without distillation. One gram of the mixture was heated with 0.1 g of cuprous bromide at 55 °C for 2.5 h with magnetic stirring. The sample was filtered on a sintered glass funnel and its composition determined by gas chromatography. This analysis showed that the mixture was 11% **8** and 89% **13**.

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Registry No. **1**, 19008-94-7; **2**, 19008-97-0; **3**, 19008-98-1; **4**, 19008-95-8; **5**, 19008-96-9; **6**, 56758-73-7; **7**, 79152-78-6; **8**, 79152-79-7; **9**, 3043-33-2; **10**, 2327-98-2; **11**, 27301-54-8; **12**, 27301-53-7; **13**, 7544-00-5; **14**, 17074-99-6; **15**, 79172-18-2; **16**, 5876-76-6; **17**, 3355-30-4; **18**, 79152-80-0; **19**, 622-76-4; **20**, 33598-22-0; 1-phenyl-2-butyn-1-ol, 32398-66-6; trimethyltin chloride, 1066-45-1; triphenyltin chloride, 639-58-7; triethyltin chloride, 994-31-0; 2,4-dinitrobenzenesulfenyl chloride, 528-76-7; chlorine, 7782-50-5; bromine, 7726-95-6.

Organometallic Chemistry of Carbon–Nitrogen Multiple Bonds. 3. Reaction of Tris(triphenylphosphine)platinum(0) with Dimethylmethyleniminium Chloride. X-ray Structures of the Products $[(Ph_3P)PtCH_2N(CH_3)_2CH_2N(CH_3)_2(Cl)]Cl$ and *cis*-$[(Ph_3P)Pt[CHN(CH_3)_2]Cl_2]$

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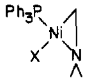
Tris(triphenylphosphine)platinum(0) reacts with $[(CH_3)_2N{=}CH_2]Cl$ in THF to yield $[(Ph_3P)PtCH_2N(CH_3)_2CH_2N(CH_3)_2(Cl)]Cl$ (A) which may be considered as a complex of the bidentate ylide ligand $^-CH_2N^+(CH_3)_2CH_2N(CH_3)_2$. When heated in acetonitrile, A converts quantitatively to the carbene complex *cis*-$\{(Ph_3P)Pt[CHN(CH_3)_2Cl_2\}$ (B) ($\nu_{C{=}N} = 1611\ cm^{-1}$) and $(CH_3)_3N$. This decomposition is dependent upon the presence of a coordinating anion as shown by the stability of the BF_4^- salt of A in CH_3CN. The results of single-crystal X-ray structures for A and B are presented. Crystal data are as follows. A: space group $P2_1/c$, $a = 13.86$ (1) Å, $b = 8.933$ (2) Å, $c = 19.52$ (1) Å, $\beta = 98.65$ (6)°, $Z = 4$, $\rho_{calcd} = 1.791\ g\ cm^{-3}$, $\rho_{exptl} = 1.77\ g\ cm^{-3}$. B: space group $R\bar{3}$, $a = 20.400$ (8) Å, $\alpha = 117.68$ (3)°, $Z = 6$, $\rho_{calcd} = 1.763\ g\ cm^{-3}$, $\rho_{exptl} = 1.77\ g\ cm^{-3}$. A has Pt–L distances of P, 2.223 (2) Å, Cl, 2.362 (2) Å, N, 2.134 (4) Å, and C, 2.017 (5) Å. The Pt–C distance is the shortest presently known for an sp^3 carbon (without fluorine substituents) bonded trans to chlorine. B has Pt–L distances of P, 2.220 (2) Å, Cl(1), 2.347 (3) Å, Cl(2), 2.345 (3) Å, and C, 1.96 (1) Å. The dihedral angle between the carbene and coordination planes is 84°.

Introduction

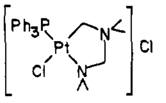
An earlier publication dealt with the syntheses of $\{(Ph_3P)Ni(X)[\eta^2\text{-}CH_2N(CH_3)_2]\}$ (X = Cl, Br, I) (I) and the single-crystal X-ray structure of the chloro complex.[1] These complexes were prepared from $(Ph_3P)_4Ni$ or $(Ph_3P)_2Ni(C_2H_4)$ and dimethylmethyleniminium halides (A) and represented the first phase of our investigations of the organometallic chemistry of iminium salts.[2] The analogous reaction of $(Ph_3P)_4Pt$ with A (X = Cl) produced a complex that analyzed for Ph_3P, Pt, and iminium salt in the ration 1:1:2. The NMR and infrared spectra of this compound did not help in the assignment of a structure. A single crystal X-ray structure shows that the complex has structure II, which may be considered as a complex of the bidentate ylide ligand $^-CH_2N^+(CH_3)_2CH_2N(CH_3)_2$. This compound converts to the carbene complex III and $(CH_3)_3N$ under mild conditions. The single-crystal X-ray structure of the carbene complex indicates that it has the cis stereochemistry. The chemistry of these complexes, details of the structures, and a discussion of the probable mechanisms of reactions of iminium salts with zero-valent d^{10} metals are the subjects of this paper.

$(>N{=}CH_2)X$

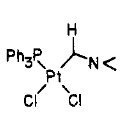
A



I



II



III

Experimental Section

Preparative work was conducted in a Vacuum Atmospheres glovebox under a nitrogen atmosphere. Solvents were distilled from drying agents under a nitrogen atmosphere. Dimethylmethyleniminium chloride[3] and $(Ph_3P)_3Pt$[4] were prepared by literature methods.

$[(Ph_3P)PtCH_2N(CH_3)_2CH_2N(CH_3)_2(Cl)]Cl$. A suspension of 0.5 g (0.4 mmol) of $(Ph_3P)_3Pt$ and 0.15 g (1.6 mmol) of $[(CH_3)_2N{=}CH_2]Cl$ in 50 mL of THF was stirred overnight. The off-white solid was collected by filtration and extracted on the frit with three 5-mL portions of CH_2Cl_2. Addition of ether to the extracts gave the product as a microcrystalline off-white material. Yield: 0.2 g or 78%. Anal. Calcd for $PtC_{24}H_{31}N_2Cl_2P$: C, 44.71; H, 4.85; N, 4.35; Cl, 11.00. Found: C, 42.89, 42.88, 43.56; H, 4.99, 4.97, 4.50; N, 4.41, 4.24; Cl, 10.87. Crystallographic quality crystals were obtained by evaporation of an acetonitrile solution of the complex.

$[(Ph_3P)PtCH_2N(CH_3)_2CH_2N(CH_3)_2Cl]BF_4$. Metathesis to the fluoroborate was accomplished by dissolving 1.25 g of the chloride in 125 mL of acetonitrile and adding a 10% excess of $NaBF_4$. After precipitated NaCl was removed the volume was reduced to half and the solution was stored at −3 °C for overnight; a second crop of NaCl was removed by filtration. After the volume

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0276-7333/82/2301-0103$01.25/0

Table I. Crystal Data for $[(Ph_3P)PtCH_2N(CH_3)_2CH_2N(CH_3)_2(Cl)]Cl$ (A) and *cis*-$\{(Ph_3P)Pt[CHN(CH_3)_2]Cl_2\}$ (B)

	A	B
mol wt	644.48	585.38
dimens, mm	0.08 × 0.25 × 0.40	0.40 × 0.40 × 0.60
space group	$P2_1/c$	$R\overline{3}$
cell constants		
a, Å	13.86 (1)	20.400 (8)
b, Å	8.933 (2)	
c, Å	19.52 (1)	
α, deg		117.68 (3)
β, deg	98.65 (6)	
no. of reflctns used to determine cell constants	15	15
and their 2θ limits, deg	$4 < 2\theta < 19$	$15.9 < 2\theta < 34.75$
Z	4	6
ρ_{calcd}, g cm^{-3}	1.791	1.763
ρ_{exptl},[a] g cm^{-1}	1.77	1.77

[a] By flotation in carbon tetrachloride/1,2-dibromoethane.

Table II. Data Collection and Refinement Details for $[(Ph_3P)PtCH_2N(CH_3)_2N(CH_3)_2(Cl)]Cl$ (A) and *cis*-$\{(Ph_3P)Pt[CHN(CH_3)_2](Cl_2)\}$ (B)

	A	B
diffractometer	Syntex $P2_1$	
monochromator (Bragg 2θ angle, deg)	graphite (12.2)	
radiation, Å	Mo K$\overline{\alpha}$, 0.71069	
take-off angle, deg	6.75	
scan method	$\theta - 2\theta$	
scan speed, min/max, deg min^{-1}	3.9/29.3	2.02/29.3
scan width, deg	2.0	
bkgd/scan time ratio (TR)[a]	1.0	
no. of standards (monitoring freq, no. of reflctns)	3[b] (97)	
2θ limits of data, deg	$4 < 2\theta < 50$	
h,k,l	$-h,0,0 \rightarrow +h,+k,+l$	$-h,-k,0 \rightarrow +h,+k,+l$: $\lvert h\rvert \leqslant l$, $\lvert k\rvert \leqslant l$
no. of data	4682	5845
no. of data used in final refinement	3316[c]	3784[d]
no. of data/no. of variables	12.2	25.1
μ,[e] cm^{-1}	64.85	63.97
$R = (\Sigma \lVert F_o\rvert - \lvert F_c\rVert)/(\Sigma \lvert F_o\rvert)$ (function minimized = $\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)^2$)	0.024	0.047
R_w	0.023[f]	0.049[g]

[a] Background counts measured before (BG1) and at the end (BG2) of the scan. Intensities determined from total scan (CT) and background (BG) counts by $I = CT - TR(BG1 + BG2)$. $\sigma_I = [CT + (TR)^2(BG1 + BG2)]^{1/2}$. $F_o = (I/Lp)^{1/2}$ where Lp is the Lorentz and polarization correction. [b] Standard reflections were as follows. A: 0,0,8; 0,2,0; 7,0,0. B: 0,0,5; 0,5,0; 5,0,0. [c] $I > 3\sigma_I$. [d] $F > 3\sigma_F$; $\sigma_F = \sigma_I/2(F)(Lp)$. [e] Data were corrected for absorption by an empirical method based on ψ scans of reflections near $\chi = 90°$; average $I_{max}/I_{min} = 2.9$ for A and 1.39 for B. [f] $R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w(\lvert F_o\rvert)^2]^{1/2}$; $w = 4I/\sigma_I$. [g] $R_w = [\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)(w^{1/2})/[\Sigma(\lvert F_o\rvert)(w^{1/2})]$; $w = n/(\sigma_F^2 + mF^2)$ in the final cycle. n was 2.86 and m was 5.1×10^{-4}.

of the filtrate was reduced to ca. 25 mL, about 10 mL of ether was added and the solution again stored at −3 °C overnight. The white crystalline fluoroborate salt was collected, washed with ether, and dried in vacuo. Anal. Calcd for $PtC_{24}H_{31}N_2PClBF_4$: C, 41.43; H, 4.49; N, 4.03. Found: C, 41.35; H, 4.52; N, 4.02.

$\{(Ph_3P)Pt[CHN(CH_3)_2]Cl_2\}$. An acetonitrile solution of $[(Ph_3P)PtCH_2N(CH_3)_2CH_2N(CH_3)_2(Cl)]Cl$ was heated at reflux for 10 min. After the solution cooled, the volume was reduced under vacuum to give white crystals of the product, which were collected, washed with ether, and dried in vacuo. Two modifications were obtained in separate preparations. One of these showed a single ν_{CN} at 1611 cm^{-1} whereas the other showed two bands at 1611 and 1622 cm^{-1} (solid state, Nujol mull). The exact conditions leading to a predictable formation of a given modification were not determined. Anal. Calcd for $PtC_{21}H_{22}NPCl_2$: C, 43.09; H, 3.79; N, 2.39. Found: C, 42.34; H, 3.93; N, 2.30. Crystals for X-ray data collection of the form having only the 1611-cm^{-1} infrared stretch were grown by addition of ether to an acetonitrile solution of the complex followed by cooling at −3 °C overnight.

Solution and Refinement of the Structures of $[(Ph_3P)PtCH_2N(CH_3)_2CH_2N(CH_3)_2(Cl)]Cl$ (A) and $\{(Ph_3P)Pt[CHN(CH_3)_2](Cl)\}$ (B). Crystal data are given in Table I and certain details of data collection and refinement in Table II. All computations were done on a CDC Cyber 70/74 computer system.

In the case of A the position of the platinum atom was determined from a Patterson synthesis and after three cycles of least-squares refinement of the scale factor and platinum coordinates $R = 0.319$. A difference Fourier map revealed the chlorine and phosphorus positions. These were included for three cycles of least-squares refinement in which the coordinates and isotropic thermal parameters of all atoms were allowed to vary ($R = 0.195$). A subsequent difference Fourier map revealed the positions of all carbon and nitrogen atoms. Inclusion of these atoms in the refinement gave $R = 0.103$ after three cycles. At this point the Pt, Cl, and P atoms were refined anisotropically for three cycles ($R = 0.059$). Hydrogen atom positions for all nonmethyl carbons were calculated by assuming sp^2 or sp^3 geometry as appropriate. The position of at least one hydrogen atom attached to each methyl carbon was determined from a difference Fourier map, and positions of the remaining ones were calculated. All hydrogen atom positions were block refined for two cycles after which their coordinates and thermal parameters were held constant. All nonhydrogen atoms were then refined anisotropically to convergence at $R = 0.024$ ($R_w = 0.023$).

Programs used included Zalkin's FORDAP Fourier summation program, Ibers NUCLS5 modification of the Busing–Martin–Levy ORFLS full-matrix least-squares program, the Busing–Martin–Levy ORFFE function and error program, and various locally written programs. For structure factor calculations the scattering factors for nonhydrogen atoms were taken from Cromer and Waber's tabulation;[5] and those for hydrogen were Stewart's.[6] Scattering factors for Pt, P, and Cl were corrected for the real and imaginary anomalous dispersion components by using the dispersion factors given by Cromer.[7] Positional and thermal parameters of nonhydrogen atoms obtained in the last least-squares cycle are given in Table III. Tables of hydrogen atom positions and structure factors have been deposited.

The structure of B was solved by direct methods. The position of the platinum atom was located via the E map showing the highest probability statistics and its positional parameters, isotropic thermal parameter, and the scale factor were subjected to three cycles of least-squares refinement, $R = 0.235$ (all computations utilized Sheldrick's Shelx-76 program package). A subsequent difference Fourier map revealed the positions of all nonhydrogen atoms. After three cycles of least-squares refinement of all positional and isotropic thermal parameters, the Pt, P, and Cl atoms were refined anisotropically for three additional least-squares cycles. At this point a difference Fourier map did not reveal any hydrogen atom positions; therefore, these were included in subsequent cycles of refinement in their calculated positions by assuming sp^2 or sp^3 hybridization of the carbon atoms as appropriate, and thermal parameters of each group (phenyl, methyl, etc.) of hydrogen atoms were treated as a unit. Least-squares refinement of hydrogen atom thermal parameters, positional and isotropic thermal parameters of phenyl group carbon atoms, and positional and anisotropic thermal parameters of the other nonhydrogen atoms was continued to convergence at $R = 0.047$ and $R_w = 0.049$. In the final cycle the thermal parameter of the C(3) hydrogen atom unit was fixed at 0.15 as it had grown steadily in previous cycles.

Scattering factors were taken from the current source;[8] those for all atoms except hydrogen were corrected for real and imaginary anomalous dispersion components.[9] Positional and thermal parameters of nonhydrogen atoms obtained in the last least-squares cycle are given in Tables IV and V. Tables of hydrogen atom positions and structure factors have been deposited.

Results

Preparation and Spectral Characterization of $[(Ph_3P)\overline{PtCH_2N(CH_3)_2N}(CH_3)_2Cl]^+$ Salts and $\{(Ph_3P)Pt[CHN(CH_3)_2Cl_2\}$. By analogy with our earlier work, in which we found that $(Ph_3P)_4Ni$ or $(Ph_3P)_2Ni(C_2H_4)$ reacted with excess $[(CH_3)_2N{=}CH_2]Cl$ in THF to give soluble $\{(Ph_3P)Ni[\eta^2\text{-}CH_2N(CH_3)_2]Cl\}$,[1] we expected a similar product from $(Ph_3P)_3Pt$. Instead, a THF-insoluble product that contained 2 equiv of iminium salt was consistently obtained, even from reactions involving 1:1 ratios of reactants. The infrared spectrum of this material contained no absorptions for vinylic CH or for C═N but gave no other information that could be used in structure assignment. The NMR spectra obtained initially varied with the solvent used and were not entirely reproducible in a given solvent, but they were not consistent with the presence of *N,N,N′,N′*-tetramethylethylenediamine which was initially considered as a possibility since reductive carbon–carbon bond formation can be achieved with certain nickel(0) reagents.[10] Poor reproducibility of the NMR spectrum was ultimately traced to the instability of the chelate complex and the presence of carbene complex in the NMR samples. Carefully handled and purified samples of both the chloro and fluoroborate complexes gave reproducible spectra (data and assignments are given in Table VI) which are consistent with the structure of the cation as determined by X-ray diffraction (vide infra). The assignments of the different methylene and methyl resonances are based on the relative sizes of the Pt coupling constants. It should be noted that the coordinated CH$_2$ resonance (δ 3.26) is at somewhat higher field than the methine resonance in *trans*-$\{(o\text{-}CH_3C_5H_4N)Pt[CH(NC_5H_4\text{-}o\text{-}CH_3)CH_2CH_2Ph]Cl_2\}$ which is at δ 5.6[11] and the $^2J_{PtH}$ value is somewhat smaller (53 vs. 112 Hz). Since only one quaternary ammonium methyl resonance is detected, the chelate ring must undergo inversion at a rate that is rapid on the NMR time scale.

When $[(Ph_3P)\overline{PtCH_2N(CH_3)_2N}(CH_3)_2(Cl)]Cl$ is heated in acetonitrile, quantitative conversion to *cis*-$\{(Ph_3P)Pt[CHN(CH_3)_2]Cl_2\}$ and $(CH_3)_3N$ occurs as shown by the NMR spectrum of the reaction mixture. This complex was easily isolated by evaporation of the acetonitrile. Its infrared spectrum contains a band at 1611 cm^{-1} for the C–N stretching absorption, which is the range observed for other secondary carbene complexes.[12] The ^{1}H NMR spectrum contains methyl resonances at δ 2.85 (singlet) and 3.52 ($^4J_{PtH} = 12$ Hz) and the carbene carbon hydrogen at δ 9.81 ($^2J_{PtH} = 22$ Hz, $^3J_{PH} = 4$ Hz). Phenyl proton resonances are multiplets at δ 7.44 and 7.73. The observation of two distinct methyl signals indicates that rotation about the C–N bond is slow as previously noted by Clark[12] for a number of other secondary carbene platinum complexes. On the basis of the detectable coupling to platinum, the low-field methyl resonance is assigned to the group trans to platinum. The small value of $^3J_{PH}$ for the hydrogen attached to the carbene carbon is consistent with the cis orientation of phosphine and carbene ligands found for the solid-state material.

The only reasonable pathway for conversion of the chelate complex to the carbene must involve chelate ring cleavage and the formation of free iminum cation which serves as an hydride abstracter. It seemed likely that either the chloride counterion or the polar solvent might promote dissociation of the amino group from the platinum atom. The fluoroborate salt of the chelate complex was synthesized to test for a counterion effect. In fact, the fluoroborate salt of the chelate complex did not yield a detectable quantity of carbene complex when heated in acetonitrile and we conclude that the chloride counterion rather than solvent is most important for the conversion. (The BF$_4^-$ salt of the chelate complex does decompose in hot acetonitrile but at a much lower rate than the conversion of the chloride salt to carbene—products were not identified.) Although the conversion of the chloride salt to carbene is rapid in CH$_3$CN, it is much slower in CHCl$_3$. This may be a result of poor solvation of the iminum cation in this medium since formation of a neutral dichloro complex should be favored by the less polar solvent.

Description of the Structure of $[(Ph_3P)\overline{PtCH_2N(CH_3)_2CH_2N}(CH_3)_2(Cl)]Cl$. The crystal structure of $[(Ph_3P)\overline{PtCH_2N(CH_3)_2CH_2N}(CH_3)_2(Cl)]Cl$ consists of four-coordinate cations and noninteracting chloride anions. The cation (see Figure 1 for an ORTEP drawing) is four-coordinate and contains the unique chelating ligand $^-CH_2N^+(CH_3)_2CH_2N(CH_3)_2$ with triphenylphosphine coordinated trans to the dimethylamino function. Selected interatomic distances and angles are given in Table VII.

Although the cation can be loosely characterized as having a square-planar arrangement of ligands about the

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Table III. Final Positional and Anisotropic Thermal Parameters[a] (with Esd's) for Nonhydrogen Atoms of $[(Ph_3P)PtCH_2N(CH_3)_2CH_2N(CH_3)_2(Cl)]Cl$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	−0.15419 (1)	0.31602 (2)	0.429869 (9)	0.02249 (9)	0.02218 (9)	0.02349 (9)	0.0013 (1)	0.00651 (5)	0.0003 (1)
Cl(1)	−0.09756 (9)	0.2439 (2)	0.54532 (6)	0.0405 (7)	0.0391 (6)	0.0272 (6)	0.0087 (6)	0.0049 (5)	0.0038 (5)
Cl(2)	0.1625 (1)	0.4505 (2)	0.24348 (8)	0.0423 (8)	0.0551 (9)	0.0564 (9)	−0.0032 (7)	0.0142 (7)	−0.0010 (8)
P	−0.30022 (8)	0.3904 (1)	0.45035 (6)	0.0236 (6)	0.0247 (6)	0.0258 (6)	0.0019 (5)	0.0063 (5)	0.0015 (5)
N(1)	−0.0150 (3)	0.2615 (5)	0.4025 (2)	0.029 (2)	0.024 (2)	0.033 (2)	0.004 (2)	0.010 (2)	0.003 (2)
N(2)	−0.0944 (3)	0.3930 (5)	0.2990 (2)	0.028 (2)	0.032 (2)	0.027 (2)	0.001 (2)	0.008 (2)	0.005 (2)
C(1)	0.0110 (4)	0.1016 (4)	0.4180 (3)	0.047 (3)	0.029 (3)	0.044 (3)	0.012 (2)	0.019 (3)	0.006 (2)
C(2)	0.0644 (3)	0.3544 (6)	0.4400 (3)	0.021 (2)	0.053 (4)	0.043 (3)	−0.005 (2)	−0.000 (2)	−0.007 (3)
C(3)	−0.0207 (3)	0.2797 (5)	0.3267 (3)	0.027 (2)	0.030 (3)	0.032 (3)	0.000 (2)	0.010 (2)	0.001 (2)
C(4)	−0.0634 (4)	0.5487 (6)	0.3192 (3)	0.042 (3)	0.025 (3)	0.051 (3)	−0.004 (2)	0.010 (3)	0.008 (3)
C(5)	−0.1077 (4)	0.3799 (7)	0.2218 (3)	0.041 (3)	0.065 (4)	0.022 (3)	0.004 (3)	0.009 (2)	0.007 (3)
C(6)	−0.1869 (4)	0.3541 (6)	0.3271 (3)	0.029 (2)	0.039 (3)	0.026 (2)	−0.002 (2)	0.012 (2)	0.001 (2)
C(7)	−0.3026 (3)	0.5931 (5)	0.4598 (2)	0.021 (2)	0.023 (3)	0.032 (3)	0.003 (2)	0.002 (2)	0.001 (2)
C(8)	−0.3328 (4)	0.6628 (6)	0.5156 (3)	0.038 (3)	0.028 (3)	0.044 (3)	0.003 (2)	0.012 (2)	−0.001 (2)
C(9)	−0.3201 (4)	0.8144 (8)	0.5248 (3)	0.058 (3)	0.037 (3)	0.054 (3)	0.005 (3)	0.011 (3)	−0.009 (3)
C(10)	−0.2797 (4)	0.8977 (6)	0.4786 (4)	0.046 (3)	0.023 (3)	0.068 (4)	0.006 (2)	0.007 (3)	0.004 (3)
C(11)	−0.2535 (4)	0.8322 (7)	0.4214 (4)	0.052 (3)	0.031 (4)	0.068 (4)	0.003 (3)	0.026 (3)	0.009 (3)
C(12)	−0.2633 (4)	0.6794 (7)	0.4121 (3)	0.050 (3)	0.035 (4)	0.048 (4)	0.010 (3)	0.022 (3)	0.012 (3)
C(13)	−0.3419 (3)	0.3157 (6)	0.5274 (2)	0.024 (2)	0.027 (2)	0.030 (2)	0.006 (2)	0.009 (2)	−0.002 (2)
C(14)	−0.2954 (3)	0.3539 (5)	0.5927 (3)	0.025 (2)	0.035 (3)	0.028 (2)	0.000 (2)	0.002 (2)	−0.001 (2)
C(15)	−0.3263 (4)	0.2955 (6)	0.6509 (3)	0.032 (2)	0.045 (3)	0.033 (3)	0.010 (3)	0.002 (2)	0.003 (3)
C(16)	−0.4029 (4)	0.1945 (7)	0.6449 (3)	0.050 (3)	0.041 (3)	0.039 (3)	0.005 (3)	0.019 (2)	0.010 (3)
C(17)	−0.4491 (4)	0.1550 (6)	0.5807 (3)	0.045 (3)	0.038 (4)	0.045 (3)	−0.011 (2)	0.018 (2)	−0.002 (2)
C(18)	−0.4196 (4)	0.2159 (5)	0.5218 (3)	0.038 (3)	0.031 (3)	0.031 (3)	−0.003 (2)	0.011 (2)	−0.002 (2)
C(19)	−0.3976 (3)	0.3381 (5)	0.3823 (2)	0.032 (2)	0.030 (3)	0.022 (2)	−0.003 (2)	0.011 (2)	−0.001 (2)
C(20)	−0.4833 (3)	0.4180 (6)	0.3679 (3)	0.027 (2)	0.038 (3)	0.034 (3)	0.003 (2)	0.006 (2)	0.003 (2)
C(21)	−0.5613 (4)	0.3624 (7)	0.3219 (3)	0.037 (3)	0.058 (4)	0.037 (3)	0.003 (3)	0.000 (2)	0.008 (3)
C(22)	−0.5530 (4)	0.2285 (8)	0.2908 (3)	0.038 (3)	0.068 (5)	0.037 (3)	−0.021 (3)	−0.002 (2)	0.000 (3)
C(23)	−0.4685 (4)	0.1467 (6)	0.3044 (3)	0.041 (3)	0.044 (4)	0.041 (3)	−0.016 (2)	0.009 (2)	−0.013 (2)
C(24)	−0.3901 (4)	0.2010 (6)	0.3500 (3)	0.040 (3)	0.033 (3)	0.033 (2)	−0.004 (2)	0.014 (2)	0.001 (2)

[a] The form of the expression defining the thermal ellipsoids is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Table IV. Final Positional and Thermal Parameters (with Esd's[a]) for Anisotropically Refined Atoms of *cis*-$\{(Ph_3P)Pt[CHN(CH_3)_2](Cl)_2\}$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt	0.19964 (4)	0.12937 (4)	0.43050 (4)	0.0282 (2)	0.0301 (2)	0.0310 (2)	0.0267 (2)	0.0254 (2)	0.0256 (2)
Cl(1)	0.2220 (3)	0.2361 (3)	0.5751 (3)	0.073 (2)	0.058 (2)	0.068 (2)	0.054 (2)	0.065 (2)	0.061 (2)
Cl(2)	0.1411 (4)	0.1746 (4)	0.3514 (4)	0.090 (2)	0.087 (2)	0.083 (2)	0.079 (2)	0.072 (2)	0.082 (2)
P	0.2683 (2)	0.0996 (2)	0.5170 (2)	0.027 (1)	0.027 (1)	0.030 (1)	0.025 (1)	0.026 (1)	0.024 (1)
N	0.268 (1)	0.101 (1)	0.333 (1)	0.070 (7)	0.087 (8)	0.073 (7)	0.074 (7)	0.067 (7)	0.069 (7)
C(1)	0.177 (1)	0.040 (1)	0.306 (1)	0.042 (6)	0.048 (6)	0.043 (6)	0.041 (5)	0.037 (5)	0.038 (5)
C(2)	0.416 (1)	0.258 (2)	0.470 (2)	0.056 (8)	0.067 (9)	0.073 (9)	0.058 (8)	0.057 (8)	0.043 (8)
C(3)	0.239 (2)	0.018 (2)	0.232 (2)	0.13 (1)	0.13 (1)	0.11 (1)	0.11 (1)	0.11 (1)	0.11 (1)

[a] The form of the expression defining the thermal ellipsoids is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Table V. Final Positional and Isotropic Thermal Parameters for Phenyl Group Carbon Atoms of *cis*-$\{(Ph_3P)Pt[CHN(CH_3)_2]Cl_2\}$

atom	x	y	z	U, Å^2
C(4)	0.4502 (9)	0.2771 (9)	0.7189 (9)	0.031 (2)
C(5)	0.568 (1)	0.395 (1)	0.786 (1)	0.036 (2)
C(6)	0.709 (1)	0.534 (1)	0.941 (1)	0.043 (2)
C(7)	0.726 (1)	0.554 (1)	1.025 (1)	0.053 (3)
C(8)	0.610 (1)	0.441 (1)	0.962 (1)	0.052 (3)
C(9)	0.470 (1)	0.300 (1)	0.807 (1)	0.045 (2)
C(10)	0.1484 (9)	−0.0220 (9)	0.4737 (9)	0.031 (2)
C(11)	0.159 (1)	−0.082 (1)	0.484 (1)	0.052 (3)
C(12)	0.070 (2)	−0.175 (2)	0.453 (2)	0.073 (4)
C(13)	−0.031 (1)	−0.210 (1)	0.411 (1)	0.055 (3)
C(14)	−0.040 (1)	−0.151 (1)	0.404 (1)	0.046 (2)
C(15)	0.046 (1)	−0.060 (1)	0.432 (1)	0.037 (2)
C(16)	0.2821 (9)	0.0204 (9)	0.4483 (9)	0.030 (2)
C(17)	0.414 (1)	0.102 (1)	0.530 (1)	0.042 (2)
C(18)	0.417 (1)	0.038 (1)	0.468 (1)	0.051 (3)
C(19)	0.282 (1)	−0.113 (1)	0.321 (1)	0.055 (3)
C(20)	0.152 (1)	−0.196 (1)	0.239 (1)	0.064 (3)
C(21)	0.148 (1)	−0.131 (1)	0.299 (1)	0.055 (3)

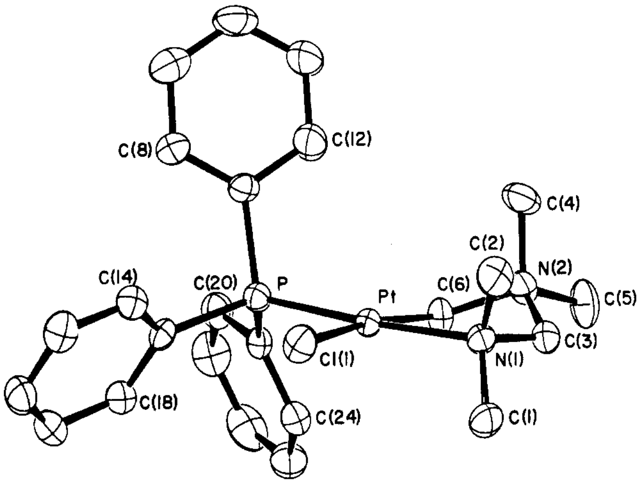

Figure 1. ORTEP drawing of the cation $[(Ph_3P)\overline{PtCH_2N(CH_3)_2CH_2N}(CH_3)_2(Cl)]^+$. Hydrogen atoms are not shown; probability ellipsoids are at the 50% level.

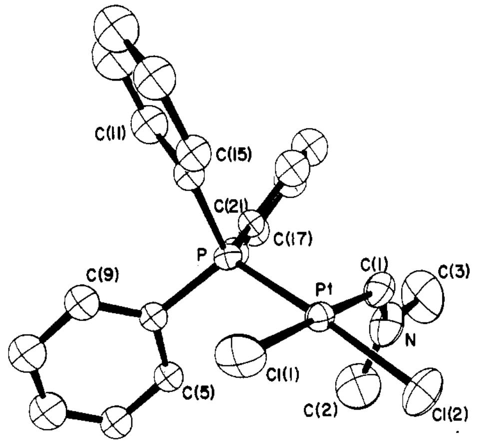

Figure 2. ORTEP drawing of *cis*-$\{(Ph_3P)Pt[CHN(CH_3)_2]Cl_2\}$. Hydrogen atoms are not shown; probability ellipsoids are at the 50% level.

platinum, the donor–Pt–donor angles are considerably different from the ideal ones. There is a slight tetrahedral distortion as shown by the deviations of the ligating atoms from the least-squares plane defined by the equation $0.304X + 0.935Y + 0.180Z - 3.075 = 0$, i.e., Cl(1), −0.059 Å; C(6), −0.076 Å; P, 0.061 Å, and N, 0.074 Å. The Pt atom is 0.008 Å out of this plane. There are also deviations in the in-plane angles from the ideal 90°; the N(1)–Pt–C(6) angle is only 82.2° whereas the Cl(1)–Pt–P and P–Pt–C(6) angles are 95.10 (7) and 93.2 (1)°, respectively. All angles and distances in the chelate and triphenylphosphine ligands are in the expected ranges.

The Pt–C distance of 2.017 (5) Å extends the range previously found for sp^3 carbon (without fluorine substituents) bonded trans to chlorine. The lower limit of this range was previously defined by values of 2.08 (1) and 2.090 (4) Å occurring in *trans*-$(Ph_3P)_2Pt(Cl)R$ (R = CH_2CN[13] and η^1-allyl[14]), respectively, and 2.081 (6) and 2.079 (14) Å in *trans*-$(Ph_2PCH_3)_2Pt(Cl)R$ (R = CH_3[15] and $CH_2Si(CH_3)_3$[16]) respectively. Although it is tempting to suggest that the shorter Pt–C distance is a result of a stronger interaction between the electronegative carbon donor (compare the Pt–C distance of 2.002 (9) Å in *trans*-$[Pt(Ph_2PCH_3)_2(C_2F_5)Cl]$[15] with the value of the CH_3 derivative given above), it is also possible that the shorter bond is partially a result of the constraint placed on the system by the chelate ring.

The Pt–P bond distance at 2.223 (2) Å is shorter than distances recorded for *trans*-bis(phosphine)platinum(II) complexes (the minimum distance is about 2.29 Å), but this is not unexpected if there is a π component to the Pt–P bond since the trans amino group would not be competitive.

The Pt–Cl distance of 2.362 (2) Å is the same as that in *tran*-$[Pt(Ph_2PCH_3)_2(CF_3)Cl]$[15] within experimental error and is considerably shorter than those in other complexes where chlorine is bonded trans to sp^3 carbon donors.[14] As noted by Bennett et al., in regard to the CF_3 complex,[15] this is probably a result of an electrostatic dipolar effect induced by the electronegative carbon substituent.

Description of the Structure of *cis*-$\{(Ph_3P)Pt$-

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[13] Del Pra, A.; Zanotti, G.; Bombieri, G.; Ros, R. *Inorg. Chem.* **1979**, *18*, 121.

[14] Kaduk, J. A.; Ibers, J. A. *J. Organomet. Chem.* **1977**, *139*, 199.

[15] Bennett, M. A.; Chee, H.-K.; Robertson, G. B. *Inorg. Chem.* **1979**, *18*, 1061.

[16] Jovanovic, B.; Manojlović-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1974**, 195.

[17] Shomaker, V.; Waser, J.; Marsh, E. R.; Bergman, G., *Acta Crystallog.* **1959**, *12*, 600.

Table VI. ^{1}H NMR Data for $[(Ph_3P)\overline{PtCH_2N(CH_3)_2CH_2N}(CH_3)_2(Cl)]$ and *cis*-$\{(Ph_3P)Pt[CHN(CH_3)_2]Cl_2\}$

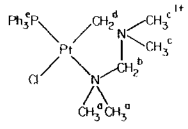
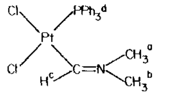
compound	solvent, anion	a	b	c	d	e
		chemical shifts (δ vs. Me_4Si) and coupling constants for proton types				
	CD_3CN, BF_4^-	δ 3.14 ($^3J_{Pt-H}$ = 23 Hz, $^4J_{P-H}$ = 2.6 Hz)	δ 4.08 ($^3J_{Pt-H}$ = 28 Hz)	δ 3.09	δ 3.26 ($^2J_{Pt-H}$ = 53 Hz, $^3J_{P-H}$ = 1.52 Hz)	δ 7.47–7.69 (m)
	CD_3CN, Cl^-	δ 3.15 ($^3J_{Pt-H}$ = 24 Hz, $^4J_{P-H}$ = 2.8 Hz)	δ 4.28 ($^3J_{Pt-H}$ = 28 Hz)	δ 3.14	δ 3.30 ($^2J_{Pt-H}$ = 54 Hz, $^3J_{P-H}$ = 1.1 Hz)	δ 7.45–7.69 (m)
	$CDCl_3$	δ 2.85	δ 3.52 ($^3J_{Pt-H}$ = 12 Hz)	δ 9.81 ($^2J_{Pt-H}$ = 22 Hz, $^3J_{P-H}$ = 4 Hz)	δ 7.30–7.87 (m)	

Table VII. Interatomic Distances (Å) and Angles (Deg) for $[(Ph_3P)\overline{PtCH_2N(CH_3)_2CH_2N}(CH_3)_2(Cl)]Cl$

Distances

Pt-P	2.223 (2)	P-C(13)	1.817 (5)
Pt-Cl(1)	2.362 (2)	C(13)-C(14)	1.382 (7)
Pt-N(1)	2.134 (4)	C(14)-C(15)	1.375 (8)
Pt-C(6)	2.017 (5)	C(15)-C(16)	1.385 (8)
		C(16)-C(17)	1.366 (9)
N(1)-C(1)	1.492 (7)	C(17)-C(18)	1.386 (8)
N(1)-C(2)	1.481 (7)	C(18)-C(13)	1.390 (7)
N(1)-C(3)	1.478 (7)		
		P-C(19)	1.806 (5)
N(2)-C(3)	1.482 (7)	C(19)-C(20)	1.378 (7)
N(2)-C(4)	1.491 (7)	C(19)-C(24)	1.390 (7)
N(2)-C(5)	1.495 (7)	C(20)-C(21)	1.389 (8)
N(2)-C(6)	1.510 (6)	C(21)-C(22)	1.354 (9)
		C(22)-C(23)	1.371 (9)
P-C(7)	1.821 (5)	C(23)-C(24)	1.385 (8)
C(7)-C(8)	1.373 (7)		
C(8)-C(9)	1.374 (8)		
C(9)-C(10)	1.354 (9)		
C(10)-C(11)	1.357 (9)		
C(11)-C(12)	1.381 (8)		
C(12)-C(7)	1.383 (7)		

Angles

Cl(1)-Pt-P	95.10 (7)	Pt-N(1)-C(3)	108.2 (3)
Cl(1)-Pt-N(1)	89.7 (1)	N(1)-C(3)-N(2)	111.8 (4)
P-Pt-C(6)	93.2 (1)	C(3)-N(2)-C(6)	106.9 (4)
N(1)-Pt-C(6)	82.2 (2)	N(2)-C(6)-Pt	108.9 (3)
P-Pt-N(1)	174.3 (1)	C(1)-N(1)-C(2)	106.8 (4)
Cl(1)-Pt-C(6)	170.9 (1)	C(4)-N(2)-C(5)	109.2 (4)

$[CHN(CH_3)_2]Cl_2\}$. The crystal structure of the carbenoid complex consists of noninteracting, nearly planar molecules which have a cis stereochemistry. A perspective drawing is shown in Figure 2 and selected interatomic distances and angles and least squares planes are given in Table VIII.

In addition to being nearly planar, there are only minor deviations of the in-plane–Pt–donor angles from 90°. Likewise, the carbenoid ligand is highly planar. Interatomic angles associated with the carbene ligand are in agreement with the notion that bonding at carbon and nitrogen involve sp^2-hybrid orbitals although the Pt–Cl–N angle is somewhat large at 129.4 (8)°. This is not unexpected in view of the large difference in sizes of the substituents on carbon (Pt vs. H). The dihedral angle between the plane of the carbene ligand and the coordination plane is 84° which is within the range found for other Pt(II)–carbene complexes (70–90°).[18]

As described in the Experimental Section, some preparations of the carbene complex exhibited two C–N stretching absorptions in the solid state (1622 and 1611 cm^{-1}). Both samples gave a single C–N absorption in $CHCl_3$ solution at 1612 cm^{-1} and had identical NMR spectra in $CDCl_3$. X-ray diffraction data were collected on a crystal from a sample that exhibited two C–N stretching absorptions in the solid state, and the structure was solved.[19] Unfortunately, the structure exhibited some inexplicable differences in bond distances that suggested there might be imperfections in the crystal so that the structure has not been included here. However, it was apparent that the dihedral angle between the carbene and coordination planes differed in the two independent molecules in the unit cell (84° vs. 65°). Comparison of the infrared data for the two forms of the carbene complex

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[18] (a) Manojlović-Muir, L.; Muir, K. W., *J. Chem. Soc., Dalton Trans.* **1974**, 2427. (b) Anderson, G. K.; Cross, R. J.; Manojlović-Muir, L.; Muir, K. W.; Wales, R. A. *Inorg. Chim. Acta* **1978**, *29*, L193.

[19] Crystal data: space group $C2/c$; a = 36.1 (3) Å, b = 9.07 (3) Å, c = 29.26 (4) Å, β = 109.42 (4)°, Z = 16. The crystal chosen for data collection was selected from a sample crystallized by cooling a saturated acetonitrile solution.

Scheme I

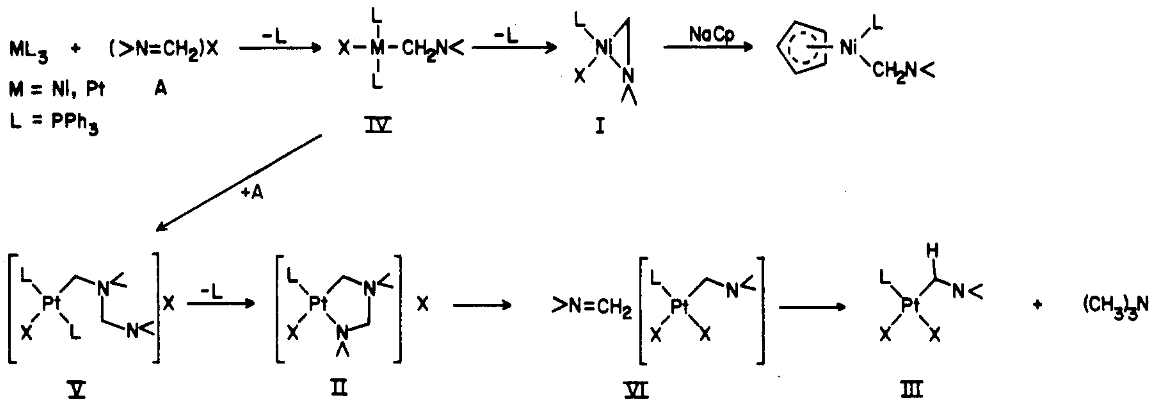

Table VIII. Selected Interatomic Distances (Å) and Angles (Deg) and Least-Squares Planes for *cis*-{(Ph$_3$P)Pt[CHN(CH$_3$)$_2$]Cl$_2$}

Distances

Pt-Cl(1)	2.347 (3)	N-C(2)	1.42 (2)
Pt-Cl(2)	2.345 (3)	N-C(3)	1.46 (2)
Pt-C(1)	1.96 (1)	P-C(4)	1.818 (9)
Pt-P	2.220 (2)	P-C(10)	1.799 (9)
C(1)-N	1.25 (1)	P-C(16)	1.828 (9)

Angles

Cl(1)-Pt-Cl(2)	89.4 (1)	C(1)-N-C(2)	124 (1)
Cl(1)-Pt-C(1)	177.7 (3)	C(1)-N-C(3)	123 (1)
Cl(1)-Pt-P	90.1 (1)	C(2)-N-C(3)	113 (1)
Cl(2)-Pt-C(1)	88.4 (3)	Pt-P-C(4)	110.8 (3)
Cl(2)-Pt-P	176.8 (1)	Pt-P-C(10)	117.0 (3)
P-Pt-C(1)	92.2 (3)	Pt-P-C(16)	113.9 (3)
Pt-C(1)-N	129.4 (8)		

Least-Squares Planes[a]

$0.435X + 0.478Y + 0.763Z = 0.328$		$0.410X - 0.816Y + 0.407Z = 4.570$	
atom	dev, Å	atom	dev, Å
Pt	−0.021	N	−0.026
Cl(1)	−0.028	C(1)	0.010
Cl(2)	0.041	C(2)	0.008
P	0.042	C(3)	0.008
C(1)	−0.033		

[a] Least-squares planes were calculated by the method described in ref 17; all atoms have unit weight. Equations refer to orthogonal axes with the *x* axis coincident with *a* and *z* with *c**.

indicates that the smaller dihedral angle results in a higher C–N stretching frequency. Since bonding between a carbenoid ligand and the metal involves back-donation from filled metal orbitals to the carbene carbon p orbital, it would seem that the maximum interaction would occur for dihedral angles of 90 or 0°. In a coordinate system where the carbenoid ligand is on the *x* axis, these limiting cases would utilize the metal d_{xz} and d_{xy} orbitals, respectively, for the π interaction with carbene carbon p orbital. The latter situation is less favorable in nonchelated systems because of steric interactions between the groups attached to the carbene carbon and cis ligands attached to the metal. The reasons for the deviations of the dihedral angles from the ideal value in may of the structurally characterized complexes are not apparent. These deviations may be a result of crystal packing effects or possibly to a trade-off between Pt–C and C–N multiple bonding.

The Pt–C(1) and C(1)–N bond distances are 1.96 (1) and 1.25 (1) Å, respectively. Both of these distances are quite short and are consistent with the presence of substantial multiple bond character to each interaction. Table VIII lists the pertinent data for other *cis*-dichloroplatinum(II) carbene structures for comparison with the present data. The distances observed for our complex are generally comparable with those of earlier structures although the present C(carbene)–N distance is significantly shorter than those in which the carbene carbon is bonded to two heteroatoms. It is only slightly different from the C–O distance in the C(OEt)CH$_2$Ph complex.[18b] Although it might be expected, on the basis of the previous discussion of the dihedral angle, that the Pt–C and C–N distances should be inversely correlated, there are insufficient structural data on similar compounds to indicate the extent of any relationship between these parameters. It might be noted that a C(carbene)–N distance of 1.266 (15) Å was found for *trans*-{[PhP(CH$_3$)$_2$]$_2$Pt(CH$_3$)[C(CH$_3$)N(CH$_3$)$_2$]}PF$_6$.[21]

Both Pt–Cl distances in the present complex are the same, which suggests similar trans influences for the carbene and triphenylphosphine ligands. The Pt–P distance is typical of those for complexes in which the phosphine is bonded trans to chlorine; the phenyl C–C distances and internal angles are normal in every sense.

Discussion

All of the products derived from reaction of dimethylmethyleniminium halides and M(PPh$_3$)$_3$ (M = Ni, Pt) and the intermediates that we believe are involved in their formation are outlined in Scheme I. Species IV has not been detected for either Ni or Pt although it is the most likely product from the initial reaction. We assume that it results from electrophilic attack of the iminium cation on the metal. In the case of nickel, species I is irreversibly formed.[1] This complex can be converted to an η^1-CH$_2$N(CH$_3$)$_2$ form by treatment with sodium cyclopentadienide, but this rearrangement cannot be accomplished by the addition of phosphorus ligands.[1] We assume either that IV does not form with platinum or that I and IV are in rapid equilibrium and IV is removed by alkylation with a second equivalent of iminium salt (to give V initially). Conversion of IV to I in the case of nickel is apparently much faster than the alkylation reaction since no evidence for a product containing the chelate ligand was ever obtained.

We view the conversion of chelate complex II to carbene complex III as proceeding by substitution of the amino group by chloride followed by dealkylation and hydride abstraction by the liberated iminium cation. Hydride abstraction in a metal complex by an iminium salt has precedent. Fong and Wilkinson reported (CO)$_4$Fe[CHN(CH$_3$)$_2$] and (CO)$_5$Cr[CHN(CH$_3$)$_2$] as the products of reaction of [(CH$_3$)$_2$C═CH$_2$]I with Fe(CO)$_4^{2-}$ and Cr(CO)$_5^{2-}$,

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[20] Badley, E. M; Muir, K. W.; Sim, G. A. *J. Chem. Soc., Dalton Trans.* **1976**, 1930.

[21] Stepaniak, R. F.; Payne, N. C. *Inorg. Chem.* **1974**, *13*, 797.

Table IX. Selected Structural Parameters in *cis*-[$Cl_2Pt(L)(carbene)$] Complexes

L	carbene	α,[a] deg	C_{sp^2}-X, Å	Pt-C, Å	Pt-Cl (trans to L), Å	Pt-Cl, Å	ref
PEt_3	C(OEt)NHPh	77	1.33 (2) O 1.33 (3) N	1.962 (18)	2.367 (7)	2.361 (5)	20
PMe_2Ph	$C(OEt)CH_2Ph$	85	1.283 (11)	1.920 (9)	2.355 (3)	2.375 (3)	19
PEt_3	$C\overline{N(Ph)CH_2CH_2N}Ph$	90	1.327 (11)	2.009 (13)	2.381 (3)	2.362 (3)	17
PPh_3	$C(H)N(CH_3)_2$	84	1.25 (1)	1.96 (1)	2.345 (3)	2.347 (3)	this work

[a] Dihedral angle between the carbene and coordination planes.

respectively.[22] These reactions apparently proceed via $(CO)_nM[\eta^1\text{-}CH_2N(CH_3)_2]^{1-}$, which reacts with a second equivalent of iminium salt. The fact that hydride abstraction has not been observed in neutral $\eta^1\text{-}CH_2N(CH_3)_2$ complexes is also consistent with the hypothesis of Cl^- involvement in the reaction of the chelate complex since proposed intermediate VI is then anionic.

We suggested earlier that the complexed $CH_2N(CH_3)_2$ moiety behaves much like the complexed allyl function.[2] This notion is further supported by the contrasting behavior of the allylnickel and -platinum complexes that are essentially analogous to I and II in the scheme. $[(\eta^3\text{-}C_3H_5)Pt(PPh_3)_2]Cl$ is apparently ionic in chloroform solution with a four-coordinate cation (assuming that the allyl group occupies two-coordination positions). However, the complex is fluxional (by NMR) in this medium even at −50 °C.[14] Since endo-exo proton interconversion in allyl complexes occurs via a σ-bonded allyl complex, this suggests that chloride ion is probably intimately involved in promoting the rearrangement (note that $[(\eta^3\text{-}C_3H_5)Pt(PR_3)Cl]$ complexes are stereochemically rigid). In fact, Kaduk and Ibers crystallized $[(\eta^1\text{-}C_3H_5)Pt(PPh_3)_2(Cl)]$ (as well as the ionic species) from a benzene–pentane solution.[14] In contrast, $[(\eta^3\text{-}C_3H_5)Ni(PPh_3)_2Cl]$ is five-coordinate and nonfluxional.[23] Thus, it appears that both η^3-allyl and η^2-iminium moieties are more strongly bonded to nickel than platinum (note that $\{(Ph_3P)_2Ni[\eta^2\text{-}CH_2N(CH_3)_2]\}^+ + Cl^-$ gives complex II).[1]

Work by Okawara and co-workers on oxidative–addition rections of $ClCH_2SCH_3$ with $(Ph_3P)_4$ M (M = Pd, Pt)[24,25] also suggests that η^2 forms of α-substituted alkyls are less stable for platinum than for the lighter group 8 elements. In both of these reactions *trans*-$[(Ph_3P)_2M(Cl)CH_2SCH_3]$ was formed (analogous to IV in the scheme) but the palladium complex was in equilibrium with $[(Ph_3P)Pd(\eta^2\text{-}CH_2SCH_3)Cl] + Ph_3P$. The η^2 complex can be isolated by removal of the dissociated phosphine. Removal of phosphine from the platinum complex gave $[(Ph_3P)Pt(\mu\text{-}CH_2SCH_3)Cl]_2$.

In view of Okawara's work, our failure to obtain complex IV with Pt is not easy to explain. However, the insolubility of the iminium salt and of the chelate complex in suitable solvents makes it difficult to make variations in reaction conditions. The fact that the chelate complex was obtained in reactions involving 1:1 ratios of $(Ph_3P)_3Pt$ and iminium salt suggests that formation of the chelate complex may be faster than oxidative–addition. Several attempts were made to prepare a $\eta^1\text{-}CH_2N(CH_3)_2$ complex using $LiCH_2N(CH_3)_2$[26] and Pt(II) starting materials but all failed in our hands.

Coupling of other unsaturates to give chelating ligands is well-known. To some extent the head-to-tail coupling of the iminium cations resembles the coupling reactions of $(CF_3)_2CO$ and $(CF_3)_2CNH$ performed by Stone and coworkers.[27] A large number of compounds of the type $L_2\overline{MXC(CF_3)_2Y}C(CF_3)_2$ (M = Ni, Pd, Pt; L = CNR, phosphorus or arsenic base; X = O, NH; Y = O, NH) were prepared, generally by addition of a second equivalent of unsaturate to a preformed π complex. It is believed, however, that these reactions occur via intermediates in which both unsaturated molecules are bonded in π fashion prior to C–N or C–O bond formation.

The process by which our chelating ligand is proposed to form is analogous to reactions of metal iminoacyls (M—CR=NR) with imidoyl halides in which the chelate complex $\overline{M\text{—}C(R)\text{=}N(R)C(R)\text{=}N}R$ is produced.[28-30]

Finally, it is interesting to note that although a much wider variety of bonding modes has been observed in phosphorus ylide complexes than is presently known for nitrogen ylides,[31] chelating forms of the former in which a neutral substituent serves as the second donor have not been prepared. One might expect, however, than an analogue of the nitrogen ylide chelate could be prepared from $[(CH_3)_2PCH_2P(CH_3)_3]^+$.[32]

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Registry No. A, 79328-81-7; B, 79328-82-8; $[(Ph_3P)\overline{PtCH_2N(CH_3)_2CH_2N}(CH_3)_2Cl]BF_4$, 79328-84-0; $(Ph_3P)_3Pt$, 13517-35-6; $[(CH_3)_2N\text{=}CH_2]Cl$, 30354-18-8.

Supplementary Material Available: Tables of final positional and isotropic thermal parameters for hydrogens atoms (both structures) and a listing of observed and calculated structure factors (both structures) (33 pages). Ordering information is given on any current masthead page.

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