ISOCYANIDE, CARBENE, AND RELATED CHEMISTRY OF
PALLADIUM(II) AND PLATINUM(II)
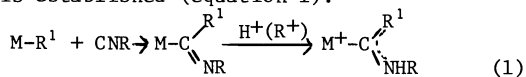
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Abstract - Previous studies of the inter-relationships between isocyanide,
imine, and carbene ligands on platinum(II), and of the stereochemistries
of the latter two ligands will be briefly reviewed. Attempts to use these
relationships to prepare platinum-olefin-carbene complexes have been
unsuccessful but have led to an interesting ortho-metallated carbene
derivative. The insertion of isocyanide into the Pd-CH$_3$ gives the stable
carbon-bonded imine ligand, e.g. Pd[C(CH$_3$)=N(p-tolyl)]. The reaction of
this ligand with dimethylacetylene dicarboxylate gives, as the major
product, a complex containing the 1-p-tolyl-3-oxo-2-E-carbomethoxy-
methylidene-2,3-dihydropyrrole ligand. The mechanism of its formation
requires the occurrence of the enamine-ketimine tautomerism.

INTRODUCTION

The chemistry of the isocyanide ligand, which is electronically similar to the carbonyl
ligand, exhibits many interesting features. In the same way, the nitrogen analogue of the
acyl group, which itself displays an interesting organometallic chemistry, may generate a
valuable new class of derivatives. Since the imidoyl ligand can be converted to a carbene
by protonation or alkylation, an inter-relationship between isocyanide, imidoyl, and carbene
ligands is established (equation 1).

$$M-R^1 + CNR \rightarrow M-C\underset{NR}{\overset{R^1}{\diagdown}} \xrightarrow{H^+(R^+)} M^+-C\underset{NHR}{\overset{R^1}{\diagdown}} \qquad (1)$$
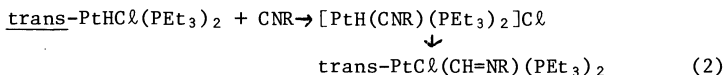
This inter-relationship, as well as some derivative chemistry, for both palladium and
platinum, will be discussed here.
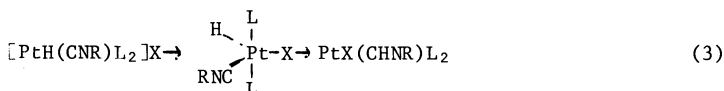
RESULTS AND DISCUSSION

Platinum(II) Formimidoyl and Carbene Complexes

Previous workers have described isocyanide insertion into the Pt-C bond (Ref.1&2), and while
our own present study was in progress Otsuka and Ataka (Ref.3) reported on the analogous
isocyanide insertion into both palladium(II) and platinum(II) - alkyl and - vinyl bonds.
Roper et.al. (Ref.4) had similarly discussed the formation of formimidoyl complexes by
isocyanide insertion into the Ru-H bond. We have found (Ref.5) that the well-known hydride,
trans-PtHCl(PEt$_3$)$_2$ undergoes a smooth sequence of reactions including that with p-tolyl
isocyanide to give firstly, the adduct [PtH(CNR)(PEt$_3$)$_2$]Cl as a crystalline solid, and then
in less polar solvents or at higher temperatures the formimidoyl complex (equation 2).

$$trans\text{-PtHCl}(PEt_3)_2 + CNR \rightarrow [PtH(CNR)(PEt_3)_2]Cl$$
$$\downarrow$$
$$trans\text{-PtCl}(CH=NR)(PEt_3)_2 \qquad (2)$$
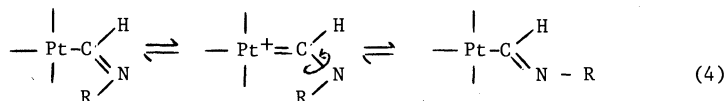
The fact that insertion is facilitated by (a) less polar solvents and (b) a good co-
ordinating anion such as chloride, led to the conclusion (Ref.5) that the mechanism involves
a neutral, five coordinate intermediate (equation 3).

$$[PtH(CNR)L_2]X \rightarrow \underset{RNC}{\overset{H}{\diagdown}}\overset{L}{\underset{L}{\underset{|}{\overset{|}{Pt}}}}-X \rightarrow PtX(CHNR)L_2 \qquad (3)$$
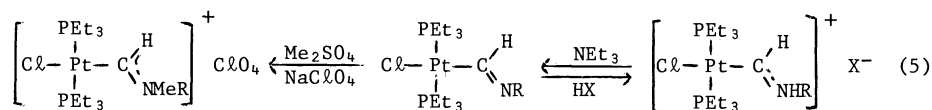
This is, of course, similar to the mechanism proposed by Treichel and Hess (Ref.2) for
isocyanide insertion into the Pt-C bond.
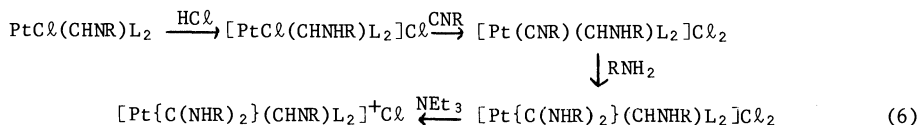
As in other investigations of imidoyl complexes, ^{1}H nmr studies showed the existence of <u>syn</u> and <u>anti</u> isomeric forms of the formimidoyl ligand, but for these platinum derivatives, the equilibrium distribution between the isomeric forms appeared to be solvent dependent and hence sensitive to small changes in solvation energies. Moreover, the ease of isomerization was observed to increase with increasing donor strength of the ligand <u>trans</u> to formimidoyl. These results are consistent with an isomerization mechanism involving a polarized transition state and rotation about the C⁓N bond (equation 4).

$$-\overset{|}{\underset{|}{Pt}}-C\overset{\diagup H}{\underset{\diagdown N}{\phantom{.}}}\diagup R \rightleftharpoons -\overset{|}{\underset{|}{Pt}}{}^{+}=C\overset{\diagup H}{\underset{\diagdown N}{\phantom{.}}}\diagup R \rightleftharpoons -\overset{|}{\underset{|}{Pt}}-C\overset{\diagup H}{\underset{\diagdown}{\phantom{.}}}N-R \qquad (4)$$

The Pt(II) formimidoyl complexes can be readily protonated with HCl or HClO₄, or methylated with dimethylsulfate, in the presence of NaClO₄ or NH₄PF₆, to generate cationic secondary carbene complexes. Moreover, protonation can be reversed by treatment of the carbene cation with triethylamine (equation 5).

$$\left[\begin{array}{c}PEt_3\\ |\\ Cl-Pt-C\\ |\\ PEt_3\end{array}\overset{H}{\underset{NMeR}{\diagdown}}\right]^{+}ClO_4 \xleftarrow{Me_2SO_4}{NaClO_4} \begin{array}{c}PEt_3\\ |\\ Cl-Pt-C\\ |\\ PEt_3\end{array}\overset{H}{\underset{NR}{\diagdown}} \overset{NEt_3}{\underset{HX}{\rightleftharpoons}} \left[\begin{array}{c}PEt_3\\ |\\ Cl-Pt-C\\ |\\ PEt_3\end{array}\overset{H}{\underset{NHR}{\diagup}}\right]^{+}X^{-} \qquad (5)$$
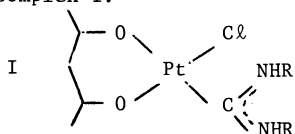
The protonation–deprotonation cycle can be usefully applied synthetically, e.g. to prepare bis (carbene), or carbene-formimidoyl complexes (equation 6).

$$PtCl(CHNR)L_2 \xrightarrow{HCl} [PtCl(CHNHR)L_2]Cl \xrightarrow{CNR} [Pt(CNR)(CHNHR)L_2]Cl_2$$
$$\Big\downarrow RNH_2$$
$$[Pt\{C(NHR)_2\}(CHNR)L_2]^{+}Cl \xleftarrow{NEt_3} [Pt\{C(NHR)_2\}(CHNHR)L_2]Cl_2 \qquad (6)$$

The ^{1}H nmr spectra of these carbene complexes show the presence of <u>cis</u> and <u>trans</u> isomers of the secondary carbene group –CHNMeR. (Ref. 4&6).
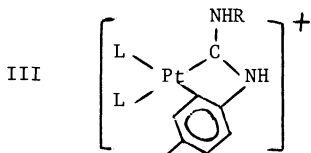

## Orthometallation of a Carbene Complex

This quite extensive chemistry based on inter-relationships between isocyanide, formimidoyl, and carbene complexes, appeared to provide a route to the preparation of Pt(II) species containing both a carbene and an olefin bound to the same metal centre. Such derivatives would be of substantial interest in connection with current studies of olefin dismutation. Although our investigations have not led to such compounds, some worthwhile chemistry has nevertheless emerged. The starting compound used is PtCl(CNR)(acac), where R=p-tolyl, acac = acetylacetonate. This, on treatment with an amine, is readily converted to the carbene complex I.
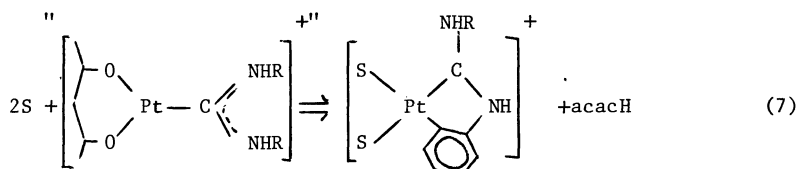


Removal of the chloride from I with AgPF₆ yields a greenish black powder whose solid state infrared spectrum reveals the presence of acetylacetonate, carbene, and PF₆⁻. We formulate this product, II, as "[Pt{C(NHR)₂}acac]⁺" although it may well be binuclear.
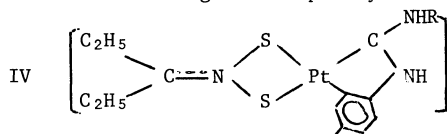
Compound II reacts instantaneously, at room temperature with one equivalent of neutral ligands such as p-tolyl isocyanide or 1,2-bisdiphenylphosphinoethane, and more slowly with coordinating solvents to give pale yellow complexes of type III.



The rate of reaction of II with solvents is dependent on their coordinating ability and was observed to be much faster for acetonitrile than acetone. The reaction with these solvents was reversible since stripping the solution to near dryness gave back the green complex II as the concentration of the higher boiling acetylacetone increased relative to the solvent (equation 7).

$$2S + \left[\begin{array}{c} \text{\textquotedbl} \\ O \\ \diagdown \\ / \\ O \end{array} Pt-C \begin{array}{c} NHR \\ \diagup \\ \diagdown\diagdown \\ NHR \end{array}\right]^{+\text{\textquotedbl}} \rightleftharpoons \left[\begin{array}{c} NHR \quad + \\ | \\ S \diagdown \quad C \\ \quad Pt \quad NH \\ S \diagup \quad \bigcirc \end{array}\right] \quad +acacH \qquad (7)$$

Similarly, compound II reacts instantaneously, at room temperature, with one equivalent of sodium dithiocarbamate to give the pale yellow complex IV.

$$IV \quad \left[\begin{array}{c} C_2H_5 \\ \diagdown \\ C \overset{\cdot\cdot\cdot}{=} N \\ \diagup \\ C_2H_5 \end{array} \begin{array}{c} S \diagdown \\ \quad Pt \\ S \diagup \end{array} \begin{array}{c} NHR \\ \diagup \\ C \\ \diagdown \\ NH \\ \bigcirc \end{array}\right]$$

Since imidoyl groups, $M-C(R_1)=NR_2$, are known (Ref.7) to be reversibly protonated at nitrogen, it was interesting to observe that, following the elimination of acetylacetone by solvent, dithiocarbamate, or other neutral ligands, ortho-metallation occurred perferentially. As might be expected, the ortho-metallation reaction may be reversed with acids. The addition of hydrochloric acid ($CH_3COC\ell$ in methanol) to $[Pt(CNR)_2\{C(NHR)(NH.C_6H_3.CH_3)\}]^+$, $[Pt(diphos)\{C(NHR)(NH.C_6H_3.CH_3)\}]^+$ and $[Pt(dtc)\{C(NHR)(NH.C_6H_3.CH_3)\}]$ gave a mixture of cis and trans $-[PtC\ell(CNR)_2\{C(NHR)_2\}]^+$, cis $-[PtC\ell(diphos)\{C(NHR)_2\}]^+$, and cis $-[PtC\ell(dtc)\{C(NHR)_2\}]$ respectively.

Subsequent removal of the chlorine from the complexes cis $-[PtC\ell(diphos)\{C(NHR)_2\}]^+$ and cis $-[PtC\ell(dtc)\{C(NHR)_2\}]$ did not regenerate the original o-metallated complexes.

That ortho-metallation involving a phenyl group of the carbene ligand has indeed occurred has been verified by a determination of the crystal structure of $[Pt\{C(NH.C_6H_3.CH_3)$ $(NHC_6H_4CH_3)\}(C_6H_5)_2PC_2H_4P(C_6H_5)_2]C\ell O_4$.

The tendency to undergo preferential ortho-metallation clearly prevents the preparation of Pt(II) carbene-olefin species, but on the other hand this is the first such example, of ortho-metallation involving a carbene ligand.
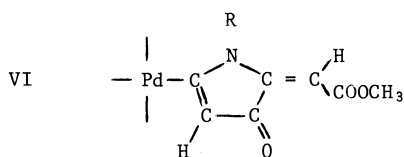

## Palladium(II) Isocyanide and Imine Complexes

Much less detailed chemistry has been explored in the analogous palladium systems, in part due to the fact that palladium hydrides are much less stable and less common than the corresponding platinum hydrides. However, as stated previously, Otsuka and Ataka (Ref.3) have studied isocyanide insertion into Pd-C bonds in the presence of a nucleophile (either $CNBu^t$ or $PPh_3$) to give $[PdX(CR^1=NBu^t)(CNBu^t)L]$. In the presence of L, insertion occurs unimolecularly being independent of the nature of L. We have similarly found that p-tolyl isocyanide reacts readily with trans $-PdC\ell(CH_3)(PEt_3)_2$ at room temperature to give trans $-PdC\ell[C(CH_3) = N(p-tolyl)](PEt_3)_2]$, V, a stable white crystalline compound.


## Enamine-Ketimine Tautomerism of the Pd-C(CH₃)=NR Group

The reaction of the palladium - imine complex V with dimethylacetylene dicarboxylate, DMA, was investigated since acetylene attack on either the metal centre or the carbon-bound imine might occur. Reaction occurred quite readily in chloroform to eliminate methanol and give ultimately, two red-orange crystalline products, VI and VII. By following the $^1$H nmr spectrum during the reaction, it was possible to show that VI was formed via an intermediate VIa which has not lost methanol. In both the infrared and $^1$H nmr spectra, VI and VII are very similar and are obviously related structurally. This is also apparent from the similarity of the $^{13}$C nmr spectra of VI and VII.
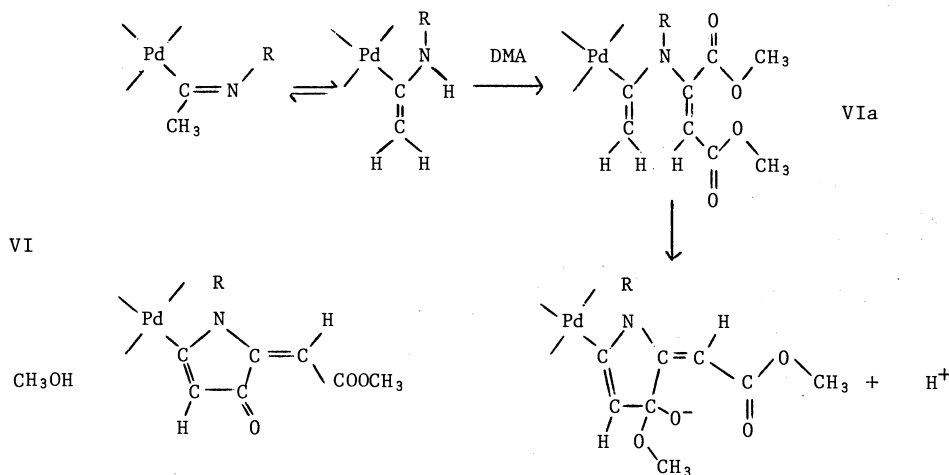
The identity of VI was established unambiguously by an X-ray crystallographic study, the structure being that shown below containing a five-membered ring with the two carbonyl groups cis about the exocyclic double bond.

$$VI \quad \begin{array}{c} R \\ | \\ | \quad N \\ -Pd-C \diagup \diagdown \diagdown C = C \diagup H \\ | \quad \diagdown\diagdown \diagup \quad \diagdown COOCH_3 \\ \quad C-C \\ \diagup \quad \diagdown\diagdown \\ H \quad O \end{array}$$

The simplest mechanism to account for this product is one which involves the enamine form of the carbon-bonded metal imine V. The N-H fragment of the enamine can add across the triple bond of the acetylene to give an intermediate which is presumably VIa. The original double

bond of the enamine can now act as a nucleophile and attack one of the carbonyl carbon atoms to eliminate methanol and form VI (See Reaction Scheme).
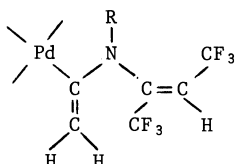
### Reaction Scheme



Experimental evidence to support this mechanism consists of the following observations:
(a)  the protons of the methyl group on the imine exchange with $D_2O$, to give deuterated species, strongly implying existence of the ketimine-enamine tautomerism.
(b)  the observed infrared and ^{1}H nmr spectroscopic data are fully consistent with this structure for VIa.
(c)  the starting imine compound V reacts with hexafluoro-2-butyne to give a somewhat unstable product whose ^{1}H and ^{19}F nmr spectra are consistent with structure VIII, which can be regarded as a fluorinated analogue of VIa with the single difference that the addition
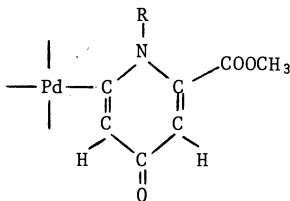


of the enamine has been _trans_ across the acetylenic triple bond.

The identity of the minor species VII has not been established conclusively, but since VI and VII are very similar spectroscopically, and since a solution of pure VI or pure VII in $CDCl_3$ will, over a few days, form small amounts of the other product, it seems that the structure shown below with the carbonyls _trans_ about the double bond would be likely.



We thus conclude that a necessary criterion for the reaction of metal carbon-bonded imines with activated acetylenes to form heterocycles is the presence of exchangeable α-protons. Such α-protons allow the presence of a ketimine – enamine tautomerism to form the reactive enamine tautomer.

## Palladium(II) Hydride – Isocyanide Insertion

The recent report (Ref.8) of a synthetic method leading to reasonably stable Pd(II) hydrides

has allowed us to commence a study of the related insertion reactions of Pd(II) hydrides with isocyanides. Our preliminary results indicate that $\underline{trans}$ – PdH(Pcy$_3$)$_2$(solvent)$^+$ and $\underline{trans}$ – PdH(NO$_3$)(Pcy$_3$)$_2$ react with p-tolylisocyanide to give only the hydrido isocyanide cation, $\underline{trans}$ – PdH(CNR)(Pcy$_3$)$_2$$^+$; there is no evidence for insertion. With $\underline{trans}$ – PdHCℓ(Pcy$_3$)$_2$, a complex reaction apparently occurs and the products have yet to be identified. However, we hope to find other methods of extending further the interesting isocyanide,– imine,– carbene chemistry of both platinum and palladium.

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