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Syntheses and Characterization of Novel *trans*-Bis(phosphoranido)platinum(II) Complexes: Reactions of Lithium Bis(naphth-1,8-diyl-8-oxy)phosphoranide with *cis*-$PtCl_2(PR_3)_2$ (R = OPh, OMe, Me)

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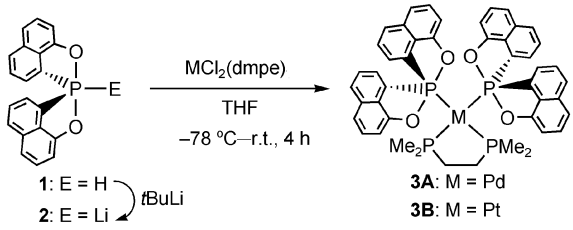
The reactions of *cis*-$PtCl_2(PR_3)_2$ (R = OPh, OMe) with 1 equiv. of lithium phosphoranide generated from a bis(naphth-1,8-diyl-8-oxy)phosphorane lead to the formation of *cis*-monophosphoranido complexes with high stereospecificity. The reaction of *cis*-$PtCl_2(PMe_3)_2$ with 1 equiv. of the lithium phosphoranide afforded a *trans*-monophosphoranido complex, exclusively. Hitherto unknown *trans*-bis(phosphoranido)-platinum(II) complexes were obtained as major products in the reactions of *cis*-$PtCl_2(PR_3)_2$ (R = OPh, OMe, Me) with an excess of the lithium phosphoranide. The stereochemistry was confirmed by X-ray structural analysis of the bis(phosphoranido) complex bearing triphenyl phosphites.

Introduction

A wide variety of ligand-substitution reactions of square-planar complexes have been investigated and mechanistic aspects have been well established.[1] Although hypervalent[2] 10–P–4[3] phosphoranides are capable of behaving as nucleophiles,[4] the stereochemical course of these reactions with square-planar complexes has been investigated to a lesser extent. Among reports on phosphoranido complexes,[5,6] there have only been a few on reactions with square-planar d^8 group 10 metal dihalides of which the phosphoranides remained intact.[6] The geometry of the resulting monophosphoranido complex was the same as that of the metal dihalide starting material. Furthermore, the formation of bis(phosphoranido) complexes was suppressed, although an unstable bis(phosphoranido)palladium(II) complex speculated from ^{31}P NMR analysis had been reported.[7] A significant factor in the synthesis and stereochemistry of phosphoranido complexes has been the steric demand of the phosphoranide ligand. From this aspect, it could be anticipated that the compact lithium bis(naphth-1,8-diyl-8-oxy)phosphoranide **2** generated from P–H phosphorane **1** would be suitable for the synthesis of these complexes.[8,9]

Recently, we reported that the reaction of one or two equiv. of phosphoranide **2** with MCl_2(dmpe) (M = Pd, Pt) gave rise to *cis*-bis(phosphoranido)palladium(II) and -platinum(II) complexes **3**, the first fully characterized square-planar complexes bearing two phosphoranide ligands (Scheme 1).[8] Consequently, the reactions of phosphoranide **2** with *cis*-$PtCl_2(PR_3)_2$ (**4**) (R = OPh, OMe, Me), in which the phosphane ligands are monodentate and not fixed *cis*, were examined. As a result, not only *cis*- and/or *trans*-monophosphoranidoplatinum(II) complexes **5**, but also unprecedented *trans*-bis(phosphoranido)platinum(II) complexes **6** were obtained. Herein, we report on the syntheses and characterization of complexes **5** and **6**. Also presented is the X-ray structure of triphenyl phosphite complex **6a**.



Scheme 1. Syntheses of *cis*-bis(phosphoranido) complexes **3**.

Results and Discussion

Syntheses and Spectroscopic Properties

Addition of 1 equiv. of lithium phosphoranide **2** to a suspension of *cis*-$PtCl_2(PR_3)_2$ (**4**) in THF resulted in the exclusive formation of monophosphoranido complexes **5**, which could be purified with silica gel chromatography (Scheme 2, Table 1). While this result is expected in light of the reaction stoichiometry, it is in contrast with the direct and exclusive formation of the bis(phosphoranido) com-

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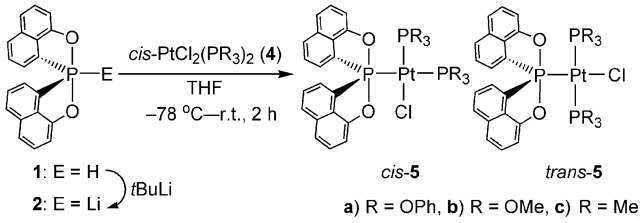
plexes **3**.[8] The reaction of the phosphoranide **2** with the phosphite complexes **4a**,**b** afforded *cis*-**5a**,**b** with high stereospecificity. By contrast, the reaction with the PMe_3 complex **4c** gave *trans*-**5c**, exclusively.



Scheme 2. Syntheses of monophosphoranido complexes **5**.

Table 1. The yields and *cis*/*trans* ratio of the complexes **5**, and cone angle of PR_3.

Complex	R	Yield [%]	*cis*/*trans*[a]	Cone angle of PR_3[b]
5a	OPh	64	91:9	128°
5b	OMe	71	91:9	107°
5c	Me	61	<1:>99	118°

[a] Determined by ^1H NMR ($CDCl_3$) spectroscopic analysis. [b] Determined for $Ni(CO)_3PR_3$.

In the ^{31}P NMR spectra, the resonances for *cis*-**5** appeared as three doublets of doublets due to low symmetry (Figure 1), while A_2X and A_2B spin systems could be assigned to the signals for the C_2 symmetric *trans*-**5a**,**b** and **5c** (Figure 2), respectively. The $^1J_{P,Pt}$ value for the phosphoranide P atom in *trans*-**5** decreases as the π-acidity of the phosphane increases (or the σ donor ability of the phosphane decreases), where the order is $P(OAr)_3 > P(OR)_3 > PR_3$ (Table 2). The reverse trend in the case of *cis*-**5** may be caused by the distortion of the structure of *cis*-**5a** in which the triphenyl phosphite ligand is also a bulky ligand. The $^1J_{P,Pt}$ value for the phosphoranide P atom in *cis*-**5** is lower than that in *trans*-**5**, which must be a consequence reflecting the larger *trans* influence of the phosphite ligand compared with that of the chloride.[10]

One might expect that the geometry of complex **5** would be partially dependent on the steric demands of the phosphane ligands, whose cone angles have been determined in the case of $Ni(CO)_3PR_3$ (Table 1).[11] However, the *cis*/*trans* ratio of complex **5** is inconsistent with the trend in steric bulk. The ratio did not significantly vary with reaction time, and the possible effect of a lithium bridge between the oxygen atoms of the phosphite ligands can be excluded since the *cis*/*trans* ratio of **5a** did not change by the addition of 12-crown-4. The *cis* and *trans*-**5a**,**b** could not be separated with silica gel chromatography or recrystallization. These results might infer that the *cis*/*trans* ratio of complexes **5** is dependent on their thermodynamic stabilities although kinetic control can not be denied.

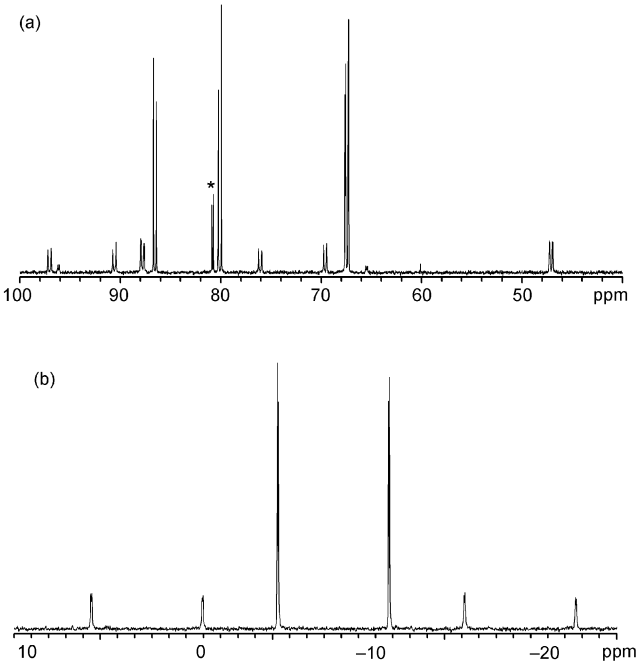


Figure 1. $^{31}P\{^1H\}$ NMR spectrum (162 MHz) of **5a** in $CDCl_3$. (a) Phosphane region. (b) Phosphoranide region for *cis*-**5a**.

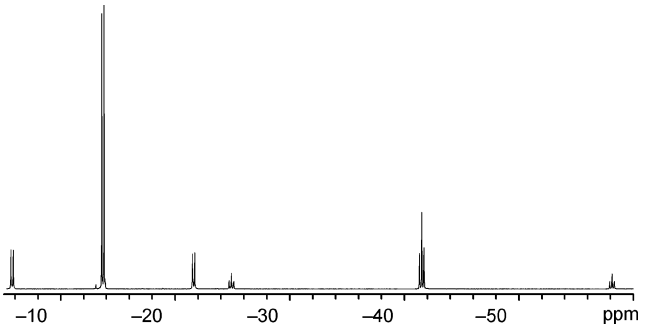


Figure 2. $^{31}P\{^1H\}$ NMR spectrum (162 MHz) of *trans*-**5c** in $CDCl_3$.

Table 2. $^{31}P\{^1H\}$ NMR spectroscopic data of the complexes **5** in $CDCl_3$.

Complex	Phosphane(*t*)[a]			Phosphane(*c*)[b]			Phosphoranide		
	δ_p [ppm]	$^2J_{P,P}$ [Hz]	$^1J_{P,Pt}$ [Hz]	δ_p [ppm]	$^2J_{P,P}$ [Hz]	$^1J_{P,Pt}$ [Hz]	δ_p [ppm]	$^2J_{P,P}$ [Hz]	$^1J_{P,Pt}$ [Hz]
cis-**5a**	83.3	1047, 51.3	3396	67.4	51.3, 9.8	6592	–8.5	1045, 9.8	3508
cis-**5b**	102.8	981, 44.0	3552	83.4	43.9, 17.1	6262	–2.2	981, 17.1	3374
trans-**5a**				80.8	24.4	4962	–45.2	24.4	4756
trans-**5b**				100.6	29.3	4539	–44.5	29.3	4988
trans-**5c**				–15.7	31.7	2563	–43.5	31.7	5378

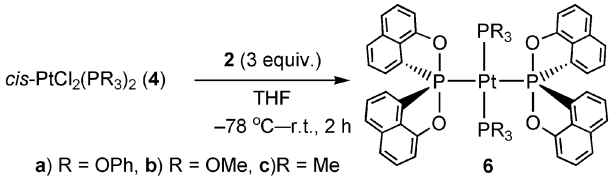
[a] The phosphane(*t*) coordinating *trans* to the phosphoranide ligand. [b] Phosphane(*c*) coordinating *cis* to the phosphoranide ligand.

Table 3. $^{31}P\{^1H\}$ NMR spectroscopic data of *trans*-bis(phosphoranido) complexes **6** in $CDCl_3$.

	Major isomer Phosphane			Phosphoranide[a]		Minor isomer Phosphane			Phosphoranide[a]	
Complex	δ_P [ppm]	$^2J_{P,P}$ [Hz]	$^1J_{P,Pt}$ [Hz]	δ_P [ppm]	$^1J_{P,Pt}$ [Hz]	δ_P [ppm]	$^2J_{P,P}$ [Hz]	$^1J_{P,Pt}$ [Hz]	δ_P [ppm]	$^1J_{P,Pt}$ [Hz]
6a	80.1	51.3	5012	–29.7	2932					
6b	101.1	51.3	4888	–25.4	3005	100.8	51.3	4810	–24.4	3040
6c	–27.3	48.8	2827	–35.5	3318	–28.0	48.8	2822	–35.0	3323

[a] The $^2J_{P,P}$ values for the phosphoranide are omitted.

The reactions of **4** with three equiv. of **2** afforded the corresponding *trans*-bis(phosphoranido)platinum(II) complexes **6** as the major products (Scheme 3, Table 3). The extremely high stereoselectivity in the formation of complex **6a** probably reflects the bulkiness of the phosphoranide ligand. Thus, when the phosphane ligand was the large PPh_3 (with a cone angle of 145°[11]), the generation of the corresponding bis(phosphoranido) complex **6** could not be observed.[12] The ^{31}P NMR spectra of the diastereomeric mixtures showed two pairs of triplets in contrast with the AA′XX′ spin system for *cis*-disposed bis(phosphoranido) complex **3**.[8] The ^{31}P NMR spectrum of *meso*-**6a**, in which the relative stereochemistry at the two pentacoordinate phosphorus atoms is *RS*(*SR*),[13] is shown in Figure 3. Similar to the case of *trans*-**5**, the $^1J_{P,Pt}$ value for the phosphoranide diminishes as the π-acidity of the phosphane ligand increases (Table 3).



Scheme 3. Syntheses of *trans*-bis(phosphoranido) complexes **6**.

The isolation of *meso* isomer of **6a** and the diastereomeric mixtures of **6b** could be achieved by silica gel chromatography (CH_2Cl_2/acetone, 20:1) in 64% and 75% (*de* 50%) yield, respectively. On the other hand, the diastereomeric mixtures of **6c** was isolated by purification with recrystallization in 46% yield (*de* 40%), since the complex **6c** decomposed on silica gel. The complexes **6** are stable in the air or even in refluxing toluene. However, they are consumed entirely in xylene at 150 °C within 8 h to give several unidentified products, while the *cis*-bis(phosphoranido) complex **3** was stable under the same conditions. The relative instability of *trans* complex **6** compared to *cis*-**3** can be explained by the simultaneous interaction of one d_π orbital on platinum with the σ*orbital on phosphorus of two phosphoranide ligands in addition to the absence of stability gained by chelation. It has been indicated that the electron density on the central atom of pentacoordinate heteroatom compounds is lessened since it bears a hypervalent bond, in which the electrons are delocalized into the apical substituents.[2] This is consistent with the phosphoranide ligand acting as π acid.[5a,5c]

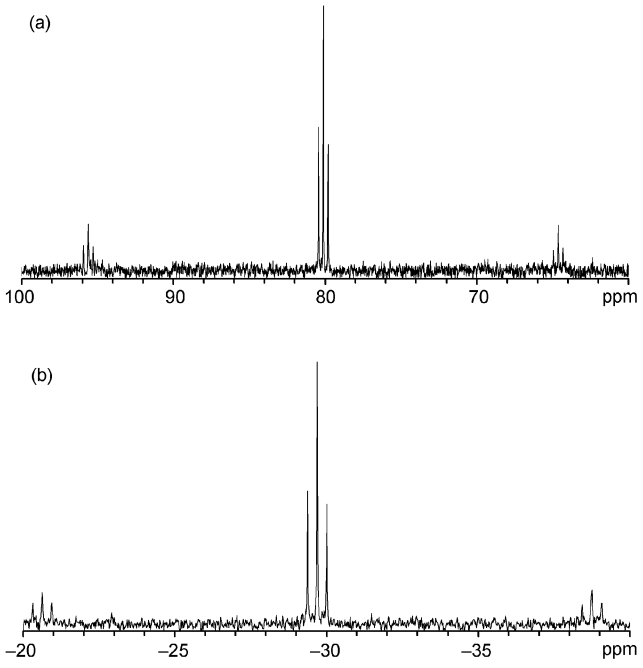


Figure 3. $^{31}P\{^1H\}$ NMR spectrum (162 MHz) of *meso*-**6a** in $CDCl_3$. (a) Phosphane region. (b) Phosphoranide region.

Crystal Structure

The crystal structure of complex **6a** could be elucidated by X-ray structural analysis (Figure 4). The geometry around the platinum atom is an ideal square-planar structure. The P–Pt bond length of 2.398(2) Å for the phosphoranide P atom is slightly longer than that [2.382(2), 2.371(2) Å] of *cis* complex **3B**.[8] This implies that the strong π-acidity of the phosphoranide ligand weakens the *trans* bond in **6a**. The geometry around the hypervalent phosphorus atom is a trigonal bipyramidal (TBP) structure with two oxygen atoms in the apical positions. Similarly to complex **3**, the equatorial C–P–C angle of 105.3° is much smaller than the ideal value (120°), while the sum of the equatorial angles is 360° and the apical O–P–O angle is 180°, which are ideal values for TBP structures. Distortion of the TBP geometry of most phosphoranes is along the Berry pseudorotation coordinate or the turnstile coordinate.[5a,9b,14] However, this rule is not necessarily applied to the metalated phosphoranes.[6a,8] The TBP geometry of complex **6a** does not distort along either permutation mechanism. The equatorial C–P–C angle of complex **6a** is slightly larger

than that of complex **3B** (101.0°, 103.9°),[8] probably due to the *trans* arrangement of the two bulky phosphoranide ligands.

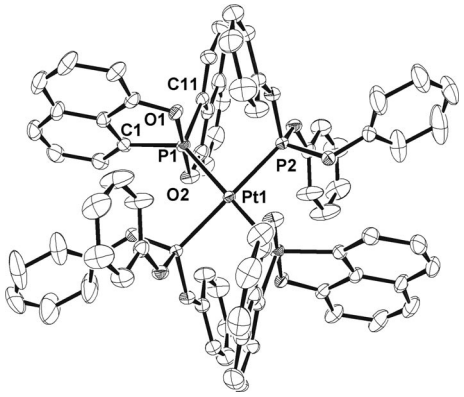


Figure 4. The ORTEP drawing of **6a** showing the thermal ellipsoids at the 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–O1 1.813(2), P1–O2 1.815(2), P1–Pt1 2.398(2), P1–C1 1.829(3), P1–C11 1.832(4), P2–Pt1 2.275(2); O1–P1–O2 179.58(12), Pt1–P1–C1 129.35(13), C1–P1–C11 105.30(17), C11–P1–Pt1 125.35(10), O1–P1–Pt1 90.16(8), O1–P1–C1 87.58(14), O1–P1–C11 92.16(15), O2–P1–Pt1 90.24(9), O2–P1–C1 92.09(14), O2–P1–C11 87.69(16), P1–Pt1–P2 86.53(3).

Conclusions

The reaction of 1 equiv. of lithium phosphoranide **2** with *cis*-$PtCl_2(PR_3)_2$ (**4**) (R = OPh, OMe, Me) gave *cis* and *trans*-monophosphoranido complexes **5**, and it is in contrast with the formation of the *cis*-bis(phosphoranido) complexes **3**. We were able to synthesize *trans*-bis(phosphoranido)platinum(II) complexes **6**, the first square-planar complex with two phosphoranide ligands in a *trans* arrangement, from *cis*-$PtCl_2(PR_3)_2$ (**4**) (R = OPh, OMe, Me) and an excess of the lithium phosphoranide **2**. These structural features could be verified by the X-ray structural analysis of complex **6a** bearing triphenyl phosphites. The *trans* complexes **6** were thermally unstable relative to the *cis* complexes **3**. Mechanistic examinations are currently underway and the results will be described in due course.

Experimental Section

General: All reagents and solvents were of standard reagent grade and were used in the syntheses without further purification except for benzene and THF. All reactions were carried out under a nitrogen atmosphere. Benzene and THF used in the syntheses were freshly distilled from CaH_2 and Na-benzophenone, respectively, and transferred under the positive pressure of nitrogen via a syringe. Phosphorane **1**[8a,9b] and $PtCl_2(COD)$[15] were prepared according to published procedures. Column chromatography was performed using Silica Gel 60N (Kanto Chemical Co., Inc., 0.063–0.210 mm particle size). Melting points were measured with a Yanaco micro melting-point apparatus and are uncorrected. ^1H and ^{31}P NMR spectra were recorded with a JEOL EX-400 spectrometer. ^1H NMR chemical shifts (δ) are given in ppm downfield from internal Me_4Si or from residual chloroform (δ = 7.26). ^{31}P NMR chemical shifts (δ) are given in ppm downfield from external 85% H_3PO_4. Elemental analyses were performed with a Perkin–Elmer 2400 CHN elemental analyzer.

General Procedure for the Preparation of *cis*-$PtCl_2(PR_3)_2$ (4): To a solution of $PtCl_2(COD)$ (1.00 g, 2.67 mmol) in benzene (10 mL) was added 2 equiv. of phosphane. After the reaction mixture was stirred for 1 h at room temperature, the resulting white crystals were filtered and washed with benzene. **4a**: yield 2.32 g, 98%. **4b**: yield 1.18 g, 86%. **4c**: yield 1.07 g, 96%. The ^{31}P NMR spectroscopic data of the complexes **4** [R = OPh (**4a**),[16] OMe (**4b**),[17] Me (**4c**)][18] agreed with the literature data.

General Procedure for the Syntheses of $PtCl\{P(C_{10}H_6O)_2\}(PR_3)_2$ (5): To a solution of **1** (200 mg, 0.632 mmol) in THF (30 mL) was added *t*BuLi (1.50 M *n*-pentane solution, 0.43 mL, 0.65 mmol) at –78 °C. After removal of the cooling bath, the solution was stirred at room temperature for 10 min and then transferred to a suspension of 1 equiv. of *cis*-$PtCl_2(PR_3)_2$ (**4**) in THF (100 mL) at –78 °C. The reaction mixture was stirred at room temperature for 2 h and then the solvents were removed under reduced pressure. Purification of the residue was carried out by silica gel column chromatography with CH_2Cl_2/acetone (20:1) as eluent. ^1H NMR spectroscopic data of *trans*-**5a**,**b** could not be assigned entirely due to the presence of these impurities.

5a: (R = OPh, *cis:trans*, 91:9): Yellow powder; yield 470 mg, 64%; m.p. 133 °C (dec.). $C_{56}H_{42}ClO_8P_3Pt$ (1166.43): calcd. C 57.66, H 3.64; found C 57.82, H 3.73. ^1H NMR ($CDCl_3$, 400 MHz): *cis* isomer δ = 7.99–7.92 (m, 2 H, Naph), 7.67 (dd, $J_{H,H}$ = 8.1, 2.7 Hz, 1 H, Naph), 7.41–7.33 (m, 4 H, Naph), 7.17–7.01 (m, 25 H, Naph and Ph), 6.98 (d, $J_{H,H}$ = 8.1 Hz, 1 H, Naph), 6.88–6.84 (m, 8 H, Naph and Ph), 6.73 (d, $J_{H,H}$ = 7.6 Hz, 1 H, Naph) ppm; *trans* isomer: δ = 7.85 (dd, $J_{H,H}$ = 7.3, $J_{H,P}$ = 11.5 Hz, 2 H, Naph), 7.52 (dd, $J_{H,H}$ = 8.1, 2.7 Hz, 2 H, Naph), 7.41–7.33 (m, 4 H, Naph), 7.17–6.84 (m, 32 H, Naph and Ph), 6.48 (d, $J_{H,H}$ = 7.6 Hz, 2 H, Naph) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): *cis* isomer: δ = 83.3 [dd, $J_{P,P}$ = 1047, 51.3, $J_{P,Pt}$ = 3396 Hz, $P(OPh)_3$], 67.4 [dd, $J_{P,P}$ = 51.3, 9.8, $J_{P,Pt}$ = 6592 Hz, $P(OPh)_3$], –8.5 [dd, $J_{P,P}$ = 1045, 9.8, $J_{P,Pt}$ = 3508 Hz, $P(C_{10}H_6O)_2$] ppm; *trans* isomer: δ = 80.8 [d, $J_{P,P}$ = 24.4, $J_{P,Pt}$ = 4962 Hz, $P(OPh)_3$], –45.2 [t, $J_{P,P}$ = 24.4, $^1J_{P,Pt}$ = 4756 Hz, $P(C_{10}H_6O)_2$] ppm.

5b: (R = OMe, *cis:trans*, 91:9): Yellow powder; yield 356 mg, 71%; m.p. 164 °C (dec.). $C_{26}H_{30}ClO_8P_3Pt$ (794.00): calcd. C 39.33, H 3.81; found C 39.25, H 3.84. ^1H NMR ($CDCl_3$, 400 MHz): *cis* isomer: δ = 7.95 (dd, $J_{H,H}$ = 6.8, $J_{H,P}$ = 10.7 Hz, 1 H, Naph), 7.89 (dd, $J_{H,H}$ = 7.8, $J_{H,P}$ = 10.7 Hz, 1 H, Naph), 7.67–7.63 (m, 2 H, Naph), 7.42–7.29 (m, 4 H, Naph), 7.09 (d, $J_{H,H}$ = 7.8 Hz, 2 H, Naph), 6.80 (d, $J_{H,H}$ = 6.8 Hz, 1 H, Naph), 6.69 (d, $J_{H,H}$ = 7.8 Hz, 1 H, Naph), 3.76 (d, $J_{H,P}$ = 12.7 Hz, 9 H, Me), 3.39 (d, $J_{H,P}$ = 13.7 Hz, 9 H, Me) ppm; *trans* isomer: δ = 7.85–7.82 (m, 2 H, Naph), 7.61–7.58 (m, 2 H, Naph), 7.42–7.08 (m, 6 H, Naph), 6.73 (d, $J_{H,H}$ = 7.8 Hz, 2 H, Naph), 3.43 (d, $J_{H,P}$ = 6.7 Hz, 18 H, Me) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): *cis* isomer: δ = 102.8 [dd, $J_{P,P}$ = 981, 44.0, $J_{P,Pt}$ = 3552 Hz, $P(OMe)_3$], 83.4 [dd, $J_{P,P}$ = 43.9, 17.1, $J_{P,Pt}$ = 6262 Hz, $P(OMe)_3$], –2.2 [dd, $J_{P,P}$ = 981, 17.1, $J_{P,Pt}$ = 3374 Hz, $P(C_{10}H_6O)_2$] ppm; *trans* isomer: δ = 100.6 [d, $J_{P,P}$ = 29.3, $J_{P,Pt}$ = 4539 Hz, $P(OMe)_3$], –44.5 [t, $J_{P,P}$ = 29.3, $J_{P,Pt}$ = 4988 Hz, $P(C_{10}H_6O)_2$] ppm.

***trans*-5c:** (R = Me): Yellow powder; yield 267 mg, 61%; m.p. 255 °C (dec.). $C_{26}H_{30}ClO_2P_3Pt$ (698.00): calcd. C 44.74, H 4.34; found C 44.43, H 4.32. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.85 (ddd, $J_{H,H}$ = 7.1, 3.7, $J_{H,P}$ = 11.0 Hz, 2 H, Naph), 7.67 (dd, $J_{H,H}$ = 8.1, 2.7 Hz, 2 H, Naph), 7.40 (t, $J_{H,H}$ = 8.1 Hz, 2 H, Naph), 7.36–7.32 (m, 2

H, Naph), 7.09 (dd, $J_{H,H}$ = 8.3, 1.7 Hz, 2 H, Naph), 6.77 (d, $J_{H,H}$ = 7.6 Hz, 2 H, Naph), 1.25 (virtual t, $J_{H,P}$ = 3.9 Hz, 18 H, Me) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = –15.7 (d, $J_{P,P}$ = 31.7, $J_{P,Pt}$ = 2563 Hz, PMe_3), –43.5 [t, $J_{P,P}$ = 31.7, $J_{P,Pt}$ = 5378 Hz, $P(C_{10}H_6O)_2$] ppm.

***meso-trans*-Pt{P($C_{10}H_6O$)$_2$}$_2${P(OPh)$_3$}$_2$ (*meso*-6a):** To a solution of **1** (500 mg, 1.58 mmol) in THF (30 mL) was added *t*BuLi (1.50 M *n*-pentane solution, 1.05 mL, 1.58 mmol) at –78 °C. After removal of the cooling bath, the solution was stirred at room temperature for 10 min and then transferred to a suspension of 1/3 equiv. of *cis*-$PtCl_2${$P(OPh)_3$}$_2$ (**4a**) (460 mg, 0.519 mmol) in THF (100 mL) at –78 °C. The reaction mixture was stirred at room temperature for 2 h and then the solvents were removed under reduced pressure. Purification of the residue was carried out by silica gel column chromatography with CH_2Cl_2 as eluent to give *meso*-**6a** as a yellow powder; yield 480 mg, 64%; m.p. 245 °C (dec.). $C_{76}H_{54}O_{10}P_4Pt$ (1446.27): calcd. C 63.11, H 3.77; found C 63.27, H 3.92. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.67 (dd, $J_{H,H}$ = 6.6, $J_{H,P}$ = 11.7 Hz, 4 H, Naph), 7.29 (d, $J_{H,H}$ = 7.6 Hz, 4 H, Naph), 7.08–6.99 (m, 26 H, Naph and Ph), 6.85 (d, $J_{H,H}$ = 8.3 Hz, 4 H, Naph), 6.75 (d, $J_{H,H}$ = 7.3 Hz, 12 H, Ph), 6.01 (d, $J_{H,H}$ = 7.6 Hz, 4 H, Naph) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ = 80.1 [t, $J_{P,P}$ = 51.3, $J_{P,Pt}$ = 5012 Hz, $P(OPh)_3$], –29.7 [t, $J_{P,P}$ = 51.3, $J_{P,Pt}$ = 2932 Hz, $P(C_{10}H_6O)_2$] ppm.

***trans*-Pt{P($C_{10}H_6O$)$_2$}$_2${P(OMe)$_3$}$_2$ (6b):** To a solution of **1** (1.53 g, 4.84 mmol) in THF (60 mL) was added *t*BuLi (1.50 M *n*-pentane solution, 3.30 mL, 4.95 mmol) at –78 °C. After removal of the cooling bath, the solution was stirred at room temperature for 10 min and then added to a suspension of 1/3 equiv. of *cis*-$PtCl_2$-$[P(OMe)_3]_2$ (**4b**) (834 mg, 1.62 mmol) in THF (100 mL) at –78 °C. The reaction mixture was stirred at room temperature for 2 h and the solvents were removed under reduced pressure. Purification of the residue was carried out by silica gel column chromatography (CH_2Cl_2/acetone, 20:1) to give the diastereomeric mixture (75:25) of **6b** as a yellow powder; yield 1.31 g, 75%; m.p. 245 °C (dec.). $C_{46}H_{42}O_{10}P_4Pt$ (1073.84): calcd. C 51.45, H 3.95; found C 51.44, H 3.87. ^1H NMR ($CDCl_3$, 400 MHz): major isomer: δ = 7.77–7.73 (m, 4 H, Naph), 7.59 (d, $J_{H,H}$ = 8.3 Hz, 4 H, Naph), 7.38 (t, $J_{H,H}$ = 8.1 Hz, 4 H, Naph), 7.34–7.27 (m, 4 H, Naph), 7.10 (d, $J_{H,H}$ = 8.1 Hz, 4 H, Naph), 6.74 (d, $J_{H,H}$ = 7.3 Hz, 4 H, Naph), 3.01 (t, $J_{H,P}$ = 6.3 Hz, 18 H, Me) ppm; minor isomer: δ = 7.82–7.78 (m, 4 H, Naph), 7.57 (d, $J_{H,H}$ = 8.3 Hz, 4 H, Naph), 7.34–7.27 (m, 8 H, Naph), 7.04 (d, $J_{H,H}$ = 8.1 Hz, 4 H, Naph), 6.70 (d, $J_{H,H}$ = 7.6 Hz, 4 H, Naph), 3.03 (t, $J_{H,P}$ = 6.3 Hz, 18 H, Me) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): major isomer: δ = 101.1 (t, $J_{P,P}$ = 51.3, $J_{P,Pt}$ = 4888 Hz, PMe_3), –25.4 [t, $J_{P,P}$ = 51.3, $J_{P,Pt}$ = 3005 Hz, $P(C_{10}H_6O)_2$] ppm; minor isomer: δ 100.8 (t, $J_{P,P}$ = 51.3, $J_{P,Pt}$ = 4810 Hz, PMe_3), –24.4 [t, $J_{P,P}$ = 51.3, $J_{P,Pt}$ = 3040 Hz, $P(C_{10}H_6O)_2$] ppm.

***trans*-Pt{P($C_{10}H_6O$)$_2$}$_2$(PMe_3)$_2$ (6c):** To a solution of **1** (909 mg, 2.87 mmol) in THF (30 mL) was added *t*BuLi (1.50 M *n*-pentane solution, 1.90 mL, 2.85 mmol) at –78 °C. After removal of the cooling bath, the solution was stirred at room temperature for 10 min and then added to a suspension of 1/3 equiv. of *cis*-$PtCl_2(PMe_3)_2$ (**4c**) (400 mg, 0.957 mmol) in THF (100 mL) at –78 °C. The reaction mixture was stirred at room temperature for 2 h and then the solvents were removed under reduced pressure. Purification of the residue was carried out by recrystallization from CH_2Cl_2/hexane to give the diastereomeric mixture (70:30) of **6c** as an orange powder; yield 435 mg, 46%; m.p. 228 °C (dec.). $C_{46}H_{42}O_4P_4Pt$ (977.84): calcd. C 56.50, H 4.34; found C 56.52, H 4.38. ^1H NMR ($CDCl_3$, 400 MHz): major isomer: δ = 7.77–7.73 (m, 4 H, Naph), 7.65 (d, $J_{H,H}$ = 8.1 Hz, 4 H, Naph), 7.47 (t, $J_{H,H}$ = 7.8 Hz, 4 H, Naph), 7.32–7.24 (m, 4 H, Naph), 7.11 (d, $J_{H,H}$ = 8.3 Hz, 4 H, Naph), 6.85 (d, $J_{H,H}$ = 7.3 Hz, 4 H, Naph), 1.06–0.98 (m, 18 H, Me) ppm; minor isomer: δ = 7.88–7.84 (m, 4 H, Naph), 7.61 (d, $J_{H,H}$ = 8.3 Hz, 4 H, Naph), 7.37 (t, $J_{H,H}$ = 7.8 Hz, 4 H, Naph), 7.32–7.24 (m, 4 H, Naph), 7.03 (d, $J_{H,H}$ = 8.3 Hz, 4 H, Naph), 6.84 (d, $J_{H,H}$ = 7.3 Hz, 4 H, Naph), 1.06–0.98 (m, 18 H, Me) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): major isomer: δ = –27.3 (t, $J_{P,P}$ = 48.8, $J_{P,Pt}$ = 2827 Hz, PMe_3), –35.5 [t, $J_{P,P}$ = 48.8, $J_{P,Pt}$ = 3318 Hz, $P(C_{10}H_6O)_2$] ppm; minor isomer: δ –28.0 (t, $J_{P,P}$ = 48.8, $J_{P,Pt}$ = 2822 Hz, PMe_3), –35.0 [t, $J_{P,P}$ = 48.8, $J_{P,Pt}$ = 3323 Hz, $P(C_{10}H_6O)_2$] ppm.

X-ray Structure Determination: The diffraction data for the complex *meso*-**6a** were measured with a Rigaku AFC-7*R* diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71069). The data were collected at 296 K using MSC/AFC diffractometer control software. The structure was solved by direct methods using SIR92.[19] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined using a riding model. Crystal data and structure refinement are summarized in Table 4.

Table 4. Crystal data and structure refinement for *meso*-**6a**.

	meso-**6a**
Empirical formula	$C_{76}H_{54}O_{10}P_4Pt$
M_r	1446.24
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	11.530(9)
b [Å]	22.048(7)
c [Å]	12.735(6)
β [°]	101.75(4)
V [Å^3]	3169.6(29)
Z	2
D_c [g cm^{-3}]	1.515
μ(Mo-K_α) [cm^{-1}]	23.682
Number of reflections collected	7618
Number of independent reflections (R_{int})	7268 (0.057)
Number of parameters	468
R_1 [$I > 2\sigma(I)$]	0.0318
wR_2 (all data)	0.0930
GOF	0.953

CCDC-743272 (for *meso*-**6a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): NMR spectra of complexes **5**, **6**, and **3B**.

[1] a) R. J. Cross, *Adv. Inorg. Chem.* **1989**, *34*, 219–292; b) M. L. Tobe, J. Burgess, *Inorganic Reaction Mechanisms*, Longman, Essex, UK, **1999**; c) J. Cooper, T. Ziegler, *Inorg. Chem.* **2002**, *41*, 6614–6622.

[2] K.-y. Akiba, *Chemistry of Hypervalent Compounds*, Wiley-VCH, New York, **1999**.

[3] C. W. Perkins, J. C. Martin, A. J. Arduengo III, W. Lau, A. Alegria, J. K. Kochi, *J. Am. Chem. Soc.* **1980**, *102*, 7753–7759.

[4] The 10–P–4 phosphoranides are also capable of functioning as electrophiles, see: a) K. Kajiyama, S. Kojima, K.-y. Akiba, *Tetrahedron Lett.* **1996**, *37*, 8409–8412; b) K. Kajiyama, M. Yoshimune, M. Nakamoto, S. Matsukawa, S. Kojima, K.-y. Akiba, *Org. Lett.* **2001**, *3*, 1873–1875; c) S. Matsukawa, S. Kojima, K. Kajiyama, Y. Yamamoto, K.-y. Akiba, S. Re, S. Nagase, *J. Am. Chem. Soc.* **2002**, *124*, 13154–13170; d) K. Kajiyama, M. Yoshimune, S. Kojima, K.-y. Akiba, *Eur. J. Org. Chem.* **2006**, 2739–2746.

[5] Review or accounts: a) C. D. Montgomery, *Phosphorus Sulfur Silicon* **1993**, *84*, 23–34; b) K. B. Dillon, *Chem. Rev.* **1994**, *94*, 1441–1456; c) H. Nakazawa, K. Kubo, K. Miyoshi, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 2255–2267.
[6] a) R. Faw, C. D. Montgomery, S. J. Rettig, B. Shurmer, *Inorg. Chem.* **1998**, *37*, 4136–4138; b) K. Toyota, Y. Yamamoto, K.-y. Akiba, *J. Chem. Res. (S)* **1999**, 386–387.
[7] I. Tkatchenko, *Phosphorus Sulfur Silicon* **1983**, *18*, 311–314.
[8] a) K. Kajiyama, Y. Hirai, T. Otsuka, H. Yuge, T. K. Miyamoto, *Chem. Lett.* **2000**, *29*, 784–785; b) K. Kajiyama, H. Yuge, T. K. Miyamoto, *Phosphorus Sulfur Silicon* **2002**, *177*, 1433–1436.
[9] a) K. Kajiyama, A. Nakamoto, S. Miyazawa, T. K. Miyamoto, *Chem. Lett.* **2003**, *32*, 332–333; b) K. Kajiyama, T. K. Miyamoto, K. Sawano, *Inorg. Chem.* **2006**, *45*, 502–504.
[10] T. G. Appleton, H. C. Clark, L. E. Manzer, *Coord. Chem. Rev.* **1973**, *10*, 335–422.
[11] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313.
[12] The formation of a 1:1 mixture of *cis* and *trans*-**5** was speculated from ^{31}P NMR analysis. However, the complexes decomposed slowly during purification by silica gel chromatography or recrystallization and were obtained as a mixture containing unidentified products.
[13] J. C. Martin, T. M. Balthazor, *J. Am. Chem. Soc.* **1977**, *99*, 152–162.
[14] R. R. Holmes, J. A. Deiters, *J. Am. Chem. Soc.* **1977**, *99*, 3318–3326.
[15] J. X. McDermott, J. F. White, G. M. Whitesides, *J. Am. Chem. Soc.* **1976**, *98*, 6521–6528.
[16] N. Ahmad, E. W. Ainscough, T. A. James, S. D. Robinson, *J. Chem. Soc., Dalton Trans.* **1973**, 1148–1150.
[17] Q.-B. Bao, T. B. Brill, *Inorg. Chem.* **1987**, *26*, 3447–3452.
[18] L. Goggin, P. R. J. Goodfellow, S. R. Haddock, J. R. Knight, F. J. S. Reed, B. F. Taylor, *J. Chem. Soc., Dalton Trans.* **1974**, 523–533.
[19] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435.

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After publication in Early View, a small error in Scheme 1 has been corrected.

