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PALLADIUM(II), PLATINUM(II) AND MERCURY(II) COMPLEXES OF AMBIDENTATE PHOSPHONIUM, ARSONIUM, SULFONIUM AND PYRIDINIUM YLIDS*

EDWARD T. WELESKI, Jr., (THE LATE) JOEL L. SILVER, MURIEL D. JANSSON and JOHN L. BURMEISTER**

Brown Chemical Laboratory, University of Delaware, Newark, Delaware 19711 (U.S.A.)

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Summary

Observations by Schweizer and Kopay (J. Org. Chem., 36 (1971) 1489) suggested the possibility of promoting ambident bonding behavior in transition metal complexes of phosphonium ylids of the type $R_3{}^+\bar{P}CR'C(O)R''$ by a judicious choice of R groups. Accordingly, we have synthesized Pd^{II}, Pt^{II} and Hg^{II} chloride—ylid complexes for ylids of the types $R_3ZCR'R''$ ($Z = P$, $R = Ph$, $R' = H$, $R'' = COPh$, $COCH_3$, $COOCH_2CH_3$, $COOCH_3$, CN; $R' = CH_3$, $R'' = COPh$, $COOCH_2 \cdot CH_3$; $R' = COPh$, $R'' = COPh$; $R = n\text{-}C_4H_9$, $R' = H$, $R'' = COPh$; $Z = As$, $R = Ph$, $R' = H$, $R'' = COPh$, $COOCH_3$), $(CH_3)_2SCHCOPh$, and $C_5H_5NCHCOPh$. The reactions of the ylids with $PdCl_2$ and $PtCl_2$ in refluxing CH_3CN yielded complexes having the general formula $[M(ylid)_2Cl_2]$, whereas reaction with $HgCl_2$ in alcohol produced dinuclear complexes of the type $[Hg_2(ylid)_2Cl_4]$, presumably involving bridging Cl^- groups. Proton NMR data for the soluble complexes revealed a downfield shift of the methine proton resonances relative to those of the free ylids. The ν(CO) frequencies of the complexes exhibited blue shifts, relative to those of the free ylids, approaching those of the completely protonated 'onium salts, which indicates coordination via the methine carbon atoms. Thiocyanate complexes of selected ylids exhibited N— and S— bonding modes, the former being favored by complexes of the least basic ylids.

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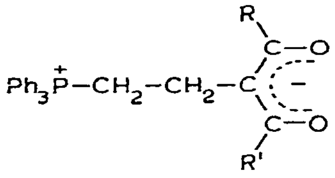
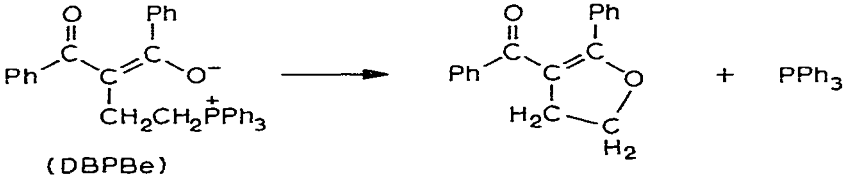
** Author to whom correspondence should be addressed.

Introduction

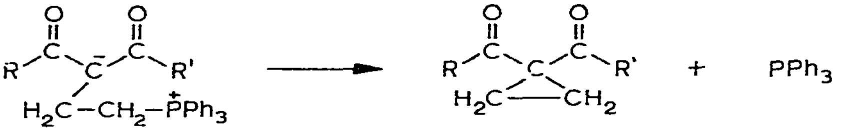
The initial interest in our laboratory in the potential ambidentate character of certain phosphonium ylids was generated by the results of studies carried out by Kopay and Schweizer [1,2]. They synthesized a number of phosphonium ylids of a special type, called betaines, wherein the positive and negative charges are on non-adjacent atoms:


(I)

Kopay and Schweizer found [1,2] that 1-(3,3-dibenzoyl) propyltriphenylphosphonium betaine (DBPBe; structure I for R = R′ = Ph) formed a dihydrofuran upon VPC pyrolysis:


(DBPBe) (1)

However, all save one of the other betaines they synthesized were found to form cyclopropanes upon VPC or solution pyrolysis:

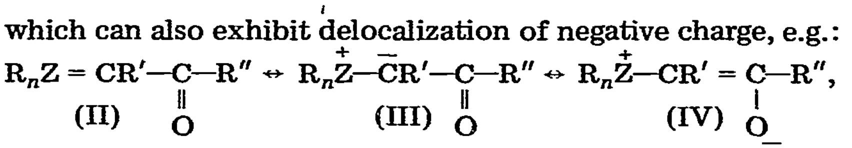

(2)

(R = Ph, R′ = OEt; R = Ph, R′ = CH_3; R = R′ = CH_3; R = CH_3, R′ = OEt)

These observations suggest that a greater localization of negative charge exists on the oxygen atoms in DBPBe, whereas a greater localization of negative charge occurs on the γ carbon atom in the betaines utilized in reaction 2.

This hypothesis is further supported by the results [1,2] of alkylation reactions of the betaines with methyl iodide. Whereas DBPBe gave only the *O*-alkylated phosphonium iodide, the other betaines gave *C*-alkylated phosphonium iodides.

These results suggested the possibility of synthesizing metal complexes of the betaines wherein bonding would selectively occur via the oxygen or carbon atoms, depending upon the nature of the R groups. Since the results of our initial experiments showed that the possibility of *O,O*′-chelation dominated the coordination chemistry of these betaines, attention was focused on the ligand properties of ambidentate ylids of the types $R_nZCR'\underset{\overset{\|}{O}}{C}R''$ (n = 3, Z = P, As; n = 2, Z = S), Ph_3PCHCN, and $C_5H_5NCH\underset{\overset{\|}{O}}{C}Ph$, which can also exhibit delocalization of negative charge, e.g.:



$$R_nZ = CR'-\underset{\overset{\|}{O}}{C}-R'' \leftrightarrow R_n\overset{+}{Z}-\overset{-}{C}R'-\underset{\overset{\|}{O}}{C}-R'' \leftrightarrow R_n\overset{+}{Z}-CR' = \underset{\overset{|}{O^-}}{C}-R'',$$

$$\text{(II)} \qquad \text{(III)} \qquad \text{(IV)}$$

but cannot chelate. The coordination chemistry of the parent phosphonium salts, e.g., $[R_3PCHR'\underset{\overset{\|}{O}}{C}R'']X$, has been described in an earlier paper [3].

Experimental

Nomenclature

At the outset, it will be helpful for the reader to set forth the abbreviations which will be used to designate the ylids and salts, because of the length of their formal nomenclature. These abbreviations are given in Table 1. In general, the first designation in the abbreviation, either one or two or three letters, represents the substitution on the carbanion. The next letter signifies the substituent on the heteroatom portion of the ylid with the following designation being the heteroatom itself. The last letter(s) in the abbreviation may be Y, which represents an ylid, or Be, representing a betaine.

Preparation of starting materials

The following phosphonium, arsonium, sulfonium, and pyridinium salts were prepared according to methods described in the literature: vinyltriphenylphosphonium bromide [4], 1-(3,3-dibenzoyl)propyltriphenylphosphonium bromide [2], benzoylmethyltriphenylphosphonium bromide [5], acetylmethyltriphenylphosphonium chloride [5], carbethoxymethyltriphenylphosphonium bromide [6], carbomethoxymethyltriphenylphosphonium bromide [7], cyanomethyltriphenylphosphonium chloride [8], carbethoxy (methyl)methyltriphenylphosphonium bromide [9], benzoyl (methyl)methyltriphenylphosphonium

TABLE 1

ABBREVIATIONS USED FOR YLIDS

Molecule	Formula	Abbreviation
1-(3,3-dibenzoyl)propyltriphenylphosphonium betaine	$(C_6H_5CO)_2C(CH_2)_2P(C_6H_5)_3$	DBPBe
Benzoylmethylenetriphenylphosphorane	$C_6H_5COCHP(C_6H_5)_3$	BPPY
Acetylmethylenetriphenylphosphorane	$CH_3COCHP(C_6H_5)_3$	APPY
Carbethoxymethylenetriphenylphosphorane	$CH_3CH_2OCOCHP(C_6H_5)_3$	CEPPY
Carbomethoxymethylenetriphenylphosphorane	$CH_3OCOCHP(C_6H_5)_3$	CMPPY
Benzoyl(methyl)methylenetriphenylphosphorane	$C_6H_5COC(CH_3)P(C_6H_5)_3$	BMPPY
Carbethoxy(methyl)methylenetriphenylphosphorane	$CH_3CH_2OCOC(CH_3)P(C_6H_5)_3$	CEMPPY
Dibenzoylmethylenetriphenylphosphorane	$(C_6H_5CO)_2CP(C_6H_5)_3$	DBPPY
Benzoylmethylenetri-n-butylphosphorane	$C_6H_5COCHPBu_3$	BBuPY
Cyanomethylenetriphenylphosphorane	$NCCHP(C_6H_5)_3$	CPPY
Benzoylmethylenetriphenylarsenane	$C_6H_5COCHAs(C_6H_5)_3$	BPAsY
Carbomethoxymethylenetriphenylarsenane	$CH_3OCOCHAs(C_6H_5)_3$	CMPAsY
Benzoylmethylenedimethylsulfurane	$C_6H_5COCHS(CH_3)_2$	BDMSY
Benzoylmethylenepyridinium ylid	$C_6H_5COCHNC_5H_5$	BPyY

bromide [10], benzoylmethyltriphenylarsonium bromide [11], carbomethoxymethyltriphenylarsonium bromide [12], benzoylmethyldimethylsulfonium bromide [13], and benzoylmethylpyridinium bromide [14].

Benzoylmethyltri-n-butylphosphonium bromide

To a solution of 0.1 mole of tri-n-butylphosphine in 100 ml of chloroform was slowly added (reaction is exothermic) 0.1 mole of phenacyl bromide ($\mathrm{Ph}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_2}\cdot$Br). The solution was stirred for 0.5 h, whereupon it was poured into 1 l of diethyl ether. The mixture was stirred for an additional 0.5 h, then filtered. The solid thus obtained was washed with diethyl ether and dried in vacuo. Yield, 68%; m.p., 123°C (Analysis Found: C, 59.71; H, 8.64. ($[C_6H_5COCH_2P(C_4H_9)_3]Br$) calcd.: C; 59.85; H, 8.54%).

The following betaine, phosphoranes, arsenanes, sulfurane, and pyridinium ylid were prepared employing the techniques described in the literature: 1-(3,3-dibenzoyl)propyltriphenylphosphonium betaine [2], benzoylmethylenetriphenylphosphorane [5], acetylmethylenetriphenylphosphorane [5], carbethoxymethylenetriphenylphosphorane [15], carbomethoxymethylenetriphenylphosphorane [7], cyanomethylenetriphenylphosphorane [8], dibenzoylmethylenetriphenylphosphorane [16], benzoylmethylenetriphenylarsenane [17], carbomethoxymethylenetriphenylarsenane [18], benzoylmethylenedimethylsulfurane [19], and benzoylmethylenepyridinium ylid [20].

Carbethoxy(methyl)methylenetriphenylphosphorane and benzoyl(methyl)methylenetriphenylphosphorane were supplied by Professor E.E. Schweizer, Department of Chemistry, University of Delaware.

Benzoylmethylenetri-n-butylphosphorane (benzene solution)

The following reaction was carried out under nitrogen. The freshly dried apparatus was assembled while hot. The benzene used was freshly distilled over sodium hydride and stored over sodium. Ten mmoles of benzoylmethyltri-n-butylphosphonium bromide, which had been dried at 110°C, was placed in a 3-neck, 250 ml round-bottom flask fitted with a nitrogen inlet and condenser. Benzene (100 ml) was added and the solution was stirred magnetically under a blanket of nitrogen. A 1.6 *M* butyllithium/hexane solution (6.2 ml) was added by means of a hypodermic syringe. The clear solution immediately took on an orange color, but no precipitation formation or gas evolution was observed. After stirring the solution at room temperature for 10 min, heat was applied by means of a heating mantle, resulting in the precipitation of LiBr. The solution was allowed to reflux for 0.5 h, then chilled. Filtration yielded a filtrate which was still cloudy. The filtrate was then shaken with five 50 ml portions of water to remove any remaining LiBr in the benzene layer, as determined by adding an $AgNO_3$ solution to the aqueous layer. The benzene solution, dried over $MgSO_4$, was used immediately in the reactions with metal salts.

Preparation of metal-ylid complexes

[Pd(DBPBe) Cl_2]

One mmole each of $PdCl_2$ (0.178 g) and DBPBe (0.512 g) were stirred at room temperature for 24 h in 50 ml of acetonitrile, then the suspension was heated to boiling. The hot solution was filtered and the filtrate evaporated to 30 ml on a rotovac at 40°C. A grey-green precipitate was collected, dried and recrystallized from acetonitrile over a period of several days. Grass-green needles were filtered from solution and dried in vacuo. Λ_m = 5.0 ohm^{-1} cm^2 mole^{-1} (10^{-3} *M* in nitromethane at 25°C).

$[Pd(BPPY)_2Cl_2]$

Ten mmoles (3.80 g) of BPPY was added to a hot solution of 5.0 mmoles (0.887 g) of $PdCl_2$ dissolved in 150 ml of hot acetonitrile. A bright orange precipitate formed immediately. After stirring for 30 min to insure complete reaction, the solid was isolated by suction filtration, washed with fresh acetonitrile and dried in vacuo over $CaSO_4$. Λ_m = 1.6 ohm^{-1} cm^2 mole^{-1} (10^{-3} *M* in nitrobenzene at 25°C).

$[Pd(BPPY)_2(NCS)_2]$

To a blood-red solution of 0.5 mmole (0.208 g) of $K_2[Pd(SCN)_4]$ [21] dissolved in 30 ml of methanol was added 1.0 mmole (0.380 g) of BPPY. The reaction mixture became turbid and an orange precipitate began to form after 5 h. The pale orange solid was separated from the red solution by suction filtration after 11 h. The product thus obtained was washed with methanol and dried in vacuo over $CaSO_4$.

$[Pt(BPPY)_2Cl_2]$

Five mmoles (1.33 g) of $PtCl_2$ was refluxed in 150 ml of acetonitrile until the solution became clear, then filtered to remove any undissolved material. To this yellow-green solution was added 10 mmoles (3.80 g) of BPPY. The reaction mixture was refluxed for 3 h, becoming orange after 2 h. The orange solution was filtered to remove any solids and the filtrate evaporated to dryness by aspiration and heating in a warm water bath. The oil which remained was slurried in diethyl ether in a Dry Ice/acetone bath, and a solid gradually formed. As the product warmed to room temperature, a tar began to form again. The tar was pumped under vacuum for two days resulting in a yellow-orange solid which was collected. Λ_m = 8.6 ohm^{-1} cm^2 mole^{-1} (10^{-3} *M* in nitrobenzene at 25°C).

$[Hg_2(BPPY)_2Cl_4]$

A solution of 2.0 mmoles (0.543 g) of $HgCl_2$ in 20 ml of ethanol was added dropwise to a solution of 4.1 mmoles (1.56 g) of BPPY in 20 ml of methanol. A white precipitate formed immediately. After stirring for 15 min at room temperature, the solid was isolated by suction filtration, washed with methanol and diethyl ether, and dried in vacuo over $CaSO_4$.

$[Pd(APPY)_2Cl_2]$

Ten mmoles (3.18 g) of APPY was added to a refluxing solution of 5.0 mmoles (0.886 g) of $PdCl_2$ dissolved in 150 ml of acetonitrile. The reaction mixture became paler in color immediately. After stirring for two h at reflux, the pale orange-yellow solution was filtered to remove some decomposition products. The filtrate was evaporated to dryness by aspiration and a warm water bath. The residue was slurried in diethyl ether in a Dry Ice/acetone bath for 1 h. The resulting yellow solid was isolated by suction filtration and dried in vacuo over $CaSO_4$. Λ_m = 35 ohm^{-1} cm^2 $mole^{-1}$ (10^{-3} *M* in nitrobenzene at 25°C).

[Pt(APPY)$_2$Cl$_2$]

A solution of 2.0 mmoles (0.532 g) of $PtCl_2$ and 4.0 mmoles (1.27 g) of APPY in 75 ml of acetonitrile was refluxed for 44 h. The reaction mixture was filtered while hot, then evaporated to dryness under reduced pressure. The yellow crystalline residue was slurried in diethyl ether in a Dry Ice/acetone bath for approximately 2 h. The solid which resulted was isolated by suction filtration, washed with fresh diethyl ether, and dried in vacuo over $CaSO_4$. Λ_m = 20 ohm^{-1} cm^2 $mole^{-1}$ (10^{-3} *M* in nitrobenzene at 25°C).

[Hg$_2$(APPY)$_2$Cl$_4$]

A warm solution of 1.0 mmole (0.271 g) of $HgCl_2$ in 10 ml of distilled water was added dropwise to a solution of 1.0 mmole (0.318 g) of APPY in 10 ml of methanol. The yellow solution lost color gradually as a white precipitate formed. After stirring for 10 min, the solid was collected in a glass-fritted funnel by suction filtration, washed with fresh methanol, distilled water, and diethyl ether, and dried in vacuo over $CaSO_4$. Mol.wt. Found: 1167, calcd: 1180; (benzene solution).

[Sn(APPY)(CH$_3$)$_3$Cl]

This complex was prepared by the method of Kato et al. [22].

[Pd(CMPPY)$_2$Cl$_2$]

$PdCl_2$ (0.166 g) was dissolved in 50 ml of hot acetonitrile in a beaker on a heater-stirrer. When dissolution was complete, the heating was stopped and CMPPY (0.669 g) was added. The reaction mixture was stirred and very slowly allowed to cool to room temperature, whereupon a yellow precipitate began to form. After stirring for 1 h, the solid was isolated by suction filtration, washed with acetonitrile and diethyl ether, and dried in vacuo over $CaCl_2$.

[Pd$_2$(CMPPY)$_2$(SCN)$_4$]

One mmole (0.334 g) of CMPPY was added to a solution of 0.5 mmole (0.208 g) of $K_2[Pd(SCN)_4]$ [21] in 25 ml of methanol. The ylid dissolved very slowly. Within 5 min the reaction mixture became turbid and an orange precipitate began to form as the blood-red color faded. After stirring for 1 h, the bright orange solid was isolated by suction filtration, washed with methanol and diethyl ether, and dried in vacuo over $CaCl_2$.

[Hg$_2$(CMPPY)$_2$Cl$_4$]

Two mmoles (0.669 g) of CMPPY were dissolved in 50 ml of methanol, warming was needed to dissolve the ylid completely. Mercury(II) chloride (1.0 mmole, 0.271 g) in 50 ml of methanol was added in portions. A white precipitate formed with stirring and gentle heating for 12 h. The product was isolated by suction filtration while the solution was still warm, washed with methanol, and dried in vacuo over $CaSO_4$.

[Pd(CEPPY)$_2$Cl$_2$]

This yellow complex was prepared by the method employed for the synthesis of the APPY complex, utilizing 1.0 mmole (0.177 g) of $PdCl_2$, 2.0 mmole (0.697 g) of CEPPY, and a refluxing period of 40 min under nitrogen.

[Pd$_2$(CEPPY)$_2$(SCN)$_4$]

This bright orange complex was prepared by the method employed for the synthesis of the BPPY—thiocyanate complex, utilizing 0.5 mmole (0.208 g) of $K_2[Pd(SCN)_4]$ [21], 1.0 mmole (0.342 g) of CEPPY, and a reaction time of 12 h.

[Pt(CEPPY)$_2$Cl$_2$]

This golden-yellow complex was prepared by the method employed for the synthesis of the APPY complex, utilizing 0.5 mmole (0.133 g) of $PtCl_2$, 1.0 mmole (0.347 g) of CEPPY, and a refluxing period of 30 min.

[Hg$_2$(CEPPY)$_2$Cl$_4$]

This white complex was prepared by the method employed for the synthesis of the BPPY complex, utilizing 1.0 mmole (0.271 g) of $HgCl_2$, 2.0 mmole (0.697 g) of CEPPY, and a reaction time of 24 h.

[Pd(DBPPY)$_2$Cl$_2$]

This complex was prepared by the method employed for the synthesis of the APPY complex, utilizing 0.5 mmole (0.0887 g) of $PdCl_2$, 1.0 mmole (0.484 g) of DBPPY, and a refluxing period of 3 h.

[Pd(DBPPY)$_2$(NCS)$_2$]

This pale orange complex was prepared by the method employed for the synthesis of the BPPY—thiocyanate complex, utilizing 0.5 mmole (0.208 g) of $K_2[Pd(SCN)_4]$ [21], 1.0 mmole (0.484 g) of DBPPY, and a reaction time of four days.

[Pt(DBPPY)$_2$Cl$_2$]

This red-orange complex was prepared by the method employed for the APPY—platinum(II) chloride complex, utilizing 0.5 mmole (0.133 g) of $PtCl_2$, 1.0 mmole (0.484 g) of DBPPY, and gentle refluxing for 24 h. The product, which was slurried as previously in diethyl ether, was allowed to warm slowly to room temperature before isolation.

[Hg$_2$(DBPPY)$_2$Cl$_4$]

The white complex was prepared by the method employed for the BPPY complex, utilizing 0.5 mmole (0.136 g) of $HgCl_2$, 1.0 mmole (0.484 g) of DBPPY, and a reaction time of 2 h.

[Pd(BMPPY)$_2$Cl$_2$]

This orange complex was prepared by the method employed for the corresponding APPY complex, utilizing 1.0 mmole of $PdCl_2$, 2.0 mmoles of BMPPY, and a refluxing period of 1 h. Λ_m = 24 ohm^{-1} cm^2 mole^{-1} (10^{-3} *M* in nitrobenzene at 25°C).

$[Hg_2(BMPPY)_2Cl_4]$

This white complex was prepared according to the method employed for the corresponding DBPPY complex, utilizing 1.0 mmole (0.271 g) of $HgCl_2$, 1.0 mmole (0.394 g) of BMPPY and a reaction time of 10 min.

$[Hg_2(CEMPPY)_2Cl_4]$

This white complex was prepared by the method employed in the previous preparation, utilizing 1.0 mmole (0.271 g) of $HgCl_2$, 2.1 mmole (0.761 g) of CEMPPY, and a reaction time of 1 h.

$[Pd(CPPY)_2Cl_2]$

To a solution of 1.0 mmole (0.177 g) of $PdCl_2$ dissolved in 40 ml of hot acetonitrile was added 2.0 mmoles (0.603 g) of CPPY. A yellow precipitate began to form after several minutes of stirring over low heat. At the end of 4 h, the yellow solid was isolated by suction filtration, washed with acetonitrile and dried in vacuo over $CaCl_2$.

$[Hg_2(CPPY)_2Cl_4]$

This white complex was prepared by the method used for the preparation of the BPPY complex, utilizing 1.0 mmole (0.271 g) of $HgCl_2$, 2.0 mmole (0.603 g) of CPPY, and a reaction time of 36 h.

$[Pd(BBuPY)_2Cl_2]$

One mmole (0.177 g) of $PdCl_2$ was dissolved in 50 ml of refluxing acetonitrile. To the filtered solution at room temperature was added 4.5 ml (ca. 2.25 mmoles) of a benzene solution of freshly-prepared BBuPY. The red-orange reaction mixture was refluxed for 15 min, then reduced to dryness using a rotary evaporator. The remaining red-orange oil was placed in vacuo for 2.5 h, after which a red-orange solid remained. The product was slurried in diethyl ether in a Dry Ice/acetone bath for 1 h. The bright yellow product was isolated by suction filtration, washed with diethyl ether, and dried in vacuo over $CaSO_4$. $\Lambda_m \cong 0$ (10^{-3} *M* in nitrobenzene at 25°C).

$[Hg_2(BBuPY)_2Cl_4]$

A solution of 6.0 mmoles of BBuPY in 30 ml of benzene was added to a solution of 3.0 mmoles of $HgCl_2$ in 30 ml of n-propanol. The mixture was boiled, additional n-propanol being added as the benzene was removed. The n-propanol solution was then evaporated to dryness in vacuo over an 18 h period, whereupon 100 ml of a 50% aqueous acetone solution was added. Vigorous stirring for 90 min converted the initially formed oil into a white solid. The product was collected by filtration, washed with water and diethyl ether, and dried in vacuo. It was then redissolved in 20 ml of acetone, 20 ml of water was slowly added, and the mixture was stirred overnight prior to isolating the solid once again. Mol.wt. Found: 1197, calcd: 1183; (benzene solution). $\Lambda_m \cong 0$ ohm^{-1} cm^2 mole^{-1} (10^{-3} *M* in nitrobenzene at 25°C).

$[Pd(BPAsY)_2Cl_2]$

This bright yellow complex was prepared according to the method used for the BPPY complex utilizing 0.5 mmole (0.0887 g) of $PdCl_2$, 1.0 mmole (0.424 g) of BPAsY, and a reaction time of one h; a precipitate formed after 15 sec.

[Pd(BPAsY)$_2$(NCS)$_2$]

The bright yellow complex was prepared by the method employed for the synthesis of the BPPY—thiocyanate complex, utilizing 0.5 mmole (0.208 g) of $K_2[Pd(SCN)_4]$ [21], 1.0 mmole (0.424 g) of BPAsY, and a reaction time of 2 h.

[Pt(BPAsY)$_2$Cl$_2$]

One-half mmole (0.133 g) of $PtCl_2$ was dissolved in 30 ml of refluxing acetonitrile. The yellow-green solution was cooled to room temperature and 1.0 mmole (0.424 g) of BPAsY was added. The reaction mixture was stirred at 50°C, for 24 h. The yellow solid which clung to the sides of the reaction flask was isolated by suction filtration, washed with acetonitrile and diethyl ether, and dried in vacuo over $CaSO_4$.

[Hg$_2$(BPAsY)$_2$Cl$_4$]

This white complex was prepared by the method employed for the preparation of the BPPY complex, utilizing 1.0 mmole (0.271 g) of $HgCl_2$, 2.0 mmole (0.849 g) of BPAsY, and a reaction time of 2 h.

[Pd(CMPAsY)$_2$Cl$_2$]

This yellow complex was synthesized according to the method employed for the preparation of the APPY complex, utilizing 0.5 mmoles (0.0887 g) of $PdCl_2$, 1.0 mmole (0.378 g) of CMPAsY, and a refluxing period of 30 min.

[Hg$_2$(BDMSY)$_2$Cl$_4$]

The off-white complex was prepared by the method employed for the BPPY complex, utilizing 0.5 mmole (0.136 g) of $HgCl_2$, 1.0 mmole (0.108 g) of BDMSY, and a reaction time of 24 h.

[Hg$_2$(BPyY)$_2$Cl$_4$]

The white complex was prepared by the method employed for the BPPY complex, utilizing 0.5 mmole (0.136 g) of $HgCl_2$, 1.0 mmole (0.197 g) of BPyY, and a reaction time of 15 h.

The formulas, yields, melting points and analytical data for the metal—ylid complexes prepared are shown in Table 2. No attempt was made to identify materials which did not precipitate from solution under the conditions of the reaction.

Physical measurements

Solid state infrared spectra in the 4000-400 cm^{-1} range were measured on a Perkin—Elmer Model 337 grating spectrophotometer. Samples were either examined as Nujol mulls suspended between potassium bromide plates, or ground up with spectral grade potassium bromide and pressed into clear disks. High resolution solid state and solution spectra of the complexes and starting materials were measured using Perkin—Elmer Models 180 and 421 spectrophotometers. For high-resolution peak assignments, a five-fold wavenumber scale expansion

TABLE 2

FORMULAS, YIELDS, MELTING POINTS AND ANALYTICAL DATA FOR THE METAL—YLID COMPLEXES

Complex	Formula	Yield (%)	Melting Point (°C)	Analyses: found (calcd.)		
				C	H	P or [N] or {Cl}
[Pd(DBPBe)Cl$_2$]	$C_{35}H_{29}Cl_2O_2PPd$	*a*	219	60.85 (60.90)	4.28 (4.24)	*a*
[Pd(BPPY)$_2$Cl$_2$]	$C_{52}H_{42}Cl_2O_2P_2Pd$	56	217-219	66.34 (66.57)	4.49 (4.51)	6.43 (6.60)
[Pd(BPPY)$_2$(NCS)$_2$]	$C_{54}H_{42}N_2O_2P_2S_2Pd$	13	233 (dec.)	66.85 (66.76)	4.15 (4.20)	[2.75] [(2.78)]
[Pt(BPPY)$_2$Cl$_2$]	$C_{52}H_{42}Cl_2O_2P_2Pt$	96	127-130	60.74 (60.82)	4.20 (4.12)	5.99 (6.03)
[Hg$_2$(BPPY)$_2$Cl$_4$]	$C_{52}H_{42}Cl_4O_2P_2Hg_2$	93	194-196	47.79 (47.90)	3.34 (3.25)	4.72 (4.75)
[Pd(APPY)$_2$Cl$_2$]	$C_{42}H_{38}Cl_2O_2P_2Pd$	98	162 (dec.)	61.75 (61.97)	4.72 (4.71)	7.39 (7.61)
[Pt(APPY)$_2$Cl$_2$]	$C_{42}H_{38}Cl_2O_2P_2Pt$	98	112	55.70 (55.88)	4.31 (4.24)	6.80 (6.75)
[Hg$_2$(APPY)$_2$Cl$_4$]	$C_{42}H_{38}Cl_4O_2P_2Hg_2$	88	206-208	42.67 (42.76)	3.41 (3.25)	5.06 (5.25) {12.01} {(12.02)}
[Sn(APPY)(CH$_3$)$_3$Cl]	$C_{24}H_{28}ClOPSn$	58	184	55.54 (55.69)	5.58 (5.45)	6.25 (5.98)
[Pd(CMPPY)$_2$Cl$_2$]	$C_{42}H_{38}Cl_2O_4P_2Pd$	54	192-194	59.41 (59.63)	4.79 (4.53)	{8.57} {(8.38)}
[Pd$_2$(CMPPY)$_2$(SCN)$_4$]	$C_{46}H_{38}N_4O_4P_2S_4Pd_2$	26	179-181	49.43 (49.60)	3.63 (3.44)	[5.25] [(5.03)]
[Hg$_2$(CMPPY)$_2$Cl$_4$]	$C_{42}H_{38}Cl_4O_4P_2Hg_2$	17	210 (dec.)	41.72 (41.63)	3.05 (3.16)	4.94 (5.11)
[Pd(CEPPY)$_2$Cl$_2$]	$C_{44}H_{42}Cl_2O_4P_2Pd$	99	72	60.33 (60.46)	4.88 (4.84)	6.94 (7.09)
[Pd$_2$(CEPPY)$_2$(SCN)$_4$]	$C_{48}H_{42}N_4O_4P_2S_4Pd_2$	48	180 (dec.)	50.39 (50.49)	3.70 (3.71)	[4.72] [(4.91)]
[Pt(CEPPY)$_2$Cl$_2$]	$C_{44}H_{42}Cl_2O_4P_2Pt$	91	113	54.87 (54.89)	4.22 (4.40)	6.56 (6.43)
[Hg$_2$(CEPPY)$_2$Cl$_4$]	$C_{44}H_{42}Cl_4O_4P_2Hg_2$	28	204 (dec.)	42.33 (42.63)	3.61 (3.42)	5.24 (5.00)
[Pd(DBPPY)$_2$Cl$_2$]	$C_{66}H_{50}Cl_2O_4P_2Pd$	95	113-115	69.30 (69.13)	4.49 (4.39)	5.56 (5.40)
[Pd(DBPPY)$_2$(NCS)$_2$]	$C_{68}H_{50}N_2O_4P_2S_2Pd$	33	212	68.29 (68.54)	4.43 (4.23)	5.00 (5.20) [2.54] [(2.35)]
[Pt(DBPPY)$_2$Cl$_2$]	$C_{66}H_{50}Cl_2O_4P_2Pt$	92	106	64.28 (64.18)	3.96 (4.08)	5.13 (5.02)
[Hg$_2$(DBPPY)$_2$Cl$_4$]	$C_{66}H_{50}Cl_4O_4P_2Hg_2$	36	190 (dec.)	52.19 (52.42)	3.43 (3.33)	4.26 (4.09)
[Pd(BMPPY)$_2$Cl$_2$]	$C_{54}H_{46}Cl_2O_2P_2Pd$	73	70	66.94 (67.13)	4.75 (4.80)	6.62 (6.41) {7.13} {(7.34)}
[Hg$_2$(BMPPY)$_2$Cl$_4$]	$C_{54}H_{46}Cl_4O_2P_2Hg_2$	36	145-147	48.56 (48.70)	3.57 (3.48)	4.48 (4.65) {10.53} {(10.65)}
[Hg$_2$(CEMPPY)$_2$Cl$_4$]	$C_{46}H_{46}Cl_4O_4P_2Hg_2$	17	179-181	44.47 (43.58)	3.71 (3.66)	5.10 (4.89)

TABLE 2 (*continued*)

Complex	Formula	Yield (%)	Melting Point (°C)	Analyses: found (calcd.)		
				C	H	P or [N] or {Cl}
$[Pd(CPPY)_2Cl_2]$	$C_{40}H_{32}Cl_2N_2P_2Pd$	48	206-208	61.38 (61.60)	4.28 (4.14)	7.74 (7.94) {9.30} {(9.09)}
$[Hg_2(CPPY)_2Cl_4]$	$C_{40}H_{32}Cl_4N_2P_2Hg_2$	9	213 (dec.)	45.77 (45.95)	2.97 (3.09)	5.70 (5.92)
$[Pd(BBuPY)_2Cl_2]$	$C_{40}H_{66}Cl_2O_2P_2Pd$	36	166-167	58.95 (58.72)	8.45 (8.13)	7.48 (7.57)
$[Hg_2(BBuPY)_2Cl_4]$	$C_{40}H_{66}Cl_4O_2P_2Hg_2$	56	142	40.41 (40.58)	5.47 (5.61)	{11.79} {(11.97)}
$[Pd(BPAsY)_2Cl_2]$	$C_{52}H_{42}As_2Cl_2O_2Pd$	87	198 (dec.)	61.12 (60.87)	3.97 (4.13)	7.12 (6.91)
$[Pd(BPAsY)_2(NCS)_2]$	$C_{54}H_{42}As_2N_2O_2S_2Pd$	61	197 (dec.)	60.32 (60.54)	4.02 (3.95)	[2.73] [(2.61)]
$[Pt(BPAsY)_2Cl_2]$	$C_{52}H_{42}As_2Cl_2O_2Pt$	9	237 (dec.)	55.76 (56.03)	3.52 (3.80)	{6.66} {(6.36)}
$[Hg_2(BPAsY)_2Cl_4]$	$C_{52}H_{42}As_2Cl_4O_2Hg_2$	20	181-183	44.74 (44.88)	3.18 (3.04)	[a]
$[Pd(CMPAsY)_2Cl_2]$	$C_{42}H_{38}As_2Cl_2O_4Pd$	42	204-205	54.28 (54.02)	4.35 (4.10)	{7.58} {(7.59)}
$[Hg_2(BDMSY)_2Cl_4]$	$C_{20}H_{24}Cl_4O_2S_2Hg_2$	31	198 (dec.)	25.41 (26.58)	2.59 (2.68)	[b]
$[Hg_2(BPyY)_2Cl_4]$	$C_{26}H_{22}Cl_4N_2O_2Hg_2$	17	186 (dec.)	32.88 (33.31)	2.29 (2.37)	[3.05] [(2.99)]

[a] Not determined. [b] %S found: 7.23, calcd: 7.10.

was employed. Matched 0.1 mm and 1.0 mm sodium chloride cavity cells were used for the solution measurements. The integrated absorption intensities of the C—N stretching frequencies of the thiocyanate complexes were determined by Ramsay's method of direct integration [23]. Proton nuclear magnetic resonance spectra were recorded on Perkin—Elmer Model R12B and Varian A-60-A spectrometers, using tetramethylsilane as an internal standard. All chemical shifts are reported in ppm relative to TMS as zero (using δ units). All deuterated solvents were obtained from Stohler Isotope Chemicals, Rutherford, New Jersey. Molar conductances, at 25°C, of 10^{-3} *M* solutions of selected complexes were determined with an Industrial Instruments, Inc., Model RC-16B2 conductivity bridge and a cell with platinized electrodes. Molecular weight determinations by the osmotic pressure method were carried out by Alfred Bernhardt, Elbach über Engelskirchen, West Germany. Melting points were measured on a Fisher—Johns melting point apparatus and a Thomas—Hoover capillary melting point apparatus and are uncorrected. Carbon, hydrogen, nitrogen, phosphorus and halogen microanalyses were performed by the following laboratories: (1) M—H—W Laboratories, Garden City, Michigan 48135; (2) Meade Microanalytical Laboratory, Amherst, Massachusetts 01002; (3) Alfred Bernhardt Microanalytisches Laboratorium, Elbach über Engelskirchen, West Germany; and (4) Micro-Analysis, Inc., Wilmington, Delaware 19808.

TABLE 3

PROTON NUCLEAR MAGNETIC RESONANCE DATA FOR SOLUTIONS OF SELECTED METAL—YLID COMPLEXES AND STARTING MATERIALS

Compound	Resonances[a,b]	Assignment
$C_6H_5COCHP(C_6H_5)_3$	4.41d(25 Hz)	—CH—[c]
	7.2-8.3m	$—C_6H_5$
$[CH_3COCH_2P(C_6H_5)_3]Cl$	2.51d(1.5 Hz)	$—CH_3$
	6.13d(11 Hz)	$—CH_2—$
	7.35-8.1m	$—C_6H_5$
$CH_3COCHP(C_6H_5)_3$	d	—CH—[e]
	2.08d(2 Hz)	$—CH_3$[e]
	7.3-8.0m	$—C_6H_5$
$[Pd(APPY)_2Cl_2]$	2.35m	$—CH_3$
	4.48d(6 Hz)	—CH—
	7.0-8.1m	$—C_6H_5$
$[Pt(APPY)_2Cl_2]$	2.22d(2 Hz)	$—CH_3$
	2.37d(2 Hz)	$—CH_3$
	4.58d(5 Hz)	—CH—
	7.3-8.0m	$—C_6H_5$
$[Hg_2(APPY)_2Cl_4]$	d	—CH—
	2.68d(2 Hz)	$—CH_3$
	7.5-8.1m	$—C_6H_5$
$[Sn(APPY)(CH_3)_3Cl]$	0.38s	$—Sn—CH_3$
	0.96d(2 Hz)	$—Sn—CH_3$
	d	—CH—
	1.99d(1.5 Hz)	$—CH_3$
	7.3-7.8m	$—C_6H_5$
$[CH_3CH_2OCOCH_2P(C_6H_5)_3]Br$	1.03t(8 Hz)	$—CH_3$
	4.01q(7 Hz)	$—OCH_2—$
	5.47d(14 Hz)	$—CH_2—$
	7.4-8.2m	$—C_6H_5$
$CH_3CH_2OCOCHP(C_6H_5)_3$	1.04t(7 Hz)	$—CH_3$[f]
	2.91s (br)	—CH—
	3.99q(7 Hz)	$—OCH_2—$[f]
	7.3-8.0m	$—C_6H_5$
$[Pd(CEPPY)_2Cl_2]$	0.99t(7 Hz)	$—CH_3$
	3.98q(7 Hz)	$—CH_2O—$
	5.32d(14 Hz)	—CH—
	7.2-8.1m	$—C_6H_5$
$[Pt(CEPPY)_2Cl_2]$	0.88t(7 Hz)	$—CH_3$
	3.70q(7 Hz)	$—OCH_2—$
	5.31(br)	—CH—
	7.0-8.4m	$—C_6H_5$
$[Pd_2(CEPPY)_2(SCN)_4]$	1.23t(7 Hz)	$—CH_3$
	3.72q(7 Hz)	$—CH_2O—$
	5.50s	—CH—
	7.1-7.9m	$—C_6H_5$
$[CH_3OCOCH_2P(C_6H_5)_3]Br$	3.53s	$—OCH_3$
	5.54d(13 Hz)	$—CH_2—$
	7.6-8.2m	$—C_6H_5$
$CH_3OCOCHP(C_6H_5)_3$	2.92s (br)	—CH—
	3.48s	$—OCH_3$
	7.1-8.0m	$—C_6H_5$
$[Pd_2(CMPPY)_2(SCN)_4]$	3.68q(7 Hz)	$—OCH_3$
	5.52s	—CH—
	7.2-7.8m	$—C_6H_5$
$[C_6H_5COCH(CH_3)P(C_6H_5)_3]Br$	1.69d(7 Hz), 2.00d(7 Hz)	$—CH_3$[g]
	5.25m	—CH—
	7.3-8.7m	$—C_6H_5$
$C_6H_5COC(CH_3)P(C_6H_5)_3$	1.73d(16 Hz)	$—CH_3$
	7.2-7.9m	$—C_6H_5$

(Table continued)

TABLE 3 (*continued*)

Compound	Resonances[a,b]	Assignment
$[Hg_2(BMPPY)_2Cl_4]$	3.74q(7 Hz)	$—CH_3$
	7.4-7.8m	$—C_6H_5$
$[CH_3CH_2OCOCH(CH_3)P(C_6H_5)_3]Br$	0.99t(7 Hz)	$—CH_3$
	1.54d(7 Hz), 1.85d(7 Hz)	$—CH_3 \alpha C^g$
	4.02q(7 Hz)	$—CH_2—$
	6.50q(8 Hz)	$—CH—$
	7.3-8.3m	$—C_6H_5$
$[Hg_2(CEMPPY)_2Cl_4]$	0.96t(7 Hz)	$—CH_2\underline{CH_3}$
	1.68m	$—CH_2—$
	4.02d(7 Hz)	$—CH_3$
	7.4-7.9m	$—C_6H_5$
$[C_6H_5COCH_2PBu_3]Br$	0.7-2.9m	—Bu
	5.03d(13 Hz)	$—CH_2—$
	7.4-8.3m	$—C_6H_5$
$C_6H_5COCHPBu_3{}^h$	0.55-2.1m	—Bu
	3.59s	$—CH—$
	i	$—C_6H_5$
$[Pd(BBuPY)_2Cl_2]$	0.6-2.8m	—Bu
	4.57s	$—CH—$
	7.25-8.55m	$—C_6H_5$
$[Hg_2(BBuPY)_2Cl_4]$	0.7-2.9m	—Bu
	4.5-4.9s (br)	$—CH—$
	7.2-7.7, m	$—C_6H_5$
$NCCHP(C_6H_5)_3$	1.68, s	$—CH—^j$
	7.2-7.9, m	$—C_6H_5$
$[C_6H_5COCH_2As(C_6H_5)_3]Br$	6.46s	$—CH_2—$
	7.4-8.5m	$—C_6H_5$
$C_6H_5COCHAs(C_6H_5)_3$	4.70s (br)	$—CH—$
	7.1-8.2m	$—C_6H_5$
$[CH_3OCOCH_2As(C_6H_5)_3]Br$	3.59s	$—OCH_3$
	5.46s	$—CH_2—$
	7.5-8.0m	$—C_6H_5$
$CH_3OCOCHAs(C_6H_5)_3$	3.19s	$—CH—$
	3.39s	$—OCH_3$
	7.3-7.9m	$—C_6H_5$
$[C_6H_5COCH_2S(CH_3)_2]Br$	3.07s	$—S—CH_3$
	5.75s	$—CH_2—$
	7.5-8.2m	$—C_6H_5$
$C_6H_5COCHS(CH_3)_2$	2.91s	$—S—CH_3$
	4.30s	$—CH—$
	7.3-8.0m	$—C_6H_5$

[a] Given as: peak position (δ), description (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, br = broad), J(P—H) (Herz). [b] Deuterochloroform solution, unless otherwise specified. [c] Lit. [24]: 4.43 δ, d, J(P—H) = 24.5 Hz. [d] Not observed. [e] Lit. [25,26]: methine H, 3.67δ, d, J(P—H) = 27 Hz; CH_3, 2.07 δ, d, J(P—H) = 1.8 Hz. [f] Lit. [27]: CH_3, 0.91δ, t; CH_2, 3.88δ, q; both at 32°C. [g] Two doublets due to partial enolization. [h] Benzene solution. [i] Obscured by benzene absorption. [j] Lit. [28]: 1.62δ, d, J(P—H) = 7Hz.

Results

The syntheses described in the Experimental Section represent only those which yielded isolable and characterizable complexes by elemental analyses within a reasonable range of accuracy. For all of the ylids represented in Table 1, syntheses were attempted with palladium(II), platinum(II) and mercury(II) chlorides. In many of the unsuccessful experiments performed, a reaction was

(continued on p. 380)

TABLE 4

SOLID STATE INFRARED ABSORPTION DATA FOR METAL—YLID COMPLEXES AND STARTING MATERIALS

Compound	Absorption Bands (1800-1500 cm^{-1})^{a,b}	Other^{a,b}
$[(C_6H_5CO)_2CH(CH_2)_2P(C_6H_5)_3]Br$	1700s, 1680s, 1600m, 1580m	
$(C_6H_5CO)_2C(CH_2)_2P(C_6H_5)_3$	1590m, 1580m, 1530m, 1500-1350s (br)	
$[Pd(DBPBe)Cl_2]$	1640s, 1570s	
$[C_6H_5COCH_2P(C_6H_5)_3]Br$	1656s, 1591s, 1584s, 1575m	
$C_6H_5COCHP(C_6H_5)_3$	1585s, 1573m, 1523s, 1511s	
$[Pd(BPPY)_2Cl_2]$	1627s, 1592m, 1584m, 1575s, 1521w	
$[Pt(BPPY)_2Cl_2]$	1672s, 1630s, 1584m, 1573m	
$[Hg_2(BPPY)_2Cl_4]$	1625s, 1585s, 1572s, 1559m	
$[Pd(BPPY)_2(NCS)_2]$	1628s (br), 1615(sh), 1591m, 1584m, 1573s, sp	2158w,^{e} 2088s (br)^f
$[CH_3COCH_2P(C_6H_5)_3]Cl$	1713s, 1700s, 1667m, 1586m, 1571w	
$CH_3COCHP(C_6H_5)_3$	1586w, 1572m, 1569m, 1536s	
$[Pd(APPY)_2Cl_2]$	1712m, 1701m, 1647s, 1584m, 1566m	
$[Pt(APPY)_2Cl_2]$	1711s, 1647s, 1585m, 1567m, 1507w	
$[Hg_2(APPY)_2Cl_4]$	1672s (br), 1643m, 1585m	
$[Sn(APPY)(CH_3)_3Cl]$	1586m (sp), 1572m (sp), 1542(sh), 1500s (br)	
$[CH_3CH_2OCOCH_2P(C_6H_5)_3]Br$	1709m (br), 1585w	
$CH_3CH_2OCOCHP(C_6H_5)_3$	1606s (br), 1587s	
$[Pd(CEPPY)_2Cl_2]$	1722s (br), 1676s (br), 1583m, 1562m	
$[Pt(CEPPY)_2Cl_2]$	1725s, 1688s (br), 1583m	
$[Hg_2(CEPPY)_2Cl_4]$	1676s (sp), 1663s (sp), 1584w	
$[Pd_2(CEPPY)_2(SCN)_4]$	1683s (sp), 1586w, 1573w	2154s (sp), ^{e}2115s (sp)^g
$[CH_3OCOCH_2P(C_6H_5)_3]Br$	1722s (sp), 1586m	
$CH_3OCOCHP(C_6H_5)_3$	1617s (br), 1585m	
$[Pd(CMPPY)_2Cl_2]$	1680s, 1584w, 1569w	
$[Hg_2(CMPPY)_2Cl_4]$	1701w, 1676s (sp), 1586w	
$[Pd_2(CMPPY)_2(SCN)_4]$	1680s (br), 1587w, 1575w, 1572w	2152s (sp), ^{e}2112s (sp)^g
$[C_6H_5COCH(CH_3)P(C_6H_5)_3]Br$	1661s, 1592m, 1583m, 1579m	
$C_6H_5COC(CH_3)P(C_6H_5)_3$	1615s, 1586m, 1543m	
$[Pd(BMPPY)_2Cl_2]$	1780, 1725, 1680, 1600	
$[Hg_2(BMPPY)_2Cl_4]$	1672m, 1616s, 1590m, 1585m, 1572m	
$[CH_3CH_2OCOCH(CH_3)P(C_6H_5)_3]Br$	1727s, 1685w, 1636m, 1585w	
$CH_3CH_2OCOC(CH_3)P(C_6H_5)_3$	1626s, 1585s, 1579(sh)	
$[Hg_2(CEMPPY)_2Cl_4]$	1705s (br), 1582m, 1570w	
$(C_6H_5CO)_2CP(C_6H_5)_3$	1584m, 1573(sh), 1523s, 1509s	
$[Pd(DBPPY)_2Cl_2]$	1667m, 1613m, 1572m, 1503s	
$[Pt(DBPPY)_2Cl_2]$	1672m, 1629m, 1593w, 1583m, 1501s	
$[Hg_2(DBPPY)_2Cl_4]$	1637s, 1587m, 1573m	
$[Pd(DBPPY)_2(NCS)_2]$	1629s (br), 1591m, 1584m, 1573m	2106(sh)^f, 2090s (br)^f
$[C_6H_5COCH_2P(Bu)_3]Br$	1676s (sp), 1596m, 1579m	
$C_6H_5COCHP(Bu)_3$	*d*	
$[Pd(BBuPY)_2Cl_2]$	1620s, 1612s, 1595s, 1574s	
$[Hg_2(BBuPY)_2Cl_4]$	1636^c, 1595^c, 1578^c	
$[NCCH_2P(C_6H_5)_3]Cl$	1830m, 1788m, 1685m, 1586s (sp), 1571m	2246(sh)^h, 2229s (sp)^h, 2131m^h
$NCCHP(C_6H_5)_3$	1587w	2136m^h
$[Pd(CPPY)_2Cl_2]$	1586m, 1570m	2248m^h, 2189s^h
$[Hg_2(CPPY)_2Cl_4]$	1610w, 1582m	2201vw^h, 2190m^h
$[C_6H_5COCH_2As(C_6H_5)_3]Br$	1650s (sp), 1591m, 1575m	
$C_6H_5COCHAs(C_6H_5)_3$	1611w, 1584m, 1506s (br), 1501s (br)	
$[Pd(BPAsY)_2Cl_2]$	1621s (sp), 1592w, 1572m	

(Table continued)

TABLE 4 (*continued*)

Compound	Absorption Bands (1800-1500 cm^{-1})[a,b]	Other[a,b]
$[Pt(BPAsY)_2Cl_2]$	1628s (br), 1591m, 1573m	
$[Hg_2(BPAsY)_2Cl_4]$	1617s (sp), 1591m, 1575m, 1571m	
$[Pd(BPAsY)_2(NCS)_2]$	1627s (sp), 1592m, 1574m	2150vw[e], 2099s (br, as)[f]
$[CH_3OCOCH_2As(C_6H_5)_3]Br$	1716(sp)	
$CH_3OCOCHAs(C_6H_5)_3$	1592(br), 1573(sh)	
$[Pd(CMPAsY)_2Cl_2]$	1660s, 1627(sh), 1581w, 1572w	
$[C_6H_5COCH_2S(CH_3)_2]Br$	1680s, 1623m, 1585s	
$C_6H_5COCHS(CH_3)_2$	1585s, 1543w, 1508s	
$[Hg_2(BDMSY)_2Cl_4]$	1632s, 1606m, 1585m	
$[C_6H_5COCH_2NC_5H_5]Br$	1691s, 1594m, 1578s	
$C_6H_5COCHNC_5H_5$	1572s, 1545m, 1520s	
$[Hg_2(BPyY)_2Cl_4]$	1634s, 1594m, 1575s	

[a] Nujol mull between KBr plates, unless specified otherwise. [b] 5/1 abscissa scale expansion. Abbreviations: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad; as, asymmetric; sp, sharp. [c] KBr disk. [d] Not isolated. [e] ν(CN) of bridging thiocyanate. [f] ν(CN) of *N*-bonded thiocyanate. [g] ν(CN) of *S*-bonded thiocyanate. [h] ν(CN) of nitrile.

TABLE 5

SOLUTION INFRARED ABSORPTION DATA FOR METAL—YLID COMPLEXES AND STARTING MATERIALS

Compound	Absorption bands (1800-1500 cm^{-1})[a,b,c]	Others
$[C_6H_5COCH_2P(C_6H_5)_3]Br$	1677s, 1606s, 1596(sh), 1586s, 1521m	
$C_6H_5COCHP(C_6H_5)_3$	1596w, 1585s, 1520s, 1509(sh)	
$[Pd(BPPY)_2Cl_2]$	1675s, 1631s, 1595m, 1585m, 1576m, 1520s	
$[Pt(BPPY)_2Cl_2]$	1676s, 1655s, 1636s, 1589(sh), 1577s	
$[Hg_2(BPPY)_2Cl_4]$	1640s, 1605s, 1584s, 1577(sh), 1519s, 1508s	
$[CH_3COCH_2P(C_6H_5)_3]Cl$	1712s, 1606s, 1543w	
$CH_3COCHP(C_6H_5)_3$	1684s, 1681(sh), 1605s, 1591(sh), 1575m, 1542s	
$[Pd(APPY)_2Cl_2]$	1717s, 1642s, 1607s, 1588m, 1565m	
$[Pt(APPY)_2Cl_2]$	1717s, 1653s, 1649(sh), 1587m, 1569m	
$[Hg_2(APPY)_2Cl_4]$	1669s, 1648(sh), 1637(sh), 1586m	
$[Sn(APPY)(CH_3)_3Cl]$	1600w, 1575vw, 1513s (br)	
$[CH_3CH_2OCOCH_2P(C_6H_5)_3]Br$	1729s (br), 1615w, 1587w	
$CH_3CH_2OCOCHP(C_6H_5)_3$	1611s (br), 1574m	
$[Pd(CEPPY)_2Cl_2]$	1728s (sp), 1679s (sp), 1587m, 1565m	
$[Pt(CEPPY)_2Cl_2]$	1728m, 1686s, 1604s, 1587s, 1572m, 1552m	
$[Hg_2(CEPPY)_2Cl_4]$	1670s (br), 1602s (br), 1515w	
$[Pd_2(CEPPY)_2(SCN)_4]$	1692s (br), 1600m, 1588(sh), 1518w	2155s (sp), [d]2114s (sp)[e]
$[CH_3OCOCH_2P(C_6H_5)_3]Br$	1735s, 1731(sh), 1588w	
$CH_3OCOCHP(C_6H_5)_3$	1613s, 1589(sh), 1573w	
$[C_6H_5COC(CH_3)HP(C_6H_5)_3]Br$	1719s, 1595s, 1589m, 1582m, 1514w	
$C_6H_5COC(CH_3)P(C_6H_5)_3$	1576vw, 1506s, 1500s	
$[Hg_2(BMPPY)_2Cl_4]$	1671m, 1623m, 1595m, 1576m, 1502s	
$[CH_3CH_2OCOCH(CH_3)P(C_6H_5)_3]Br$	1727s, 1632m, 1602m, 1585m	
$CH_3CH_2OCOC(CH_3)P(C_6H_5)_3$	1625s, 1586s	
$[Hg_2(CEMPPY)_2Cl_4]$	1708s, 1675s, 1600m, 1587m	
$(C_6H_5CO)_2CP(C_6H_5)_3$	1585s, 1510s	
$[Pd(DBPPY)_2Cl_2]$	1673s (sp), 1624m, 1596m, 1577m, 1514s (sp)	

(Table continued)

TABLE 5 (*continued*)

Compound	Absorption bands (1800-1500 cm^{-1})^{a,b,c}	Others
[Pt(DBPPY)$_2$Cl$_2$]	1674s (sp), 1634s, 1596m, 1585s, 1576m, 1512s (sp)	
[Hg$_2$(DBPPY)$_2$Cl$_4$]	1638s (sp), 1595w, 1587w, 1578m, 1516s	
[Pd(DBPPY)$_2$(NCS)$_2$]	1629s (br), 1591m, 1584m, 1573m	2106(sh)^f, 2090s (br)^f
[C$_6$H$_5$COCH$_2$PBu$_3$] Br	1712w, 1675s, 1596m, 1580m	
[Pd(BBuPY)$_2$Cl$_2$]	1621s, 1613s, 1595s (sp), 1574s (sp)	
[NCCH$_2$P(C$_6$H$_5$)$_3$] Cl	1709w, 1601w, 1590w, 1437s	2146s^g
NCCHP(C$_6$H$_5$)$_3$	1483m, 1437s	2146s^g
[C$_6$H$_5$COCH$_2$As(C$_6$H$_5$)$_3$] Br	1668s, 1653(sh), 1596m, 1579m	
C$_6$H$_5$COCHAs(C$_6$H$_5$)$_3$	1710m, 1583m, 1502m	
[Pd(BPAsY)$_2$(NCS)$_2$]	1626s (sp), 1600s(sp), 1576m	2155^d, 2103m^f
[CH$_3$OCOCH$_2$As(C$_6$H$_5$)$_3$] Br	1727s, 1710s, 1635w, 1601w	
CH$_3$OCOCHAs(C$_6$H$_5$)$_3$	1710m, 1632m, 1598s, 1575(sh)	
[C$_6$H$_5$COCH$_2$S(CH$_3$)$_2$] Br	1682s, 1627m, 1596m, 1586s	
C$_6$H$_5$COCHS(CH$_3$)$_2$	1585s, 1539m, 1510s	
C$_6$H$_5$COCHNC$_5$H$_5$	1580s, 1547m, 1514s	

[a] Measured in 1.0 mm matched sodium chloride solution cells. [b] Chloroform solution. [c] 5/1 abscissa scale expansion. [d] ν(CN) of bridging thiocyanate. [e] ν(CN) of *S*-bonded thiocyanate. [f] ν(CN) of *N*-bonded thiocyanate. [g] ν(CN) of nitrile.

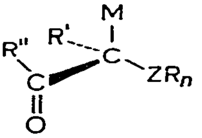
observed to occur because of color changes of the reaction mixtures, but stable complexes either could not be isolated or elemental analyses were unsatisfactory. Melting points were observed over wide ranges because of the tendency of the complexes to decompose with discoloration over a large temperature range. Even metal—ylid complexes of high purity, as determined by elemental analyses, gave poor melting points. This was probably due to the instability of the ylid-structure restraint created by the complex formation.

Proton nuclear magnetic resonance data for the salts, ylids, and metal—ylid complexes are given in Table 3. Many of the complexes prepared were insoluble in deuterochloroform while others had only minimal solubility. Thus, a complete overview of the complexes was unattainable.

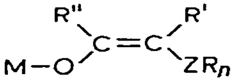
The infrared absorption bands in the carbonyl stretching and carbon—carbon double bond stretching regions, along with other pertinent absorption bands, of the spectra exhibited by the metal—ylid complexes in the solid state and, for those which exhibited sufficient solubility, in solution are shown in Tables 4 and 5, respectively.

Discussion

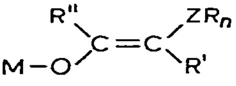
With the use of soft metal ions such as Pd^{II}, Pt^{II} and Hg^{II} as coordination sites, it was anticipated that bonding would occur most readily via resonance structure III because a carbanion is a softer Lewis base than oxygen. In addition to the possibility of either metal—carbon or metal—oxygen bond formation, any oxygen-bonded metal complexes could involve coordination in either a *cisoid* or *transoid* configuration:



(V)



cisoid
(VI)



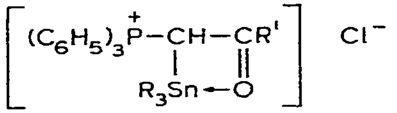
transoid
(VII)

The methine proton resonance was found to be a very good indicator of coordination of the ylid to the metal. In the proton NMR spectrum of each of the complexes studied in this manner (see Table 3) there is a downfield shift of the methine proton resonance toward the low-field position of the completely protonated 'onium salt. No spin—spin coupling between the methine proton and the ^{195}Pt nucleus could be observed because of poor solubility of the complexes or poor resolution. Koezuka et al. [29], have determined the coupling constants between the methine proton and the ^{195}Pt nucleus for a series of platinum(II)—sulfur ylid, [$CH_3(C_6H_5)SCHC(O)C_6H_4Cl$-*p*], complexes. The coupling constants were 124.7, 126.1 and 118.8 Hz for the dichloro, dibromo, and diiodo complexes, respectively. These data provide strong support for the existence of a direct platinum—carbon bond when compared with the value of 123 Hz for the ^{195}Pt—H (methine) coupling constant for K[Pt(acac)$_2$Cl] [30], which contains a direct platinum—carbon bond to one acetylacetonate group, the other functioning as a normal *O,O'*-bonded chelate (^{195}Pt—H (methine) = 2 Hz). Koezuka et al. [29] observed the same order for the methine chemical shifts, i.e., δ(free ylid) $<$ δ(complex) $<$ δ('onium salt), as that found in the present study.

In the proton nuclear magnetic resonance spectra for many of the complexes, the methine proton resonance was very broad or not present at all, as was the situation for some of the APPY complexes. These broad unresolved methine proton resonances exhibited by the complexes may be due to a rapid proton exchange between the ylid and a trace of the parent 'onium salt, as has been pointed out and demonstrated by Randall and Johnson [24]. In summary, the downfield shift of the methine proton resonance for the complexes studied is due to the inductive effect of the metal atom, implying coordination of the ylid to the metal and a close proximity of the metal atom, most probably via coordination through the methine carbon atom.

Considering the resonance forms which the free ylid may assume (structures II, III and IV), one might predict that oxygen-bonding (structures VI and VII), should cause a decrease in the carbonyl stretching frequency relative to the frequency exhibited by the free ylid. Conversely, if carbon-bonding were the bonding mode of the ylid in the complex, structure V, one would predict an increase in the carbonyl stretching frequency to one which would approach that of the free 'onium salt. The infrared absorption bands tabulated in Tables 4 (solid state) and 5 (solution) show a general increasing trend of the carbonyl stretching frequencies of the palladium(II), platinum(II), and mercury(II) complexes relative to that exhibited by the corresponding free ylid. The general trend may be described as an increase in the carbonyl stretching frequency in going from the free ylid to the metal—ylid complex to the free 'onium salt.

Koezuka et al. [29] have prepared palladium(II) and platinum(II) halide complexes, $[Pd(Sy)_2X_2]$ and $[Pt(R_2S)(Sy)X_2]$ ($X = Cl, Br, I$; $R = CH_3, CH_3CH_2$; $Sy = CH_3(C_6H_5)SCHC(O)C_6H_4Cl$-*p*) with a stable sulfur ylid. The sulfur ylid employed, *p*-chlorobenzoylmethylenemethylphenylsulfurane (Sy), can be described by the same resonance structures shown previously. The carbonyl stretching frequency of this ylid at 1578 cm^{-1} suggests a large contribution of the enolate resonance form in which the lone-pair electrons on the ylid methine carbon are considerably delocalized toward the oxygen atom. The carbonyl stretching frequencies of the complexes are observed [29] at higher frequencies (1628-1652 cm^{-1}) than that of the free ylid. In addition, the *p*-chlorobenzoylmethylmethylphenylsulfonium cation, which is totally protonated at the methine carbon, exhibits a carbonyl stretching frequency at 1677 cm^{-1} [29]. Thus, along with the methine proton NMR data cited earlier for these complexes, the high frequency shift of the carbonyl stretching frequencies implies that coordination takes place via the methine carbon in the palladium(II), platinum(II) and mercury(II) complexes, with the obvious exception of the $[Pd(DBPBe)Cl_2]$ complex, which in order to be square planar, must be *O,O′*-chelated. Examples of authentic oxygen-bonded metal complexes of carbonyl-stablized ylids of this type were sought in order to complement this conclusion. Kato et al. [22] have found that a dichloromethane solution of *para*-substituted benzoylmethylenetriphenylphosphoranes treated with an equimolar amount of trimethyltin chloride yielded isolable compounds which could be characterized by elemental analyses and infrared spectral data. The infrared spectra of the 1/1 adducts exhibited a very intense carbonyl-stretching absorption band in the region 1470-1495 cm^{-1}. These carbonyl stretching bands are shifted to a lower frequency relative to that of the free ylids, indicative of a strong coordination of the carbonyl oxygen to the trimethyltin moiety. Such a large shift of the carbonyl stretching frequency to a lower wave number was suggested by the authors to imply structure VIII, a



$$\left[\begin{array}{l}(C_6H_5)_3\overset{+}{P}-CH-CR' \\ \qquad\qquad\;\; | \quad\;\; \| \\ \qquad\quad R_3Sn\leftarrow O\end{array}\right] \quad Cl^-$$

(VIII)

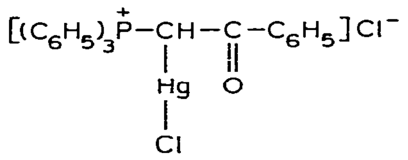
phosphonium salt similar to those structures proposed by Nesmeyanov et al. [31,32] for mercurated phosphonium and arsonium salts. This proposed structure is ambiguous and shows a hesitancy on behalf of the authors to describe the bonding mode unequivocally as being through the oxygen atom alone. Also, they have ignored the possibility of a neutral coordination compound of tin.

The most significant and relevant work to date in this connection is that of Buckle and Harrison [33,34]. With triorgano-tin and -lead halides, carbonyl-stabilized ylids such as BPPY, APPY, CMPPY, CMMPPY (carbomethoxymethylmethylenetriphenylphosphorane), and BPAsY yielded crystalline 1/1 adducts, $R_3MX \cdot$ (ylid), irrespective of the ylid or the metal halide employed. The adducts exhibit an intense absorption band in the range 1465-1510 cm^{-1} which represents a shift to a lower frequency and therefore the ylid residue is considered to be attached to the trimethyltin chloride moiety through the carbonyl oxygen.

More importantly, the assignment of bonding modes of these ylids in metal complexes via an increase or decrease in the infrared carbonyl stretching frequency, relative to the free ylid, has been confirmed by an X-ray crystal structure analysis [34]. Buckle et al. [34] have determined the structure of the trimethyltin chloride complex of acetylmethylenetriphenylphosphorane by single-crystal X-ray diffraction. The ylid residue is attached to tin through the carbonyl oxygen rather than the methine carbon atom. Also, the complex is a neutral species with a coordinated chloride ion, rather than an ionic phosphonium salt. The configuration around tin is trigonal bipyramidal with the more electronegative groups, chloride and oxygen, in the axial positions and the trimethyltin moiety being essentially planar.

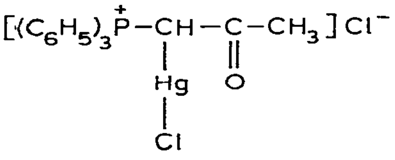
The infrared spectral data and proton nuclear magnetic resonance data for the synthesized complexes, in conjunction with the data concerning the *O*-bonded structure of the tin—ylid complexes, clearly demonstrate than the bonding mode of the ylids in the palladium(II), platinum(II) and mercury(II) complexes is through the methine carbon atom. These complexes can thus be classified as true organometallic complexes.

One of the few reports of metal—ylid complexes of this type to appear in the literature previous to this work is that of Nesmeyanov et al. [31,32,35] who prepared a series of metal—ylid complexes of mercury(II) using carbonyl-stablized phosphonium ylids and mercury(II) chloride. Elemental analyses indicated the complexes were 1/1 adducts with the proposed structures being, for example IX and X. They proposed that the HgCl group which was introduced into the



$[(C_6H_5)_3\overset{+}{P}-\underset{\underset{Cl}{|}}{\underset{Hg}{|}}{CH}-\underset{\underset{O}{\|}}{C}-C_6H_5]Cl^-$

(IX)



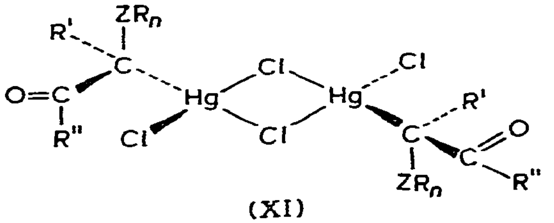
$[(C_6H_5)_3\overset{+}{P}-\underset{\underset{Cl}{|}}{\underset{Hg}{|}}{CH}-\underset{\underset{O}{\|}}{C}-CH_3]Cl^-$

(X)

IX: ν(CO) 1645 cm^{-1} (KBr disk), 1661 cm^{-1} (parent phosphonium bromide), 1527 cm^{-1} (free ylid)

X: ν(CO) 1680 cm^{-1} (KBr disk), 1672 cm^{-1} ($CHCl_3$ solution), 1720 cm^{-1} (parent phosphonium salt), 1527 cm^{-1} (free ylid)

phosphorane to form a mercurated phosphonium salt raised the frequency of the carbonyl group relative to the free ylid because of conjugation between the Hg—C and C=O bonds. Their formulation of the mercury(II)—ylid complexes as phosphonium salts ignores the possibility of their being neutral organometallic compounds. Conductivity measurements of solutions of the isolated compounds would quite easily differentiate between the non-conductive organometallic compound and the ionic phosphonium salt. Measurements performed in our laboratory unequivocally show that only an undissociated species exists in nitrobenzene solution. With these data available, the possibility also arises that the 1/1 adduct (by elemental analyses) may be, in fact, a dinuclear species. Molecular weight determinations for the representative compounds $[Hg_2(APPY)_2Cl_4]$ and $[Hg_2(BBuPY)_2Cl_4]$ in benzene solution definitely indicate that the 1/1 adducts are actually dinuclear species, presumably chloride-bridged:



(XI)

Arnup and Baird [36] have also synthesized a series of transition metal—BPPY complexes. They concluded that the complexes involved metal—carbon bonding.

Of the thiocyanate complexes isolated and characterized, only the CMPPY and CEPPY complex are thiocyanate-bridged dinuclear $[Pd_2(ylid)_2(SCN)_4]$ species (bonding mode assignments of the SCN^- group are based on well-established [37] ν(CN) frequency trends). All of the others are mononuclear $[Pd(ylid)(NCS)_2]$ complexes. The terminal thiocyanates were found to be *S*- and *N*-bonded, respectively. A rationale for this bonding pattern can be understood by considering the relative basicities of the various ylids. Bestmann [38] has studied basicity by measuring the equilibria between the ylids and their parent phosphonium salts, the transylidation reaction. An increase in the acidity of an 'onium salt represents a decrease in the basicity of the corresponding ylid. The phosphonium salts decrease in acidity in the order $C_6H_5CO— > —COOCH_3 > C_6H_5— >$ alkyl groups.

The first quantitative data were published by two groups: Speziale and Ratts [39], and Fliszar, Hudson and Salvadori [40]. They potentiometrically determined the acidity of ketophosphonium salts. Thus, BPPBr and CEPPBr were found to have pK_a values of 6.0 and 9.2, respectively. Aksnes and Songstad [41] potentiometrically measured the ionization constants of a variety of ketophosphonium, ketoarsonium, and ketosulfonium salts, in particular finding the pK_a of BPAsBr to be approximately 8.0. The DBPPBr salt has a pK_a value of 2.69 in 80% ethanol solution [42]. Interestingly, the least basic ylids, BPPY, BPAsY, and DBPPY, are the same ylids which show only nitrogen-bonding in the thiocyanate complexes. This tendency toward the formation of *N*-bonded thiocyanates in palladium(II) complexes as the basicity of other groups in the coordination sphere is reduced has been noted previously, e.g., $[Pd(1,10\text{-phenanthroline})(SCN)_2]$ [43] versus $[Pd(2,2'\text{-bipyridine})(NCS)_2]$ [43] (pK_a's of 4.96 and 4.37, respectively) [44], $[Pd(1,10\text{-phenanthroline})(SCN)_2]$ versus $[Pd(5\text{-}NO_2\text{-}1,10\text{-phen})(NCS)_2]$ [45] and $[Pd(4,4'\text{-dimethyl-}2,2'\text{-bipy})(SCN)(NCS)]$ [46] versus $[Pd(2,2'\text{-bipy})(NCS)_2]$.

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