Metal–Ylide Complexes. Part I. Metallation Reactions of *N*-(1-Pyridinio)benzamidate and Related Compounds with Palladium(II), Platinum(II), Rhodium(III), and Iridium(III)

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The reaction of various ylides of general formula $RCO\cdot\overset{-}{X}\cdot\overset{+}{Y}$ [R = Ph or *m*- or *p*-MeC_6H_4; X = N or CH; Y = pyridine, NMe_3, or PPh_3 (most work has been carried out with $PhCO\cdot\overset{-}{N}\cdot\overset{+}{N}H_5C_5$ = L)] with halide salts of palladium(II), platinum(II), rhodium(III), and iridium(III) affords products containing metallated betaines. Spectroscopic data (i.r., ^1H, and ^{13}C n.m.r.) show unambiguously that the aryl group R has become metallated in a position *ortho* to the carbonyl group and also that the ylide is bidentate (L′) *via* the group X. There is good evidence to indicate that the mechanism of the reaction involves preliminary co-ordination of the ylide followed by intramolecular electrophilic attack by the metal. Palladium tends to give di-μ-halogeno-complexes, $[\{Pd(L')Y\}_2]$, whereas in the case of platinum it is possible to prepare $[PtL'_2]$ which has *cis*-Pt–C bonds. Rhodium affords ionic complexes, *cis*-$[RhL'_2(H_2O)_2]Z$ (Z = Cl, Br, I, or BPh_4), which with 2,2′-bipyridyl give $[RhL'_2(bipy)]Cl$. Iridium gives a non-ionic derivative, $[IrL'_2(H_2O)Cl],3H_2O$. Reactions of the complexes with Ph_3P or $Bu^n{}_3P$ give new complexes containing phosphine oxide such as $[PdL'\{P(O)Ph_3\}Cl]$, $[PtL'\{P(O)Ph_3\}Cl]$, $[RhL'_2\{P(O)Bu^n{}_3\}Cl]$, and $[IrL'_2\{P(O)Ph_3\}Cl]$. The Pd–Cl and Pt–Cl bonds are *trans* to nitrogen when L = $PhCO\cdot\overset{-}{N}\cdot\overset{+}{N}H_5C_5$. Carbon monoxide reacts reversibly with palladium and iridium complexes of $PhCO\cdot\overset{-}{N}\cdot\overset{+}{N}H_5C_5$ to give $[PdL'(CO)Cl]$ and $[IrL'_2(CO)_2]Cl$. I.r. evidence suggests CO to be *cis* to the Pd–C bond in the palladium complex and other observations suggest that the mode of formation is not simple.

An increasing number of papers reporting the interaction of metal-containing species with ylides are appearing. Examples include instances where the ligated ylide arises through a rearrangement as in the case of the platinum-(II) and -(IV) complexes of $C_5H_5\overset{+}{N}-\overset{-}{C}H(Et)$ [1,2] or by reaction of a co-ordinated ligand as in the recently reported {1-aza-4-azoniabicyclo-[2.2.2]octane-4-methoxy(phenyl)methanide}pentacarbonylchromium(0) [3] and other related examples.[4,5] More usually the reports detail reactions between metal complexes and the more stable ylides.[4]

The majority of the information available concerns phosphorus ylides. Thus the compound $Ph_3\overset{+}{P}-\overset{-}{C}=C=O$ reacts with $[(OC)_5M(NCMe)]$ (M = Cr, Mo, or W), the resulting pentacarbonylylide complexes functioning as a source of carbonylmethylene under thermolysis conditions.[6] Reactions of hexaphenylcarbodiphosphorane with tungsten carbonyl have been reported [7] and tri-

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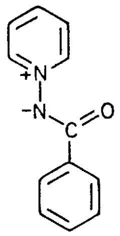
methylphosphoniomethanide affords a range of novel compounds with nickel(II),[8] copper(I),[9] silver(I),[9] gold(I),[10] and chromium(III).[11] In all cases the ligand present is in fact dimethylphosphoniodimethanide; also when triphenylphosphoniomethanide is treated with a chromium(III) aryl, the ligated ylide has one metallated phenyl ring.[11] Resonance-stabilised ylides such as $\mathrm{Ph_3\overset{+}{Y}{-}\overset{-}{C}HCOR}$ [Y = P or As; R = Me, Ph, or (methoxycarbonyl)methylene] afford co-ordination complexes with tri- and di-organotin(IV) compounds,[12] and (for Y = P) with a variety of transition-metal complexes in which the anionic carbon atom is bonded to the metal.[13]

Far fewer reports have dealt with sulphur or nitrogen ylides. Copper–ylide interaction is proposed as a step in the Lewis-acid-promoted thermal decomposition of dimethylsulphoniophenacylide [14,15] and iron carbonyl–ylide interaction may be involved when the reaction of iron carbonyls with *N*-(1-pyridinio)phenacylide affords 1,4-diphenylbutane-1,4-dione and [(py)Fe(CO)$_4$] (py = pyridine).[16] Resonance-stabilised sulphonioylides (p-$\mathrm{XC_6H_4CO\overset{-}{C}H{-}\overset{+}{S}Me_2}$: X = H, Me, or OMe) have been treated recently with bis(acetonitrile)palladium(II) chloride to yield bis(ylide) complexes of *trans*-configuration in which the donor atom is carbon.[17] *N*-(1-Pyridinio)amidates are not ylides in the strict sense but may be accepted as such for our purposes.[18] They may be photoisomerised to 1*H*-1,2-diazepines which in turn can give π-complexes with iron and ruthenium.[19,20] Our interest in *N*-(1-pyridinio)benzamidate arose from a desire to study the influence of metal ions on the thermal stability of the N–N bond. In addition the geometry of the betaine suggested that in some instances the *ortho*-metallation reaction should be observed. In this paper we describe the reactions of this betaine, and of related substances, with rhodium(III), iridium(III), palladium(II), and platinum(II). A preliminary report has appeared.[21]



EXPERIMENTAL

N-(1-Pyridinio)benzamidate was prepared by a literature method [22] starting with 1-aminopyridinium iodide obtained by the Gösl method.[23] The corresponding *m*- and *p*-toluamidates were prepared by the following modified literature [24a] procedure. 1-Aminopyridinium iodide [23] (8·8 g, 0·04 mol) was dissolved in a mixture of ethanol (100 cm^3) and methanol (100 cm^3). To this solution were added, dropwise and concurrently, solutions of potassium hydroxide (4·5 g, 0·08 mol) in methanol (100 cm^3) and *m*-toluoyl chloride (12·0 g, 0·08 mol) in methanol (20 cm^3). The reaction mixture was stirred constantly and the rate of addition of the KOH solution was regulated to maintain a blue-violet colouration during the addition of *m*-toluoyl chloride. On completion of the addition of reagents, the solution was stirred for a further 2 h after which it was reduced to dryness on a rotatory film evaporator. The solid residue was dissolved in 10% aqueous potassium carbonate solution and extracted with dichloromethane. The organic extract was dried with sodium sulphate after which the solution was concentrated and treated with diethyl ether to afford a white precipitate. The latter was recrystallised from benzene after treatment with animal charcoal. Yield of *N*-(1-pyridinio)-*m*-toluamidate 71%, m.p. 88—89 °C (lit.,[24b] 87—88 °C); *N*-(1-pyridinio)-*p*-toluamidate, 71%, m.p. 166—167 °C (lit.,[24b] 164—166 °C). 2-Benzoyl-1,1,1-trimethylhydrazinium iodide and the corresponding betaine were prepared using Hinman and Flores' method.[25] Benzoyl(triphenylphosphine)methylene was prepared following the literature.[26]

The ligands gave satisfactory analyses and i.r., ^{1}H n.m.r., and mass spectra.

Preparation of Metal Derivatives.—(a) *Palladium complexes. Chloro*[N-(1-*pyridinio*)*benzamidate*-NC^2]*palladium*(II), (I). Palladium(II) chloride (1·0 g, 5 mmol) was dissolved in hot water (200 cm^3) and filtered. *N*-(1-Pyridinio)benzamidate (2·0 g, 10 mmol) was added to the warm solution which was then heated under reflux for 2 h with vigorous stirring. The yellowish green *product* was recrystallised from water, yield 1·85 g, 97%. Addition of sodium perchlorate to the filtrate from the reaction mixture afforded crystals of the perchlorate salt of the protonated betaine, $\mathrm{[C_5H_5N{\cdot}\overset{+}{N}H{\cdot}COPh][ClO_4]}$. The product could also be recrystallised from ethanol, chloroform, and dichloromethane. Products obtained from dichloromethane contained variable amounts of solvent (analysis, i.r., and ^{1}H n.m.r. spectra) and were yellow, in contrast to the greenish yellow products obtained from water or ethanol. The product from chloroform was also yellow. No differences in i.r., ^{1}H n.m.r., or mass spectra were observed between the

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green and yellow forms. The analogous bromide was prepared by heating under reflux a suspension of the above product (either form) in water containing an excess of lithium bromide. The dark green product was washed and recrystallised from dibromomethane.

Dichlorobis[N-(1-*pyridinio*)*benzamidate*-N]*palladium*(II), (II). Dipotassium tetrachloropalladate(II) (0·98 g, 3 mmol) and sodium acetate (0·49 g, 6 mmol) were dissolved in water (75 cm^3). *N*-(1-Pyridinio)benzamidate (1·2 g, 6 mmol) was added and the reaction mixture was stirred at room temperature for 2 h and set aside overnight. The amber coloured *product* was washed with water, methanol, and diethyl ether and dried *in vacuo*.

Chloro[N-(1-*pyridinio*)*benzamidate*-N][N-(1-*pyridinio*)-*benzamidate*-NC^2]*palladium*(II) *dihydrate*, (III). The above procedure was followed with the exception that the solution was stirred for 2 h under reflux. The amber material changed to a greenish yellow *product* which was filtered off, washed with water, methanol, and diethyl ether, and dried *in vacuo*.

The above two products could be converted to chloro-[*N*-(1-pyridinio)benzamidate-*NC*^{2}]palladium(II) by heating under reflux in benzene for 3—4 h.

Chloro[N-(1-*pyridinio*)-m-*toluamidate*-NC^2]- *and chloro*-[N-(1-*pyridinio*)-p-*toluamidate*-NC^2]-*palladium*(II), (I). These complexes were prepared by heating under reflux 1 : 1 mixtures of palladium(II) dichloride and the betaine in water. The product derived from the *m*-toluamidate was recrystallised from chloroform–methanol and that from the *p*-toluamidate was recrystallised from acetone. It was noted that the reaction with the *m*-toluamidate was complete in a very short time. When the reactions of the benzamidate, *m*-toluamidate, and *p*-toluamidate were compared under the same conditions it was observed that the reaction rates were, qualitatively, *m*-toluamidate $\gg$ benzamidate $>$ *p*-toluamidate.

Chloro[(*trimethylammonio*)*benzamidate*-NC^2]*palladium*-(II), (I). Palladium(II) dichloride (1·8 g, 10 mmol) and lithium chloride (0·85 g, 20 mmol) were dissolved in methanol (40 cm^3) giving an homogeneous solution to which was added (trimethylammonio)benzamidate (1·8 g, 10 mmol) in methanol 10 cm^3) and sodium acetate (0·82 g, 10 mmol). The mixture was heated under reflux for 2 h when a dirty green residue separated out. This material was filtered off and recrystallisation from acetone afforded a green crystalline *product*.

Chloro[(*triphenylphosphonio*)*phenacylide*-CC^2]*palladium*-(II), (I). Benzoyl(triphenylphosphine)methylene (1·9 g, 5 mmol) was dissolved in anhydrous methanol (50 cm^3) containing sodium acetate (0·41 g, 5 mmol). To this solution was added, with stirring, palladium(II) dichloride (0·89 g, 5 mmol), and the resulting mixture was then heated under reflux for 2 h. A greenish product contaminated with a black material separated out. This material was treated with dichloromethane and filtered to remove the black contaminant. The filtrate, on concentration in a rotatory film evaporator, gave a green *product*.

(b) *Platinum complexes*. *Chloro*[N-(1-*pyridinio*)*benzamidate*-N][N-(1-*pyridinio*)*benzamidate*-NC^2]*platinum*(II) *dihydrate*, (III). Dipotassium tetrachloroplatinate(II) (1·0 g, 2·4 mmol) in water (75 cm^3) was treated with *N*-(1-pyridinio)benzamidate (1·2 g, 6 mmol) and the resulting mixture was heated under reflux for 2 h. The yellowish *product* was separated and recrystallised from ethanol. Addition of a hot aqueous solution of sodium tetraphenylborate to the filtrate from the reaction afforded the tetraphenylborate salt of the protonated betaine.

Bis[N-(1-*pyridinio*)*benzamidate*-NC^2]*platinum*(II), (IV). A mixture of dipotassium tetrachloroplatinate(II) (1·6 g, 4 mmol), sodium acetate (0·66 g, 8 mmol), and *N*-(1-pyridinio)benzamidate (1·6 g, 8 mmol) in water (75 cm^3) was heated under reflux for 4 h. The greenish yellow solid which separated was found to be a mixture by t.l.c. Extraction of material (2·2 g) with dry benzene (150 cm^3) in a Soxhlet apparatus gave the complex (1·1 g) described above and a yellowish orange residue. Dichloromethane extraction afforded an amber material (0·4 g) (not yet characterised) and the greenish yellow residue was shown to be pure by t.l.c. and characterised as the bis(metallated) complex (0·7 g).

(c) *Rhodium complexes*. *Diaquabis*[N-(1-*pyridinio*)*benzamidate*-NC^2]*rhodium*(III) *chloride*, (V). Rhodium(III) trichloride hydrate (0·5 g) and *N*-(1-pyridinio)benzamidate (2·0 g) were dissolved in water (75 cm^3) containing ethanol (10 cm^3) and heated under reflux for 2 h. The product separated during the reaction and was recrystallised from ethanol–benzene. The addition of sodium acetate gave the same product in slightly shorter time. The analogous bromide and iodide were prepared by heating under reflux an aqueous suspension of the chloride in the presence of excess of sodium bromide or sodium iodide. The products could be recrystallised from ethanol–benzene. Aqueous solutions of the chloride, bromide, or iodide when treated with aqueous sodium tetraphenylborate afforded, immediately, a precipitate of the tetraphenylborate salt of the title cation. A similar complex was prepared from the reaction of rhodium(III) chloride and *N*-(1-pyridinio)-*p*-toluamidate.

(d) *Iridium complexes*. *Aquachlorobis*[N-(1-*pyridinio*)*benzamidate*-NC^2]*iridium*(III) *trihydrate*, (VI). An exactly similar preparative procedure to that for the rhodium(III) chloride was followed, replacing rhodium(III) chloride hydrate by sodium (or ammonium) hexachloroiridate(IV). A similar complex was prepared using *N*-(1-pyridinio)-*p*-toluamidate.

(e) *Reactions with Tertiary Phosphines and other Lewis Bases*.—The same conditions were used for all complexes prepared. The betaine–metal complex was treated with the tertiary phosphine (1 : 4 molar ratio) in benzene solution under nitrogen {in the case of $[\mathrm{Pd(C_6H_4{\cdot}CO{\cdot}\overset{-}{N}{\cdot}\overset{+}{N}H_5C_5)Cl}]$, 1,4-dioxan was used as solvent}. The reaction mixtures were then heated under reflux for 30—40 min. In this manner the following complexes were formed: $[\mathrm{Pd(L')Cl\{P(O)Ph_3\}}],n\mathrm{C_6H_6}$ [$n = 0$ (VIII) or 1 (IX), L$'$ = *N*-(1-pyridinio)benzamidate-*NC*^{2} or (trimethylammonio)benzamidate-*NC*^{2}]; $[\mathrm{Pt(L')Cl\{P(O)Ph_3\}}],n\mathrm{C_6H_6}$ ($n = 0$ or 1); $[\mathrm{RhL'_2\{P(O)Bu^n_3\}Cl}]$, (XI); and $[\mathrm{IrL'_2\{P(O)Ph_3\}Cl}]$ (XIII) [L$'$ = *N*-(1-pyridinio)benzamidate-*NC*^{2}]. The formulation of these complexes as phosphine oxide derivatives is supported by analysis, and i.r. and mass spectroscopy; this point is discussed later.

(2,2$'$-*Bipyridylbis*[N-(1-*pyridinio*)*benzamidate*-NC^2]-*rhodium*(III) *chloride*, (XII). The complex $[\mathrm{Rh(}o\text{-}\mathrm{C_6H_4{\cdot}CO{\cdot}\overset{-}{N}{\cdot}\overset{+}{N}H_5C_5)_2(H_2O)_2}]\mathrm{Cl}$ (0·57 g, 1 mmol) dissolved in hot dichloromethane (100 cm^3) was treated with 2,2$'$-bipyridyl (0·94 g, 6 mmol) and heated under reflux for 1·5 h. After concentration and addition of n-hexane, a yellow product was obtained which was recrystallised from dichloromethane–n-heptane (1 : 2 v/v).

(f) *Reactions with Carbon Monoxide*.—The reactions were carried out at room temperature and atmospheric pressure.

Palladium complexes. The complexes $[Pd(o\text{-}C_6H_4\cdot CO\cdot\overset{-}{N}\cdot\overset{+}{N}H_5C_5)X]$ ($X = Cl$ or Br) in suspension in dry benzene were treated with carbon monoxide over 4 h. After this time gas uptake was complete and a greenish product had formed *via* a colourless intermediate which decomposed when isolation was attempted. It was noted that the products of some experiments were contaminated with palladium metal and also that the reaction was readily reversible. Thus, although the complex would take up carbon monoxide in acetone (excess of CO), recrystallisation of the product $[Pd(o\text{-}C_6H_4\cdot CO\cdot\overset{-}{N}\cdot\overset{+}{N}H_5C_5)(CO)Cl]$ from acetone in the absence of CO afforded a compound in which co-ordinated acetone replaced CO. The co-ordinated carbon monoxide is readily lost on heating the complexes.

Iridium complex. The rhodium complexes were totally unreactive to carbon monoxide under the above conditions yet, by contrast, $[Ir(o\text{-}C_6H_4\cdot CO\cdot\overset{-}{N}\cdot\overset{+}{N}H_5C_5)_2(H_2O)Cl],3H_2O$ underwent a rapid (10 min) and clean reaction to afford $[Ir(o\text{-}C_6H_4\cdot CO\cdot\overset{-}{N}\cdot\overset{+}{N}H_5C_5)_2(CO)_2]Cl$. Experiments involving a gas burette confirmed the uptake of 2 mol carbon monoxide but suggest that at first *four* mol are consumed with the subsequent release of two mol to give the observed product. Heating the dicarbonyl complex in water under reflux regenerated the starting iridium complex.

The complex $[Pt(o\text{-}C_6H_4\cdot CO\cdot\overset{-}{N}\cdot\overset{+}{N}H_5C_5)(PhCO\cdot\overset{-}{N}\cdot\overset{+}{N}H_5C_5)Cl]$ reacted slowly and incompletely with carbon monoxide at room temperature and pressure. Analytical data for the new complexes are presented in Table 1.

Physical Measurements.—I.r. spectra (4 000—250 cm^{-1}) were recorded for KBr discs using a Perkin-Elmer 457 instrument. Far-i.r. spectra (400—200 cm^{-1}) were measured for Nujol mulls in caesium iodide supports with a Perkin-Elmer 225 spectrophotometer. ^1H N.m.r. spectra were recorded for the ligands [dimethyl sulphoxide (dmso) or $CDCl_3$ solutions] and for the complexes (dmso solutions) at 100 MHz with Perkin-Elmer R14 and Varian HA 100 D instruments. Chemical shifts were measured relative to the methyl resonance of dmso which was set at τ 7·36. ^{13}C N.m.r. spectra were measured for the ligands $PhCO\cdot\overset{-}{N}\cdot\overset{+}{N}H_5C_5$ and $p\text{-}MeC_6H_4\cdot CO\cdot\overset{-}{N}\cdot\overset{+}{N}H_5C_5$ and their rhodium(III) chloride complexes in [$^2H_6$]dmso solution with $SiMe_4$ as external reference using a Varian XL 100-FT spectrometer operating at 25·2 MHz. We are much indebted to Mr. M. I. M. Wazeer at the University of East Anglia for these measurements. Mass spectra were recorded at 70 eV with an AEI MS 9 instrument.* Conductivity measurements were made with a Henelec bridge, but attempts to obtain molecular-weight data using a Mechrolab vapour-phase osmometer failed due to the limited solubility of our complexes at 37 °C. Some *X*-ray powder data were obtained using Cu(*K*) radiation. This data established isomorphism for the series $[RhL'_2(H_2O)_2]X$ ($X = Cl$, Br, or I; $L' = o\text{-}C_6H_4\cdot CO\cdot\overset{-}{N}\cdot\overset{+}{N}H_5C_5$) and also indicated that $[RhL'_2(H_2O)_2]Cl$ and $[IrL'_2(H_2O)Cl],3H_2O$ are *not* isomorphous.

RESULTS AND DISCUSSION

Spectroscopic data (i.r. and ^1H n.m.r.) relevant to the discussion are gathered into Table 1 and some ^{13}C n.m.r. data for two betaines and their rhodium(III) chloride derivatives are presented in Table 2. The analytical data for complexes derived from the reaction of palladium, platinum, rhodium, and iridium salts with various resonance-stabilised ylides suggest that, in some cases, the organic substrate has lost one proton. We present below [section (*b*)] a summary of the evidence that leads us to believe that these complexes provide further examples of the *ortho*-metallation reaction. However the formation of the complexes and their stereochemistry will be discussed initially.

(a) *The Formation and Structure of the Complexes*.—The metallation reactions referred to above occurred smoothly in aqueous media and, in the case of the palladium complexes, it was possible by slight variation of the experimental conditions to isolate (II) and (III) which may be regarded as intermediates in the path to the final product, (I), since it is possible to convert both to (I). We believe, therefore, that the first step is

$$PdCl_2 + 2L \longrightarrow \underset{(II)}{[Pd(L)_2Cl_2]} \longrightarrow \underset{(III)}{[PdL(L')Cl]} \longrightarrow \underset{(I)}{\frac{1}{n}\Big[Pd(L')Cl\Big]} \quad (1)$$

formation of a simple co-ordination compound, and the ligand then undergoes internal metallation. As recently pointed out,[27] if substituents in the phenyl ring are to be used to aid mechanistic studies, the results will be more readily interpreted if an electron-releasing substituent is *meta* (*i.e. ortho* or *para* to the position attacked by the metal). We therefore compared the rates of formation of complexes [I; $L' =$ *N*-(1-pyridinio)-benzamidate-, -*m*-toluamidate-, and -*p*-toluamidate-*NC*^{2}] and found the relative rates to be *m*-toluamidate $\gg$ benzamidate $>$ *p*-toluamidate. Thus the *meta*-methyl substituent gives the greater rate, suggesting strongly that the metallation involves electrophilic attack by the palladium on the *N*-co-ordinated ligand.

Complex (I) was obtainable in greenish yellow or bright yellow modifications (see Experimental section), yet spectral differences between the forms were minimal. In view of the fact that the modification obtained is a function of crystallisation solvent and that the yellow form can trap solvent molecules (more open structure?), we incline to the view that they are dimorphic forms rather than isomers or differing oligomeric forms. The *X*-ray powder photographs differed, but this would be expected whatever the difference between the materials. The evidence for the presence of chloride bridges is good. Thus ν(PdCl) at 344 and 292 cm^{-1} compares well with data for corresponding azobenzene derivatives;[28] also reaction with triphenylphosphine affords complexes [(VIII) and (IX)] which probably arise from a bridge-splitting reaction. It is of interest to note that both

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* 1 eV $\approx 1{\cdot}60 \times 10^{-19}$ J.

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TABLE 1

Analytical and spectroscopic data for the ylides and their metal derivatives

				Analyses (%) [a]						I.r. data/cm^{-1}					
Compound	Yield (%)	Colour	M.p. (θ_c/°C)	C	H	N	Halogen	Metal	Λ/[b] (Solvent) S cm^2 mol^{-1}	$\tilde{\nu}$(OH)	$\tilde{\nu}$(CO)	$\tilde{\nu}$(NN)	$\tilde{\gamma}$(CH) (phenyl)	$\tilde{\nu}$(MX)	^{1}H N.m.r. data (τ, nH) [c]
L = $\mathrm{PhCO{\cdot}\overset{-}{N}{\cdot}\overset{+}{N}H_5C_5}$	91	White	178—179	72·5 (72·7)	5·15 (5·05)	14·1 (14·1)					1 550	1 335	690, 715 (sh)		d (1·1, 2H), m (1·65—1·93, 3H), t (2·05, 2H), m (2·40—2·60, 3H)
$\mathrm{[PhCO{\cdot}\overset{+}{N}H{\cdot}NH_5C_5]I}$											1 698	1 285	688, 716 (sh)		d (0·60, 2H), t (1·10, 1H), t (1·54, 2H), m (1·72—2·00, 2H), m (2·06—2·44, 3H)
$\mathrm{[PhCO{\cdot}\overset{+}{N}H{\cdot}NH_5C_5][ClO_4]}$											1 700	1 285	684 (sh), 715 (sh)		d (0·64, 2H), t (1·12, 1H), t (1·56, 2H), m (1·75—2·00, 2H), m (2·04—2·40, 3H)
$\mathrm{[\{Pd(L')Cl\}_{\mathit{n}}]}$ [d] (I)	97	Yellow-green	266—267 (decomp.)	42·7 (42·5)	2·75 (2·95)	8·25 (8·25)	10·3 (10·4)	31·1 (31·3)	5 ($\mathrm{MeNO_2}$)		1 645	1 315	738 (sh)	344, 292	d (1·03, 2H), t (1·43, 1H), m (1·73—2·03, 3H), m (2·43—2·60, 1H), m (2·70—2·90, 2H)
$\mathrm{[\{Pd(L')Br\}_{\mathit{n}}]}$ (I)	98	Green	245 (decomp.)	37·4 (37·6)	3·35 (2·35)	6·70 (7·30)	19·7 (20·8)	27·9 (27·8)	4 ($\mathrm{MeNO_2}$)		1 640	1 312	735 (sh)		d (1·02, 2H), t (1·46, 1H), m (1·71—2·02, 3H), m (2·36—2·60, 1H), m (2·63—2·86, 2H)
$\mathrm{[Pd(L)_2Cl_2]}$ (II)	87	Amber	195—196 (decomp.)	49·0 (50·2)	3·70 (3·50)	9·40 (9·75)	11·9 (12·4)		2 ($\mathrm{HCONMe_2}$)		1 620	1 338	659 (sh), 722 (sh)	338	m (1·00, 2H), m (1·30—1·70, 1H), m (1·73—2·10, 4H), m (2·24—2·59, 2H), m (2·60—2·90, 1H)
$\mathrm{[PdL'(L)Cl],2H_2O}$ (III)	98	Green-yellow	165—166 (decomp.)	51·1 (51·9)	3·50 (3·80)	9·85 (10·1)	6·50 (6·40)		5 ($\mathrm{MeNO_2}$)	3 420	1 610, 1 630	1 320	695, 718(sh), 735	346	d(1·06), m (1·29—2·24), m (2·30—3·06)
$\mathrm{[Pt(L')_2]}$ (IV)	80	Green-yellow	280—282 (decomp.)	48·2 (48·9)	3·25 (3·05)	9·25 (9·50)		33·4 (33·1)	5 ($\mathrm{MeNO_2}$)		1 630	1 285	730		d (1·15, 2H), m (1·54—3·00, 7H)
$\mathrm{[PtL'(L)Cl],2H_2O}$ (III)	60	Yellow	218—219 (decomp.)	45·3 (43·5)	3·80 (3·50)	8·60 (8·45)	5·40 (5·35)	30·2 (29·5)		3 450	1 620, 1 650	1 320	690 (sh), 719 (sh), 748 (sh)	333	
$\mathrm{[RhL'_2(H_2O)_2]Cl}$ (V)	77	Green-yellow	273—275 (decomp.)	50·8 (50·7)	3·90 (3·85)	9·75 (9·85)	6·25 (6·25)	18·7 (18·1)	91 ($\mathrm{H_2O}$) [e]	3 400—3 140	1 609	1 332	755 (sh)		d (0·66, 2H), t (1·53, 1H), t (1·93, 2H), m (2·36—2·74, 2H), m (2·79—3·17, 2H)
$\mathrm{[RhL'_2(H_2O)_2]Br}$ (V)	88	Green-yellow	>300	47·5 (47·0)	3·60 (3·60)	9·45 (9·15)	13·5 (13·0)	17·4 (17·1)	106 ($\mathrm{H_2O}$) [f]	3 600—3 140	1 600	1 330	750		d(0·66, 2H), t (1·50, 1H), t (1·91, 2H), m (2·30—2·71, 2H), m (2·72—3·10, 2H)
$\mathrm{[RhL'_2(H_2O)_2]I}$ (V)	90	Yellow	>300	42·3 (43·6) [g]	3·25 (3·35)	7·80 (8·50)	18·8 (19·2)		99 ($\mathrm{HCONMe_2}$)	3 620—3 200	1 600	1 325	738		d (0·68, 2H), t (1·51, 1H), t (1·94, 2H), m (2·40—2·78, 2H), m (2·80—3·20, 2H)
$\mathrm{[RhL'_2(H_2O)_2][BPh_4]}$ (V)	95	Yellow	>300	68·0 (67·6)	5·20 (4·95)	6·80 (6·55)			60 ($\mathrm{HCONMe_2}$)						
$\mathrm{[IrL'_2(H_2O)Cl],3H_2O}$ (VI)	47	Red-orange	>300	41·7 (41·5)	3·55 (3·75)	7·95 (8·05)	4·75 (5·10)	27·6 (27·7)	7 ($\mathrm{HCONMe_2}$)	3 660—3 100	1 590	1 325	740 (sh), 758 (sh)	341	m (0·57—0·90), m (1·24—1·60), m (1·65—2·15), m (2·25—2·69), m (2·70—3·13)
$\mathrm{[PdL'(CO)Cl]}$ (VII)	35	Green	265 (decomp.)	43·2 (42·5)	3·45 (2·45)	7·80 (7·65)			4 ($\mathrm{MeNO_2}$)		2 110, 1 650	1 318	740 (sh)	273	
$\mathrm{[PdL'(CO)Br]}$ (VII)	80	Pale yellow	232—235 (decomp.)	36·9 (37·9)	2·60 (2·20)	6·30 (6·80)	18·5 (19·4)		5 ($\mathrm{MeNO_2}$)		2 108, 1 645	1 315	738 (sh)		
$\mathrm{[PdL'\{P(O)Ph_3\}Cl]}$ (VIII)	80	Pale yellow	170—180 (decomp.)	58·3 (58·3)	4·20 (4·05)	4·20 (4·55)	6·25 (5·75)	5·05 (5·00) [h]	3 ($\mathrm{MeNO_2}$)						
$\mathrm{[PdL'\{P(O)Ph_3\}Cl],C_6H_6}$ (IX)	70	White	180—187 (decomp.)	61·4 (62·2)	5·30 (4·30)	4·05 (4·05)	5·25 (5·10)	4·50 (4·45) [h]	5 ($\mathrm{MeNO_2}$)	1 098 [ν(PO)]	1 638	1 315	738 (sh)	318	

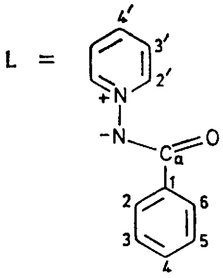
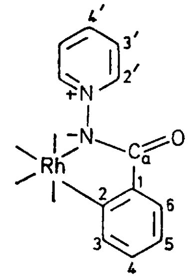
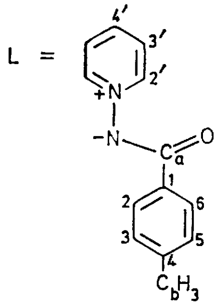
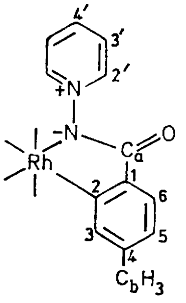
TABLE 1 (*Continued*)

Compound	Yield (%)	Colour	M.p. (θ_c/°C)	Analyses (%) [a]					Λ/[b] (Solvent) S cm^2 mol^{-1}	I.r. data/cm^{-1}					^{1}H N.m.r. data (τ, nH) [c]
				C	H	N	Halogen	Metal		$\tilde{\nu}$(OH)	$\tilde{\nu}$(CO)	ν(NN)	$\tilde{\gamma}$(CH) (phenyl)	$\tilde{\nu}$(MX)	
$[\mathrm{PtL'\{P(O)Ph_3\}Cl}]$ (VIII)	40	Yellow	190—200 (decomp.)	51·8 (51·0)	3·45 (3·40)	4·10 (3·95)	5·75 (5·00)		4 ($\mathrm{MeNO_2}$)						
$[\mathrm{PtL'\{P(O)Ph_3\}Cl}],\mathrm{C_6H_6}$ (IX)	60	Cream	183—185 (decomp.)	54·8 (55·1)	4·55 (3·85)	3·45 (3·55)	4·35 (4·50)	3·65 (3·95) [h]	5 ($\mathrm{MeNO_2}$)	1 098 [ν(PO)]	1 645	1 310	740 (sh)	290	d (1·05, 2H), m (1·30—1·50, 1H), m (1·70—1·95, 2H), m (2·10—2·90, 19H)
$[\mathrm{RhL'_2\{P(O)Bu^n_3\}Cl}]$ (XI)	82	Green-yellow	205 (decomp.)	57·6 (57·6)	6·10 (6·00)	7·60 (7·45)	5·40 (4·70)		20 ($\mathrm{MeNO})_2$	1 092 [ν(PO)]	1 615	1 308	738 (sh)	353	
$[\mathrm{RhL'_2(bipy)}]\mathrm{Cl}$ (XII)	80	Yellow	270—290	59·6 (59·3)	3·90 (3·80)	12·3 (12·2)	5·65 (5·15)		82 ($\mathrm{MeNO_2}$)		1 610	1 320	745		
$[\mathrm{IrL'_2\{P(O)Ph_3\}Cl}]$ (XIII)	99	Yellow	230—233 (decomp.)	56·3 (56·0)	4·10 (3·65)	5·80 (6·20)	3·75 (3·95)		7 ($\mathrm{HCONMe_2}$)	1 088 [ν(PO)]	1 620	1 300	740, 755 (sh)	351	
$[\mathrm{IrL'_2(CO)_2}]\mathrm{Cl}$ (XIV)	98	Amber	>300	46·0 (46·0)	3·20 (2·65)	7·45 (8·25)	5·80 (5·25)		3 ($\mathrm{MeNO_2}$)		2 000, 1 985, 1 632	1 300	750		
$\mathrm{L = PhCO{\cdot}\overset{-}{N}{\cdot}\overset{+}{N}Me_3}$	98	White	168—169	67·2 (67·4)	7·75 (7·85)	15·6 (15·7)					1 600	1 332	690, 728		m (2·23—2·48, 2H), m (2·86—3·14, 3H), s (6·90, 9H) (in $\mathrm{CDCl_3}$)
$[\mathrm{Ph{\cdot}CO{\cdot}\overset{+}{N}H{\cdot}NMe_3}]\mathrm{I}$											1 695	1 280	690, 718		
$[\{\mathrm{Pd(L')Cl}\}_n]$ (I)	88	Green	220 (decomp.)	38·0 (37·5)	4·05 (4·35)	8·85 (8·80)	10·5 (10·5)	31·8 (31·5)	3 ($\mathrm{MeNO_2}$)		1 640	1 290	740	360, 321	m (1·80—2·15, 1H), m (2·25—2·75, 3H), Me resonance masked by solvent
$[\mathrm{PdL'\{P(O)Ph_3\}Cl}]$ (VIII)	98	Pale green	195—200 (decomp.)	57·2 (56·3)	5·20 (4·70)	4·70 (4·70)	5·70 (5·95)	5·05 (5·20) [h]	6 ($\mathrm{MeNO_2}$)	1 095 [ν(PO)]	1 628	1 300	740	285	
$\mathrm{L = PhCO{\cdot}\overset{-}{C}H{\cdot}\overset{+}{P}Ph_3}$											1 524	1 382 (PCCO) [i]	688, 710, 745		m (1·90—2·40, 15H), m (2·45—2·60, 5H), d [5·43, 1H, *J*(PH) 24·3 Hz]
$[\mathrm{PhCO{\cdot}\overset{+}{C}H_2{\cdot}PPh_3}]\mathrm{Br}$											1 662		685, 715 (sh), 745		m (1·70—2·50, 20H), d [3·55, 2H, *J* (PH) 13·7 Hz]
$[\{\mathrm{Pd(L')Cl}\}_n]$ (I)	75	Green	250—255 (decomp.)	58·8 (59·8)	3·60 (4·00)		7·00 (6·80)	5·75 (5·95) [h]	3($\mathrm{MeNO_2}$)		1 630		682, 715, 745, 770	328, 295	m (1·60—2·03), methine proton not detected due to dilute solution
$\mathrm{L} = m\text{-}\mathrm{MeC_6H_4{\cdot}CO{\cdot}\overset{-}{N}{\cdot}\overset{+}{N}H_5C_5}$											1 545	1 335	740, 855		d (1·25, 2H), m (1·92—2·10, 1H), m (2·14—2·77, 6H), s (7·63, 3H)
$[\{\mathrm{Pd(L')Cl}\}_n]$ (I)	99	Yellow	229—230 (decomp.)	43·6 (44·2)	3·30 (3·10)	7·60 (7·95)	9·62 (10·0)		3 ($\mathrm{MeNO_2}$)		1 630, 1 608	1 302	760	344 ,289	d (1·01, 2H), t (1·44, 1H), t (1·86, 2H), s (2·66, 1H), m (2·81—2·96, 2H) (in $\mathrm{CDCl_3}$)
$\mathrm{L} = p\text{-}\mathrm{MeC_6H_4{\cdot}CO{\cdot}\overset{-}{N}{\cdot}\overset{+}{N}H_5C_5}$											1 545	1 330	745, 832		d (1·20, 2H), d (1·90, 2H), t (2·15, 1H), t (2·40, 2H), d (2·77, 2H), s (7·62, 3H)
$[\{\mathrm{Pd(L')_2Cl}\}_n]$ (I)	96	Green-yellow	255—257 (decomp.)	44·3 (44·2)	3·45 (3·10)	7·65 (7·95)	9·65 (10·0)		4 ($\mathrm{MeNO_2}$)		1 640	1 308	835		d (0·83, 2H), m (1·00—1·33, 1H), m (1·50—1·90, 3H)
$[\mathrm{RhL'_2(H_2O)_2}]\mathrm{Cl}$ (V)	83	Green	>300	50·9 (52·3) [g]	4·15 (4·35)	9·15 (9·40)	5·95 (5·95)		108 ($\mathrm{H_2O}$) [j]	3 400—3 120	1 585	1 320	835		d (0·75, 2H), t (1·61, 1H), t (2·01, 2H), d (2·70, 1H), m (2·90—2·98, 1H), m (3·20—3·33, 1H), s (7·81, 3H) (in [$^2\mathrm{H_6}$]dmso)
$[\mathrm{IrL'_2(H_2O)Cl}],3\mathrm{H_2O}$ (VI)	23	Red-brown	210—220 (decomp.)	40·2 (43·2)	3·70 (4·15)	7·30 (7·75)	4·75 (4·90)		4 ($\mathrm{MeNO_2}$)	3 600—3 200	1 585	1 315	830	375	

[a] Calculated values are given in parentheses. [b] 10^{-3}M Solution. [c] dmso Solution; $\mathrm{SiMe_4}$ as internal standard. [d] L′ represents the ligand L when co-ordinated in a bidentate manner, through C(2) of the benzamidate or toluamidate Ph group; *e.g.* when $\mathrm{L = PhCO{\cdot}\overset{-}{N}{\cdot}\overset{+}{N}H_5C_5}$, L′ = *N*-(1-pyridinio)benzamidate-*NC*^{2}. [e] 12 ($\mathrm{HCONMe_2}$) and 10 ($\mathrm{MeNO_2}$). [f] 21 ($\mathrm{MeNO_2}$). [g] Replicate analyses failed to improve on the poor carbon figures; however, the complexes gave satisfactory spectra. [h] % P. [i] See ref. 13. [j] S ($\mathrm{MeNO_2}$).

TABLE 2

^{13}C N.m.r. data at 25·2 MHz. Spectra in [$^2H_6$]dmso with ^{1}H nucleus spin decoupler; chemical shifts (p.p.m.) relative to [^{13}C]SiMe$_4$ as external reference

Complex	C(a)	C(b)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(2′)	C(3′)	C(4′)
	168·4		137·5			127·4	127·2	126·3	143·1	129·4	137·8
	174·9 d, *J* 5 Hz		126·6	159·5 d, *J* 32·5, Hz	126·0	133·0	121·5	129·2	146·3	137·5	141·9
	168·6	22·8	135·3			126·8	128·0	128·5	143·6	138·2	139·4
	177·6	23·4	136·9	160·5 d, *J* 33·0 Hz	135·6	124·6	127·9	128·5	148·3	140·5	143·8

i.r. and mass spectroscopy [29] are quite conclusive that (VIII) and (IX) contain Ph_3PO. It is possible, but not proved, that catalytic oxidation of the phosphine has occurred.[30] It was not possible to rupture the Pd–N bond by treatment with Lewis bases and, in this respect, our complexes differ from the well known azobenzene derivatives.[28] The position of ν(PdCl) for complex (IX) suggests the chlorine to be *trans* to nitrogen rather than to carbon.[28] That [{Pd(L′)Br}$_n$] [L′ = *N*-(1-pyridinio)benzamidate-*NC*^{2}]} showed no ν(PdBr) above 200 cm^{-1} is consistent with a di-μ-bromo-structure.[28]

The single ν(PdCl) for complex (II) suggests a *trans*-dichloro-structure and the position of this vibration (346 cm^{-1}) for (III) implies the palladium–chlorine bond to be *trans* to nitrogen; [28] similarly for the platinum analogue the Pt–Cl bond is *trans* to nitrogen. No analogue of complex (I) was prepared in the platinum case. Presumably (I) arises *via* nucleophilic displacement of the non-metallated ligand from (III); this reaction is likely to be slow for platinum with the result that internal metallation of the second ylide molecule may proceed at a rate which is at least comparable to that of the displacement reaction to give a reasonable yield of complex (IV). The two metallated ligands of

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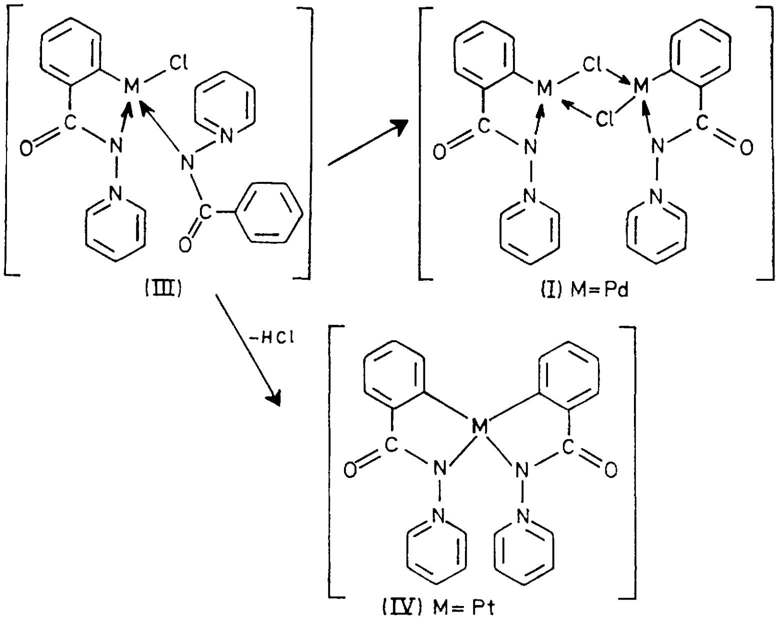
[29] D. H. Williams, R. S. Ward and R. G. Cooks, *J. Amer. Chem. Soc.*, 1968, **90**, 966.

[30] R. K. Poddar and V. Agarwala, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 785.

this complex are equivalent (^{1}H n.m.r.) and, in view of the structure suggested for (III; M = Pt), *cis*-Pt–C bonds may be present. The structure may be distorted from planarity for steric reasons. Nucleophilic displacement of L from complex (III; M = Pt) can, however, occur as shown by the formation of (VIII) and (IX) (M = Pt).



(III)

(I) M=Pd

(IV) M=Pt

Available data suggest that the palladium complexes of other ylides (L′ = $\mathrm{PhCO\cdot\bar{N}\cdot\overset{+}{N}Me_3}$, $\mathrm{PhCO\cdot\bar{C}H\cdot\overset{+}{N}Ph_3}$, m-$\mathrm{MeC_6H_4\cdot CO\cdot\bar{N}\cdot\overset{+}{N}H_5C_5}$, and p-$\mathrm{MeC_6H_4\cdot CO\cdot\bar{N}\cdot\overset{+}{N}H_5C_5}$) are similar, structurally speaking, to (I). This statement is supported by i.r. and ^{1}H n.m.r. data (Table 1) and also by bridge-splitting reactions with $\mathrm{Ph_3P}$ which again give complexes of $\mathrm{Ph_3PO}$. It therefore appears that the metallation reaction is general for compounds $\mathrm{\overset{+}{Y}\cdot\bar{X}\cdot COR}$ (R = aryl; X = CH or N); however it does not occur for $\mathrm{C_5H_5\overset{+}{N}\cdot\bar{N}\cdot SO_2Ph}$.[31]

The evidence that the chloride of complex (V; M = Rh) is as formulated in Table 1 may be briefly summarised. The complex dissociates as a 1 : 1 electrolyte in water and the chloride may be replaced by bromide, iodide, or tetraphenylborate to afford other 1 : 1 electrolytes. The chloride, bromide, and iodide are isomorphous and their i.r. spectra are substantially similar from 4 000 to 200 cm^{-1}; *i.e.* no band may be assigned as ν(Rh–halogen). The chloride and bromide give low conductivities in organic solvents, an observation we attribute to strong ion-pair formation possibly involving hydrogen bonding which, from ν(OH), is undoubtedly of importance in the solid state. A *cis*-configuration for complexes (V) is likely on steric grounds and the facile reaction with 2,2′-bipyridyl to displace water and give [RhL′$_2$(bipy)]Cl, (XII), is consistent with this view. Both ^{1}H and ^{13}C n.m.r. studies showed the metallated ligands $\mathrm{PhCO\cdot\bar{N}\cdot\overset{+}{N}H_5C_5}$ and p-$\mathrm{MeC_6H_4\cdot\bar{N}\cdot\overset{+}{N}H_5C_5}$ to be equivalent; thus the Rh–C bonds must be mutually *cis* or mutually *trans*. We cannot press the interpretation of our data further, but it may be noted that a bis(azobenzene) complex of rhodium(III)[32e] has *cis*-Rh–C bonds and, from the steric viewpoint, this seems a preferable arrangement in this case. The iridium(III) complex (VI) is not isomorphous with (V) and the ^{1}H n.m.r. data strongly imply the ligands to be magnetically inequivalent. The complex is a non-electrolyte and a band at 341 cm^{-1} may be assigned as ν(IrCl); thus the formulation [Ir(L′)$_2$Cl(H$_2$O)],3H$_2$O follows. Our data do not allow us to specify the stereochemistry about iridium, but *cis*-Ir–C bonds seem plausible. Both (V) and (VI) reacted with phosphines to give phosphine oxide complexes, (XI) and (XIII); these materials require no further comment. We observed that heating the chloride (V; M = Rh) produced a reversible colour change (to amber), involving a modification to the ν(OH) region of the spectrum consistent with disruption of the hydrogen-bonded network of the lattice.

(b) ortho-*Metallation*.—Since the original discovery[33,34] of direct metallation of an aromatic ring

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[31] L. Y. Chia, S. A. Dias, and W. R. McWhinnie, unpublished work; see also ref. 21.

[32] See, for example, (*a*) J. M. Guss and R. Mason, *Chem. Comm.*, 1971, 58; (*b*) M. I. Bruce, B. L. Goodall, M. Z. Iqbal, F. G. A. Stone, R. J. Doedeus, and R. G. Little, *ibid.*, p. 1595; (*c*) R. W. Siekman and D. L. Weaver, *ibid.*, 1968, 1021; (*d*) R. J. Hoare and O. S. Mills, *J.C.S. Dalton*, 1972, 2141; (*e*) A. R. M. Craik, G. R. Knox, and P. L. Pauson, *Chem. Comm.*, 1971, 168; (*f*) M. I. Bruce, J. Howard, I. W. Nowell, G. Shaw, and P. Woodward, *J.C.S. Chem. Comm.*, 1972, 1041; (*g*) C. W. Bradford, R. S. Nyholm, G. J. Gainsford, J. M. Guss, P. R. Ireland, and R. Mason, *ibid.*, p. 87.

[33] J. Kleiman and M. Dubeck, *J. Amer. Chem. Soc.*, 1963, **85**, 1544.

[34] A. C. Cope and R. W. Siekman, *J. Amer. Chem. Soc.*, 1965, **87**, 3272.

there have been numerous other examples discovered.[35] Several complexes have been the subject of *X*-ray crystallographic determinations,[32] and the formation of a transition metal to carbon bond by direct metallation is now a very well authenticated process for many types of organic substrate including, for example, derivatives of nitrogen such as azo-compounds,[33,34] oximes,[36] 2-phenylpyridine,[37] amines,[38] and benzo[*h*]quinoline;[39,40] several examples from phosphorus are known, *e.g.* refs. 39—44, and more recently, some derivatives of organosulphur compounds.[45,46]

(i) *I.r. evidence.* It is well known that mono- and 1,2-disubstituted benzenes have characteristic spectra in the γ(CH) region of the spectrum.[47] *ortho*-Metallation of *N*-(1-pyridinio)benzamidate in the phenyl ring will generate a 1,2-disubstituted benzene and should lead to characteristic changes in the 680—800 cm^{-1} region; this criterion has also been used by other workers.[34,37,48,49] Table 1 shows that, in all cases where the analytical data suggest loss of a ligand proton, changes characteristic of the metallation reaction are noted in the i.r. spectrum; in particular two bands (ligand phenyl) at *ca.* 690 and 715 cm^{-1} are replaced by one band at *ca.* 740 cm^{-1}. Also when both metallated and unmetallated ligand molecules are present as in complexes (III), this fact is clearly evident from the i.r. spectrum. In the case of complexes (I; M = Pd, L′ = *m*- and $p\text{-MeC}_6\text{H}_4\cdot\text{CO}\cdot\bar{\text{N}}\cdot\overset{+}{\text{N}}\text{H}_5\text{C}_5$) and (V) and (VI) ($\text{L}' = p\text{-MeC}_6\text{H}_4\cdot\text{CO}\cdot\bar{\text{N}}\cdot\overset{+}{\text{N}}\text{H}_5\text{C}_5$) (see Table 1) the changes in i.r. spectra observed are consistent with the change from a 1,3-di- to a 1,2,4-tri-substituted benzene or from a 1,4-di- to a 1,2,5-tri-substituted benzene.

The *ortho*-metallation reaction is generally accompanied by formation of a chelate ring, and preferably a five-membered planar ring.[50] Inspection of *N*-(1-pyridinio)benzamidate indicates that planar five-membered chelate rings could be formed by co-ordination through the benzamidate nitrogen atom or *via* the carbonyl oxygen atom. It has been observed that protonation on the benzamidate nitrogen atom results in a considerable shift to higher energy of ν(CO)[51] (see Table 1), whereas co-ordination of, say cobalt(II), *via* the carbonyl oxygen atom causes a lowering of ν(CO) compared to the free base.[31] Since ν(CO) undergoes a shift to higher frequency in the complexes considered here, co-ordination *via* nitrogen is indicated. A recent paper[52] assigns ν(NN) for *N*-(2,4,6-trimethyl-1-pyridinio)benzamidate at 1 341 cm^{-1}; we agree with this assignment and place ν(NN) in a similar spectral region for the three pyridinio- and the trimethylammonio-compounds considered here. This band shifts to lower wavenumber on protonation and also showed a downward shift in the metal derivatives reported here. This is consistent with co-ordination through nitrogen and also implies a weakening of the N–N bond in the complexes. The phosphorus ylide $\text{PhCO}\cdot\bar{\text{C}}\text{H}\cdot\overset{+}{\text{P}}\text{Ph}_3$ showed an increase in ν(CO) on complex formation in complex (I; M = Pd), thus implying co-ordination *via* the anionic carbon atom. Arnup and Baird[13] reported no example of *ortho*-metallation reactions with this ylide. Possibly our experimental conditions were more forcing.

(ii) *N.m.r. evidence.* The ^{1}H n.m.r. spectrum of *N*-(1-pyridinio)benzamidate is known.[24] The resonance of the α protons of the pyridine ring is well separated downfield from other resonances in the aromatic region, a fact which enabled us to perform meaningful integrations of the spectra. Thus the ratio of the low-field doublet (*J* 7 Hz) to the other aromatic resonances was 2 : 8 for the free ylide, but in complexes (I; M = Pd), (IV), and (V) ($\text{L}' = \text{PhCO}\cdot\bar{\text{N}}\cdot\overset{+}{\text{N}}\text{H}_5\text{C}_5$) the ratio was 2 : 7. In complex (II), however, the ratio 2 : 8 was seen, consistent with the view that this is a simple co-ordination compound. In the cases where two ylide molecules were present, the results indicated that these molecules are magnetically equivalent. However, in the case of the iridium(III) complex (VI; $\text{L}' = \text{PhCO}\cdot\bar{\text{N}}\cdot\overset{+}{\text{N}}\text{H}_5\text{C}_5$) it was not possible to carry out a meaningful integration of the spectrum based on the α doublet, a result which supports the non-equivalence of the ligands implied by the formula in Table 1. The α doublet of the pyridine ring underwent a shift to low field on protonation of the benzamidate nitrogen atom, indicating that the α protons become more deshielded. The same resonance underwent a very slight downfield shift in the Pd$^{\text{II}}$ and Pt$^{\text{II}}$ complexes, but in complexes of the tripositive ions Rh$^{\text{III}}$ and Ir$^{\text{III}}$ the degree of deshielding produced was comparable to that produced by a proton. We interpret these observations as being consistent with the view

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that the benzamidate nitrogen atom is the point of attachment of the ligand to the metal ion. It may also be remarked that the ^1H n.m.r. data show the metallation to be in the phenyl and not in the pyridine ring and also, together with i.r. data, confirm that the ylide has undergone no major rearrangement on co-ordination and metallation. The ^1H n.m.r. data also provided adequate proof of the metallation reactions with the other ligands (Table 1).

^{13}C N.m.r. data should provide unambiguous proof of the metallation reaction, the rhodium complexes of $C_5H_5\overset{+}{N}\cdot\overset{-}{N}\cdot COR$ (R = Ph or *p*-MeC_6H_4) being selected for study (Table 2). The proton-decoupled spectra showed a single sharp band for each magnetically distinct carbon atom; thus $C_5H_5\overset{-}{N}\cdot\overset{+}{N}\cdot COPh$ showed eight resonances. The metallated complex has ten magnetically inequivalent carbon atoms and the spectrum of $[RhL'_2(H_2O)_2]Cl$ ($L' = PhCO\cdot\overset{-}{N}\cdot\overset{+}{N}H_5C_5$) showed ten distinct resonances one of which had undergone a large downfield shift and was split into a doublet [*J*(RhC) 32·5 Hz]. The deshielding indicates that this is the resonance due to C(2) (Table 2) and the splitting is of the order expected for *J*(RhC).[53] The data for *p*-$MeC_6H_4\cdot CO\cdot\overset{-}{N}\cdot\overset{+}{N}H_5C_5$ and the corresponding complex (V) were very similar and it is noted that the resonance of the methyl carbon is a sharp singlet thus confirming that the two ligand molecules are magnetically equivalent. A small splitting (5 Hz) of the carbonyl resonance for $PhCO\cdot\overset{-}{N}\cdot\overset{+}{N}H_5C_5$ complex was noted. The consensus of other evidence suggests the two ligand molecules are equivalent; hence the possibility of long-distance coupling with ^{103}Rh must be considered. For the *p*-$MeC_6H_4\cdot CO\cdot\overset{-}{N}\cdot\overset{+}{N}H_5C_5$ complex resonance was single. The assignments of C(a), C(b), C(1), and C(2) were most definite (Table 2). The assignment of C(a) and C(1) was established by rapid pulsing which attenuates all signals relaxing slowly (mostly those arising from carbon atoms with no attached protons).

(c) *Reaction of the Complexes with Carbon Monoxide.*—Some of the complexes described here reacted reversibly with carbon monoxide under ambient conditions. In the case of the palladium complexes, side reactions leading to reduction to metallic palladium occurred but it was possible to isolate materials of stoicheiometry [PdL′(CO)X] (X = Cl or Br). Complex (VII; X = Cl) showed ν(PdCl) at 273 cm^{-1}, implying that the chloride ligand is *trans* to carbon. This is in contrast to the product derived from the reaction of Ph_3P with complex (I; M = Pd, $L' = PhCO\cdot\overset{-}{N}\cdot\overset{+}{N}H_5C_5$) which had a chloride ligand *trans* to nitrogen; this is more expected since as a di-μ-chloro-complex it would be anticipated that the ligands *trans* to carbon would be more labile. However the reaction with carbon monoxide was not simple since a colourless intermediate, which we could never isolate pure, was involved (see Experimental section). Thus products such as (VII) should not be regarded as necessarily arising from a bridge-splitting reaction. The platinum complex (III) reacted very slowly with CO and only mixtures with ν(CO) at 2 080 cm^{-1} were isolated.

The rhodium complexes were totally unreactive to CO under ambient conditions yet, by contrast, the iridium complex (VI; $L' = PhCO\cdot\overset{-}{N}\cdot\overset{+}{N}H_5C_5$) underwent a smooth and quantitative reaction to afford $[IrL'_2(CO)_2]Cl$, (XIV), which we believe to be a *cis*-dicarbonyl complex [two ν(CO) at 2 000 and 1 985 cm^{-1}]. The starting material, (VI), may be regenerated by heating (XIV) under reflux in water. We followed the uptake of CO in some experiments and confirmed that two moles of gas were consumed per mole of (VI); however, initially, considerably more CO was taken up with the excess being released as the reaction neared completion. Thus the mechanism of formation is not simple and it will be the subject of further study.

To date, preliminary studies with the carbonyl complexes have given no evidence for the carbonyl-insertion reaction. There are examples of the reaction with *ortho*-metallated complexes,[54–57] but the only evidence we have so far that this is a possible reaction for our complexes comes from mass-spectroscopic investigations of (III). In both cases a fragment of stoicheiometry $C_8H_5NO_2$ was found (*m*/*e* 147·03270; calc. 147·03203) which is not present in the mass spectra of the free ylide [58] or in the spectra of other complexes. This ion is reasonably assumed to be derived from phthalimide which would arise from (*i*) rupture of the N–N bond of the non-metallated ylide (we have good evidence that this process is much easier for the co-ordinated than the free ylide [42]), (*ii*) removal of CO from N·COPh either before or after rearrangement to phenyl isocyanate, and (*iii*) carbonyl insertion followed by release of the organic fragment; *i.e.* we regard the fragment $C_8H_5NO_2$ to arise during pyrolysis of the complex.

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