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Synthesis of *ortho*-Metalated Palladium(II) and Platinum(II) Complexes of Phosphonium, Arsonium and Sulfonium Ylids

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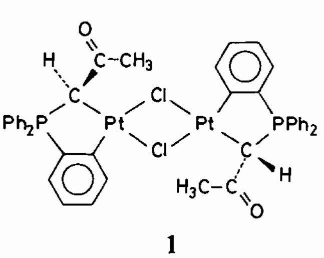
Abstract

We have found that the reactions of $PdCl_2$ and/or $PtCl_2$ with ylids of the type $Ph_nZCHC(O)CH_3$ ($n = 3$, $Z = P$, As; $n = 2$, $Z = S$) in refluxing CH_3CN produce dinuclear C-bound, *ortho*-metalated complexes analogous to the $[\overline{Pt(\mu\text{-}Cl)(CH_3CO\dot{C}HP(C_6H_4)}(C_6H_5)_2]_2$ complex previously reported by our laboratory. In addition, we have succeeded in forming a 'back-door' C-bound, *ortho*-metalated dinuclear complex by refluxing $PdCl_2$ and the ylid $(n\text{-}C_4H_9)_3PCHC(O)Ph$ in CH_3CN: $[\overline{Pd(\mu\text{-}Cl)(C_6H_4CO\dot{C}HP}(n\text{-}C_4H_9)_3]_2$. This and the preceding complexes' syntheses and structures are discussed in terms of their ^1H, ^{13}C, and ^{31}P NMR spectra, as well as those produced by additional reactions of $PtCl_2$ and $PdCl_2$ in CH_3CN with ylids of the type $PhCOCHZPh_3$ ($Z = P$, As), *i.e.*, ylids having both a 'front-door' and a 'back-door' available for *ortho*-metalation.

Introduction

An earlier report [1] from our laboratory discussed the formation of Pd(II), Pt(II), and Hg(II) complexes of ambidentate ylids of the type $R_nZCR'C(O)R''$ ($n = 3$, $Z = P$, As, N; $n = 2$, $Z = S$), concluding that the ylids were C-bound. Prompted by our discovery [2] that the Pt(II) complex of $(C_6H_5)_3PCHC(O)CH_3$ (APPY) actually involved both C-bonding and *ortho*-metalation, resulting in the formation of compound 1, we have undertaken a reinvestigation of the other ylid complexes described in the initial study [1], as well as of related ylid complexes.



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In so doing , we have sought to assess the effects of the following variables in our attempt to define the limits of this cyclometalation reaction: the effect of the metal atom (reaction of $PdCl_2$ with the APPY ylid), the effect of the heteroatom (reactions of $PdCl_2$ with the arsenic and sulfur analogs of the APPY ylid) and the effect of changing the point of *ortho*-metalation, including competitive *ortho*-metalation reactions (reaction of $PdCl_2$ and $PtCl_2$ with $Bu^n_3PCHC(O)C_6H_5$ (BBuPY), $(C_6H_5)_3PCHC(O)C_6H_5$ (BPPY), and $(C_6H_5)_3AsCHC(O)C_6H_5$ (BPAsY)). We now wish to report the first results of these studies.

Experimental

Synthesis of 'Onium Salts

The following phosphonium, arsonium, and sulfonium salts were prepared according to procedures given in the literature: benzoylmethyltriphenylphosphonium bromide [3], acetylmethyltriphenylphosphonium chloride [3], benzoylmethyl-tri-n-butylphosphonium bromide [4], benzoylmethyltriphenylarsonium bromide [5], benzoylmethyldimethylsulfonium bromide [6].

Preparation of acetylmethyltriphenylarsonium bromide

20 mmol (6.1 g) of triphenylarsine and 22 mmol (1.84 ml) of bromoacetone were added to a hot solution consisting of 24 ml of absolute ethanol and 6 ml of water. After 18 h of refluxing, a yellow tint could be seen in the solution. After 20 h, the solution was cooled and filtered into 500 ml of diethyl ether. A fine white precipitate could be seen and a brown oil began to form at the bottom of the flask. The oil was separated from the ether by extraction with water in a separatory funnel and discarded. The white precipitate was then collected from the remaining ether solution by suction filtration. Yield, 63%; melting point (m.p.), 150–151 °C.

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TABLE I. Names, Formulas and Abbreviations of Ylids used in this Study

Benzoylmethylenetriphenylphosphorane	$C_6H_5COCHP(C_6H_5)_3$	BPPY
Acetylmethylenetriphenylphosphorane	$CH_3COCHP(C_6H_5)_3$	APPY
Benzoylmethylenetri-n-butylphosphorane	$C_6H_5COCHP(C_4H_9)_3$	BBuPY
Benzoylmethylenetriphenylarsenane	$C_6H_5COCHAs(C_6H_5)_3$	BPAsY
Acetylmethylenetriphenylarsenane	$CH_3COCHAs(C_6H_5)_3$	APAsY
Acetylmethylenediphenylsulfurane	$CH_3COCHS(C_6H_5)_2$	APSY

Preparation of acetylmethyldiphenylsulfonium chloride

42 mmol (3.4 ml) of chloroacetone and 42 mmol (4.6 ml) of diphenylsulfide were heated to reflux in 30 ml of chloroform. During the two hour reflux, the solution color changed from pale yellow to orange. After the two hours, the solution was cooled and then reduced in volume on a Rotovapor. An oil was thus obtained, which would not solidify. Yield, 89%.

Preparation of the Ylids

The names, formulas, and abbreviations of the ylids utilized in this study are shown in Table I. The following phosphoranes, arsenanes, and sulfuranes were prepared according to procedures given in the literature: benzoylmethylenetriphenylphosphorane [3], acetylmethylenetriphenylphosphorane [3], benzoylmethylene-tri-n-butylphosphorane [4], benzoylmethylenetriphenylarsenane [7], benzoylmethylenedimethylsulfurane [8].

Preparation of acetylmethylenetriphenylarsenane

4.5 mmol (2.0 g) of acetylmethyltriphenylarsonium bromide was dissolved in 450 ml of distilled water and cooled to 5 °C. To this was added 50 ml of a 50% aqueous NaOH solution, also cooled to 5 °C. The addition caused an immediate formation of a white precipitate that was collected using suction filtration and then water washed. Yield, 100%, m.p., 103–105 °C.

Preparation of acetylmethylenediphenylsulfurane

15 mmol (6.5 g) of acetylmethyldiphenylsulfonium bromide was mixed with 40 ml of acetonitrile under dinitrogen. To this was added dropwise 16 mmol of a butyllithium solution (7 ml of 2.2 M). Upon the completion of the addition of butyllithium, the solution had changed from light yellow to black. The solution was then filtered to remove an insoluble precipitate and then stored in a refrigerator until use.

Preparation of Metal–Ylid Complexes

Preparation of $[\overline{Pd(\mu\text{-}Cl)CH_3COC}HP(C_6H_4)(C_6H_5)_2]_2$, $(Pd_2(APPY\text{-}H)_2Cl_2)$

5 mmol (0.888 g) of palladium(II) chloride and 10 mmol (3.181 g) of acetylmethylenetriphenylphosphorane (APPY) were allowed to reflux together in 150 ml of acetonitrile for two hours. The solution was then filtered to remove some black decomposition product. The filtrate was rotovaped to dryness, leaving a yellow–orange precipitate, which was collected and slurried in diethyl ether in a dry ice/acetone bath for an hour. A yellow precipitate was collected by suction filtration and stored 24 h under vacuum. It was then stirred in distilled water for 24 h and recollected by suction filtration. Yield, 55%; m.p., 212–215 °C decomposition (dec.).

Preparation of $[\overline{Pd(\mu\text{-}Cl)CH_3COC}HAs(C_6H_4)(C_6H_5)_2]_2$, $(Pd_2(APAsY\text{-}H)_2Cl_2$

1 mmol (0.362 g) of acetylmethylenetriphenylarsenane (APAsY) and 0.5 mmol of palladium(II) chloride were allowed to reflux together in 60 ml of acetonitrile for one hour. The solution was then filtered to remove some black decomposition product, leaving an orange filtrate. The filtrate was then poured into 600 ml of diethyl ether, resulting in the immediate formation of a precipitate. The yellow–orange precipitate was collected by suction filtration, stirred in distilled water for 24 h, reisolated, and dried 24 h under a vacuum. Yield, 56%; m.p., 120–121 °C (dec.).

Preparation of $[\overline{Pd(\mu\text{-}Cl)CH_3COC}HS(C_6H_4)(C_6H_5)]_2$, $(Pd_2(APSY\text{-}H)_2Cl_2)$

2.5 mmol (0.444 g) of palladium(II) chloride was added to a solution containing 15 mmol (6.5 g) of acetylmethylenediphenylsulfurane (APSY) in 40 ml of acetonitrile. The mixture was allowed to reflux for two hours. The solution was then filtered to remove some black decomposition product, leaving a red–black filtrate. The filtrate was rotovaped to dryness yielding a dark red precipitate, which was stored under a vacuum for 24 h. The precipitate changed into a red oil. The oil was added to diethyl ether and slurried in a dry ice/acetone bath for one hour. A light orange precipitate was collected by suction filtration and stored under a vacuum for 24 h. The precipitate was stirred 24 h in distilled water and then collected by suction filtration. Yield, 57%; m.p., 163 °C (dec.).

Preparation of $[\overline{Pd(\mu\text{-}Cl)(C_6H_4)COC}HP(C_4H_9)_3]_2$, $(Pd_2(PBuPY\text{-}H)_2Cl_2)$

1 mmol (0.181 g) of palladium(II) chloride was added to a solution containing 2.25 mmol of

benzoylmethylenetri-n-butylphosphorane (BBuPY) in 17 ml of benzene. An additional 50 ml of acetonitrile was added and the mixture was allowed to reflux for 30 min. The solution was filtered to remove some black decomposition product, leaving a red solution. The solution was rotovaped down to an oil and stored under a vacuum for 24 h. The oil solidified under the vacuum and was collected and added to diethyl ether to be slurried while sitting in a dry ice/acetone bath. After one hour of stirring, the yellow–orange product was collected by suction filtration and stored under a vacuum for 24 h. The product was then stirred in distilled water for 24 h and collected by suction filtration. Yield, 51%; m.p., 162–165 °C (dec.).

Preparation of $[\overline{Pt(\mu\text{-}Cl)(C_6H_4)COCH}P(C_6H_5)_3]_2$, $(Pt_2(BPPY\text{-}H)_2Cl_2)$

1 mmol (0.260 g) of platinum(II) chloride and 3 mmol (1.138 g) of benzoylmethylenetriphenylphosphorane (BPPY) were allowed to reflux together in 70 ml of acetonitrile for three hours. The solution was filtered to remove some black decomposition product, leaving an orange filtrate. The solution was rotovaped down to dryness and the yellow–orange precipitate thus obtained was slurried in distilled water for 24 h. The product was collected by suction filtration. Yield, 60%; m.p., 130–134 °C (dec.).

Elemental Analysis

Carbon, hydrogen, phosphorus, and chlorine elemental analyses were performed by Guelph Chemical Laboratories, Ltd., Guelph, Ontario N1H1E7.

Proton, Carbon-13 and Phosphorus-31 Nuclear Magnetic Resonance Spectra

All nuclear magnetic resonance spectra were recorded on a Brüker 250 MHz spectrometer, using phosphoric acid as an internal standard for ^{31}P spectra and tetramethylsilane as an internal standard for both proton and ^{13}C spectra. All chemical shifts are reported in parts-per-million, relative to their internal standard as zero. Deuterated solvents were obtained from Norell, Inc., Landisville, New Jersey.

Melting Point Determinations

Melting points were measured on a Thomas-Hoover Capillary Melting Point Apparatus, and are uncorrected.

TABLE II. Elemental Analyses for Metal–Ylid Complexes

Compound	Element	Found (%)	Calculated for binuclear *ortho*-metalated (%)	Calculated for mononuclear square planar (ML_2Cl_2) (%)
$Pd_2(APPY\text{-}H)_2Cl_2$	C	54.86	54.93	61.97
	H	3.98	3.95	4.70
	P	6.92	6.75	7.61
$Pt_2(APPY\text{-}H)_2Cl_2$ [a]	C	45.97	46.04	55.88
	H	3.34	3.31	4.24
	P	5.25	5.65	6.75
$Pd_2(APAsY\text{-}H)_2Cl_2$	C	48.88	50.13	55.93
	H	3.83	3.60	4.26
$Pd_2(APSY\text{-}H)_2Cl_2$	C	46.91	47.01	54.43
	H	3.91	3.43	4.27
$Pd_2(BBuPY\text{-}H)_2Cl_2$	C	52.25	52.06	58.72
	H	7.44	7.01	8.11
	P	6.12	6.71	7.54
$Pt_2(BPPY\text{-}H)_2Cl_2$	C	51.32	51.19	60.81
	H	3.62	3.31	4.10
	P	5.10	5.08	6.03
$Pd(BPAsY)_2Cl_2$ [b]	C	59.74	55.24	60.87
	H	4.31	3.57	4.13
	Cl	7.94	6.27	6.91
$Pt(BPAsY)_2Cl_2$ [b]	C	54.50	47.74	56.03
	H	3.97	3.09	3.80
	Cl	6.93	5.42	6.36

[a] Experimental data taken from ref. 2. [b] Water-washed samples originally prepared by Weleski, *et al.* [1].

TABLE III. Proton Nuclear Magnetic Resonance Data for Solutions of Ylid Salts, Ylids and Metal–Ylid Complexes[a]

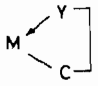
Compound	Aromatic	Methine	Methyl	Other
$APPYH^+Cl^-$	7.9–7.5m	6.15d (11)	2.54d (2)	
APPY	7.8–7.5m	3.68d (27)	2.08d (2)	
$Pd_2(APPY\text{-}H)_2Cl_2$	8.0–7.0m	4.32d (5)	2.12d (2)	
$Pt_2(APPY\text{-}H)_2Cl_2$	8.0–7.0m	4.59d (5)	2.20d (2)	
$APAsYH^+Br^-$	7.9–7.6m	6.22	2.54	
APAsY	7.7–7.4m	3.95	2.10	
$Pd_2(APAsY\text{-}H)_2Cl_2$	7.8–7.2m	5.80	2.17	
$APSYH^+Br^-$ [b]	7.5–7.0m	3.62	1.83	
APSY	c	c	c	
$Pd_2(APSY\text{-}H)_2Cl_2$ [b]	7.7–7.2m	2.17	1.53	
$BBuPYH^+Br^-$	8.21d, 7.6–7.4m	5.02d (12)	0.95br	1.51br, 2.63br
BBuPY	c	c	c	c
$Pd_2(BBuPY\text{-}H)_2Cl_2$ [b]	8.36d, 7.5–7.4m	4.6m	0.94br	1.51br, 2.10br
$BPPYH^+Br^-$	8.4–7.3m	6.37d (11)		
BPPY	8.0–7.3m	4.4br		
$Pt_2(BPPY\text{-}H)_2Cl_2$	8.0–7.2m	4.5br		
$BPAsYH^+Br^-$	8.5–7.4m	6.46		
BPAsY	8.2–7.1m	4.70br		
$Pd(BPAsY)_2Cl_2$	d	d		
$Pt(BPAsY)_2Cl_2$	d	d		

[a] Shifts are given in parts-per-million, relative to TMS. All solutions are in deuterochloroform, unless otherwise noted. Peak description: d = doublet, m = multiplet, br = broad. [b] Deuteroacetone solution. [c] Made *in situ* – not isolated, proton NMR spectrum not determined. [d] Insoluble in deuterochloroform, deuteroacetone, and deuterodimethylsulfoxide.

The results of the elemental analyses for the metal ylid complexes prepared, as well as the theoretical results for both the binuclear *ortho*-metalated and mononuclear square planar complex formulations are shown in Table II. Tables III, IV, and V contain, respectively, the ^1H, ^{13}C, and ^{31}P NMR data for all of the 'onium salts, ylids, and metal complexes prepared.

Discussion

Cyclometalated organometallic compounds represent a relatively new class of compounds which contain the following ring system **2** [9]:



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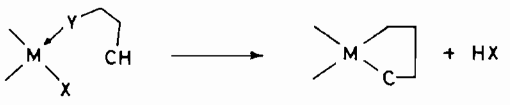
This ring system includes two bonds of special interest: a covalent metal–carbon (M–C) bond, in which the metal is a transition element, and (usually) a coordinate covalent (M ← Y) bond, with the Y donor frequently being a Group 15 (N, P, As) or Group 16 (O, S) element. In the formation of the ring system **1**, the coordinate covalent bond is first established, followed by C–H bond cleavage, yielding the cyclic structure. The first such cyclometalated compound was described by Kleinmann and Dubeck [10] in 1963. The compound **3**, shown below, was formed by the reaction of azobenzene with nickelocene.



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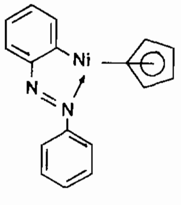

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Structure **3** is also an example of a special class of cyclometalated compounds involving *ortho*-metalation. This occurs when the metal–carbon covalent bond is formed at the *ortho* position of a phenyl ring. The phenomenon of *ortho*-metalation is of significance to a broad spectrum of current research topics, such as organic synthesis of heterocycles [11], including regiospecific reactions [12], homogeneous catalytic activation of C–H bonds under mild conditions [13], other reactions of

TABLE IV. Carbon-13 Nuclear Magnetic Resonance Data for Solutions of Ylid Salts, Ylids and Metal–Ylid Complexes[a]

Compound	Carbonyl	Aromatic	Methine	Methyl	Other
$APPYH^+Cl^-$	201.0d (25)	135–118m	40.1d (59)	32.4d (6)	
APPY	190.7	133–126m	51.6d (107)	28.4d (23)	
$Pd_2(APPY\text{-}H)_2Cl_2$	201.7	138–118m	40.4d (19)	31.1d (9)	
$Pt_2(APPY\text{-}H)_2Cl_2$	201.3d (25)	146–118m	e	30.1d (10)	
$APAsYH^+Br^-$	202.0	134–130m	44.2	31.7	
APAsY	187.3	134–128m	57.1	26.3	
$Pd_2(APAsY\text{-}H)_2Cl_2$	202.4	134–128m	43.7	31.8	
$APSYH^+Br^-$	c	c	c	c	
APSY	d	d	d	d	
$Pd_2(APSY\text{-}H)_2Cl_2$	c	c	c	c	
$BBuPYH^+Br^-$	193.4d (6)	135.5, 135.4, 134.7, 129.4, 129.0	32.0d (54)	13.4	19.9d (48), 23.9d (15)
BBuPY	d	d	d	d	
$Pd_2(BBuPY\text{-}H)_2Cl_2$[b]	197.1d (3)	140.5m (18) 131–127m	e	13.7	20.7–21.9m, 22.5–24.9m
$BPPYH^+Cl^-$	192.4d (5)	135–128m	35.5d (61)		
BPPY	184.7	133–126m	50.0d (112)		
$Pt_2(BPPY\text{-}H)_2Cl_2$	185.3	133–127m	50.6d		
$BPAsYH^+Br^-$[f]	c	c	c	c	
BPAsY	c	c	c	c	
$Pd(BPAsY)_2Cl_2$	c	c	c	c	
$Pt(BPAsY)_2Cl_2$	c	c	c	c	

[a] Shifts are given in parts-per-million, relative to TMS. All solutions are in deuterochloroform, unless otherwise noted. Peak description: d = doublet, m = multiplet, br = broad. [b] Deuteroacetone solution. [c] Insoluble in deuterochloroform, deuteroacetone, and deuterodimethylsulfoxide. [d] Made *in situ* – not isolated, ^{13}C NMR spectrum not determined. [e] Not found. [f] Deuterodimethylsulfoxide solution.

TABLE V. Phosphorus-31 Nuclear Magnetic Resonance Data for Solutions of Ylid Salts, Ylids and Metal–Ylid Complexes[a]

Compound	P
$APPYH^+Cl^-$	20.4
APPY	15.3
$Pd_2(APPY\text{-}H)_2Cl_2$	19.9
$Pt_2(APPY\text{-}H)_2Cl_2$	25.6
$BBuPYH^+Br^-$	33.5
BBuPY	c
$Pd_2(BBuPY\text{-}H)_2Cl_2$[b]	30.9
$BPPYH^+Br^-$	21.9
BPPY	17.0
$Pt_2(BPPY\text{-}H)_2Cl_2$	29.5

[a] Shifts are given in parts-per-million, relative to H_3PO_4. All solutions are in deuterochloroform, unless otherwise noted. [b] Deuteroacetone solution. [c] Made *in situ* – not isolated, ^{31}P NMR spectrum not determined.

transition metal–C bonds [11, 14], elucidation of organometallic reaction mechanisms [9, 11, 15, 16] and CO or alkane insertion into transition metal–carbon bonds [17]. Several reference-rich reviews on *ortho*-metalation have appeared [11, 18] and the synthesis and reactions of *ortho*-metalated complexes continue to receive considerable attention [19, 20].

Most of the *ortho*-metalated structures reported in the literature contain a coordinate covalent bond to the metal from the donor heteroatom, as shown in **2**. Very few structures have been reported wherein an *ortho*-metalated compound contains *two* covalent metal–carbon bonds in the ring instead of one. Our laboratory succeeded [2] in synthesizing one of these by accident, by the reaction of platinum(II) chloride with the ylid acetylmethylenetriphenylphosphorane (APPY), producing the dinuclear *ortho*-metalated complex $Pt_2(APPY\text{-}H)_2Cl_2$ (**1**).

Our original study [1] of this reaction resulted in the product's being mis-identified as *trans*-$[Pt(APPY)_2Cl_2]$, due to the fact that the two mol of $APPYH^+Cl^-$ formed as a by-product of reaction (2) was still mixed with the actual product **1**, *i.e.*, the

$$2PtCl_2 + 4APPY \xrightarrow[\text{reflux}]{CH_3CN} \underset{\mathbf{1}}{Pt_2(APPY\text{-}H)_2Cl_2} + 2APPYH^+Cl^- \qquad (2)$$

analysis of a 1:2 mixture of **1** and $APPYH^+Cl^-$ is identical to the theoretical analytical results for *trans*-$[Pt(APPY)_2Cl_2]$. This was confirmed by an analysis [2] of the water-washed product **1**, (water-washing removes the $APPYH^+Cl^-$ by-product) and a single crystal X-ray diffraction study [2] of the purified product **1**.

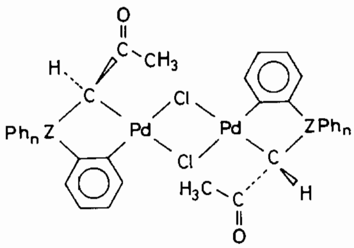
We therefore became intrigued by the possibility that some (or all) of the other phosphonium, arsonium, and sulfonium ylids investigated in the original study [1] had also undergone *ortho*-metalation reactions under the same conditions. Accordingly, we have reinvestigated several of these reactions in the context of the variables outlined in the Introduction. It should be noted that, of the ylids studied in the present work (see Table I), two (APAsY and APSY) were not included in the original study.

Several lines of evidence indicate that, in point of fact, $PdCl_2$ also undergoes an analogous *ortho*-metalation reaction with APPY, as well as with its arsenic and sulfur analogs, APAsY and APSY. Likewise, $PdCl_2$ will *ortho*-metalate a phenyl ring attached to the acetyl group, in its reaction with BBuPY. *ortho*-Metalation also occurs in the reaction of $PtCl_2$ with BPPY although, as we shall see, the point of *ortho*-metalation has not yet been determined. Of the six ligands studied, only BPAsY, the arsenic analog of BPPY, did not undergo *ortho*-metalation in refluxing acetonitrile.

The most direct evidence for *ortho*-metalation, or the lack thereof, emanates from the analytical results (see Table II), which clearly distinguish between the alternative *ortho*-metalation and simple coordination (ML_2Cl_2) formulations. The pattern described in the preceding paragraph is clearly supported by these results.

Where the proton NMR data are available (see Table III), the methine and methyl proton resonances of the APPY, APAsY, and APSY derivatives follow the same pattern: 'onium salt > *ortho*-metalated complex > free ylid, suggesting a commonality of structure for these *ortho*-metalated species. The ^{13}C resonances (see Table IV) for the carbonyl, methine, and methyl carbon atoms of the APPY and APAsY complexes are very similar to those of the corresponding 'onium salts, but are quite different from those of the corresponding free ylids. Likewise, the ^{31}P resonances (see Table V) of the APPY complexes are closer to that exhibited by $APPYH^+Cl^-$. It would appear, therefore, that the structure of the $Pd_2(APPY\text{-}H)_2Cl_2$ complex **4** is quite analogous to that of **1**, as are those of the $Pd_2(APAsY\text{-}H)_2Cl_2$ and $Pd_2(APSY\text{-}H)_2Cl_2$ complexes, **5** and **6**, respectively.

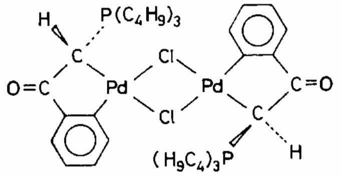
Colloquially, we refer to **1**, **4**, **5**, and **6** as 'front-door' complexes, with the point of *ortho*-metalation being on a phenyl ring attached to the Z heteroatom. In this sense, *ortho*-metalation of the phenyl ring attached to the carbonyl group in the ylid BBuPY would produce a 'back-door' complex. As noted above, the analytical results (Table II) indicate that this did, in fact, occur.



4, Z = P, *n* = 2
5, Z = As, *n* = 2
6, Z = S, *n* = 1

A now familiar trend was observed in the proton NMR spectra (see Table III) of this complex and the $BBuPYH^+Br^-$ salt. The methine proton resonance at 4.60 ppm for the complex is upfield, relative to that of the ylid salt, which exhibits a chemical shift of 5.02 ppm. This trend was observed in all four examples of *ortho*-metalation discussed previously.

No comparison of the methine ^{13}C resonances (see Table IV) could be made, due to the lack of any signal being observed for the methine carbon of the complex. The carbonyl carbon resonances, though, do offer a comparison with the complex exhibiting a chemical shift of 197.1 ppm and the $BBuPYH^+Br^-$ salt producing a chemical shift of 193.4 ppm. The similarity of these two shifts would indicate that *ortho*-metalation has taken place as in the four previous examples. It should also be noted that, in the ^{13}C spectrum of the complex, an aromatic carbon resonance is observed downfield (at 140.8 ppm) from the resonances of the remaining aromatic carbons. This has already been shown [2] to be a good indicator of *ortho*-metalation. We would therefore conclude that **7** is the structure of the $Pd_2(BBuPY\text{-}H)_2Cl_2$ complex.



7

Lastly, we sought to investigate the possibility of competitive *ortho*-metalation in an ylid containing both 'front' and 'back-doors', *i.e.*, phenyl rings on both the Z heteroatom and the carbonyl group, as is the case in the ylids BPPY and BPAsY.

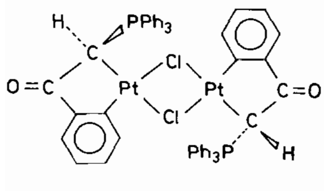
Several lines of circumstantial reasoning lead to the tentative conclusion that *ortho*-metalation of the BPPY ylid took place via the 'back-door', *i.e.*, the benzoyl phenyl group, in its reaction with $PtCl_2$. The analytical data (Table II) clearly indicate that a dinuclear, *ortho*-metalated complex ($Pt_2(BPPY\text{-}H)_2Cl_2$) formed. Unlike the proton NMR trends (see Table III) exhibited by the 'front door' APPY, APAsY, and APSY complexes, wherein the methine proton chemical shifts of the complex, ylid salt and free ylid are quite different, that of the Pt–BPPY complex is virtually identical to that of the free BPPY ylid.

In a similar vein, the ^{13}C NMR data (see Table IV) also appear to support *ortho*-metalation via the 'back-door'. Unlike the ^{13}C NMR trends exhibited by the 'front-door' APPY and APAsY complexes, wherein the methine ^{13}C resonances of the complexes and the ylid salts are quite similar (and very different from those of the free ylids), the methine ^{13}C resonance of the Pt–BPPY complex is very similar to that of the free BPPY ylid and very different from that of the ylid salt. Likewise, the carbonyl ^{13}C resonances of the APPY and APAsY complexes are quite similar to those of the ylid salts (and very different from those of the free ylids), whereas the carbonyl ^{13}C resonance of the Pt–BPPY complex is very similar to that of the free BPPY ylid and quite different from that of the ylid salt.

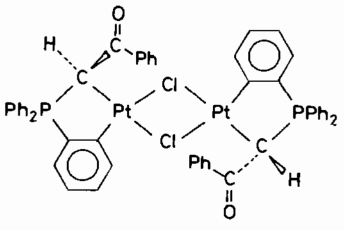
Unfortunately, two facts tend to undermine the conclusion of 'back-door' *ortho*-metalation for the Pt–BPPY complex. Although the carbonyl ^{13}C resonance for the confirmed 'back-door' Pd–BBuPY complex is also quite different than that exhibited by the ylid salt, the order is reversed from that exhibited by the Pt–BPPY complex and its ylid salt.

Although the preceding discrepancy is minor, especially in view of the fact that two different metals are involved, that found in the ^{31}P NMR data (see Table V) is more troublesome. The 'front-door' Pt–APPY complex exhibits a ^{31}P resonance which is found farther downfield than that of its ylid salt, as does the supposed 'back-door' Pt–BPPY complex. Finally, it should be noted that the ^{13}C NMR spectrum of the Pt–BPPY complex does not contain the downfield-shifted aromatic carbon resonance which is usually characteristic of *ortho*-metalation, the results of the elemental analysis notwithstanding.

In order to resolve this dilemma, we attempted to grow a crystal suitable for single crystal X-ray analysis, but were unsuccessful in this endeavor. Consequently, the two possible structures (**8**, **9**) are shown below for the complex $Pt_2(BPPY\text{-}H)_2Cl_2$.



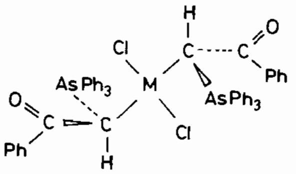
8 ('back-door')



9 ('front-door')

It should be noted that the *ortho*-metalated structures **1**, **4**, **7**, and **8**/**9** represent reformulations of products originally identified by Weleski, *et al.* [1] as being simple ML_2Cl_2 complexes. It is surmised that all of these earlier, erroneous conclusions were a consequence of the chain of events described earlier in this paper (and, in greater detail, by Illingsworth, *et al.* [2]), based on the commonality of the synthetic procedures originally employed [1].

However, the circle is completed in the reactions of the 'either door' ylid BPAsY with $PdCl_2$ and $PtCl_2$. Unlike its phosphorus analog **8**, **9** and, indeed, all of the other ylids discussed in this paper, BPAsY apparently does not undergo an *ortho*-metalation reaction with $PdCl_2$ or $PtCl_2$ in refluxing acetonitrile. The products originally prepared by Weleski, *et al.* [7] still exhibited analyses (see Table II) after repeated water washings that most closely resembled the theoretical values for the simple $M(BPAsY)_2Cl_2$ formulations (structures **10** and **11**, with the choice of the *trans*-C-bound structures being based on their original infrared data [1].



10, M = Pd
11, M = Pt

Obviously, much work remains to be done in this area if we are eventually to be able to identify the characteristics of the ylids that lead to *ortho*-metalation reactions. We intend to explore the reactions of these ylids with other metal salts, including those of hard metal ions that would have a tendency, such as that already demonstrated [21] for Sn(IV), to bond to the oxygen atom of the ylid. We also intend to investigate the reactions of nitronium ylids, the potential effects of varying the R groups on the carbonyl, the methine carbon and the heteroatom, and the mechanism of the *ortho*-metalation reaction. The results of these studies will be reported in due course.

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