Journal of Organometallic Chemistry, 71 (1974) 299—308
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THE CRYSTAL AND MOLECULAR STRUCTURE OF *trans*-$PtI(CMe{=}NC_6H_4Cl)(PEt_3)_2$: A COMPOUND DERIVED FROM THE INSERTION OF AN ISOCYANIDE INTO A METAL—CARBON BOND

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(Received November 6th, 1973)

Summary

The title compound, obtained from the reaction of the platinum alkyl compound, $PtI(Me)(PEt_3)_2$, and *p*-chlorophenyl isocyanide, crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell with dimensions *a* 20.903(3), *b* 8.531(1), *c* 15.176(2)Å and $\beta = 107.76(1)°$. Its crystal and molecular structure was determined, and refined by full-matrix isotropic-anisotropic least squares on 1791 independent counter data, to a final unweighted *R* factor of 3.8%. The structure of this species consists of discrete molecular units, in which the platinum atom assumes its expected four-coordinate square planar geometry with Pt—P distances of 2.314(3) and 2.321(3)Å, a Pt—I distance of 2.712(1)Å, and a Pt—C distance of 2.027(11)Å. The intramolecular Pt—N distance, the distance between the nitrogen of the acylimino-group and the metal atom, is found to be 3.042(10)Å. This is clearly a non-bonding distance, refuting an earlier suggestion based on PMR data that the metal atom achieves pseudo five-coordination in these species through coordination to this atom. No unusual intermolecular distances are observed in this structure, with the closest Pt—Pt distance being 8.531 Å.

Introduction

The room temperature PMR spectra of the compounds *trans*-$MI(CMe{=}NC_6H_{11})(PPhMe_2)_2$ (M = Pd [1], Pt [2]) has been reported to show non-equivalence of the phosphine methyl groups. This result was initially interpreted in terms of a five-coordinate platinum complex, with the acylimino-group functioning as a bidentate ligand coordinated to one metal through both carbon and nitrogen. In view of the predisposition of platinum(II) complexes to assume four- rather than five-coordination, this suggestion seemed of dubious merit. Moreover it is clear that any restriction of Pt—C bond rotation, regardless of coordination of nitrogen to the metal, could explain the PMR data [3].

Nonetheless, it appeared to us that the best resolution of the question of four- vs. five-coordination could be accomplished by a single crystal X-ray structural determination of one of these complexes. Such a study was clearly within the bounds of our current interest in isocyanide insertion reactions, which has recently been described in several papers [3—5]. We selected as the subject for this study the complex $PtI(CMe{=}NC_6H_4Cl)(PEt_3)_2$, which happened to yield crystals acceptable for this work. Herein we describe the crystal and molecular structure for this species. A prior communication on this work has appeared [6].

Experimental

Single Crystal X-ray Data

Well-formed pale yellow crystals were obtained by vapor diffusion of diethyl ether into a dichloromethane solution of *trans*-$PtI(CMe{=}NC_6H_4Cl)(PEt_3)_2$ [4] at room temperature. The crystal used for data collection had an approximately rectangular cross section with dimensions (each defined by the perpendicular distance between the opposite pair of crystal faces) of 0.50 mm (100) × 0.15 mm $(\bar{1}01)$ × 0.08 mm (010). The crystal was accurately centered on a Syntex $P\bar{1}$ four circle computer controlled diffractometer equipped with a graphite monochromator, such that its (100) axis was approximately coincident with the instrumental ϕ axis. After careful alignment of the crystal with the X-ray tube, fifteen diffraction maxima were automatically centered in 2θ, χ and ω. Mo-K_α radiation (λ 0.7107 Å) was used throughout the alignment and data collection procedures. After these reflections were assigned correct indices they were used in a least-squares procedure to give the best lattice and orientation parameters [7].

The measured lattice constants ($\approx 23°$) with their estimated standard deviations for the indicated monoclinic unit cell with C_{2h} $(2/m)$ Laue symmetry are a 20.903(3), b 8.531(1), c 15.176(2) Å, and $\beta = 107.760(10)°$. The unit cell volume is 2577.1(6) Å^3, yielding a calculated density of 1.832 g·cm^{-3} for M 710.89 and Z 4, which agrees well with the measured density of 1.828 g·cm^{-3}, determined by flotation in a mixture of carbon tetrachloride and methyl iodide. The total number of electrons per unit cell, $F(000)$, is 1368.

Intensity data were collected by the θ—2θ scan technique with stationary crystal-stationary counter background counts taken at the beginning and end of each scan. The normal Syntex procedure was used, wherein variable scan rates and scan ranges are determined according to the intensity and width of the peak being measured. For each peak the total time spent in taking the two background counts was set equal to the total scan time [7]. A total of 2480 reflections were collected, distributed through the two octants hkl and $\bar{h}kl$ ($3.0° \leqslant 2\theta \leqslant 40.0°$), of which 2355 reflections were Laue independent. The two standard reflections $(\bar{1}31)$ and $(4\bar{2}2)$ were monitored every 50 reflections as a check of electronic and crystal stability. During the entire data collection process, the intensity of the standard reflections varied by only ± 2% as measured on I, and therefore no corrections for crystal decay were necessary.

The data were corrected for Lorentz and polarization effects [8] and then converted to structure factor amplitudes $|F_o| = (I/L{\cdot}p)^{1/2}$ with $\sigma(F_o)$ taken as $\sigma(I)/2F_o{\cdot}L{\cdot}p$. A given reflection was considered statistically unobserved if the net intensity I was less than twice the standard deviation of the intensity $\sigma(I)$, these being calculated from standard expressions [9]. The instrument instability or "ignorance" factor E was set equal to 0.003 and is introduced into $\sigma^2(I)$ to avoid overweighting the strong reflections in least squares. The merged [8] data set gave a total of 1791 observed reflections, all of which were used in the structure determination.

Transmission factors, based on the linear absorption coefficient [10] for Mo-K_α radiation of 71.69 cm^{-1}, varied from 0.31 to 0.60 and accordingly the appropriate absorption corrections were made [11].

The data showed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, consistent only with the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5); No. 14).

Solution and refinement of the structure

The solution of the structure was accomplished by the heavy atom method and required the location of one molecule as the independent unit. A Fourier synthesis [12], phased on the location of the platinum and iodine atoms obtained from the interpretation of a three-dimensional Patterson map [13], gave initial coordinates for the two phosphorus atoms and the chlorine atom. After three preliminary cycles of least squares refinement [14], varying individual positional and isotropic thermal parameters, the discrepancy indices R_1 and R_2* were 15.7% and 18.9% respectively. A three-dimensional Fourier difference map revealed the positions of the remaining 21 non-hydrogen atoms and 12 of the 37 hydrogen atoms in the crystallographic asymmetric unit. This map also indicated very strong thermal anisotropy about the platinum and iodine atoms. Three cycles of full-matrix least squares refinement on all non-hydrogen atoms varying both positional and isotropic parameters and including ideal coordinates** for all hydrogen atoms, except for those on C(8), as fixed atom contributions (B_{iso} 6.0 Å^2), resulted in $R_1 = 8.8\%$ and $R_2 = 11.0\%$. A second difference map, phased on the non-hydrogen atoms only, located all the hydrogen atoms except H(15), H(18) and H(21). Two final cycles of full-matrix least squares refinement including all atoms, with anisotropic temperature factors for the Pt, I, Cl and P atoms and anomalous dispersion corrections for the Pt and I atoms***, resulted in convergence with $R_1 = 3.8\%$ and $R_2 = 4.6\%$. No value of shift/error > 0.08 was observed in the final cycle. The final data to parameter ratio was approximately 7/1.

All least-squares refinements were based on the minimization of $\Sigma w_i \| F_o | - | F_c \|^2$. The atomic scattering factors used for all non-hydrogen atoms were those compiled by Hanson et al. [17], while those used for hydrogen atoms were from Stewart et al. [18]. The calculated and observed structure factor amplitudes

(continued on p. 305)

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*Defined as $R_1 = [\Sigma \| F_o | - | F_c \| / \Sigma | F_o |] \times 100$ and $R_2 = [\Sigma w_i(|F_o| - |F_c|)^2 / \Sigma w_i |F_o|^2]^{1/2} \times 100$ using individual weights $w_i = 1/(\sigma(F_o))^2$.

**See ref. 15. All C—H distances were set at 1.0 Å; the phenyl hydrogen atoms were placed in the plane of the ring and those of the ethyl groups were placed tetrahedrally about each carbon with the methylene and methyl hydrogen atoms staggered with respect to each other. The C(8)-methyl group was idealized to tetrahedral geometry in an orientation that conformed closest to that observed in the first Fourier difference map.

***See Ref. 16. Both real and imaginary components were included with values Pt: —1.9, 9.6 and I: —0.5, 2.4 respectively.

TABLE 1

FINAL ATOMIC PARAMETERS FOR *trans*-PtI(CMe=NC_6H_4Cl)(PEt_3)$_2$ [a]

	x	y	z	B (Å^2)
Pt	21471(2)	1161(5)	31236(3)	*b*
I	15031(4)	−26842(9)	29004(6)	*b*
Cl	4646(2)	741(6)	8100(3)	*b*
P(1)	3038(2)	−1032(3)	4235(2)	*b*
P(2)	1214(2)	1167(4)	2031(2)	*b*
N	3051(5)	2938(11)	3195(6)	3.8(2)
C(1)	2796(6)	−1800(15)	5186(8)	4.4(3)
C(2)	2475(8)	−611(19)	5661(10)	6.3(3)
C(3)	3393(6)	−2740(14)	3822(7)	4.1(2)
C(4)	3615(8)	−2428(18)	2976(10)	6.6(4)
C(5)	3751(6)	199(14)	4781(8)	4.1(3)
C(6)	4321(7)	−535(18)	5569(9)	5.7(3)
C(7)	2578(5)	2257(13)	3430(7)	3.0(2)
C(8)	2307(6)	3157(15)	4081(7)	4.1(3)
C(9)	3388(6)	2305(13)	2623(7)	3.4(2)
C(10)	3124(6)	1379(14)	1843(8)	4.4(3)
C(11)	3501(6)	903(14)	1294(8)	4.1(3)
C(12)	4158(6)	1308(15)	1530(8)	4.6(3)
C(13)	4452(7)	2201(16)	2296(9)	5.5(3)
C(14)	4065(7)	2732(15)	2833(8)	4.8(3)
C′(1)	1327(7)	3153(17)	1627(9)	5.3(3)
C′(2)	720(8)	3899(19)	935(10)	6.8(4)
C′(3)	472(7)	1197(17)	2428(10)	6.2(3)
C′(4)	543(8)	1973(21)	3321(11)	7.6(4)
C′(5)	881(7)	53(14)	966(8)	4.5(3)
C′(6)	1379(9)	−293(19)	475(11)	7.0(4)
H(1)[c]	3205	−2232	5642	
H(2)	2467	−2676	4933	
H(3)	2347	−1120	6167	
H(4)	2058	−185	5186	
H(5)	2796	259	5896	
H(6)	3037	−3568	3685	
H(7)	3784	−3087	4352	
H(8)	3804	−3407	2787	
H(9)	3969	−1589	3114	
H(10)	3222	−2070	2446	
H(11)	3574	1150	5011	
H(12)	3941	538	4267	
H(13)	4690	235	5818	
H(14)	4504	−1484	5335	
H(15)	4137	−872	6079	
H(16)	2582	2922	4731	
H(17)	1830	2843	3989	
H(18)	2329	4303	3960	
H(19)	2645	1015	1696	
H(20)	3291	283	710	
H(21)	4939	2480	2473	
H(22)	4272	3377	3389	
H(23)	1697	3073	1340	
H(24)	1475	3821	2193	
H(25)	848	4975	776	
H(26)	351	3995	1223	
H(27)	574	3247	370	
H(28)	350	71	2482	
H(29)	112	1725	1939	
H(30)	111	1908	3463	
H(31)	668	3092	3272	
H(32)	906	1437	3815	

(continued)

TABLE 1 (Continued)

	x	y	z	$B(\text{Å}^2)$
H(33)	493	670	572	
H(34)	707	−958	1153	
H(35)	1161	−896	−109	
H(36)	1766	−895	871	
H(37)	1552	734	290	

[a] The Pt and I positional parameters have been multiplied by 10^5, all others by 10^4. The estimated standard deviations in the last digit is given in parenthesis in this and the following tables. [b] Anisotropic temperature factors of the form $\exp\{-[\beta_{11}\cdot h^2 + \beta_{22}\cdot k^2 + \beta_{33}\cdot l^2 + 2\beta_{12}\cdot hk + 2\beta_{13}\cdot hl + 2\beta_{23}\cdot kl]\}$ were used for these atoms. The resulting thermal coefficients with their estimated standard deviations are as follows:

	$10^5\times\beta_{11}$	$10^5\times\beta_{22}$	$10^5\times\beta_{33}$	$10^5\times\beta_{12}$	$10^5\times\beta_{13}$	$10^5\times\beta_{23}$
Pt	148(2)	757(9)	385(3)	1(2)	86(2)	−8(3)
I	263(3)	1005(15)	803(6)	−137(5)	75(3)	62(7)
Cl	322(13)	3025(91)	873(25)	206(30)	284(15)	70(41)
P(1)	178(10)	932(49)	418(16)	76(18)	87(10)	90(23)
P(2)	156(9)	1244(56)	405(17)	67(19)	73(10)	0(24)

[c] The hydrogen parameters are the idealized coordinates used for the final two least squares cycles.

TABLE 2

INTERATOMIC DISTANCES AND BOND ANGLES

A. Bonding intramolecular distances (Å)

Metal—halogen:	Pt—I	2.712(1)		
Metal—phosphorus:	Pt—P(1)	2.314(3)		
	Pt—P(2)	2.321(3)		
		2.318(av)		
Metal—carbon:	Pt—C(7)	2.027(11)		
Isocyanide bonds:	Inserted methyl group			
	C(7)—C(8)	1.492(16)		
	Nitrogen—carbon			
	N—C(7)	1.287(13)		
	N—C(9)	1.383(14)		
	Chlorine—carbon			
	Cl—C(12)	1.774(13)		
	Phenyl ring			
	C(9)—C(10)	1.389(15)	C(13)—C(14)	1.388(18)
	C(9)—C(14)	1.401(16)	C(11)—C(12)	1.354(15)
	C(10)—C(11)	1.372(16)	C(12)—C(13)	1.369(16)
Phosphine bonds:	Phosphorus—carbon			
	P(1)—C(1)	1.792(12)	P(2)—C′(1)	1.842(15)
	P(1)—C(3)	1.830(12)	P(2)—C′(3)	1.827(15)
	P(1)—C(5)	1.806(12)	P(2)—C′(5)	1.820(12)
	Carbon—carbon			
	C(1)—C(2)	1.515(19)	C′(1)—C′(2)	1.517(18)
	C(3)—C(4)	1.516(18)	C′(3)—C(4)	1.475(20)
	C(5)—C(6)	1.540(18)	C′(5)—C′(6)	1.483(22)

B. Intermolecular distances < 3.8 Å (Å)

Cl···Cl	3.474[a]	C(8)···C′(6)	3.738[b]
C(8)···C(11)	3.612[b]	C(2)···C′(1)	3.794[b]
C(6)···C(13)	3.737[b]		

TABLE 2 (Continued)

C. Selected nonbonding intramolecular distances (Å)			
Pt···N	3.042(10)	C(10)···C′(1)	3.968
C(5)···C(14)	3.861	C(10)···C′(6)	3.871
C(8)···C(5)	3.828	H(19)···H(36)	2.488
C(8)···C(2)	3.954	H(11)···H(16)	2.496
C(8)···C′(1)	3.668	H(17)···H(31)	2.350
C(8)···C′(4)	3.658	H(17)···H(32)	2.221
D. Intramolecular angles (Deg.)			
Angles centered on platinum			
I—Pt—P(1)	88.65(8)	I—Pt—P(2)	88.51(8)
P(1)—Pt—P(2)	176.76(10)	I—Pt—C(7)	172.47(30)
P(2)—Pt—C(7)	91.93(29)	C(7)—Pt—P(1)	90.68(28)
Angles centered on phosphorus			
Pt—P(1)—C(1)	112.3(4)	Pt—P(2)—C′(1)	115.4(4)
Pt—P(1)—C(3)	114.1(4)	Pt—P(2)—C′(3)	112.5(5)
Pt—P(1)—C(5)	117.2(4)	Pt—P(2)—C′(5)	116.3(4)
C(1)—P(1)—C(3)	103.2(5)	C′(1)—P(2)—C′(3)	107.7(6)
C(1)—P(1)—C(5)	103.8(5)	C′(1)—P(2)—C′(5)	103.7(5)
C(3)—P(1)—C(5)	104.8(5)	C′(3)—P(2)—C′(5)	99.6(6)
Ethyl group angles			
P(1)—C(1)—C(2)	114(1)	P(2)—C′(1)—C′(2)	117(1)
P(1)—C(3)—C(4)	114(1)	P(2)—C′(3)—C′(4)	117(1)
P(1)—C(5)—C(6)	117(1)	P(2)—C′(5)—C′(6)	114(1)
Imino group angles			
Pt—C(7)—C(8)	112.5(8)	N—C(7)—C(8)	115.4(10)
Pt—C(7)—N	131.9(8)	N—C(9)—C(10)	127.6(11)
C(7)—N—C(9)	125.4(10)	N—C(9)—C(14)	115.3(10)
C(9)—C(14)—C(13)	121(1)	C(12)—C(11)—C(10)	120(1)
C(10)—C(9)—C(14)	117(1)	C(13)—C(12)—C(11)	122(1)
C(11)—C(10)—C(9)	122(1)	C(14)—C(13)—C(12)	119(1)
Cl—C(12)—C(11)	119(1)	Cl—C(12)—C(13)	119(1)

[a,b] The distances are given from the indicated atoms in one molecule to those in another molecule related by the symmetry operations: (*a*), $1-x, -y, -z$; (*b*), $x, 1/2-y, 1/2-z$.

TABLE 3

EQUATIONS OF BEST LEAST-SQUARES PLANES, DISTANCES OF SELECTED ATOMS FROM THESE PLANES, AND DIHEDRAL ANGLES BETWEEN THESE PLANES[a,b]

A. Equations of Planes and Distances (Å) of Selected Atoms from the Planes

(a). Plane containing Pt, I, P(1) and P(2)

$$0.657X - 0.237Y - 0.716Z + 1.276 = 0$$

Pt	0.02	P(1)	−0.01
I	0.00	P(2)	−0.01
C(7)	−0.24	N	0.59

(b). Plane containing Pt, N, C(7) and C(9)

$$-0.460X + 0.386Y - 0.800Z + 4.970 = 0$$

Pt	−0.001	C(7)	0.003
N	−0.003	C(9)	0.001

(c). Plane containing C(9) through C(14)

$$-0.085X + 0.826Y - 0.558Z + 0.986 = 0$$

C(9)	0.00	C(12)	0.00
C(10)	−0.01	C(13)	−0.01
C(11)	0.01	C(14)	0.01

B. Dihedral angles (°) between normals to planes

(a) and (b)	79.72	(b) and (c)	36.50
(a) and (c)	81.52		

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[a] The equations of the planes are given in an orthogonal Ångström coordinate system (X, Y, Z) which is related to the fractional coordinates (x, y, z) of the monoclinic unit cell by the transformation $X = ax + cz \cos\beta$, $Y = by$, $Z = cz \sin\beta$. [b] Unit weights were used for all atoms in the application of the Smith least-squares planes program.

obtained from the last cycle of the anisotropic least squares refinement are available*. The positional and thermal parameters for all atoms are given in Table 1. Interatomic bonding distances and bond angles, with estimated standard deviations calculated with the Busing—Martin—Levy function and error program [19] from the full inverse matrix are presented in Table 2. Equations of least squares planes and the dihedral angles between the normals to these planes are listed in Table 3 [20].

Results and discussion

The compound *trans*-PtI(CMe=NC$_6$H$_4$Cl)(PEt$_3$)$_2$ consists of discrete molecules separated by normal van der Waals distances. The closest Pt—Pt distance is 8.531 Å, ruling out possible metal—metal chain interactions.

The molecular structure of this species is shown in Fig. 1 [21]. The coordination around platinum is essentially square planar, although the bond angles about the central metal show slight distortion (see Table 2*D*). The phosphine ligands are in a *trans* configuration, as had been predicted earlier from PMR data. The Pt, I and the two P atoms lie in a well-defined plane; the phosphorus—platinum—iodine angles are slightly less than 90°. The acylimino carbon atom, C(7), is situated below this plane (by 0.24 Å), while the nitrogen atom bonded to it is 0.60 Å above this plane. The plane defined by C(7), N, and C(9), compo-

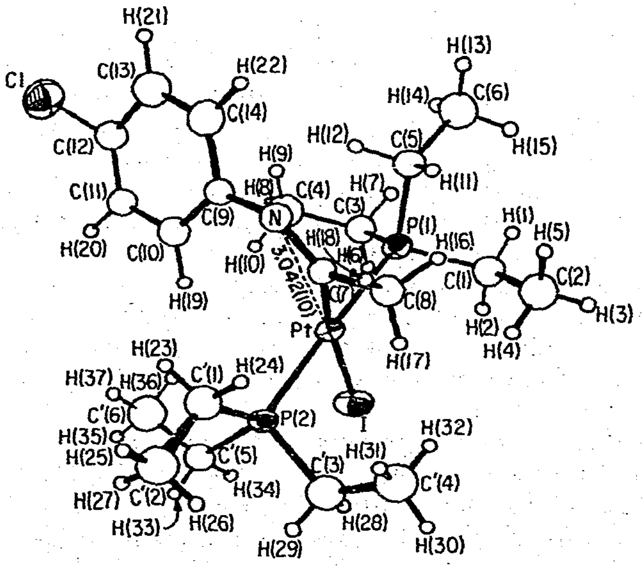

Fig. 1. A view of *trans*-PtI(CMe=NC$_6$H$_4$Cl)(PEt$_3$)$_2$ showing the overall stereochemistry and the atom numbering scheme.

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*The table of structure factors has been deposited as NAPS Document No. 02295, with ASIS/NAPS, c/o Microfiche Publications, 305 E. 46th Street, New York, New York 10017. A copy may be secured by citing the document number and remitting $1.50 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications.

nent atoms of the acylimino-group, and the metal atom has a normal at 79.72° to the plane containing the metal, both phosphorus atoms, and the iodine atom. The Pt—C(7)—N and C(7)—N—C(9) angles are 131.9(8)° and 125.4(10)° respectively. These measured values are somewhat higher than the values expected for the simple representation of sp^2 hybridization at each atom.

The two platinum—phosphorus bond lengths of 2.314(3) and 2.321(3) Å are comparable to other known distances in platinum—phosphorus compounds wherein phosphines are in a *trans* configuration; viz., the Pt—P distances in $Pt(NO_2)_2(PEt_3)_2$ [2.31(1) and 2.30(1) Å] [22], and in $PtX_2(PEt_3)_2$ [X = Cl, 2.298(18) Å and X = Br, 2.315(4) Å] [23]. The platinum—iodine distance in $PtI(CMe{=}NC_6H_4Cl)(PEt_3)_2$ is 2.712(1) Å. This value may be compared with platinum—iodine bond lengths in the platinum(IV) compounds $Pt(acac)_2I_2$ [24] and $(PtI_4)_\infty$ [25] which are found to be 2.667(1) and 2.62 Å (Pt—I terminal distance) respectively. The only platinum(II) species for which a platinum—iodine bond length is recorded is *trans*-$Pt[C_6H_4(AsMe_2)_2]_2I_2$; in this species the axial metal—iodine bonds are substantially longer, at a value of 3.50(1) Å [26]. The Pt—C distance of 2.027(11) Å is similar to those of 1.98(2) and 2.00(3) Å in the imido complex *cis*-$PtCl_2[C(OEt)NHPh]PEt_3$ [27] and in the carbene complex *trans*-$PtCl_2[C(NPhCH_2)_2]PEt_3$ [28] respectively, and does not appear to be unusual.

The primary purpose for carrying out this structural determination was to ascertain whether the imino nitrogen was bonded to the metal atom, with the latter thus achieving five-coordination. The results clearly confirmed our earlier expectations that this coordination does not occur, and that the acylimino group is bonded to the metal in the expected manner. The imino nitrogen atom is found at a distance from the metal of 3.042(10) Å, approximately 0.9 Å longer than ordinary bonding distances. There appears to be no constraint imposed which brings the nitrogen atom close to the platinum; indeed the platinum—carbon—nitrogen angle of 131.9(8)° seems somewhat larger than anticipated for the expected carbon atom geometry. It should be pointed out that in such instances where a hydrocarbon ligand containing a heteroatom is known to coordinate to a metal, the structure is inevitably distorted to give a metal—heter atom distance smaller than the metal—carbon distance. For example, in the structure of $(PhCH{=}CH{-}CH{=}NPh)Fe(CO)_3$, the nitrogen atom is found to be about 0.1 Å closer to the metal than are the carbon atoms in the ligand [29]. For a ligand $MeC{\equiv}N^+Ph$ to bond to platinum there is no reason not to expect the same observation to apply, i.e., if there were a bonding interaction, nitrogen ought to be closer to the metal than is carbon.

We think it fair to assume that this type of structure is appropriate for other $PtX(CR{=}NR')L_2$ species including the complex $PtMe(CMe{=}NC_6H_{11}Cl)(PPhMe_2)_2$ [5] for which PMR indicated a dissimilarity of phosphine methyl groups. This being so, assignment of the PMR results to asymmetry within the molecule resulting only from a restriction of rotation of the platinum to carbon bond is reasonable. As pointed out earlier in this paper, no bonding of platinum to nitrogen need be implied in this description.

The structural data here does suggest the possibility of restricted rotation of the platinum—carbon bond as a result of steric factors. The statistically significant but slight distortion of the I—Pt—P(1) and I—Pt—P(2) angles, from the idealized 90° to the observed values of 88.65(8)° and 88.51(8)° respectively, is a measure of the non-bonding steric interaction of the methyl-imino group and the phosphine ligands. The latter are bent away from the imino group. This may be considered as evidence for some steric crowding and in accord with the proposed restricted rotation about the platinum—carbon bond in this type of complex. The closest non-bonding interaction between elements of the phosphine and imino group are still quite large however. The shortest C—C distance found is 3.66 Å and the closest H—H approach is 2.22 Å (see Table 2*C*). The effective van der Waals radius for a methyl or methylene group is 2.0 Å.

It would be interesting to look next at the products derived from bis-insertion of an isocyanide into a metal—carbon bond. For the palladium species, with the ligand $PPhMe_2$, the same dissimilarity of phosphine methyl groups is noted.

Acknowledgement

We acknowledge the financial support of the National Science Foundation (GP 17207) and the University of Wisconsin Graduate School for this work. The acquisition of a Syntex Diffractometer System, available for our use, was made possible by a National Science Foundation major instrument grant to the Department.

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