105.90 ppm ($^2J_{PP}$ = 37 Hz, $^1J_{PPt}$ = 4070 Hz, *trans* to phosphite ligand) and a triplet at 122.60 ppm ($^2J_{PP}$ = 37 Hz, $^1J_{PPt}$ = 2818 Hz, *trans* to I) of the starting complex **8** disappeared and new two signals at 93.63 ppm (d, $^2J_{PP}$ = 15 Hz, $^1J_{PPt}$ = 3508 Hz) and 70.43 ppm (t, $^2J_{PP}$ = 15 Hz, $^1J_{PPt}$ = 5170 Hz) were observed. The ^{195}Pt satellite value of the triplet ($^1J_{PPt}$ = 5170 Hz) of the product was larger than the corresponding value of the starting complex **8** ($^1J_{PPt}$ = 2818 Hz). This large Pt–P coupling constant suggests the substitution of a methyl group for a ligand having weaker *trans* influence.

We tried to isolate complexes formed in the reaction of complexes **7** and **8** with $BF_3{\cdot}OEt_2$. A methyl complex, $[PtMe\{P(NMeCH_2)_2(OMe)\}_3]X$ (X = Cl: **7**, I: **8**), was treated with an equimolar amount of $BF_3{\cdot}OEt_2$ at room temperature for 2 h and then with $NaBPh_4$ in CH_2Cl_2 to afford the halogeno complex $[PtX\{P(NMeCH_2)_2(OMe)\}_3]BPh_4$ (X = Cl: **11**, I: **12**) as a result of the Me/X substitution reaction on the Pt center [Eq. (8)].



(8)

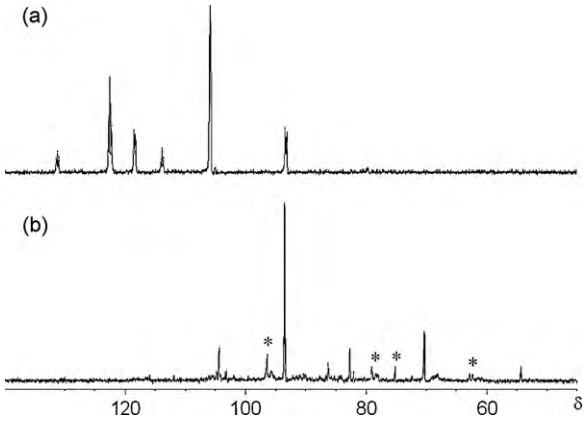


Fig. 7. The $^{31}P\{H\}$ NMR spectra of **8** (a) and **8** with BF_3OEt_2 (after 2 h) (b) at 25 °C in CH_2Cl_2. Peaks with asterisks are impurity.

X-ray structure analyses of **11** and **12** were undertaken. The ORTEP drawings of **11** and **12** are displayed in Figs. 8 and 9, respectively. Crystal data and selected bond distances and angles are summarized in Tables 5 and 6. Both platinum complexes take a normal square-planar geometry with three $P(NMeCH_2)_2(OMe)$ and one X ligands (X = Cl for **11**, I for **12**). Although the structure of a cationic part of **12** is similar to that of **6**, the anion part is composed of a tetraphenylborate anion. The P–OMe bond distances of **12** (1.598(9)–1.614(10) Å) are similar to those of **6** (1.589(3)–1.596(4) Å) and of the corresponding complexes reported previously (1.59–1.6387 Å) [3,4,6,11,24]. The X-ray analyses revealed that preferential Me substitution on the Pt center takes place and the OMe group on the phosphite remains intact.

Two plausible reaction pathways from **7**, **8** to **11**, **12** are shown in Scheme 1. Along Path A, BF_3 reacts with X^- to give

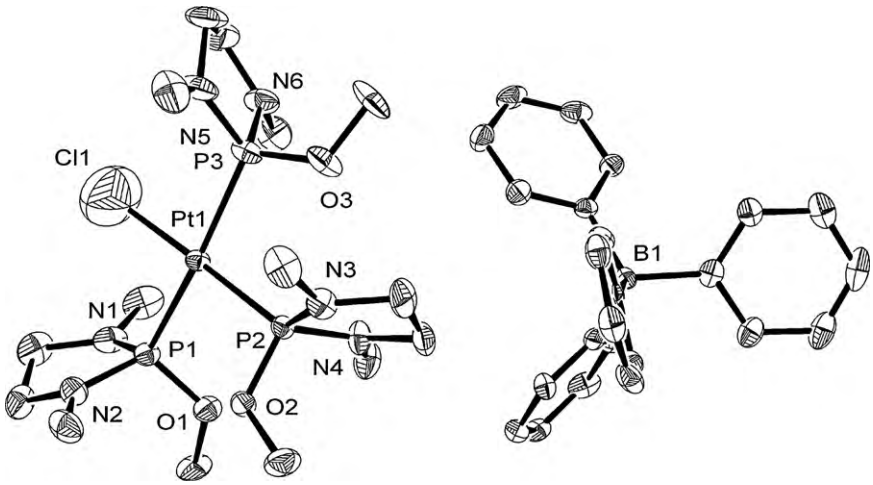


Fig. 8. Crystal structure of **11**·CH_2Cl_2 with 50% thermal ellipsoidal plots. The hydrogen atoms and CH_2Cl_2 were omitted for simplicity.

Table 5
Crystal data and experimental parameters used for the intensity data collection of **11** and **12**. Procedure and final results of the structure determination.

Empirical formula	$C_{40}H_{61}N_6O_3BCl_3P_3Pt$ **11**	$C_{40}H_{61}N_6O_3BCl_2IP_3Pt$ **12**
Formula weight	1079.11	1170.56
T (K)	100(1)	100(1)
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	13.0976(18)	13.1133(17)
b (Å)	13.6179(18)	13.7843(18)
c (Å)	14.6613(19)	14.4299(19)
α (°)	102.513(2)	101.684(4)
β (°)	102.661(4)	103.378(4)
γ (°)	104.213(4)	103.742(4)
Volume (Å^3)	2370.0(5)	2371.6(5)
Z	2	2
ρ_{calcd} (mg m^{-3})	1.512	1.639
μ (cm^{-1})	3.273	3.865
F(000)	1092	1164
Crystal size (mm^3)	0.10 × 0.10 × 0.02	0.31 × 0.20 × 0.10
Reflections collected	18440	18573
R(int)	10288 (0.0501)	10305 (0.0674)
R ($I > 2\sigma(I)$)	0.0673	0.0787
w$R2$	0.1269	0.2192
Goodness of fit	1.186	1.063

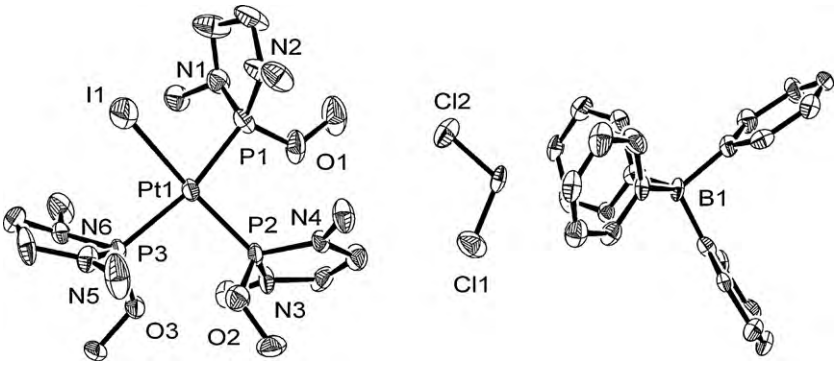


Fig. 9. Crystal structure of **12**·CH_2Cl_2 at the 50% ellipsoidal level. The hydrogen atoms are omitted for simplicity.

Table 6
Selected bond lengths (Å) and bond angles (°) for **11** and **12**.

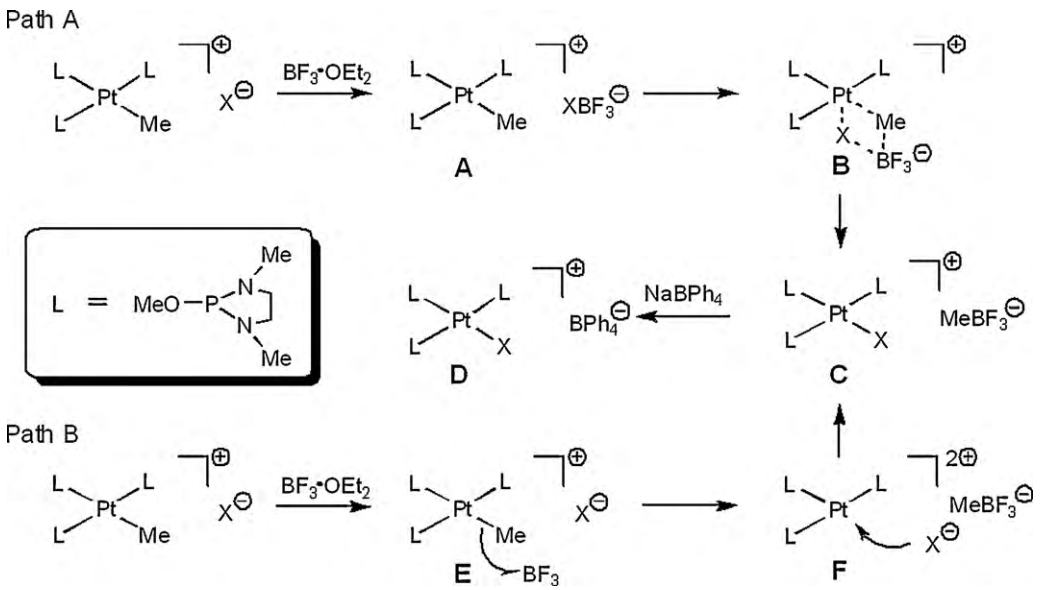
	11	**12**
Pt1–P1	2.3000(19)	2.287(3)
Pt1–P2	2.2756(17)	2.262(3)
Pt1–P3	2.274(2)	2.310(3)
Pt1–Cl1 (I1 for 12)	2.232(5)	2.5870(13)
P1–O1	1.603(5)	1.614(10)
P2–O2	1.611(5)	1.598(9)
P3–O3	1.585(6)	1.605(8)
P1–Pt1–P2	95.35(6)	95.67(11)
P2–Pt1–P3	95.76(7)	95.65(10)

XBF_3^- (**A**), and then a metathesis reaction between the Pt–Me and X–BF_3^- bonds takes place (**B** → **C**). The counter anion $MeBF_3^-$ is exchanged by BPh_4^- to give the final product (**C** → **D**). Alternatively in Path B, the Me^- group on the Pt center instead of the OMe^- group on the P atom is abstracted by BF_3 to generate a dicationic complex and $MeBF_3^-$ (**E** → **F**). Then a halogeno anion coordinates to the Pt center (**F** → **C**), and a subsequent pathway is similar to Path A. Path A is highly likely because of the advantage of avoiding the formation of the unstable dicationic intermediate **F**. However, Path B cannot be ruled out.

Through this work it was found that the platinum complexes with diamino-substituted phosphorus compounds were not converted into the corresponding phosphenium complexes in the reaction with a Lewis acid, whereas some other transition metal complexes were. The role of the platinum is not clear now, and is under investigation.

3. Conclusion

We found that a reaction of platinum complex with $P(NMeCH_2)_2(R')$ (R' = OMe, NEt_2) produces the corresponding cationic complex or neutral *cis*- or *trans*-complex depending on the substrate on the Pt center and the bulkiness of diamino-substituted phosphorus ligand. Reactions of cationic methyl platinum complexes **7** and **8** with BF_3·OEt_2 clearly showed that the predominant Me/X



Scheme 1. Plausible pathway of formation of $[PtX\{P(NMeCH_2)_2(OMe)\}_3]BPh_4$ (X = Cl: **11**, I: **12**).

substitution on the Pt center takes place and the OMe group on the P atom remains intact.

4. Experimental section

4.1. General considerations

All reactions were carried out under an atmosphere of dry nitrogen by using standard Schlenk tube techniques. Solvents except CH_2Cl_2 were distilled from sodium metal and were stored under nitrogen atmosphere. CH_2Cl_2 was distilled from CaH_2 under dry nitrogen prior to use. [$PtMe_2$(cod)] [16(a)], [Pt(*p*-tol)$_2$(cod)] [16(b)], [PtMeX(cod)] (X = Cl, I [16(b)]), [PtI_2(cod)] [21], and [$P(NMeCH_2)_2$(R')] (R' = OMe [17], NEt_2 [18]) were synthesized according to the reported procedures. NMR spectra (^1H, ^{13}C, ^{31}P) were measured on JEOL JNM-AL400 spectrometer at 25 °C. ^1H and ^{13}C NMR data were referred to residual peaks of solvent as an internal standard. Peak position of the ^{31}P NMR spectrum was referenced to an external 85% H_3PO_4.

4.2. Syntheses of complexes 1–12

4.2.1. cis-[Pt(Me)$_2${P(NMeCH$_2$)$_2$(OMe)}$_2$]: 1

A benzene solution of Pt(Me)$_2$(cod) (300 mg, 0.90 mmol) was slowly added to [$P(NMeCH_2)_2$(OMe)] (296 mg, 2.00 mmol) at 25 °C. The mixture was stirred for 1 h at ambient temperature. Volatile materials were removed under reduced pressure, and the resulting residue was washed with a small amount of hexane, collected by filtration, and dried *in vacuo* to give a white solid of **1** (463 mg, 0.88 mmol, 98%). Single-crystals of **1** were obtained by solvent diffusion over a few days from an acetone layer containing **1** and an overlayer of hexane. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.42 (apparent t, J_{PH} = 7.3 Hz, J_{PtH} = 67.4 Hz, 6H, PtMe), 2.49 (d, J_{PH} = 10.7 Hz, 12H, NMe), 3.18 (dt, J_{PH} = 5.9 Hz, J_{HH} = 8.3 Hz, 4H, NCH_2), 3.30 (d, J_{PH} = 10.7 Hz, 6H, OMe), 3.37 (br, 4H, NCH_2). $^{13}C\{^1H\}$ NMR (100.4 MHz, $CDCl_3$, δ, ppm): 1.27 (dd, J_{PC} = 12.5, 138.7 Hz, J_{PtC} = 563.8 Hz, PtMe), 33.49 (apparent t, J_{PC} = 7.5 Hz, J_{PtC} = 10.8 Hz, NMe), 50.83 (apparent t, J_{PC} = 5.0 Hz, J_{PtC} = 15.0 Hz, OMe), 52.42 (apparent t, J_{PC} = 1.7 Hz, J_{PtC} = 11.6 Hz, NCH_2). $^{31}P\{^1H\}$ NMR (161.7 MHz, $CDCl_3$, δ, ppm): 125.07 (s, J_{PtP} = 2860 Hz). Elemental Analysis. Calcd. For $C_{12}H_{32}N_4O_2P_2Pt$: C, 27.64; H, 6.19; N, 10.74; Found: C, 27.31; H, 6.08; N, 10.45%.

4.2.2. cis-[Pt(p-tol)$_2${P(NMeCH$_2$)$_2$(OMe)}$_2$]: 2

In a procedure analogous to that outlined above, Pt(*p*-tol)$_2$(cod) (346 mg, 0.71 mmol) and $P(NMeCH_2)_2$(OMe) (259 mg, 2.42 mmol) gave a gray powder of **2** (389 mg, 0.58 mmol, 81%). Single-crystals of **2** were obtained from an acetone-hexane solution containing **2**. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.12 (s, 6H, Ph*Me*), 2.53 (d, J_{PH} = 10.3 Hz, 12H, NMe), 2.82 (dt, J_{PH} = 5.4 Hz, J_{HH} = 7.8 Hz, 4H, NCH_2), 3.22 (d, J_{PH} = 10.3 Hz, 6H, OMe, and overlapped 4H of NCH_2), 6.71 (d, J_{HH} = 6.8 Hz, 4H, *m*-Ph), 7.04 (t, J_{HH} = 7.3 Hz, J_{PtH} = 56.6 Hz, 4H, *o*-Ph). ^{13}C $\{^1H\}$ NMR (100.4 MHz, $CDCl_3$, δ, ppm): 21.20 (s, Ph*Me*), 33.09 (apparent t, J_{PC} = 7 Hz, NMe), 50.07 (apparent t, J_{PC} = 5 Hz, OMe), 51.83 (s, NCH_2), 126.72 (t, J_{PC} = 4 Hz, J_{PtC} = 63 Hz, *o*-Ph), 129.67 (s, *p*-Ph), 137.63 (t, J_{PC} = 2 Hz, J_{PtC} = 38 Hz, *m*-Ph), 157.77 (dd, J_{PC} = 18, 164 Hz, J_{PtC} = 830 Hz, PtC). ^{31}P $\{^1H\}$ NMR (161.7 MHz, $CDCl_3$, δ, ppm): 118.56 (s, J_{PPt} = 2809 Hz). Elemental Analysis. Calcd. For $C_{24}H_{40}N_4O_2P_2Pt$: C, 42.79; H, 5.99; N, 8.32; Found: C, 42.74; H, 6.04; N, 8.00%.

4.2.3. cis-[Pt(Me)$_2${P(NMeCH$_2$)$_2$(NEt$_2$)}$_2$]: 3

In a procedure analogous to that outlined above, Pt(Me)$_2$(cod) (284 mg, 0.85 mmol) and [$P(NMeCH_2)_2$(-NEt_2)] (322 mg, 1.70 mmol) gave a gray powder of **3** (359 mg, 0.60 mmol, 70%). Single-crystals of **2** were obtained by a saturated hexane solution at −20 °C. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.36 (m, J_{PtH} = 66.4 Hz, 6H, PtMe), 0.95 (t, J_{HH} = 7.3 Hz, 12H, $NCH_2C\underline{H}_3$), 2.47 (d, J_{PH} = 11.2 Hz, 12H, NMe), 2.95 (d, J_{PH} = 5.9 Hz, J_{PtH} = 17.6 Hz, 4H, NCH_2), 3.07 (dq, J_{HH} = 7.3 Hz, J_{PH} = 9.8 Hz, 8H, $NC\underline{H}_2CH_3$), 3.18 (br, 4H, NCH_2). ^{13}C $\{^1H\}$ NMR (100.4 MHz, $CDCl_3$, δ, ppm): 4.13 (dd, J_{PC} = 11.5, 129 Hz, J_{PtC} = 567 Hz, PtMe), 14.32 (s, $NCH_2\underline{C}H_3$), 34.76 (apparent t, J_{PC} = 5 Hz, NMe), 38.87 (m, $N\underline{C}H_2CH_3$), 52.14 (s, J_{PtH} = 4 Hz, NCH_2). ^{31}P $\{^1H\}$ NMR (161.7 MHz, $CDCl_3$, δ, ppm): 120.13 (s, J_{PtP} = 2860 Hz). Elemental Analysis. Calcd. For $C_{18}H_{46}N_6P_2Pt$: C, 35.82; H, 7.68; N, 13.92; Found: C, 36.09; H, 7.72; N, 13.79%.

4.2.4. cis-[Pt(p-tol)$_2${P(NMeCH$_2$)$_2$(NEt$_2$)}$_2$]: 4

In a procedure analogous to that outlined above, Pt(*p*-tol)$_2$(cod) (238 mg, 0.49 mmol) and [$P(NMeCH_2)_2$(NEt_2)] (315 mg, 1.66 mmol) gave a white solid of **4** (327 mg, 0.44 mmol, 90%). ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.02 (t, J_{HH} = 7.3 Hz, 12H, $NCH_2C\underline{H}_3$), 2.07 (s, 6H, Ph*Me*), 2.24 (d, J_{PH} = 7.3 Hz, 12H, NMe), 3.03 (s, 8H, NCH_2), 3.22 (dq, J_{HH} = 7.3 Hz, J_{PH} = 3.4 Hz, 8H, $NC\underline{H}_2CH_3$), 6.61 (d, J_{HH} = 6.8 Hz, 4H, *m*-Ph), 7.03 (d, J_{HH} = 5.9 Hz, J_{PtH} = 55.2 Hz, 4H, *o*-Ph). ^{13}C $\{^1H\}$ NMR (100.4 MHz, $CDCl_3$, δ, ppm): 14.16 (s, $NCH_2\underline{C}H_3$), 21.13 (s, Ph*Me*), 33.81 (apparent t, J_{PC} = 5 Hz, NMe), 38.93 (apparent t, J_{PC} = 5 Hz, $N\underline{C}H_2CH_3$), 51.21 (s, NCH_2), 126.77 (t, J_{PC} = 3 Hz, J_{PtC} = 66 Hz, *o*-Ph), 128.43 (t, J_{PC} = 9 Hz, *p*-Ph), 137.57 (t, J_{PC} = 17 Hz, *m*-Ph), 156.44 (dd, J_{PC} = 15, 143 Hz, J_{PtC} = 804 Hz, PtC). ^{31}P $\{^1H\}$ NMR (161.7 MHz, $CDCl_3$, δ, ppm): 107.40 (s, J_{PtP} = 2688 Hz). Elemental Analysis. Calcd. For $C_{30}H_{54}N_6P_2Pt$: C, 47.67; H, 7.20; N, 11.12; Found: C, 47.68; H, 7.21; N, 10.94%.

4.2.5. [PtCl{P(NMeCH$_2$)$_2$(OMe)}$_3$]Cl: 5

In a procedure analogous to that outlined above, $PtCl_2$(cod) (224 mg, 0.60 mmol) and [$P(NMeCH_2)_2$(OMe)] (266 mg, 1.79 mmol) gave a white powder of **5** (387 mg, 0.54 mmol, 91%). ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.75 (m, 6H, NMe), 2.80 (t, J_{PH} = 5.9 Hz, 12H, NMe), 3.24 (m, 2H, NCH_2), 3.39 (t, J_{PH} = 3.4 Hz, 3H, OMe), 3.41-3.48 (m, 6H, OMe and 6H, NCH_2), 3.51 (m, 4H, NCH_2). $^{13}C\{^1H\}$ NMR (100.4 MHz, $CDCl_3$, δ, ppm): 33.00 (m, overlapped NMe of three P ligands), 50.62 (d, J_{PC} = 4 Hz, OMe on assignable P *trans* to Cl), 51.26 (t, J_{PC} = 4 Hz, OMe on assignable P *cis* to Cl), 52.21 (m, overlapped NCH_2 of three P ligands). ^{31}P $\{^1H\}$ NMR (161.7 MHz, $CDCl_3$, δ, ppm): 71.24 (t, J_{PP} = 13 Hz, J_{PtP} = 5375 Hz, *trans* to Cl), 99.17 (d, J_{PP} = 13 Hz, J_{PtP} = 3633 Hz, *cis* to Cl). Elemental Analysis. Calcd. For

$C_{15}H_{39}N_6O_3P_3Cl_2Pt$: C, 25.36; H, 5.53; N, 11.83; Found: C, 23.34; H, 5.90; N, 10.68%.

4.2.6. [PtI{P(NMeCH$_2$)$_2$(OMe)}$_3$]I: 6

In a procedure analogous to that outlined above, PtI_2(cod) (557 mg, 1.00 mmol) and [P(NMeCH$_2$)$_2$(OMe)] (445 mg, 3.00 mmol) gave a white solid of **6** (868 mg, 0.97 mmol, 97%). Single-crystals of **6** were obtained by solvent diffusion over a few days from a CH_2Cl_2 layer containing **6** and an overlayer of hexane. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.62 (apparent t, J_{PH} = 6.0 Hz, 12H, NMe), 2.66 (d, J_{PH} = 11.2 Hz, 6H, NMe), 3.17 (m, 2H, NCH_2), 3.29 (m, 4H, NCH_2), 3.34 (d, J_{PH} = 12.4 Hz, OMe, 3H), 3.35 (apparent t, J_{PH} = 6.0 Hz, 6H, OMe), 3.39 (m, 4H, NCH_2), 3.45 (m, 2H, NCH_2). ^{13}C{^{1}H} NMR (100.4 MHz, $CDCl_3$, δ, ppm): 32.68 (m, J_{PtC} = 159 Hz, NMe of assignable P *cis* to I), 32.77 (m, NMe of assignable P *trans* to I), 50.23 (m, OMe on assignable P *cis* to I), 51.15 (m, OMe of assignable P *trans* to I), 51.63 (m, overlapped NCH_2 of three P ligands). ^{31}P{^{1}H} NMR (161.7 MHz, $CDCl_3$, δ, ppm): 70.43 (t, J_{PP} = 15 Hz, J_{PPt} = 5158 Hz, *trans* to I), 93.63 (d, J_{PP} = 15 Hz, J_{PPt} = 3512 Hz, *cis* to I). Elemental Analysis. Calcd. For $C_{15}H_{39}N_6O_3P_3I_2Pt$: C, 20.17; H, 4.40; N, 9.41; Found: C, 20.44; H, 4.38; N, 9.06%.

4.2.7. [Pt(Me){P(NMeCH$_2$)$_2$(OMe)}$_2$]$_3$Cl: 7

In a procedure analogous to that outlined above, PtMeCl(cod) (175 mg, 0.50 mmol) and [P(NMeCH$_2$)$_2$(OMe)] (220 mg, 1.49 mmol) gave a gray powder of **7** (304 mg, 0.44 mmol, 89%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.31 (dt, J_{PH} = 7.3, 8.8 Hz, J_{PtH} = 56.0 Hz, 3H, PtMe), 2.69 (d, J_{PH} = 11.2 Hz, 6H, NMe), 2.73 (t, J_{PH} = 5.9 Hz, 12H, NMe), 3.17 (m, 2H, NCH_2), 3.30–3.33 (m, 3H, OMe and 6H, NCH_2), 3.42 (t, J_{PH} = 5.9 Hz, 6H, OMe), 3.57 (m, 4H, NCH_2). ^{13}C{^{1}H} NMR (100.4 MHz, $CDCl_3$, δ, ppm): −3.00 (dt, J_{PC} = 106 Hz, J_{PC} = 9 Hz, J_{PtC} = 443 Hz, PtMe), 32.75 (t, J_{PC} = 7 Hz, NMe), 33.12 (d, J_{PC} = 14 Hz, J_{PtC} = 9 Hz, NMe), 50.83 (d, J_{PC} = 13 Hz, OMe), 51.40 (apparent t, J_{PC} = 9 Hz, OMe), 51.63 (s, J_{PtC} = 10 Hz, NCH_2), 52.20 (s, J_{PtC} = 18 Hz, NCH_2). ^{31}P {^{1}H} NMR (161.7 MHz, $CDCl_3$, δ, ppm): 106.06 (d, J_{PP} = 37 Hz, J_{PtP} = 4070 Hz, *cis* to Me on the Pt), 122.78 (t, J_{PP} = 37 Hz, J_{PtP} = 2818 Hz, *trans* to Me on the Pt). Elemental Analysis. Calcd. For $C_{16}H_{42}N_6O_3P_3ClPt$: C, 27.85; H, 6.14; N, 12.18; Found: C, 26.80; H, 6.30; N, 11.51%.

4.2.8. [Pt(Me){P(NMeCH$_2$)$_2$(OMe)}$_3$]I: 8

In a procedure analogous to that outlined above, PtMeI(cod) (146 mg, 0.32 mmol) and [P(NMeCH$_2$)$_2$(OMe)] (145 mg, 0.98 mmol) gave a gray powder of **8** (237 mg, 0.30 mmol, 94%). Single-crystals of **8** were obtained by solvent diffusion over a few days from a CH_2Cl_2 layer containing **8** and an overlayer of hexane. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.22 (dt, J_{PH} = 7.3, 8.8 Hz, J_{PtH} = 56.0 Hz, 3H, PtMe), 2.63 (d, J_{PH} = 24.4 Hz, 6H, NMe), 2.71 (t, J_{PH} = 4.8 Hz, 12H, NMe), 3.15 (m, 2H, NCH_2), 3.23 (d, J_{PH} = 11.6 Hz, 6H, OMe and overlapped 1H of NCH_2), 3.42 (d, J_{PH} = 5.2 Hz, 3H, OMe and overlapped 1H and 4H of NCH_2), 3.56 (br, 4H, NCH_2). ^{13}C {^{1}H} NMR (100.4 MHz, $CDCl_3$, δ, ppm): 3.27 (dt, J_{PC} = 8, 106 Hz, J_{PtC} = 442 Hz, PtMe), 32.48 (t, J_{PC} = 7 Hz, J_{PtC} = 10 Hz, NMe), 32.85 (d, J_{PC} = 8 Hz, J_{PtC} = 15 Hz, NMe), 50.60 (d, J_{PC} = 12 Hz, J_{PtC} = 15 Hz, OMe), 51.26 (d, J_{PC} = 5 Hz, J_{PtC} = 22 Hz, OMe), 51.33 (s, J_{PtC} = 8 Hz, NCH_2), 51.85 (s, J_{PtC} = 19 Hz, NCH_2). ^{31}P {^{1}H} NMR (161.7 MHz, $CDCl_3$, δ, ppm): 105.97 (d, J_{PP} = 37 Hz, J_{PPt} = 4003 Hz, *cis* to Me on the Pt), 122.73 (t, J_{PP} = 37 Hz, J_{PPt} = 2818 Hz, *trans* to Me on the Pt). Elemental Analysis. Calcd. For $C_{16}H_{42}N_6O_3P_3IPt$: C, 24.59; H, 5.42; N, 10.75; Found: C, 24.76; H, 5.38; N, 10.55%.

4.2.9. cis-[Pt(Me)(Cl){P(NMeCH$_2$)$_2$(NEt$_2$)}$_2$] and trans-[Pt(Me)(Cl){P(NMeCH$_2$)$_2$(NEt$_2$)}$_2$]: 9

In a procedure analogous to that outlined above, PtMeCl(cod) (365 mg, 1.03 mmol) and [P(NMeCH$_2$)$_2$(NEt$_2$)] (391 mg, 2.07 mmol) gave a white powder of **9** (550 mg, 0.88 mmol, 85%, *trans*: *cis* = *ca.* 2:1). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.47 (apparent t, J_{PH} = 6.8 Hz, J_{PtH} = 86.4 Hz, 3H, PtMe), 0.71 (dd, J_{PH} = 2.0, 8.8 Hz, J_{PtP} = 49.3, 3H, PtMe), 0.99 (t, J_{PH} = 7.3 Hz, 12H, $NCH_2C\underline{H}_3$), 1.05 (t, J_{PH} = 7.3 Hz, 12H, $NCH_2C\underline{H}_3$), 2.47 (d, J_{PH} = 11.7 Hz, 4H, NCH_2), 2.65 (d, J_{PH} = 10.3 Hz, 4H, NCH_2), 2.72 (t, J_{PH} = 5.4 Hz, 16H, $NC\underline{H}_2CH_3$), 2.98–3.29 (m, 8H, NCH_2 and 24H, NMe). ^{13}C{^{1}H} NMR (100.4 MHz, $CDCl_3$, δ, ppm): −17.92 (t, J_{PtC} = 678 Hz, J_{PC} = 8 Hz, PtMe *trans* to chloride), 9.80 (dd, J_{PC} = 6, 123 Hz, J_{PtC} = 455 Hz, PtMe, *trans* to phosphine), 14.50 (d, J_{PC} = 2 Hz, $NCH_2\underline{C}H_3$), 14.81 (d, J_{PC} = 2 Hz, $NCH_2\underline{C}H_3$), 15.11 (s, $NCH_2\underline{C}H_3$), 34.63 (t, J_{PC} = 4 Hz, NMe), 35.02 (d, J_{PC} = 8 Hz, NMe), 35.53 (d, J_{PC} = 9 Hz, NMe), 39.69 (d, J_{PC} = 7 Hz, $N\underline{C}H_2CH_3$), 39.79 (d, J_{PC} = 5 Hz, $N\underline{C}H_2CH_3$), 40.70 (d, J_{PC} = 7 Hz, $N\underline{C}H_2CH_3$), 50.95 (s, NCH_2), 51.67 (d, J_{PC} = 2 Hz, NCH_2), 52.07 (d, J_{PC} = 3 Hz, NCH_2). ^{31}P{^{1}H} NMR (161.7 MHz, C_6D_6, δ, ppm): 82.84 (d, J_{PP} = 22 Hz, J_{PtP} = 6037 Hz, *trans* to Cl), 102.20 (s, J_{PtP} = 3938 Hz, *trans* to P), 116.60 (d, J_{PP} = 22 Hz, J_{PtP} = 2651 Hz, *trans* to Me). Elemental Analysis. Calcd. For $C_{17}H_{43}N_6P_2ClPt$: C, 32.72; H, 6.95; N, 13.47; Found: C, 32.10; H, 6.83; N, 13.06%.

4.2.10. trans-[Pt(Me)(I){P(NMeCH$_2$)$_2$(NEt$_2$)}$_2$]: 10

In a procedure analogous to that outlined above, PtMeI(cod) (482 mg, 0.97 mmol) and [P(NMeCH$_2$)$_2$(NEt$_2$)] (367 mg, 1.94 mmol) gave a gray powder of **10** (627 mg, 0.88 mmol, 90%). Single-crystals of **10** were obtained by solvent diffusion over a few days from a CH_2Cl_2 layer containing **10** and an overlayer of hexane. ^{1}H NMR (400 MHz, C_6D_6, δ, ppm): 0.73 (t, J_{PH} = 6.4 Hz, J_{PtH} = 83.5 Hz, 3H, PtMe), 1.05 (t, J_{HH} = 6.8 Hz, 12H, $NCH_2C\underline{H}_3$), 2.74 (t, J_{PH} = 5.4 Hz, 12H, NMe), 3.15–3.23 (m, 8H, NCH_2 and 8H, $NC\underline{H}_2CH_3$). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, δ, ppm): −9.09(t, J_{PC} = 8 Hz, J_{PtC} = 678 Hz, PtMe), 14.72 (s, $NCH_2\underline{C}H_3$), 35.80 (t, J_{PC} = 4 Hz, NMe), 39.72 (t, J_{PC} = 5 Hz, $N\underline{C}H_2CH_3$), 51.10 (s, NCH_2). ^{31}P {^{1}H} NMR (161.7 MHz, C_6D_6, δ, ppm): 103.24 (s, J_{PtP} = 3850 Hz). Elemental Analysis. Calcd. For $C_{17}H_{43}N_6P_2Pt$: C, 28.16; H, 5.98; N, 11.45; Found: C, 28.54; H, 6.06; N, 11.75%.

4.2.11. [PtCl{P(NMeCH$_2$)$_2$(OMe)}$_3$]BPh$_4$: 11

$BF_3{\cdot}OEt_2$ (38 μl, 0.3 mmol) was slowly added to a CH_2Cl_2 solution of **7** (207.0 mg, 0.3 mmol) at 25 °C. The mixture was stirred for 1 h at room temperature, and $NaBPh_4$ (102.7 mg, 0.3 mmol) was added. After stirred for 1 h at room temperature, this mixture was filtrated. Volatile materials in the filtrate were removed under

reduced pressure to give a colorless oil. Single-crystals of **11** (134.2 mg, 0.14 mmol, 45%) were obtained by solvent diffusion over a few days from a CH_2Cl_2 layer containing a colorless oil and an overlayer of hexane. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.63 (t, J_{PH} = 10.7 Hz, 6H, NMe), 2.68 (t, J_{PH} = 5.9 Hz, 9H, NMe), 2.75 (t, J_{PH} = 5.9 Hz, 3H, NMe), 3.02–3.07 (m, 2H, NCH_2), 3.21(m, 4H, NCH_2), 3.24 (d, J_{PH} = 11.7 Hz, 3H, OMe), 3.29–3.30 (m, 2H, NCH_2), 3.32 (t, J_{PH} = 5.9 Hz, 6H, OMe), 3.43 (m, 4H, NCH_2), 6.93 (t, J_{HH} = 7.3 Hz, 4H, *p*-Ph), 7.08 (t, J_{HH} = 7.3 Hz, 8H, *m*-Ph), 7.44 (br, 8H, *o*-Ph). ^{13}C{^{1}H} NMR (100.4 MHz, $CDCl_3$, δ, ppm): 32.74 (apparent t, J_{PC} = 7 Hz, NMe), 33.12 (d, J_{PC} = 15 Hz, NMe), 51.27 (m, OMe), 51.50 (m, OMe), 52.16 (t, J_{PC} = 10 Hz, NCH_2, and overlapped other NCH_2), 121.64 (s, *p*-Ph), 125.50 (q, J_{BC} = 3 Hz, *o*-Ph), 136.37 (s, *m*-Ph), 164.33 (q, J_{BC} = 49 Hz, *ipso*-Ph). ^{31}P{^{1}H} NMR (161.7 MHz, $CDCl_3$, δ, ppm): 71.35 (t, J_{PP} = 22 Hz, J_{PPt} = 5342 Hz, *trans* to Cl), 99.09 (d, J_{PP} = 22 Hz, J_{PPt} = 3583 Hz, *cis* to Cl). Elemental Analysis. Calcd. For $C_{39}H_{59}BClN_6O_3P_3Pt$: C, 44.52; H, 5.70; N, 7.79; Found: C, 44.97; H, 5.87; N, 7.73%.

4.2.12. *[PtI{P(NMeCH$_2$)$_2$(OMe)}$_3$]BPh$_4$:* **12**

$BF_3{\cdot}OEt_2$ (38 μl, 0.3 mmol) was slowly added to a CH_2Cl_2 solution of **8** (234.4 mg, 0.3 mmol) at 25 °C. The mixture was stirred for 2.5 h at room temperature, and $NaBPh_4$ (102.7 mg, 0.3 mmol) was added. After stirred for 1 h at room temperature, this mixture was filtrated. Volatile materials in the filtrate were removed under reduced pressure to give a yellow oil. Single-crystals of **12** (136.8 mg, 0.13 mmol, 42%) were obtained by solvent diffusion over a few days from a CH_2Cl_2 layer containing a yellow oil and an overlayer of hexane. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.63 (d, J_{PH} = 11.7 Hz, 6H, NMe), 2.68 (t, J_{PH} = 5.9 Hz, 12H, NMe), 2.93–3.03 (m, 4H, NCH_2), 3.24 (d, J_{PH} = 13.7 Hz, 3H, OMe), 3.28 (t, J_{PH} = 6.4 Hz, 6H, OMe), 3.34–3.46 (m, 8H, NCH_2), 6.92 (t, J_{HH} = 7.3 Hz, 4H, *p*-Ph), 7.07 (t, J_{HH} = 7.3 Hz, 8H, *m*-Ph), 7.43 (br, 8H, *o*-Ph). ^{13}C{^{1}H} NMR (100.4 MHz, $CDCl_3$, δ, ppm): 32.85 (d, J_{PC} = 12 Hz, NMe), 33.20 (t, J_{PC} = 7 Hz, NMe), 50.64 (d, J_{PC} = 3 Hz, OMe), 50.98 (m, OMe), 52.26 (s, overlapped NCH_2 of three P ligands), 121.96 (s, *p*-Ph), 125.78 (q, J_{BC} = 3 Hz, *o*-Ph), 136.60 (s, *m*-Ph), 164.54 (q, J_{BC} = 49 Hz, *ipso*-Ph). ^{31}P{^{1}H} NMR (161.7 MHz, $CDCl_3$, δ, ppm): 70.54 (t, J_{PP} = 15 Hz, J_{PPt} = 5173 Hz, *trans* to I), 93.68 (d, J_{PP} = 15 Hz, J_{PPt} = 3524 Hz, *cis* to I). Elemental Analysis. Calcd. For $C_{39}H_{59}BIN_6O_3P_3Pt$: C, 43.15; H, 5.48; N, 7.74; Found: C, 43.53; H, 5.64; N, 7.41%.

4.3. *X-ray crystallography measurements*

X-ray intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo-Kα radiation. Calculations were performed with the CrystalClear software package of Molecular Structure Corporation. The structures were solved by direct methods and expanded using Fourier techniques. The structures were refined by full matrix least-squares technique using the program SHELXL-97 [25]. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Complexes **1**–**3**, **6**, **8**, and **10**–**12** have been deposited with the Cambridge Crystallographic Data Centre under CCDC 761300, 761301, 761302, 761303, 761304, 761305, 761306, and 761307, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; tel.; +44 1223 336408; fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk).

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