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Reaction of "Cyclenphosphorane" with *cis*-Dichlorobis(triphenylphosphine)platinum(II). Formation of Bidentate and Monodentate Phosphoranide Adducts and X-ray Crystal Structure of (η^2-cyclenP)PtClPPh$_3$

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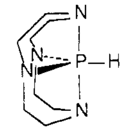
The reaction of cyclenphosphorane (cyclenPH) with *cis*-dichlorobis(triphenylphosphine)platinum(II) leads to two Pt-containing products, (η^2-cyclenP)PtClPPh$_3$ (**1**) and [*cis*-(H$_2$cyclenP)PtCl$_2$PPh$_3$]Cl (**2**), in >95% yield each. Both **1** and **2** are stable to atmospheric oxygen; however, **2** is hygroscopic. The X-ray crystal structure of **1** was obtained and shows the four ligated atoms to Pt to all lie in the same plane as Pt; the sum of the cis angles about Pt is 359.6 (8)°. The cyclenP ligand in **1** is in an approximate trigonal-bipyramidal geometry. There is one long P–N bond (in the P–Pt–N triangle) of 1.872 (11) Å while the other three P–N bonds are between 1.68 and 1.70 Å. $C_{26}H_{31}ClN_4P_2Pt$ is monoclinic, space group $P2_1/n$. Unit cell parameters: $a = 11.562$ (2) Å, $b = 14.272$ (2) Å, $c = 15.556$ (2) Å, $\beta = 94.01$ (1)°, $Z = 4$; $R = 0.039$, $R_w = 0.046$. By addition of HCl, **1** can be converted to **2**.

Introduction

Recently, examples of molecules featuring pentacoordinated group 15 atoms bonded to a single transition-metal species, i.e. R$_4$E–M (R = main-group moiety, E = group 15 atom, M = transition-metal species), have been reported. These molecules have been synthesized by a variety of methods, including nucleophilic substitution at a pentacoordinated phosphorus by transition-metal carbonyl anions[2] and oxidative addition to a metallo-substituted R$_2$E–M species.[3] Other, less straightforward, syntheses involve proton abstraction from polycyclic, bidentate ligands with coordinated P and N atoms[4] and reaction of a pentacoordinated phosphorane with transition-metal carbonyl dimers.[5]

We herein report the synthesis of two platinum compounds, one containing a bidentate and the other a monodentate phosphoranide,[6] R$_4$P:$^-$, ligand from the reaction of cyclenPH[5,7,8] with *cis*-Cl$_2$Pt(PPh$_3$)$_2$.



cyclenPH

Results and Discussion

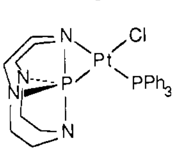
1. Synthesis. When cyclenPH is allowed to react with *cis*-Cl$_2$Pt(PPh$_3$)$_2$ in a 1:1 molar ratio in THF solution, two Pt-containing products are formed, **1** and **2**, as well as free PPh$_3$. The mass of the free PPh$_3$ isolated indicates the stoichiometry of the reaction to be

$$2\text{cyclenPH} + 2\,cis\text{-}Cl_2Pt(PPh_3)_2 \rightarrow 2PPh_3 + \mathbf{1} + \mathbf{2} \quad (1)$$

The solubilities of **1** and **2** are markedly different: **1** is soluble in most polar organic solvents such as THF and CH$_2$Cl$_2$ while **2** is soluble only in dimethyl sulfoxide (Me$_2$SO). Both compounds are stable, though **2** is hygroscopic.

Spectral data for the starting materials and products are collected in Table I. The $^{31}P\{^1H\}$ NMR spectra of **1** and **2** are very similar and feature one resonance in the pentacoordinated phosphorus region (upfield, negative δ) and another resonance in the complexed PPh$_3$ region. Each resonance shows ^{195}Pt satellites. In addition, the peaks are split into doublets due to two-bond phosphorus–phosphorus coupling. The fact that the peaks are doublets indicates that only one cyclenP and one PPh$_3$ are bonded to Pt in both **1** and **2**. Moreover, the small values of $^2J_{PP}$ suggest a cis arrangement of phosphorus atoms.[9] The ^1H NMR spectra of **1** and **2** show no upfield resonances, ruling out the possibility of a direct Pt–H bond in both compounds.

A single band in the ν_{Pt-Cl} region of the IR spectrum is observed for **1** (see Table I). Also, its (EI) mass spectrum shows a molecular ion at m/e 691 and corresponds to (cyclenP)PtClPPh$_3^+$. These data suggest the following structure for **1**:



1

The bidentate nature of the cyclenP phosphoranide ligand,[5,10] as well as related ligands,[4] has been observed before. The structure of **1** was confirmed by X-ray crystallography (see below).

From the above balanced equation, **2** would be expected to have the empirical formula **1**·2HCl. (This presumes that hydrogen is not lost as H$_2$, and we find no evidence of any gas being evolved.) The elemental analysis obtained (see Experimental Section) agrees with this formulation. The most likely (non-Pt) sites for the protons are the nitrogens; however, we find no obvious peak in

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(1) (a) Southern Methodist University. (b) Present address: Vanderbilt University. (c) The University of Texas at Austin.

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(5) Lattman, M.; Chopra, S. K.; Cowley, A. H.; Arif, A. M. *Organometallics* **1986**, *5*, 677.

(6) Phosphoranide anions have been isolated: (a) Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 7434. (b) Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 4623.

(7) The cyclic molecule 1,4,7,10-tetraazacyclododecane has been termed "cyclen" (Collman, J. P.; Schneider, P. W. *Inorg. Chem.* **1966**, *5*, 1380). The word "cyclenphosphorane" has been used to describe the pentacoordinated phosphorus molecule bonded to the cyclen macrocycle (see ref 8). We use the abbreviation cyclenPH for this molecule.

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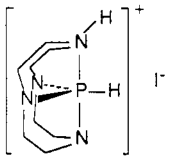
Table I. Spectral Data[a]

compd	^{31}P/ppm	^{13}C/ppm		^{1}H/ppm	IR/cm^{-1}
		cyclen	Ph		ν_{PtCl}
cyclenPH[b]	-55 ($^1J_{PH}$ = 623 Hz)	44.2 ($^2J_{PC}$ = 10 Hz)		2.77, 3.00 (m, CH_2, 16 H)	
				6.77 (d, PH, 1 H, $^1J_{PH}$ = 623 Hz)	
PPh_3	-6		128.4 ($^2J_{PC}$ = 7 Hz)	7.45 (br s)	
			128.6		
			133.6 ($^3J_{PC}$ = 20 Hz)		
			137.2 ($^1J_{PC}$ = 11 Hz)		
cis-$Cl_2Pt(PPh_3)_2$	14 ($^1J_{PtP}$ = 3672 Hz)		127.6–135.2[c]	7.1–7.5 (comp m)	279, 303 (s)
1	-55 (PN, $^1J_{PtP}$ = 3612 Hz)	44.5, 44.8, 45.2	127.8 ($^2J_{PC}$ = 10 Hz)	2.2–3.6 (comp m, CH_2, 16 H)	249 (s)
	21 (PC, $^1J_{PtP}$ = 4702 Hz)	45.4, 47.4, 50.1	130.1	7.33, 7.62 (m, CH, 15 H)	
	($^2J_{PP}$ = 2 Hz)		132.1 ($^1J_{PC}$ = 62 Hz)		
			134.4 ($^3J_{PC}$ = 12 Hz)		
2	-59 (PN, $^1J_{PtP}$ = 5567 Hz)	(39.8, 40.2, 40.6)[d]	127.9 ($^2J_{PC}$ = 10 Hz)	1.7–3.5 (comp m, CH, 16 H)	275, 300 (s)
	15 (PC, $^1J_{PtP}$ = 4070 Hz)	41.7, 42.1, 42.8	130.7	$\left.\begin{array}{l}\text{7.50 (br s, CH)}\\ \text{7.79 (m, CH and NH)}\end{array}\right\}$ (17H)	
	($^2J_{PP}$ = 10 Hz)	43.5	130.8 ($^1J_{PC}$ = 62 Hz)		
			135.4 ($^3J_{PC}$ = 10 Hz)		

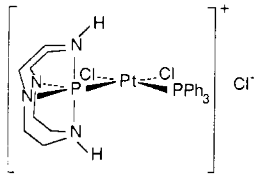
[a] All NMR data recorded in $CDCl_3$ except those for **2** (Me_2SO-d_6). IR data recorded in Nujol mulls between polyethylene plates. [b] Reported data:[8a] ^{31}P, δ -54.5 ($^1J_{PH}$ = 621 Hz); ^{13}C, δ 45.0 ($^2J_{PC}$ = 8.8 Hz); ^1H, δ 6.88 (d, 1 H, $^1J_{PH}$ = 628 Hz), 3.03, 2.83 (m, 16 H). ^1H chemical shifts move upfield with increasing concentration. [c] Complex; Ph groups not equivalent. [d] Peaks in parentheses overlap with solvent peaks.

the ^1H NMR spectrum of **2** to assign to N^+–H. In the ^1H NMR spectrum of $[cyclenPH_2]I$,[5] the N^+–H resonance appeared as a broad, low-intensity peak at δ 7.4 that moved downfield and broadened, almost into the base line, as the concentration decreased. We observe no such phenomenon here, though **2** is not highly soluble in Me_2SO. What is found is an anomaly in the integration of the CH vs. CH_2 region of the ^1H NMR spectrum: the integrated phenyl region is *larger* than the methylene region. In fact, a CH/CH_2 proton ratio of 17/16 (instead of 15/16) is observed. When D_2O is added to the NMR tube, the resulting spectrum shows that the "phenyl" peak at δ 7.79 has diminished in intensity and the integrated phenyl/methylene region is in the expected 15/16 ratio. Thus, the N^+–H resonance must be broad and coincident with the phenyl resonance at δ 7.79. No change in the ^{31}P NMR spectrum is observed with the D_2O addition. The ν_{PtCl} region in the IR spectrum of **2** shows two bands and looks very similar to the corresponding region in the starting material, *cis*-$Cl_2Pt(PPh_3)_2$ (see Table I). This observation, coupled with the fact that a conductometric titration of **2** with $AgNO_3$ in Me_2SO showed the presence of only one ionic Cl, suggests two covalent Pt–Cl bonds.



$[cyclenPH_2]$ I

The above evidence leads to the following structure for **2**:



2

All attempts to obtain an X-ray structure of **2** have, thus far, failed. The pentacoordinated phosphorus is drawn as a trigonal bipyramid (tbp), which is consistent with previous structures: cyclenPH,[11a] cyclenPF,[11b] and the dimer cyclenP–Pcyclen[12] have been found to have distorted tbp geometries about phosphorus. Protonation of the axial nitrogens is consistent with their basic nature since one axial nitrogen is found to coordinate to the metal atom in many complexes such as **1**, (η^2-cyclenP)MoCp$(CO)_2$ (Cp = η^5-C_5H_5), and (η^2-cyclenP)$Co(CO)_3$.[5,10] Also, the structure of cyclenPH·$2BH_3$ has been obtained[13] and shows a tbp geometry for cyclenPH with each BH_3 coordinated to an axial nitrogen. Finally, cyclenPH can be protonated at one of the nitrogen atoms to form the $cyclenPH_2^+$ cation without rupture of the P–N bond.[5]

Nitrogen atoms bonded to phosphorus are, in general, not very nucleophilic.[9a,14,15] However, this appears not to be the case for the axial nitrogens in cyclenP derivatives. This increased basicity may arise from two sources: first of all, the ring structure of the cyclenP group fixes the axial nitrogens in a more pyramidal geometry compared to the equatorial nitrogens, as has been shown in cyclenPF[11b] and cyclenP–Pcyclen.[12] Secondly, the so-called "hypervalent" three-center four-electron bond places significantly more electron density at the axial positions compared to the equatorial positions in a tbp.[16] This may result in higher energy lone-pair orbitals on the axial nitrogens compared to the equatorial nitrogens. Alternatively, the hypervalent bond may serve as a polarizable source of electrons to stabilize the positive charge on nitrogen.

At present, the mechanism of this reaction is unknown but must involve a species that can add HCl, ultimately leading to **2**. A number of molecules in this reaction are potential candidates: some tetracoordinate Pt(II) molecules are known to oxidatively add HCl.[17] However, no reaction occurred when HCl was bubbled into a CH_2Cl_2 solution of *cis*-$Cl_2Pt(PPh_3)_2$. cyclenPH adds HI to form $[cyclenPH_2]I$ (though the reaction pathway was

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(11) (a) A structure of poor quality was obtained for cyclenPH: Hamerlinck, J. H. H.; Schipper, P.; Buck, H. M. *J. Am. Chem. Soc.* **1983**, *105*, 385. (b) Richman, J. E. *Tetrahedron Lett.* **1977**, 559.

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(15) A few (non-cyclenP) examples of tetracoordinated nitrogen bonded to phosphorus are known: (a) Febvay, J.; Casabianca, F.; Riess, J. G. *J. Am. Chem. Soc.* **1984**, *106*, 7985. (b) Grec, D.; Hubert-Pfalzgrapf, L. G.; Riess, J. G. *J. Am. Chem. Soc.* **1980**, *102*, 7133. (c) Milbrath, D. S.; Verkade, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 6607. (d) Laube, B. L.; Bertrand, R. D.; Casedy, G. A.; Compton, R. D.; Verkade, J. G. *Inorg. Chem.* **1967**, *6*, 173. (e) White, D. W.; Karcher, B. A.; Jacobson, R. A.; Verkade, J. G. *J. Am. Chem. Soc.* **1979**, *101*, 4921. (f) Kroshefsky, R. D.; Verkade, J. G.; Pipal, J. R. *Phosphorus Sulfur* **1979**, *6*, 377. (g) Fleming, S.; Parry, R. W. *Inorg. Chem.* **1972**, *11*, 1. (h) Fleming, S.; Lupton, M. K.; Jekot, K. *Inorg. Chem.* **1972**, *11*, 2534. See also ref 4.

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(17) (a) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1962**, 5075. (b) Glockling, F.; Hooton, K. A. *J. Chem. Soc. A* **1968**, 826. (c) See also: Hartley, F. R. *The Chemistry of Platinum and Palladium*; Halsted: New York, 1973.

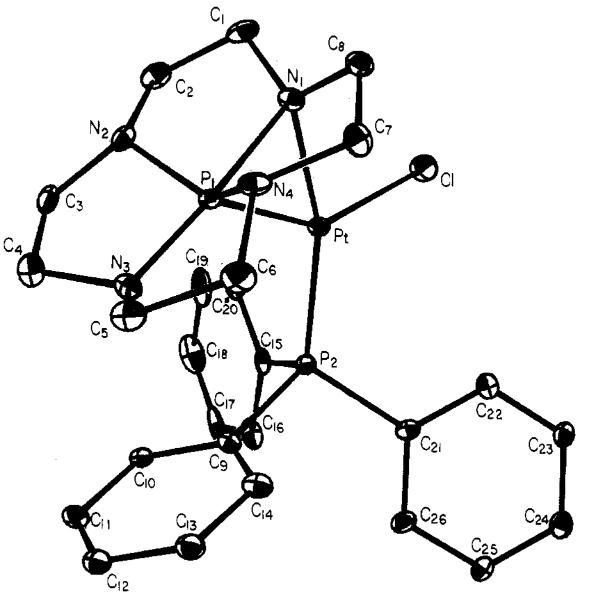

Figure 1. ORTEP view of (η^2-cyclenP)PtClPPh$_3$ (**1**) showing the atom-numbering scheme.

not by direct addition of HI to cyclenPH).[5] Furthermore, the fact that **1** differs from **2** by 2 mol of HCl led us to try to convert **1** directly to **2** by HCl addition. This reaction occurs smoothly; an immediate white precipitate of **2** forms when HCl is added to a THF solution of **1**. An attempt was made to convert **2** to **1** by heating under vacuum, but this only led to decomposition of **2** at about 130 °C.

2. Structure of 1. The structure of **1** is illustrated in Figure 1. Atomic positional parameters are listed in Table II and selected bond distances and angles in Table III. All four atoms directly bonded to Pt lie approximately in the same plane as the metal atom, as is clear from the sum of the bond angles about Pt, 359.6 (8)°. However, due to the constraint of the P1–Pt–N1 triangle, the four cis bond angles deviate significantly from 90° each. The geometry about P1 is distorted trigonal bipyramidal, with N1 and N3 the axial atoms and N2, N4, and Pt the equatorial atoms. The N1–P1–N3 angle is 175.2 (5)° while the N2–P1–N4 angle is 128.4 (6)°. The three equatorial atoms do not lie in the same plane as P1 [sum of equatorial angles about P1 is 350 (1)°]. There is one very long P–N bond, P1–N1 = 1.872 (11) Å, while the other three P–N bond lengths fall in the range 1.68–1.70 Å. This is the usual geometry for cyclenP when the phosphorus and one of the nitrogen atoms are bound to the same metal.[5,10] No significant difference is found in the two Pt–P bond lengths. The only bond length in **1** that is unusual is the Pt–Cl bond of 2.440 (4) Å, which is quite long. This is consistent with the relatively low $\nu_{\text{Pt-Cl}}$ of 249 cm^{-1} (see Table I). These data are similar to those obtained for *trans*-ClPt(SiMePh$_2$)(PMe$_2$Ph)$_2$ with a Pt–Cl bond length of 2.45 (1) Å and $\nu_{\text{Pt-Cl}}$ of 242 cm^{-1}.[18] The latter results were taken to indicate a high trans effect for silicon. We hesitate to invoke a similar effect here for the pentacoordinated phosphorus since the $\nu_{\text{Pt-Cl}}$ frequencies of **2** and *cis*-Cl$_2$Pt(PPh$_3$)$_2$ are very similar. The long bond length and low stretching frequency in **1** may arise more from the steric and/or electronic demands of the P–N–Pt three-membered ring, which significantly distorts the square-planar angles.

Table II. Positional Parameters and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	B/Å^2
Pt	0.30050 (4)	0.19600 (4)	0.81968 (3)	2.448 (8)
Cl	0.5018 (3)	0.2350 (3)	0.8626 (3)	5.02 (9)
P1	0.1747 (3)	0.1273 (2)	0.7252 (2)	2.46 (6)
P2	0.2164 (3)	0.2298 (2)	0.9394 (2)	2.41 (6)
N1	0.3279 (9)	0.1419 (8)	0.6958 (7)	3.1 (2)
N2	0.201 (1)	0.0106 (7)	0.7289 (7)	3.4 (2)
N3	0.0334 (9)	0.1095 (9)	0.7438 (7)	3.6 (3)
N4	0.1367 (9)	0.1940 (9)	0.6391 (6)	3.5 (2)
C1	0.390 (1)	0.053 (1)	0.693 (1)	4.5 (3)
C2	0.321 (1)	−0.016 (1)	0.742 (1)	4.3 (3)
C3	0.120 (1)	−0.038 (1)	0.780 (1)	4.1 (3)
C4	0.005 (1)	0.012 (1)	0.759 (1)	5.0 (4)
C5	−0.049 (1)	0.157 (1)	0.6836 (9)	4.4 (3)
C6	0.021 (1)	0.236 (1)	0.642 (1)	4.7 (4)
C7	0.224 (1)	0.259 (1)	0.6119 (9)	4.4 (3)
C8	0.339 (1)	0.208 (1)	0.6242 (8)	3.9 (3)
C9	0.060 (1)	0.2141 (9)	0.9321 (7)	2.6 (3)
C10	0.008 (1)	0.1348 (9)	0.9657 (8)	2.7 (3)
C11	−0.114 (1)	0.122 (1)	0.9532 (9)	3.8 (3)
C12	−0.179 (1)	0.187 (1)	0.9043 (8)	3.9 (3)
C13	−0.126 (1)	0.266 (1)	0.8719 (9)	4.0 (3)
C14	−0.008 (1)	0.281 (1)	0.8841 (9)	4.0 (3)
C15	0.266 (1)	0.1551 (9)	1.0302 (8)	2.9 (3)
C16	0.222 (1)	0.166 (1)	1.1108 (8)	4.2 (3)
C17	0.258 (1)	0.101 (1)	1.1772 (9)	5.7 (4)
C18	0.332 (2)	0.027 (1)	1.163 (1)	7.1 (5)
C19	0.372 (1)	0.018 (1)	1.083 (1)	6.4 (4)
C20	0.341 (1)	0.079 (1)	1.014 (1)	4.2 (3)
C21	0.235 (1)	0.3500 (9)	0.9811 (7)	2.8 (3)
C22	0.328 (1)	0.4024 (9)	0.9562 (8)	3.0 (3)
C23	0.343 (1)	0.4933 (9)	0.9874 (9)	3.4 (3)
C24	0.268 (1)	0.531 (1)	1.0439 (9)	3.8 (3)
C25	0.175 (1)	0.478 (1)	1.067 (1)	4.3 (3)
C26	0.156 (1)	0.387 (1)	1.0360 (9)	3.8 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[\alpha^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table III. Selected Bond Distances (Å) and Angles (deg) for **1**[a]

	Bond Distances		
Pt–Cl	2.440 (4)	P1–N3	1.698 (11)
Pt–P1	2.223 (3)	P1–N4	1.676 (11)
Pt–P2	2.214 (3)	P2–C9	1.814 (12)
Pt–N1	2.120 (10)	P2–C15	1.829 (13)
P1–N1	1.872 (11)	P2–C21	1.841 (13)
P1–N2	1.694 (11)		
	Angles		
Cl–Pt–P1	148.1 (1)	C9–P2–C15	103.5 (6)
Cl–Pt–P2	100.7 (1)	C9–P2–C21	103.2 (6)
Cl–Pt–N1	97.6 (3)	C15–P2–C21	104.4 (6)
P1–Pt–P2	110.3 (1)	Pt–N1–P1	67.3 (4)
P1–Pt–N1	51.0 (3)	Pt–N1–C1	116.4 (8)
P2–Pt–N1	161.2 (3)	Pt–N1–C8	118.9 (9)
Pt–P1–N1	61.7 (3)	P1–N1–C1	112.5 (9)
Pt–P1–N2	107.7 (4)	P1–N1–C8	112.9 (8)
Pt–P1–N3	123.1 (4)	C1–N1–C8	118 (1)
Pt–P1–N4	113.6 (4)	P1–N2–C2	115.8 (9)
N1–P1–N2	87.0 (5)	P1–N2–C3	111.4 (9)
N1–P1–N3	175.2 (5)	C2–N2–C3	117 (1)
N1–P1–N4	86.6 (5)	P1–N3–C4	114 (1)
N2–P1–N3	91.0 (6)	P1–N3–C5	114.3 (9)
N2–P1–N4	128.4 (6)	C4–N3–C5	114 (1)
N3–P1–N4	91.2 (5)	P1–N4–C6	113.3 (9)
Pt–P2–C9	114.4 (4)	P1–N4–C7	116.4 (8)
Pt–P2–C15	112.9 (4)	C6–N4–C7	114 (1)
Pt–P2–C21	116.9 (4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant figures.

Experimental Section

The synthesis was carried out in an atmosphere of prepurified nitrogen. Solvents were rigorously dried over appropriate drying agents and distilled and deoxygenated prior to use unless otherwise noted. Glassware was flame-dried under vacuum. IR spectra were recorded on a Perkin-Elmer 283 infrared spectrophotometer and NMR spectra on an IBM WP200SY multinuclear NMR spectrometer resonating at 200.132 (^{1}H), 50.327 (^{13}C), and 81.026 (^{31}P) MHz. All ^{13}C and ^{31}P spectra are proton-decoupled unless otherwise indicated. ^{1}H and ^{13}C peak positions were measured relative to solvent peaks, referenced to Me$_4$Si. ^{31}P peak positions were measured relative to external 85% H$_3$PO$_4$. Mass spectra were

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(18) (a) McWeeny, R.; Mason, R.; Towl, A. D. C. *Discuss. Faraday Soc.* **1969**, *47*, 50. (b) Chatt, J.; Eaborn, C.; Ibekwe, S. *Chem. Commun.* **1966**, 700.

Table IV. Crystallographic and Intensity Data Collection Parameters for (η^2-cyclenP)PtClPPh$_3$ (**1**)

formula	$C_{26}H_{31}ClN_4P_2Pt$
fw	692.06
cryst system	monoclinic
space group	$P2_1/n$
cryst dimens/mm	0.28 × 0.2 × 0.20
color and habit	colorless prisms
a/Å	11.562 (2)
b/Å	14.272 (2)
c/Å	15.556 (2)
β/deg	94.01 (1)
ρ(calcd)/g cm^{-3}	1.795
Z	4
temp/K	298
λ(Mo Kα, graphite monochromated)/Å	0.71069
μ(Mo Kα)/cm^{-1}	8.96
scan technique	$\theta/2\theta$
scan width/deg	$0.8 + 0.35 \tan \theta$
2θ range/deg	3.0 to 46.0
octants	$+h,\pm k,\pm l$
scan speed/deg min^{-1}	2–7
no. of check reflcns	2, measd every 30 min
decay of std	<1%
no. of reflcns measd	3931
no. of reflcns collected	3931 total yielding 2780 unique
no. of obsd data [$I > 3\sigma(I)$]	2462
agreement factor for av reflcns	0.025
R^a	0.039
$R_w{}^b$	0.046

${}^aR = \sum(|F_o| - |F_c|)/\sum|F_o|^2$. ${}^bR_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$.

recorded on a Hewlett-Packard 5988A GC/MS system.

cyclenPH was prepared as described previously.[5] HCl gas (technical) and *cis*-$Cl_2Pt(PPh_3)_2$ were obtained commercially and used without further purification.

1. Synthesis. A mixture of cyclenPH (0.570 g, 2.85 mmol) and *cis*-$Cl_2Pt(PPh_3)_2$ (2.25 g, 2.85 mmol) in 35 mL of THF was stirred for 12 h, yielding a white precipitate and colorless solution. The volatiles were removed under vacuum. The residue was washed with 10 × 10 mL of hexane (to dissolve the PPh_3), followed with 10 × 10 mL of THF (to dissolve **1**). The two washings and the residue, **2**, were pumped dry separately. **1** and **2** were then heated to 90 °C under vacuum to remove the last traces of impurities. Both **1** and **2** are white solids. Yields and melting points: PPh_3, 0.75 g (97%); **1**, 0.99 g (97%), 205–220 °C dec; **2**, 1.09 g (96%), 305–315 °C dec. Anal. Calcd for $C_{26}H_{31}ClN_4P_2Pt$ (**1**): C, 45.12; H, 4.52; N, 8.10; Cl, 5.12. Found: C, 46.01; H, 4.55; N, 7.90; Cl, 5.12. Calcd for $C_{26}H_{33}Cl_3N_4P_2Pt$ (**2**): C, 40.82; H, 4.36; N, 7.33; Cl, 13.90. Found: C, 40.63; H, 4.50; N, 7.31; Cl, 14.06. Mass spectrum (EI) of **1**: molecular ion *m/e* 691 (0.2%), base peak *m/e* 199 (cyclenP$^+$).

2. Conductometric Titrations. The apparatus used consisted of a 50-mL beaker with a dip cell connected to an R/C bridge (Industrial Instruments, Inc., Model RC 16B2). Me_2SO (Aldrich, Gold Label, Spectrophotometric Grade) was used without further purification. The Me_2SO solutions to be titrated were made up in the beaker and stirred while a 0.101 M $AgNO_3$ solution in Me_2SO was added dropwise. As a standard, KCl (9.7 mg, 0.13 mmol) in 40 mL of Me_2SO was titrated. This solution gave an initial conductance of 1.08 mS before $AgNO_3$ addition, and 1.3 mL of the $AgNO_3$ solution was needed to reach the end point (end point calculated 1.3 mL). A solution of **2** (91.8 mg, 0.120 mmol) in 40 mL of Me_2SO gave an initial conductance of 0.92 mS before $AgNO_3$ addition. A volume of 1.2 mL of $AgNO_3$ was needed reach the end point (end point calculated for one ionic Cl 1.2 mL). As a final test, a solution of **1** (87.4 mg, 0.126 mmol) in 40 mL of Me_2SO was made up, giving an initial conductance of 0.082 mS before $AgNO_3$ addition. As $AgNO_3$ was added, a smooth rise in conductance with no abrupt change in slope was observed, indicating no ionic Cl. Graphs of the titrations appear as supplementary material.

3. Conversion of 1 to 2. In the atmosphere, an HCl solution in THF was added dropwise to a THF solution of **1**. An immediate precipitate formed. The precipitate was separated, washed thoroughly with THF, and pumped dry. ^1H and ^{31}P NMR spectra of the precipitate were identical with those of **2**. Care was taken not to add excess HCl. If the reaction is conducted by bubbling HCl gas into a THF solution of **1**, the ^1H NMR spectrum of the resulting product shows some anomalies due, most likely, to excess HCl present in the product.

4. X-ray Structure Analysis of 1. Compound **1** was recrystallized by gas-phase diffusion of pentane into a THF solution of **1**. Pertinent crystallographic data are summarized in Table IV. A suitable single crystal was sealed in a Lindemann capillary under nitrogen. Initial lattice parameters were obtained from a least-squares fit to 25 reflections, 20° ≤ 2θ ≤ 26°, accurately centered on an Enraf-Nonius CAD 4-F diffractometer and subsequently refined by using higher angle data. The final scan speed was determined from the net intensity gathered in an initial prescan at 10° min^{-1}. The space group was uniquely determined as $P2_1/n$ due to the following systematic absences: $0k0$ absent for k odd and $h0l$ absent for $h + l$ odd.

Data were corrected for Lorentz and polarization effects. An empirical absorption correction was also applied. The position of the platinum atom was revealed from a Patterson map, and all of the non-hydrogen atoms were located from a subsequent difference Fourier map. All non-hydrogen atoms were refined with the use of anisotropic thermal parameters. Final refinement using full-matrix, least-squares methods converged smoothly to produce the R values given in Table IV. No chemically significant peaks were present in the final difference map. Complex neutral-atom scattering factors were used throughout.[19] All calculations were performed on a DEC PDP 11/44 computer using Enraf-Nonius SDP Plus structure solution programs.[20]

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Registry No. **1**, 108148-24-9; **2**, 108148-25-0; *cis*-$Cl_2Pt(PPh_3)_2$, 15604-36-1.

Supplementary Material Available: Graphs of the conductometric titrations and tables of bond lengths, bond angles, and thermal parameters (9 pages); a listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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