

Crystal and Molecular Structure of a Dinuclear Ortho-Metalated Platinum Ylid Complex, $[\text{Pt}(\mu\text{-Cl})\text{CH}_3\text{COCHP}(\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)_2]_2 \cdot 2\text{CDCl}_3$

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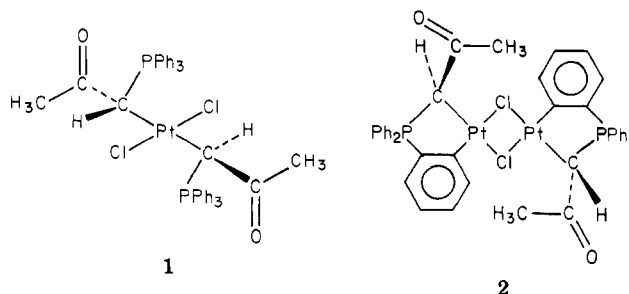
The product of the reaction between PtCl_2 and APPY (APPY = acetylmethylenetriphenylphosphorane, $(\text{C}_6\text{H}_5)_3\text{PCHC}(\text{O})\text{CH}_3$), upon heating a 1:2 mole ratio at reflux in acetonitrile for 44 h, was originally formulated as $\text{Pt}(\text{APPY})_2\text{Cl}_2$ (1) on the basis of elemental analysis and infrared and proton NMR spectral data. However, this product has now been shown by X-ray crystallography to have undergone ortho-metalation of an APPY ligand and dimerization to form $[\text{Pt}(\mu\text{-Cl})\text{CH}_3\text{COCHP}(\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)_2]_2$ (2). The $\text{APPYH}^+\text{Cl}^-$ formed in the process was identified by its IR, ^1H , ^{13}C , and ^{31}P NMR spectra and removed by washing the original sample with water. Yellow monoclinic crystals of compound 2 and two molecules of deuteriochloroform, space group C_{2h}^2-C2/c were obtained by slow evaporation of a deuteriochloroform solution of the original reaction product. The unit-cell parameters at 26 °C are $a = 21.33$ (1) Å, $b = 18.453$ (3) Å, $c = 14.337$ (6) Å, $\beta = 122.93$ (2)°, and $Z = 4$. The structure has been refined to an R index on F of 0.070 for 3214 observations and 263 parameters. The two platinum atoms and the two chlorine atoms of compound 2 are planar, due to a crystallographically imposed inversion center (i) located between the two platinum atoms and the two bridging chlorine atoms. The coordination about each of the platinum atoms is square planar with a platinum-to-platinum nonbonding distance of 3.599 Å. The two deuteriochloroform molecules are weakly interacting with the carbonyl oxygen of the ortho-metalated APPY ligand, $\text{O}\cdots\text{D} = 2.339$ Å. The ortho-metalating APPY ligand is puckered, as would be expected for a five-membered chelate containing only single bonds. The significant ^1H , ^{13}C , and ^{31}P NMR and IR spectral data for this compound are also discussed.

Introduction

Beginning approximately 18 years ago, IR and ^1H NMR spectroscopic evidence¹ and X-ray structural data² were obtained which showed that carbonyl-containing ylids could behave as ambidentate ligands, capable of either C or O coordination. As part of this laboratory's program to develop improved physical methods for characterizing transition-metal complexes of such ligands,³ an X-ray crystal structure determination was undertaken to corroborate the results of a multinuclear NMR investigation that is still in progress.

The product of the reaction between PtCl_2 and APPY (APPY = acetylmethylenetriphenylphosphorane, $(\text{C}_6\text{H}_5)_3\text{PCHC}(\text{O})\text{CH}_3$), obtained by heating a 1:2 mole ratio at reflux in acetonitrile for 44 h, was originally formulated to be $\text{Pt}(\text{APPY})_2\text{Cl}_2$ (1) on the basis of elemental analysis and infrared and proton NMR spectral evidence.^{1c} The presence of more than one signal in both the methine and methyl regions of the proton NMR spectrum suggested, however, that isomerization might be taking place. Thus, in order to discern which isomers might be present, crystals of the reaction product were obtained by slow evaporation of the deuteriochloroform solution. Solution of the structure indicated, however, that the title com-

ound, 2, had actually been formed during the original synthesis.



This X-ray crystal structure (Figure 1) was received with some surprise because of the significantly different elemental analysis that would be expected for compound 2. The analysis of the original sample, however, remained in agreement with that calculated for compound 1. The presence of a 1:2 stoichiometric amount of compound 2 and $\text{APPYH}^+\text{Cl}^-$ in the initial reaction product was therefore hypothesized, and, upon thorough washing of the sample with water, the expected elemental analysis corresponding to compound 2 was obtained for the residue.

Standard physical and spectral data for the purified product, 2, are reported herein. The mitigating factors for orthometalation of the APPY ligand in this system, and the significance of this result to our study and to others are also discussed.

Experimental Section

The yellow material to be recrystallized was taken from an elementally analyzed, spectrally characterized $\text{Pt}(\text{APPY})_2\text{Cl}_2$ sample previously reported.^{1c} The decomposition point (112 °C) and ^1H NMR spectrum were confirmed, as was the elemental analysis. (Anal. Calcd for $[\text{Pt}(\text{CH}_3\text{C}(\text{O})\text{CHP}(\text{C}_6\text{H}_5)_2)_2\text{Cl}_2]$: C, 55.88; H, 4.24; P, 6.75. Found (originally): C, 55.70; H, 4.31; P, 6.80. Found (currently): C, 55.84; H, 4.19; P, 6.55.

(1) (a) Nesmeyanov, N. A.; Novikov, V. M.; Reutov, O. A. *J. Organomet. Chem.* 1965, 4, 202. (b) Buckle, J.; Harrison, P. G. *Ibid.* 1973, 49, C17. (c) Weleski, E. T., Jr.; Silver, J. L.; Jansson, M. D.; Burmeister, J. L. *Ibid.* 1975, 102, 365. (d) Bravo, P.; Fronza, G.; Ticozzi, C. *Ibid.* 1976, 111, 361; Bravo, P.; Fronza, G.; Ticozzi, C.; Gaudiano, G. *Ibid.* 1974, 74, 143. (e) Kozuka, H.; Matsubayashi, G.; Tanaka, T. *Inorg. Chem.* 1976, 15, 417.

(2) Buckle, J.; Harrison, P. G.; King, T. J.; Richards, J. A. *J. Chem. Soc., Chem. Commun.* 1972, 1104.

(3) Kargol, J. A.; Crecely, R. W.; Burmeister, J. L. *Inorg. Chem.* 1979, 18, 2532. Pan, W.-H.; Fackler, J. P., Jr.; Kargol, J. A.; Burmeister, J. L. *Inorg. Chim. Acta* 1980, 44, L95. Fultz, W. C.; Burmeister, J. L.; Cheng, C. P.; Brown, T. L. *Inorg. Chem.* 1981, 20, 1734.

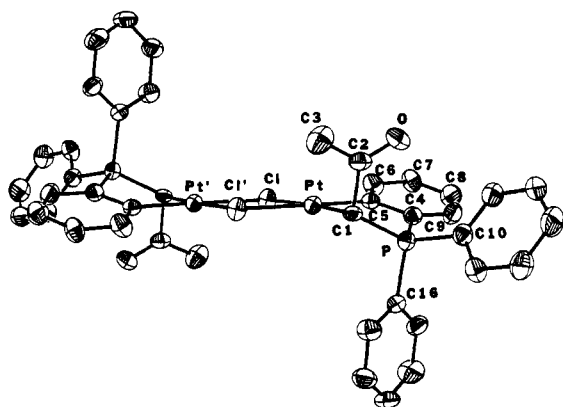


Figure 1. Structure and labeling scheme for $[\text{Pt}(\mu\text{-Cl})\text{-CH}_3\text{COCHP}(\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)_2]_2 \cdot 2\text{CDCl}_3$ (thermal ellipsoids; 35% probability). All hydrogens and solvent molecules are removed for clarity.

Table I. Crystal and Intensity Data Collection Summary

mol formula	$[\text{Pt}(\mu\text{-Cl})\text{CH}_3\text{COCHP}(\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)_2]_2 \cdot 2\text{CDCl}_3$
fw	667.27
mol wt	1334.54
<i>a</i> , Å	21.33 (1)
<i>b</i> , Å	18.453 (3)
<i>c</i> , Å	14.337 (6)
β , deg	122.93 (2)
<i>V</i> , Å ³	4736 (3)
space group	C_2/c
ρ (calcd), g cm ⁻³	1.871
<i>Z</i>	4 (8 half molecules)
cryst dimens, mm	0.2 × 0.2 × 0.3
radiation	Mo $K\alpha$ (graphite monochromated)
abs coeff μ (Mo $K\alpha$), cm ⁻¹	67.6
temp, °C	26
scan speed, deg min ⁻¹	variable; 4.0–20.0
scan type	ω
scan range	0.8° below $2\theta(K\alpha_1)$ to 0.8° above $2\theta(K\alpha_2)$
stds monitored	3 stds every 147 reflections
2θ limits, deg	3.0–50.0
reflectns collected	$\pm h, k, l$
no. of reflectns collected	4612
unique reflectn	4180
unique reflectns used	3214 with $F_0^2 > 3.00\sigma(F_0)^2$
ignorance factor, <i>g</i>	0.00203
<i>R</i> (<i>F</i>)	0.0703
<i>R</i> _w (<i>F</i>)	0.0703
GOF	1.224

Crystals of $[\text{PtCl}(\text{C}_{21}\text{H}_{18}\text{OP})]_2 \cdot 2\text{CDCl}_3$ suitable for X-ray diffraction were obtained by slow evaporation from deuteriochloroform. The yellow crystals were attached to a glass fiber and encapsulated with epoxy cement to prevent the loss of molecules of solvation. Data were collected on a Nicolet R3 diffractometer using graphite-monochromated Mo $K\alpha$ radiation. The reflections were collected by an ω scan technique over a range of 3–50° in 2θ . A summary of pertinent crystallographic parameters is presented in Table I.

The structure was solved and refined by using the Nicolet SHELXTL (Version 3.0) programs. An empirical absorption correction was applied to the data by using ψ -scan data from close-to-axial (i.e., $\chi = 90$ or $270 \pm 10^\circ$) reflections (absorption coefficient 67.6 cm⁻¹). The ψ -scan data were refined by a six-parameter procedure to define a pseudoellipsoid used to calculate the corrections (transmission coefficient, max/min = 0.266/0.133). A profile-fitting procedure was applied to the data to improve the precision of the measurement of weak reflections. No correction for decay was required.

The direct methods technique (SOLV) yielded the heavy-atom position but related to a displaced origin. The origin definition

Table II. Final Atom Coordinates ($\times 10^4$)

atom	<i>x</i>	<i>y</i>	<i>z</i>
Pt	9117 (1)	4791 (1)	3750 (1)
P	8036 (2)	4302 (2)	1357 (3)
Cl	10234 (2)	5501 (2)	4323 (3)
O	7530 (6)	5751 (7)	1536 (10)
C(1)	8628 (7)	5037 (7)	2102 (11)
C(2)	8203 (9)	5757 (9)	1912 (11)
C(3)	8631 (11)	6431 (10)	2170 (15)
C(4)	7711 (7)	4013 (8)	2217 (11)
C(5)	8213 (7)	4213 (8)	3335 (11)
C(6)	8017 (8)	3987 (10)	4076 (12)
C(7)	7367 (8)	3616 (10)	3740 (14)
C(8)	6896 (10)	3417 (10)	2632 (14)
C(9)	7077 (8)	3622 (9)	1861 (13)
C(10)	7265 (8)	4461 (9)	-68 (11)
C(11)	6590 (9)	4703 (10)	-290 (14)
C(12)	6033 (10)	4860 (11)	-1362 (14)
C(13)	6119 (11)	4772 (13)	-2208 (14)
C(14)	6788 (10)	4509 (11)	-2008 (13)
C(15)	7361 (8)	4357 (10)	-916 (11)
C(16)	8587 (8)	3589 (8)	1267 (11)
C(17)	9151 (8)	3758 (10)	1104 (13)
C(18)	9535 (9)	3214 (10)	974 (14)
C(19)	9352 (10)	2482 (10)	1000 (14)
C(20)	8806 (11)	2331 (9)	1208 (16)
C(21)	8406 (9)	2889 (9)	1294 (12)
ClA ^a	10250 (4)	1079 (4)	-68 (5)
ClB ^a	11177 (5)	2251 (5)	1150 (8)
ClC ^a	10714 (7)	2024 (9)	-1119 (9)
C ^a	10975 (12)	1656 (15)	124 (17)
D ^a	11434	1406	368

^a Solvent.

was determined by fixing the inversion center through the special position (0, $1/2$, $1/2$). All other non-hydrogen atoms were located by difference-Fourier techniques. All non-hydrogen atoms were refined anisotropically by using blocked-cascade, least-squares refinement methods.⁴ The hydrogens were calculated by using a riding model ($d(\text{C-H}) = 0.96$ Å; $U = 1.2U$ for the carbon atom to which it is attached). The final discrepancy indices are $R(F) = 7.0\%$ and $R_w(F) = 7.0\%$. The final difference map showed several peaks greater than $1 \text{ e } \text{Å}^{-3}$ that were generally less than 1.10 Å from the platinum atoms. All attempts to eliminate these peaks proved unsuccessful.

Following the solution of this structure, the original sample of “[Pt(APPY)₂Cl₂]” was washed with water and the water evaporated, repeatedly, until the washings no longer produced any white residue of APPYH⁺Cl⁻. The analysis of the completely washed sample (decomp pt 150 °C) agreed with that calculated

for compound 2. (Anal. Calcd for $[\text{Pt}(\mu\text{-Cl})\text{CH}_3\text{COCHP}(\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)_2]_2$: C, 46.04; H, 3.31; P, 5.65. Found: C, 45.97; H, 3.34; P, 5.25).

Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada. Infrared spectra were obtained as KBr pellets on a Perkin-Elmer Model 180 spectrophotometer. NMR spectra of deuteriochloroform solutions were measured by using a Bruker WM 250 spectrometer. Melting points were obtained on a Hoover-Thomas capillary melting point apparatus and are uncorrected.

Results and Discussion

Perhaps owing to the strong case for orthometalation which can be made from deuterium exchange⁵ and/or spectroscopic evidence^{1b,c,6} (including ¹H NMR integration,

(4) SHELXTL User Manual, Revision 3, July 1981, p 9.01.

(5) (a) Cope, A. C.; Siekman, R. W. *J. Am. Chem. Soc.* **1965**, *87*, 3272. (b) Gehrig, K.; Hugentobler, M.; Klaus, A. J.; Rys, P. *Inorg. Chem.* **1982**, *21*, 2493.

(6) Gill, D. F.; Mann, B. E.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1973**, 270. Ahmad, N.; Ainscough, E. W.; James, T. A.; Robinson, S. D. *Ibid.* **1973**, 1151. Hiraki, K.; Onishi, M.; Ohnuma, K.; Sugino, K. *J. Organomet. Chem.* **1981**, *216*, 413. Stewart, R. P., Jr.; Isbrandt, L. R.; Benedict, J. J.; Palmer, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 3215. Stewart, R. P., Jr.; Isbrandt, L. R.; Benedict, J. J. *Inorg. Chem.* **1976**, *15*, 2011.

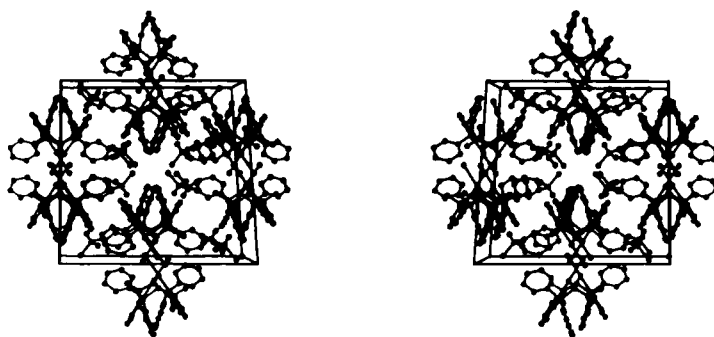


Figure 2. Stereopacking diagram of all atoms, including solvent molecules, for $[\text{Pt}(\mu\text{-Cl})\text{CH}_3\text{COCHP}(\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)_2]_2 \cdot 2\text{CDCl}_3$, as viewed down the c axis.

Table III. Selected Interatomic Distances (Å) and Angles (deg) for $[\text{PtCl}(\text{C}_{21}\text{H}_{18}\text{OP})]_2 \cdot 2\text{CDCl}_3$ with Estimated Standard Deviations

Bond Distances			
Pt-Cl	2.438 (4)	C2-C3	1.467 (25)
Pt-Cl'	2.384 (4)	C5-C4	1.409 (17)
Pt-C1	2.048 (15)	C5-C6	1.398 (28)
Pt-C5	1.990 (15)	C6-C7	1.378 (24)
P-C1	1.762 (13)	C7-C8	1.390 (22)
P-C4	1.792 (20)	C8-C9	1.408 (33)
P-C10	1.820 (12)	C9-C4	1.363 (23)
P-C16	1.815 (18)	Pt...Pt'	3.599
C1-C2	1.547 (22)	Cl...Cl'	3.223
C2-O	1.228 (21)	C-C(av) ^a	1.37 (3)
Bond Angles			
Cl-Pt-Cl'	83.4 (2)	C1-P-C10	118.0 (7)
Cl-Pt-C1	93.5 (4)	C1-P-C16	108.8 (7)
Cl-Pt-C5	178.1 (5)	C4-P-C10	111.7 (8)
Cl'-Pt-C1	176.1 (5)	C4-P-C16	109.9 (8)
Cl'-Pt-C5	94.8 (4)	C10-P-C16	105.1 (7)
Pt-C1-C5	88.3 (6)	P-C4-C5	111.5 (12)
Pt-Cl-Pt'	96.6 (2)	P-C4-C9	125.2 (12)
Pt-C1-P	106.1 (8)	C5-C4-C9	123.3 (18)
Pt-C1-C2	106.0 (11)	C5-C6-C7	122.8 (14)
P-C1-C2	113.3 (9)	C6-C7-C8	119.7 (20)
Pt-C5-C4	119.5 (13)	C7-C8-C9	119.3 (17)
Pt-C5-C6	124.9 (9)	C8-C9-C4	119.3 (14)
C4-C5-C6	115.5 (14)	C-C-C(av) ^a	120 (2)
C1-P-C4	103.3 (8)		

^a In phenyls not interacting with Pt.

¹³C NMR, ³¹P NMR, and substituted benzene IR patterns), there is a scarcity of X-ray data for ylid coordination compounds. The final atomic coordinates are shown in Table II. Selected bond distances and angles are given in Table III. Other results are available as supplementary material, as specified in the paragraph at the end of this article.

The compound $[\text{Pt}(\mu\text{-Cl})\text{CH}_3\text{COCHP}(\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)_2]_2 \cdot 2\text{CDCl}_3$ is shown and labeled in Figure 1. A stereopacking diagram is provided in Figure 2. The unit cell contains eight half molecules as well as eight deuteriochloroform molecules of solvation. The distances between the deuteriochloroform molecules and the oxygen atoms of the ylid ligands are significantly short for nonbonded interactions ($\text{Cl}_3\text{CD-O} = 2.339 \text{ \AA}$).

The complex possesses crystallographic site symmetry $C_i\bar{1}$, in which there is half of a complex molecule and one deuteriochloroform molecule per crystallographically independent unit. The whole complex and two deuteriochloroform molecules are generated by the inversion center. The two platinum(II) atoms are bridged by two chlorine atoms ($\text{Pt-Cl} = 2.438 (4)$ and $2.384 (4) \text{ \AA}$). The bond angles $\text{Pt-Cl-Pt}' (96.6 (2)^\circ)$ and $\text{Cl-Pt-Cl}' (83.4 (2)^\circ)$ are consistent with a nonbonding repulsive interaction between the metal atoms ($\text{Pt}\cdots\text{Pt}' = 3.599 \text{ \AA}$). These ob-

servations are consistent with those of a similar $\text{Pt}_2(\mu\text{-Cl})_2$ structure, $[\text{Pt}(\mu\text{-Cl})\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2\text{P}(t\text{-C}_4\text{H}_9)_2]_2$, reported by Mason et al.: $\text{Pt-Cl} = 2.460 \text{ \AA}$, $\text{Pt-Cl}' = 2.402 \text{ \AA}$, $\text{Pt-Cl-Pt}' = 97.3^\circ$, $\text{Cl-Pt-Cl}' = 82.7^\circ$, and $\text{Pt}\cdots\text{Pt}' = 3.650 \text{ \AA}$ (calculated).⁷ The elongation of the metal-metal axis would cause the $\text{Cl-Pt-Cl}'$ angle to decrease while the $\text{Pt-Cl-Pt}'$ angle would become larger, as is observed. The two platinum atoms and the two chlorine atoms are found in a crystallographically imposed plane. The coordinated carbons C(1) and C(5) are only slightly displaced from this plane (-0.0224 and 0.0013 \AA , respectively).

As can be seen in Figure 1, the five-membered chelate ring is puckered. This distortion, as well as the bond angles about C(1) and P, confirms the sp^3 hybridization of both C(1) (as is found for other C-bound ylids)^{1d,1e,8} and P. The phenyl ring that is ortho-metalated is also slightly distorted. The C(5) carbon is shifted toward the metal atom, causing the $\text{C}(4)\text{-C}(5)\text{-C}(6)$ angle to contract ($115.5 (14)^\circ$) while the $\text{C}(5)\text{-C}(6)\text{-C}(7)$ and $\text{C}(5)\text{-C}(4)\text{-C}(9)$ angles expand ($123.2 (18)^\circ$ and $122.8 (14)^\circ$, respectively). The potential optical activity of the asymmetric ylid carbon atoms is negated by the crystallographic inversion center. The similarity of the $\text{Pt-C}(1)$ and $\text{Pt-C}(5)$ bond lengths and the presence of a $\text{P-C}(4)$ single bond⁹ in the chelate ring through which no resonance is occurring indicate that both carbon donor atoms carry a full negative charge. Thus, the two bridging chlorine atoms impart a third negative charge to the coordination sphere of each platinum. However, both platinum atoms evidently remain Pt(II) by virtue of their square-planar geometries, as in PtCl_4^{2-} . There are two positive charges in the complex that are not in either platinum coordination sphere; these charges reside on the two phosphorus atoms and produce a complex that is neutral overall.

Factors that contribute to orthometalation have recently been summarized elsewhere.¹⁰⁻¹² These factors are pri-

(7) Mason, R.; Textor, M.; Al-Salem, N.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* 1976, 292. For comparison, a typical Pt(III)-Pt(III) single-bond distance has been given as $2.471 (1) \text{ \AA}$ [see: Cotton, F. A.; Falvello, L. R.; Han, S. *Inorg. Chem.* 1982, 21, 2889].

(8) Oosawa, Y.; Saito, T.; Sasaki, Y. *Chem. Lett.* 1975, 1259. Heydenreich, F.; Mollbach, A.; Wilke, G.; Dreeskamp, H.; Hoffmann, E. G.; Schroth, G.; Seevogel, K.; Stempfle, W. *Isr. J. Chem.* 1972, 10, 293. Keeton, M.; Mason, R.; Russell, D. R. *J. Organomet. Chem.* 1971, 33, 259. (All are ylid X-ray references.)

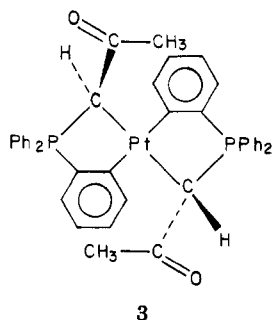
(9) The $\text{P-C}(4)$ bond distance of $1.791 (20) \text{ \AA}$, where C(4) is sp^2 hybridized, compares favorably with the P-C single bond distance of $1.837 (2) \text{ \AA}$, where C is an ethyl carbon (sp^3) [see: Ibers, J. A.; DiCosimo, R.; Whitesides, G. M. *Organometallics* 1982, 1, 13]. This is in contrast to the P-C bond distances of $1.660 (9) \text{ \AA}$ [see: Kroto, H. W.; Nixon, J. F.; Taylor, M. J.; Frew, A. A.; Muir, K. W. *Polyhedron* 1982, 1, 89] and $1.69 (1) \text{ \AA}$ [see: Schmidbaur, H.; Deschler, U.; Zimmer-Gasser, B.; Neugebauer, D.; Schubert, U. *Chem. Ber.* 1980, 113, 902] ascribed to be double bonds.

(10) Bruce, M. I. *Angew. Chem.* 1977, 89, 75; *Angew. Chem., Int. Ed. Engl.* 1977, 16, 73 (especially section 9.2).

(11) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* 1976, 18, 327 (especially section E).

marily steric in nature: (a) bulky groups have less internal rotational entropy to lose upon cyclization and (b) the enthalpy effect (stronger M-donor atom bond) will be especially favorable due to the smaller number of (or smaller repulsive forces within) sterically hindered configurations upon cyclization. The expressions "gem-dialkyl effect",¹² in the case of carbon, and "gem-tert-butyl effect",¹² in the case of larger atoms such as phosphorus, have been used to describe the steric bulkiness necessary to cause cyclization. The occurrence of orthometalation in the current system clearly shows that the steric bulkiness need not be situated at the donor atom. (The ylid C donor atom has the nonchelate ring groups H and C-(O)CH₃). Formation of a five-membered ring has also been shown to be a favorable factor in most cases.^{5b,10,13} Under reaction conditions similar to those employed here such as reflux in polar solvents, orthometalation has also been postulated (from non X-ray crystallographic data) for the ylid complexes Pt-N-pyridinio ylid¹⁴ and Cr-phosphonium methylide ylid.¹⁵ The latter is presumed to have five-membered chelate rings as does **2**. In the former case, however, the orthometalation occurs on the carbonyl substituent away from the ylidic group.

The question of why a *dinuclear* species was formed, as opposed to a mononuclear such as **3**, where **1** would lose two molecules of HCl, must now be addressed. In the



observed process, two molecules of **1** must lose two molecules of APPY as well as two molecules of HCl. Since free APPY is basic, formation of the salt APPYH⁺Cl⁻ may contribute to the driving force of the reaction. Otherwise, the reason may be kinetic, e.g., only intermolecular collisions being sufficiently energetic at this temperature to initiate cyclization.

It is also interesting to note that, despite the similar arrangement of donor atoms in the *N,N*-dimethyldithiocarbamate and APPY ligands, the O of the latter ligand is evidently less inclined to bridge two Pt atoms than is chlorine, whereas the S of the former ligand is evidently more inclined to bridge than chlorine.¹⁶

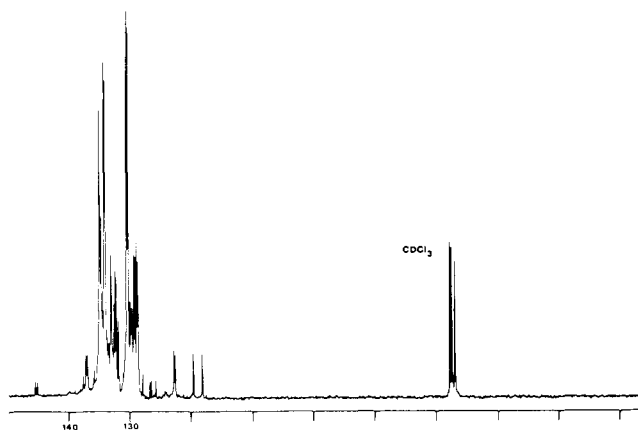


Figure 3. The aromatic region of the ¹³C NMR spectrum of the original reaction product containing **2** and APPYH⁺Cl⁻, labeled in parts per million downfield from SiMe₄.

The incongruity between the original and current analyses of the original sample, which agreed with the formula for compound **1**, and the observed structure of compound **2** can be resolved by reviewing the synthetic procedure employed.^{1c} Orthometalation undoubtedly occurred during the 44-h time period that the PtCl₂ and APPY were allowed to react, in a 1:2 ratio, in refluxing acetonitrile. Complete reaction would have produced compound **2** and APPYH⁺Cl⁻ in a 1:2 ratio. This ratio would have been maintained in the solid state, since the sample was isolated by evaporating the filtered reaction mixture (filtered while hot) to dryness. The 2-h stirring period in diethyl ether that followed would have served to homogenize the mixture and remove any organic impurities. In accord with this hypothesis, the original sample was found^{1c} to exhibit a molar conductance of 20 Ω⁻¹ cm² mol⁻¹ in nitrobenzene (10⁻³ M) at 25 °C, corresponding to a 1:1 salt.

When the elemental components of **2**, [PtCl(C₂₁H₁₈O-P)]₂, are added to those of two APPYH⁺Cl⁻, 2-(C₂₁H₂₀O)PCl, the resulting elemental composition is exactly two times that of **1**, Pt(APPY)₂Cl₂, i.e., Pt₂Cl₄C₈₄H₇₆O₄P₄ and PtCl₂C₄₂H₃₈O₂P₂, respectively, thus giving the same elemental analyses. Removal of the APPYH⁺Cl⁻ from the sample by repeated water washings produced a yellow residue whose analysis agreed with that calculated for **2**.

Pertinent spectral data for the compounds in question are summarized in Table IV. The originally proposed^{1c} spectral indicators of C-coordination of the APPY ligand, i.e., the appearance of a ν_{C=O} stretching frequency, not seen in the IR spectrum of the free ligand, and a downfield methine proton chemical shift, relative to that of the free ligand, remain applicable for **2**. ¹³C and ³¹P NMR corroboration of C-coordination is also indicated by the downfield shift of the carbonyl carbon resonance and the downfield shift of the ³¹P singlet—both in opposite directions compared to those exhibited by the O-coordinated [Sn(APPY)(CH₃)₃Cl] complex, whose structure has also been determined² by X-ray crystallography. It should be noted that the ¹H, ¹³C, and ³¹P NMR spectra of the original sample also contain the appropriate resonances, in the proper intensity ratios, of the APPYH⁺Cl⁻ byproduct.

Upon closer inspection, additional evidence of metalation also becomes apparent from the ¹³C NMR spectrum of the original reaction mixture. The chemical shift of the ortho-metalated carbon, when bound to nuclear spin zero isotopes of platinum, is observed at 136.9 ppm downfield from Me₄Si (slightly further downfield than the other aromatic carbon resonances). This signal is split into a

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Table IV. Spectral Data for the Title Compound, 2, and Related Compounds

$^1\text{H NMR}^{a-c}$				
sample/assignt	aromatic	methine	methyl	
original reaction product				
lit. ^d	7.3–8.0 m	4.58 d (5) ^e	2.37 d (2), 2.22 d (2)	
this work	7.0–8.0 m	5.82 d (11), ^{f,g} 4.59 d (5)	2.46 d (2), ^g 2.20 d (2)	
APPYH ⁺ Cl ⁻				
lit. ^d	7.35–8.1 m	6.13 d (11)	2.51 d (1.5)	
this work	7.5–7.9 m	6.15 d (11) ^f	2.54 d (2)	
water-washed reaction product (2) ^h	7.0–8.0 m	4.59 d (5)	2.20 d (2)	
APPY				
lit. ^d	7.3–8.0 m	3.67 d (27) ⁱ	2.07 d (2)	
this work	7.5–7.8 m	3.68 d (27) ^f	2.08 d (2)	
Sn(APPY)(CH ₃) ₃ Cl				
lit. ^d	7.3–7.8 m	<i>j</i>	1.99 d (1.5) ^k	
this work	7.5–7.7 m	4.0 d (25) ^f	1.99 d (1.5) ^k	
$^{13}\text{C NMR}^{a-c}$				
sample/assignt	carbonyl	aromatic	methine	methyl
original reaction product				
this work	201.4, 201.3, 201.1	118–146 m ^l	40.1 d (59) ^m	32.7 d (8), 30.1 d (10)
APPYH ⁺ Cl ⁻				
this work	201.1, 201.0	118–135 m	40.1 d (59)	32.4 d (6)
APPY				
this work	190.7	126–133 m	51.6 d (107)	28.4 d (23)
Sn(APPY)(CH ₃) ₃ Cl				
this work	188.0	132 m, 129 m, 125 d (94)	60.8 d (101)	28.4 d (23) ⁿ
$^{31}\text{P NMR}^{a,c,o}$				
sample/assignt	PPh ₃			
original reaction product, this work	25.6, 20.1			
APPYH ⁺ Cl ⁻ , this work	20.4			
APPY, this work	15.3			
Sn(APPY)(CH ₃) ₃ Cl, this work	14.8			

Infrared^{c,p}

sample/assignt	$\nu_{\text{CO}} \text{ cm}^{-1}$
original reaction product ^d	1711 (s), 1647 (s)
APPYH ⁺ Cl ^{-d}	1713 (s), 1700 (s), 1667 (m)
water-washed product, this work	1647 (s)
APPY ^d	<i>j</i>
Sn(APPY)(CH ₃) ₃ Cl ^d	<i>j</i>

^a δ in ppm (*J* in Hz), CDCl₃ as solvent, room temperature. ^b Me₄Si internal reference. ^c Abbreviations: m = multiplet, d = doublet, (s) = strong, (m) = medium, (w) = weak. ^d Reference 1c. ^e Methylene resonance due to APPYH⁺Cl⁻ not observed in low-resolution (Varian A60), ¹H NMR spectrum. ^f Signal disappears following addition of D₂O. ^g Reference 17. ^h Reference 18. ⁱ Reference 19. ^j Not observed. ^k SnCH₃ resonance observed at 0.38 ppm. ^l Includes ortho-metalated aromatic carbon. ^m Methine resonance for ortho-metalated product not observed. ⁿ SnCH₃ resonance observed at 3.5 ppm. ^o H₃PO₄ external reference. ^p KBr pellets.

doublet by the secondary coupling of the phosphorus atom (²J_{P-C-C-Pt} = 14 Hz), as shown in Figure 3. This doublet is flanked on one side by a smaller doublet (²J = 14 Hz) at 145 ppm downfield from Me₄Si. This smaller doublet is due to the coupling of the ¹⁹⁵Pt isotope, which is 34% abundant and has a nuclear spin of 1/2, to the ortho-metalated carbon. The other ¹⁹⁵Pt–C doublet that would be expected to appear approximately 8 ppm upfield from the central doublet, at 129 ppm, is obscured by the intense aromatic carbon multiplet centered at 130 ppm. The primary coupling constant for ¹⁹⁵Pt and the ortho-metalated carbon (¹J_{Pt-C}) is therefore estimated to be just over 1000 Hz, which is in reasonable agreement with a value (1216 Hz) reported earlier for another ortho-metalated platinum compound.²⁰

Two intriguing questions pertaining to this spectrum still remain unanswered: while ortho-metalated carbon resonances are expected to be further downfield than the other aromatic carbon resonances, the downfield shift in δ has typically been 20–30 ppm for platinum and other metal

ortho-metalated compounds.²¹ Why is the downfield change in δ so small for (2)? Also, since the Pt–C resonances and ¹⁹⁵Pt–C coupling are evident for the ortho-metalated C in this ¹³C NMR spectrum, why is not a Pt–C resonance and a ¹⁹⁵Pt–C coupling evident for the methine C, which is present in the same abundance? Further NMR studies pertaining to these points are in progress.

In conclusion, the structure of 2 is significant because of the broad spectrum of current research topics to which structural information can be applied such as organic synthesis of heterocycles,¹⁰ including regiospecific reactions,^{5b} homogeneous catalytic activation of C–H bonds under mild conditions,²² other reactions of transition metal–C bonds,^{10,23} and elucidation of the mechanisms of

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orthometalation,^{1e,10,11,24} square-planar Pt ligand substitution,²⁵ and CO or alkane insertion into Pt-C bonds.²⁶ Several reference-laden reviews on orthometalation have also appeared.^{10,12,24b}

Further elucidation of the mechanisms of orthometalation, dimerization, and ligand substitution at square-planar Pt may also be possible with these new data. Synthesis and reactions of ortho-metalated complexes are continuing to receive considerable attention at present.^{21,27} Still other researchers will be interested, as we are, in the

various modes of isomerism in ylid complexes^{1d,e,12,28} such as ligand cis-trans isomerism, stereoisomers derived from the asymmetric C donor atom, Pt cis-trans isomerism, and ligand inequities resulting from steric crowding prior to orthometalation. Identification of these isomeric forms may lead to a recognition of which isomer is most important in the orthometalation process.

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Registry No. 2, 86846-87-9; Sn(APPY)(CH₃)₃Cl, 38856-46-1; PtCl₂, 10025-65-7; APPY, 1439-36-7; APPYH⁺Cl⁻, 1235-21-8.

Supplementary Material Available: Tables and bonds and angles, anisotropic thermal parameters, hydrogen coordinates, and structure factors (24 pages). Ordering information is given on any current masthead page.

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Synthesis of (1,2,3,4-Tetramethylfulvene)palladium(0) Complexes from (η^5 -Pentamethylcyclopentadienyl)palladium(II) Precursors. The Crystal Structure of [Pd(PMe₃)₂(η^2 -CH₂=C₅Me₄)]

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[Pd(η^3 -allyl)(η^5 -C₅Me₅)] complexes react with tertiary phosphines and phosphites in a stepwise manner to give initially (η^1 -allyl)palladium complexes of the type [PdL(η^1 -allyl)(η^5 -C₅Me₅)]. Reaction with a second ligand molecule leads to transfer of a hydrogen atom from a ring-methyl group to the allyl group to give the (tetramethylfulvene)palladium(0) complex [PdL₂(η^2 -CH₂=C₅Me₄)]. The coordination of the fulvene molecule to the metal through the exo-methylene group has been established by an X-ray crystal structure determination of the trimethylphosphine adduct (space group *P*₂₁/*a*, *a* = 12.139 (2) Å, *b* = 13.468 (2) Å, *c* = 12.294 (1) Å, β = 105.874 (8)°, *Z* = 4).

Introduction

In recent years the chemistry of organotransition-metal complexes containing the η^5 -C₅Me₅ ring has received considerable attention. Maitlis in particular has shown that the substitution of the cyclopentadienyl hydrogen atoms by alkyl groups is frequently associated with a stabilization of the complexes formed by group 8 transition metals.²

Bercaw, Brintzinger, et al.³ were the first to point out that the introduction of the C₅Me₅ group offers access to the 1,2,3,4-tetramethyl-5-methylene-1,3-cyclopentadiene (tetramethylfulvene) system and to suggest that [Ti(η^5 -C₅Me₅)₂] undergoes a kinetically favored rearrangement to give a species (tentatively formulated as [TiH(η^2 -

CH₂=C₅Me₄)(η^5 -C₅Me₅)] in which a hydrogen atom has been transferred from a methyl group to the metal. Subsequently, Bottomley et al.⁴ isolated a related complex, in which the CH₂=C₅Me₄ group bridges two titanium atoms, from the reaction of [Ti(η^5 -C₅Me₅)₂] with N₂O and confirmed the structure by an X-ray analysis.

Our interest in this area stems from investigations on the reaction of [Pd(η^3 -allyl)(η^5 -C₅H₅)] and [Pd(η^3 -allyl)]₂ complexes with donor ligands.⁵⁻⁸ We have shown that,

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