# Reactions of Methyl- and Phenylplatinum(II) Complexes with Isocyanides. Mechanism of the Insertion Reaction

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Reactions of several PtX(R)(phos)$_2$ (X = Br, I; R = CH$_3$, C$_6$H$_5$; phos = several phosphines) complexes with methyl and *p*-chlorophenyl isocyanide were carried out. Initially an isolable 1:1 adduct of these reagents was formed; because solutions of these species had conductivity values appropriate to 1:1 electrolytes, we propose the ionic formulation [PtR(CNR')-phos$_2$]X. Heating these species which had been either isolated previously or prepared *in situ* usually gave a product in which the isocyanide inserted into the alkyl- (or aryl-) platinum bond, *viz.*, PtX{C(R)=NR'}(phos)$_2$. Deviations from this general pattern of behavior occurred in only three instances. The ionic [PtC$_6$F$_5$(CNCH$_3$){(C$_6$H$_5$)$_3$P}$_2$]Br was unstable with respect to isocyanide loss and was not isolable as a pure substance; on refluxing PtBr(C$_6$F$_5$){(C$_6$H$_5$)$_3$P}$_2$ and CH$_3$NC in benzene, PtCN(C$_6$F$_5$){(C$_6$H$_5$)$_3$P}$_2$ was formed. Dealkylation of the isocyanide also occurred with the complexes [Pt(CH$_3$)-(CNCH$_3$){(C$_2$H$_5$)$_3$P}$_2$]X; in the case of X = Br only PtCN(CH$_3$){(C$_2$H$_5$)$_3$P}$_2$ was isolated. For X = I, three products were found: PtCN(CH$_3$){(C$_2$H$_5$)$_3$P}$_2$, PtI{C(CH$_3$)=NCH$_3$}{(C$_2$H$_5$)$_3$P}$_2$, and [PtI{C(CH$_3$)=N(CH$_3$)$_2$}{(C$_2$H$_5$)$_3$P}$_2$]I. The third product apparently arises from alkylation of the imino nitrogen in the inserted product by the methyl iodide generated in the dealkylation reaction.

## Introduction

About 2 years ago we initiated a general study on iso-cyanide complexes of platinum.[1-3] Our investigations were first directed to insertion reactions of methyl isocyanide with platinum(II) methyl and phenyl species; we described our earlier work in a communication.[1] Herein we report further studies on this subject.

Preceding our work, several examples of reactions involving isocyanide insertion into metal-carbon σ bonds had been re-ported.[4] Yamamoto and coworkers[5,6] were the first to describe this phenomenon, reporting reactions of several iso-cyanides with the compounds C$_5$H$_5$Ni{(C$_6$H$_5$)$_3$P}CH$_3$ and C$_5$H$_5$Mo(CO)$_3$R (R = CH$_3$, CH$_2$C$_6$H$_5$). Subsequently Otsuka, *et al.*,[7] reported novel oxidative addition reactions of several isocyanide complexes of nickel(0) and palladium(0), for which they postulated the initial formation of alkylmetal isocyanide complexes; these complexes subsequently re-arranged to give insertion of one or more isocyanides into the carbon-metal bond. The reactions described were of particular interest, in that they provided a model which ex-plained the polymerization of isocyanides in certain metal systems.

It is to be noted, however, that the low stability of the initial reaction products, with respect to isocyanide insertion, precluded a detailed study of the early steps in this reaction. Our work[1] served to complement the studies of Otsuka, *et al.*,[7] in that the initial steps of these insertion reactions could be detailed more precisely.

Since our communication appeared, there has been a gen-eral resurgence of interest in insertion reactions of metal alkyl and aryl species. Much of this work, though not all, has been directed to the nickel group metals and particularly

to palladium and platinum. Yamamoto, *et al.*,[8a] described reactions with the palladium complexes PdI(CH$_3$)(PR$_3$)$_2$ (PR$_3$ = P(C$_6$H$_5$)$_3$, P(C$_6$H$_5$)(CH$_3$)$_2$) and cyclohexyl isocy-anide; it is interesting to note that multiple insertion into the palladium-carbon bond was observed in this work, analogous to earlier work,[7] but in contrast to our study with platinum in which only one isocyanide was shown to insert. Yamamoto, *et al.*, have also reported briefly on analogous reactions with platinum and have verified our original ob-servations.[8b] More recently Clark and coworkers[9,10] have described, in several papers, the reactions of platinum(II) alkyl species with several acetylenes and with tetrafluoro-ethylene in which insertion into the metal-carbon bond was sometimes observed.

## Experimental Section

All reactions were carried out under a nitrogen atmosphere. Melting points were taken on a Kofler hot-stage apparatus and are uncorrected. Infrared spectra (4000-550 cm$^{-1}$) were recorded on a Perkin-Elmer Model 421 spectrometer using Nujol mulls. A Beckman IR-10 spectrometer was used for the remainder of the spectrum down to 250 cm$^{-1}$. Proton nmr spectra were obtained on a Varian T-60 or on a JEOL-NM-MH-100 spectrometer, using chloroform-$d_1$ solu-tions and tetramethylsilane, τ 10.0, as an internal standard. Con-ductivity measurements were made on dichloromethane and aceto-nitrile solutions with a Beckman conductivity bridge, Model RC-18A, and a Beckman conductivity cell with cell constant $k$ = 0.20; these data are given in Table I. Molecular weight determinations on the nonionic compounds were made on chloroform solutions using a Mechrolab osmometer, Model 301A. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by Meade Microanalytical Laboratories, Amherst, Mass.

The starting platinum complexes *trans*-PtXR{(C$_6$H$_5$)$_3$P}$_2$ (R = CH$_3$, C$_6$H$_5$, X = I; R = C$_6$F$_5$, X = Br) were prepared from Pt-[(C$_6$H$_5$)$_3$P]$_4$ and RX;[11] *trans*-PtCl(C$_6$H$_5$){(C$_6$H$_5$)$_3$P}$_2$ was synthesized by decarbonylating the benzoyl complex PtCl(COC$_6$H$_5$){(C$_6$H$_5$)$_3$P}$_2$ obtained from Pt[(C$_6$H$_5$)$_3$P]$_3$ and C$_6$H$_5$COCl,[12] and the bromo com-plex PtBr(C$_6$H$_5$){(C$_6$H$_5$)$_3$P}$_2$ was prepared from this by a metathetical reaction using NaBr in aqueous acetone. The complexes *trans*-PtX-(CH$_3$){(C$_2$H$_5$)$_3$P}$_2$ and *trans*-PtX(CH$_3$){(C$_6$H$_5$)$_2$(CH$_3$)P}$_2$ (X = Cl, Br, I) were prepared from *cis*- or *trans*-PtCl$_2${(C$_2$H$_5$)$_3$P}$_2$, or PtCl$_2$-

(1) P. M. Treichel and R. W. Hess, *J. Amer. Chem. Soc.*, 92, 4731 (1970).

(2) P. M. Treichel, W. J. Knebel, and R. W. Hess, *J. Amer. Chem. Soc.*, 93, 5424 (1971).

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(4) This subject has recently been reviewed: Y. Yamamoto and H. Yamazaki, *Coord. Chem. Rev.*, 8, 225 (1972).

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Table I. Conductivity Data on Ionic Complexes

| Complex[a] | $\Lambda_M$, ohm$^{-1}$ cm$^2$ mol$^{-1}$ | |
|---|---|---|
| | CH$_3$CN[b] | CH$_2$Cl$_2$[c] |
| [PtCH$_3$(CNCH$_3$){(C$_6$H$_5$)$_3$P}$_2$]I | 130.2 | 56.2 |
| [PtC$_6$H$_5$(CNCH$_3$){(C$_6$H$_5$)$_3$P}]I | 132.4 | 53.8 |
| [PtC$_6$H$_5$(CNCH$_3$){(C$_6$H$_5$)$_3$P}]Cl | $\cdots$ | 56.7 |
| [PtC$_6$H$_5$(CNCH$_3$){(C$_6$H$_5$)$_3$P}]PF$_6$ | 131.7 | $\cdots$ |
| [PtCH$_3$(CNCH$_3$){(C$_6$H$_5$)$_2$(CH$_3$)P}$_2$]I | | 56.7 |
| [PtCH$_3$(CNCH$_3$){(C$_6$H$_5$)$_2$(CH$_3$)P}$_2$]Br | | 69.7[d] |
| [PtCH$_3$(CNCH$_3$){(C$_2$H$_5$)$_3$P}$_2$]I | | 51.4 |
| [PtCH$_3$(CNCH$_3$){(C$_2$H$_5$)$_3$P}$_2$]Br | | 45.3[e] |
| [PtCH$_3${CNC$_6$H$_4$Cl}{(C$_6$H$_5$)$_2$(CH$_3$)P}$_2$]I | | 50.7 |
| [PtCH$_3${CNC$_6$H$_4$Cl}{(C$_6$H$_5$)$_2$(CH$_3$)P}$_2$]Br | | 53.8 |
| [PtCH$_3${CNC$_6$H$_4$Cl}{(C$_6$H$_5$)$_2$(CH$_3$)P}$_2$]PF$_6$ | | 57.5 |
| [PtCH$_3${CNC$_6$H$_4$Cl}{(C$_2$H$_5$)$_3$P}$_2$]I | | 58.1 |
| [PtCH$_3${CNC$_6$H$_4$Cl}{(C$_2$H$_5$)$_3$P}$_2$]Br | | 60.3 |
| [PtCH$_3${CNC$_6$H$_4$Cl}{(C$_2$H$_5$)$_3$P}$_2$]PF$_6$ | | 53.4 |
| [PtI{C(CH$_3$)=N(CH$_3$)$_2$}{(C$_2$H$_5$)$_3$P}$_2$]I | 153.3 | 22.6 |
| [PtI{C(CH$_3$)=N(CH$_3$)$_2$}{(C$_6$H$_5$)$_3$P}$_2$]I | 127.0 | 40.18 |

[a] Concentrations (4-7) × 10$^{-4}$ $M$ unless otherwise indicated.
[b] For [(C$_2$H$_5$)$_4$N]ClO$_4$ (5 × 10$^{-4}$ $M$), $\Lambda_M$ = 151.4. [c] For [(C$_4$H$_9$)$_4$N]ClO$_4$ (5 × 10$^{-4}$ $M$), $\Lambda_M$ = 52.9. [d] 3.63 × 10$^{-4}$ $M$. [e] 9.33 × 10$^{-4}$ $M$.

{(C$_6$H$_5$)$_2$(CH$_3$)P}$_2$ and CH$_3$MgX.[13a] Methyl isocyanide[13b] and *p*-chlorophenyl isocyanide[13c] were prepared by the literature methods.

**Preparation of Ionic Platinum(II)-Isocyanide Addition Complexes.** The preparation of [PtCH$_3$(CNCH$_3$){(C$_6$H$_5$)$_3$P}$_2$]I from PtI(CH$_3$){(C$_6$H$_5$)$_3$P}$_2$ and methyl isocyanide illustrates the general procedure used.

*trans*-[PtCH$_3$(CNCH$_3$){(C$_6$H$_5$)$_3$P}$_2$]I. To a suspension of PtI(CH$_3$){(C$_6$H$_5$)$_3$P}$_2$ (0.798 g, 0.93 mmol) in 1:1 benzene-hexane was added methyl isocyanide (0.04 g, 1 mmol) in 15 ml of benzene dropwise while stirring at room temperature. The white suspension turned a bright yellow. (Note: Only for the triphenylphosphine complexes was a yellow color observed.) The solvent was evaporated to give a yellow solid which dissolved in chloroform to give a colorless solution. Recrystallization from chloroform-benzene or chloroform-hexane gave the product as white needles (0.695 g, 83%) (melting point data: began to melt at 95°, resolidified at 120°, and remelted at 230-235° with decomposition). The infrared spectra of the initial yellow solid and the recrystallized white needles were identical.

*Anal.* Calcd for C$_{39}$H$_{36}$NP$_2$PtI·0.5CHCl$_3$:[14] C, 49.3; H, 3.88; N, 1.45; P, 6.44. Found: C, 49.6; H, 3.82; N, 1.61; P, 6.50.

Ir: 2220 (s) (C≡N), 1585 (w), 1480 (s), 1435 (s), 1310 (w), 1155 (w), 1092 (s), 1033 (w), 995 (w), 762 (m), 746 (m), 737 (m, sh), 702 (s), 685 (s), 675 (s), 612 (w), 513 (s), 500 (s, sh) cm$^{-1}$. Pmr: $\tau$ 9.84 (t* of t, $J_{Pt-H}$ = 60 Hz, $J_{P-H}$ = 7.0 Hz, Pt-C$H_3$), $\tau$ 7.33 (s, broad, CNC$H_3$), $\tau$ 2.42 (m, C$_6H_5$).

Utilizing a similar procedure, PtCl(CH$_3$){(C$_6$H$_5$)$_3$P}$_2$ (0.39 g, 0.507 mmol) and methyl isocyanide (0.04 g, 1 mmol) gave only a dark pink solution which precipitated a light purple solid that was not further investigated.

Data on other compounds prepared by this route are tabulated below.

[PtC$_6$H$_5$(CNCH$_3$){(C$_6$H$_5$)$_3$P}$_2$]I: yellow solid; 84% yield; mp 90-100°, resolidified 120°, remelted 220-230°.

*Anal.* Calcd for C$_{44}$H$_{38}$NP$_2$PtI: C, 54.8; H, 3.84; N, 1.46; P, 6.43. Found: C, 54.9; H, 4.09; N, 1.54; P, 6.26.

Ir: 2220 (s) (C≡N) 1600 (w), 1588 (w), 1572 (m), 1478 (s), 1430 (s), 1307 (w), 1238 (w), 1212 (w), 1180 (w), 1153 (w), 1092 (s), 1065 (w), 1022 (m), 993 (m), 750 (s, sh), 740 (s), 732 (s, sh), 703 (s), 690 (s), 680 (s), 668 (s), 612 (w), 520 (s), 507 (s), 494 (m) cm$^{-1}$. Pmr: $\tau$ 7.37 (t*,[15] $J_{Pt-H}$ = 12 Hz, CNC$H_3$), $\tau$ 3.50 (m, Pt-C$_6H_5$), $\tau$ 2.53 (m, P-C$_6H_5$).

[PtC$_6$H$_5$(CNCH$_3$){(C$_6$H$_5$)$_3$P}$_2$]Br: white solid; 90% yield; mp 235-237°.

(13) (a) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959); (b) R. E. Schuster, J. E. Scott, and J. Casanova, *Org. Syn.*, 46, 75 (1966); (c) I. Ugi and R. Meyr, *Chem. Ber.*, 93, 239 (1960).
(14) In a number of instances, products prepared here retained some solvent on recrystallization. In our early work we verified solvent presence and approximate amount of solvent incorporated by nmr spectra and simply took this into account on analyses. Later we found that careful drying on heating under vacuum would generally remove solvent.
(15) t* here denotes 1:4:1 "triplet," arising from coupling to $^{195}$Pt (abundance 34%).

*Anal.* Calcd for C$_{44}$H$_{38}$NP$_2$PtBr·0.15CHCl$_3$: C, 56.7; H, 4.11; N, 1.50; P, 6.62. Found: C, 56.8; H, 4.23; N, 1.35; P, 6.50.

Ir: same as for the iodide salt above. Pmr: $\tau$ 7.32 (t*, $J_{Pt-H}$ = 12 Hz, CNC$H_3$), $\tau$ 3.55 (m, Pt-C$_6H_5$), $\tau$ 2.53 (m, P-C$_6H_5$).

[PtC$_6$H$_5$(CNCH$_3$){(C$_6$H$_5$)$_3$P}$_2$]Cl: white; 87% yield; mp 234-236°.

*Anal.* Calcd for C$_{44}$H$_{38}$NP$_2$PtCl·0.2CHCl$_3$: C, 59.2; H, 4.29; N, 1.56. Found: C, 59.3; H, 3.83; N, 1.49.

Ir: same as for the iodide salt above except $\nu_{C≡N}$ 2215 (s) cm$^{-1}$. Pmr: $\tau$ 7.28 (t*, $J_{Pt-H}$ = 12 Hz, CNC$H_3$), $\tau$ 3.53 (m, Pt-C$_6H_5$), $\tau$ 2.58 (m, P-C$_6H_5$).

This complex was converted to the hexafluorophosphate salt by a metathetical reaction with NH$_4$PF$_6$ in acetone. The product (96%) gave white needles, mp 226-228°, on recrystallization from chloroform. Its infrared spectrum was identical with that for the chloride except for the PF$_6^-$ absorptions 830 (vs) and 550 (m) cm$^{-1}$.

*Anal.* Calcd for C$_{44}$H$_{38}$NP$_3$PtF$_6$: C, 53.8; H, 3.90; N, 1.43. Found: C, 54.3; H, 3.79; N, 1.38.

[PtCH$_3$(CNCH$_3$){(C$_6$H$_5$)$_2$(CH$_3$)P}$_2$]I: white platelets, recrystallized with difficulty from benzene-hexane; 98% yield; mp 162-165°.

*Anal.* Calcd for C$_{29}$H$_{32}$INP$_2$Pt: C, 44.74; H, 4.14; N, 1.80; P, 7.96. Found: C, 44.30; H, 4.20; N, 1.64; P, 7.13.

Ir: 2221 (s) (C≡N), 1484 (m, sh), 1436 (s), 1180 (w), 1150 (w), 1101 (m), 910 (w), 898 (m), 891 (m), 833 (w), 750 (w, sh), 740 (m, sh), 735 (m), 694 (m, sh), 686 (m), 504 (s), 477 (m), 434 (w), 405 (m) cm$^{-1}$. Pmr: $\tau$ 9.80 (t*, $J_{Pt-H}$ = 60 Hz, $J_{P-H}$ not resolved, Pt-C$H_3$), $\tau$ 7.68 (m, P-C$H_3$), $\tau$ 7.48 (t*, $J_{Pt-H}$ = 12 Hz, CNC$H_3$), $\tau$ 2.50 (m, P-C$_6H_5$).

[PtCH$_3$(CNCH$_3$){(C$_6$H$_5$)$_2$(CH$_3$)P}$_2$]Br: white needles; 82% yield; mp 136-137°.

*Anal.* Calcd for C$_{29}$H$_{32}$BrNP$_2$Pt: C, 46.62; H, 4.41; N, 1.91. Found: C, 46.46; H, 4.24; N, 1.70.

Ir: identical with that of the iodide salt. Pmr: $\tau$ 9.78 (t* of t, $J_{Pt-H}$ = 60 Hz, $J_{P-H}$ = 7.5 Hz, Pt-C$H_3$), $\tau$ 7.66 (m, P-C$H_3$), $\tau$ 7.30 (t*, $J_{Pt-H}$ = 12 Hz, CNC$H_3$), $\tau$ 2.48 (m, P-C$_6H_5$).

An attempt to prepare [PtCH$_3$(CNCH$_3$){(C$_6$H$_5$)$_2$(CH$_3$)P}$_2$]Cl gave a clear oil which could not be crystallized to give a pure product. Attempts to derivatize the oil with NH$_4$PF$_6$ gave a solidified oil after pumping under vacuum for a few hours. No crystalline product could be obtained. Ir (Nujol) showed coordinated isocyanide at 2220 (s) cm$^{-1}$ (C≡N) and PF$_6^-$ at 830 cm$^{-1}$.

[PtCH$_3$(CNCH$_3$){(C$_2$H$_5$)$_3$P}$_2$]I: white precipitate; 96% yield; recrystallized from benzene-ethyl ether; mp 112-113°.

*Anal.* Calcd for C$_{15}$H$_{36}$INP$_2$Pt: C, 29.3; H, 5.91; N, 2.28. Found: C, 28.1; H, 5.79; N, 2.47.

Ir: 2230 (s) (C≡N) and 1416 (s), 1265 (m), 1256 (m), 1235 (w), 1146 (w), 1111 (w), 1030 (vs), 1000 (m), 757 (s), 730 (s), 722 (s), 717 (sh), 710 (sh), 629 (m), 490 (w), 452 (m), 404 (m) cm$^{-1}$. Pmr: $\tau$ 9.68 (t* of t, $J_{Pt-H}$ = 61 Hz, $J_{P-CH_3}$ = 7 Hz, Pt-C$H_3$), $\tau$ 8.83 (pentet, $|^2J_{P-H} + {}^4J_{P-H}|$ = 7.5 Hz, trans P-CH$_2$C$H_3$), $\tau$ 8.0 (m, P-CH$_2$), $\tau$ 6.30 (t*, $J_{Pt-H}$ = 12.5 Hz, CNC$H_3$).

[PtCH$_3$(CNCH$_3$){(C$_2$H$_5$)$_3$P}$_2$]Br: white needles; 49% yield; recrystallized from acetone-ethyl ether, mp 108-109°.

*Anal.* Calcd for C$_{15}$H$_{36}$BrNP$_2$Pt: C, 31.80; H, 6.41; N, 2.47. Found: C, 31.01; H, 6.40; N, 2.28.

Ir: 2220 (s) (C≡N) and 1416 (s), 1255 (m), 1235 (w), 1153 (w), 1112 (w), 1033 (s), 1000 (m), 770 (sh), 756 (s), 737 (s), 727 (s), 707 (w), 642 (w), 630 (m), 532 (w), 458 (m) cm$^{-1}$. The pmr spectrum is identical with that of the iodide.

An attempt to prepare [PtCH$_3$(CNCH$_3$){(C$_2$H$_5$)$_3$P}$_2$]Cl gave a very ether-soluble yellow oil which could not be crystallized but showed the presence of coordinated isocyanide in the ir spectrum.

[PtCH$_3$(CNC$_6$H$_4$Cl){(C$_6$H$_5$)$_2$(CH$_3$)P}$_2$]I: yellow crystals; 90% yield; recrystallized from acetone-hexane; mp 148-149°.

*Anal.* Calcd for C$_{34}$H$_{33}$ClINP$_2$Pt·0.3C$_6$H$_6$: C, 47.98; H, 3.92; N, 1.55. Found: C, 47.67; H, 3.99; N, 1.72.

Ir: 2156 (s) (C≡N) and 1484 (s), 1432 (s), 1405 (w), 1306 (w), 1237 (w), 1143 (w), 1100 (m), 1090 (m), 1026 (w), 1009 (w), 890 (vs), 835 (m), 805 (w), 745 (m), 735 (m), 731 (m), 692 (sh), 687 (m), 673 (sh), 498 (s), 482 (m), 455 (m) cm$^{-1}$. Pmr: $\tau$ 9.63 (t, $J_{Pt-H}$ = 60 Hz, $J_{P-H}$ not resolved, Pt-C$H_3$), $\tau$ 7.52 (s, broad, P-C$H_3$), $\tau$ 3.24 (AB pattern, $J$ = 9 Hz, $J/\Delta\nu$ = 0.24, ClC$_6H_4$NC), $\tau$ 2.62 (benzene), $\tau$ 2.50 (m), P-C$_6H_5$.

[PtCH$_3$(CNC$_6$H$_4$Cl){(C$_6$H$_5$)$_2$(CH$_3$)P}$_2$]Br: colorless prisms; 84% yield; recrystallized from benzene-hexane; mp 134-136°.

*Anal.* Calcd for C$_{34}$H$_{33}$BrClNP$_2$Pt: C, 49.32; H, 4.02; N, 1.69; P, 7.48. Found: C, 48.73; H, 3.96; N, 1.72; P, 7.13.

Ir: 2162 (s) (C≡N), other bands identical with those for the iodide. Pmr: $\tau$ 9.62 (t*, $J_{Pt-H}$ = 60 Hz, Pt-C$H_3$), $\tau$ 7.55 (s, broad, P-C$H_3$), $\tau$ 3.17 (AB pattern, $J$ = 9 Hz, $J/\Delta\nu$ = 0.23, ClC$_6H_4$NC), $\tau$

2.53 (m), $\tau$ 2.35 (m), P-C$_6$H$_5$. At 100 MHz and below 0°, the broad singlet at $\tau$ 7.55 can be resolved into a t* of t ($J_{Pt-H}$ = 34 Hz, $J_{P-H}$ = 4 Hz), indicating mutually trans phosphine ligands.

Attempts to isolate the chloride analog gave oils which would not crystallize but ir data showed a coordinated isocyanide to be present (ir (CHCl$_3$): 2125 (s) cm$^{-1}$). However, derivatization with NH$_4$PF$_6$ gave the following compound.

[PtCH$_3$(CNC$_6$H$_4$Cl){(C$_6$H$_5$)$_2$(CH$_3$)P}$_2$]PF$_6$: white crystals; 60% yield; recrystallized from acetone-ether; mp 108-110°.

*Anal.* Calcd for C$_{34}$H$_{33}$ClF$_6$NP$_3$Pt·0.8CH$_3$COCH$_3$: C, 46.6; H, 4.05; N, 1.49; P, 9.89. Found: C, 46.4; H, 4.01; N, 1.04; P, 9.37. Acetone could not be driven off by heating at 65° for 2 days under vacuum.

Ir: 2178 (s) (C≡N), 1483 (s), 1433, 1308 (w), 1291 (w), 1175 (w), 1100 (m), 1090 (m), 1010 (w), 992 (w), 893 (s), 870 (m), 830 (vs, br), 730 (s), 695 (sh), 685 (s), 548 (s), 498 (s), 478 (m), 443 (m) cm$^{-1}$. Pmr: $\tau$ 9.64 (t* of t, $J_{Pt-H}$ = 60 Hz, $J_{P-H}$ = 8.5 Hz, Pt-CH$_3$), $\tau$ 8.73 (acetone), $\tau$ 7.94 (t* of t, $J_{Pt-H}$ = 15 Hz, $J_{P-H}$ = 3.5 Hz, P-CH$_3$), $\tau$ 3.23 (AB pattern, $J/\Delta\nu$ = 0.22, ClC$_6$H$_4$NC), $\tau$ 2.50 (m, P-C$_6$H$_5$).

[PtCH$_3$(CNC$_6$H$_4$Cl){(C$_2$H$_5$)$_3$P}$_2$]I: colorless plates; 52% yield; mp 118-120°.

*Anal.* Calcd for C$_{20}$H$_{37}$ClINP$_2$Pt: C, 33.79; H, 5.25; N, 1.97; P, 8.71. Found: C, 33.78; H, 5.21; N, 2.15; P, 8.70.

Ir: 2158 (s) (C≡N) and 1485 (m), 1412 (m), 1403 (m), 1112 (w), 1098 (sh), 1090 (s), 1035 (s), 1005 (m), 840 (m), 800 (w), 760 (sh), 748 (s), 733 (s), 726 (s), 703 (w), 630 (w), 510 (w), 495 (w), 405 (m) cm$^{-1}$. Pmr: $\tau$ 9.51 (t* of t, $J_{Pt-H}$ = 62 Hz; $J_{P-H}$ = 6.5 Hz, Pt-CH$_3$), $\tau$ 8.78 (pentet, |$^2J_{P-H}$ + $^4J_{P-H}$| = 7.5 Hz, trans P-CH$_2$CH$_3$), $\tau$ 7.90 (m, P-CH$_2$), $\tau$ 2.35 (AB pattern, $J/\Delta\nu$ = 0.89, ClC$_6$H$_4$NC).

[PtCH$_3$(CNC$_6$H$_4$Cl){(C$_2$H$_5$)$_3$P}$_2$]Br: white prisms; 22% yield; recrystallized from benzene-hexane; mp 101-102°.

*Anal.* Calcd for C$_{20}$H$_{37}$BrClNP$_2$Pt: C, 36.18; H, 5.62; N, 2.11; P, 9.33. Found: C, 35.71; H, 5.59; N, 2.41; P, 9.55.

The ir and pmr spectra were identical with spectra of the iodide. Attempts to isolate the chloride analog gave only uncrystallizable oils. Derivatization with NH$_4$PF$_6$ in the usual way gave [PtCH$_3$(CNC$_6$H$_4$Cl){(C$_2$H$_5$)$_3$P}$_2$]PF$_6$: 85% yield; recrystallized from 1:1 methanol-ethyl ether and hexane; mp 150-151°.

*Anal.* Calcd for C$_{20}$H$_{37}$ClF$_6$NP$_3$Pt: C, 32.95; H, 5.12; N, 1.93. Found: C, 32.84; H, 5.13; N, 2.03.

Ir: 2162 (s) (C≡N) and 1484 (s), 1413 (w), 1409 (w), 1183 (w), 1153 (w), 1120 (w), 1097 (m), 1039 (m), 1015 (w), 878 (w), 835 (vs, br), 761 (sh), 756 (s), 737 (m), 731 (m), 630 (w), 548 (m), 506 (m), 495 (m), 402 (m) cm$^{-1}$. Pmr: $\tau$ 9.57 (t* of t, $J_{Pt-H}$ = 60 Hz, $J_{P-H}$ = 7.5 Hz, Pt-CH$_3$), $\tau$ 8.84 (pentet, |$^2J_{P-H}$ + $^4J_{P-H}$| = 7.5 Hz, trans P-CH$_2$CH$_3$), $\tau$ 8.00 (m, P-CH$_2$), $\tau$ 3.52 (s, AB pattern collapsed, ClC$_6$H$_4$NC).

Reaction of [PtBr(C$_6$F$_5$){(C$_6$H$_5$)$_3$P}$_2$] with Methyl Isocyanide. To a refluxing solution of *trans*-PtBr(C$_6$F$_5$){(C$_6$H$_5$)$_3$P}$_2$ (1.12 g, 1.16 mmol) in benzene was added methyl isocyanide (0.048 g, 1.2 mmol) in benzene dropwise with stirring. After 1 hr, the solvent was evaporated and the resulting white solid recrystallized from benzene-hexane to give PtCN(C$_6$F$_5$){(C$_6$H$_5$)$_3$P}$_2$ (0.85 g, 83%), mp 305-308°. The reaction between PtBr(C$_6$F$_5$){(C$_6$H$_5$)$_3$P}$_2$ and KCN in methanol gave the same compound.

*Anal.* Calcd for C$_{43}$H$_{30}$NP$_2$PtF$_5$: C, 56.6; H, 3.39; N, 1.54; P, 6.80; mol wt 912. Found: C, 56.9; H, 3.32; N, 1.67; P, 6.66; mol wt 908.

Ir: 2135 (m) (C≡N), 1610 (w), 1590 (w), 1575 (w), 1500 (s), 1480 (m), 1434 (s), 1308 (w), 1183 (w), 1156 (w), 1095 (s), 1055 (w), 1023 (w), 996 (w), 956 (s), 856 (w), 790 (m), 752 (m), 738 (m), 706 (s), 698 (s), 522 (s), 510 (s), 498 (m) cm$^{-1}$.

PtCN(C$_6$F$_5$){(C$_6$H$_5$)$_3$P}$_2$ was recovered quantitatively when this compound was treated with a second equivalent of CH$_3$NC in benzene under reflux.

In an attempt to isolate an isocyanide intermediate in the formation of PtCN(C$_6$F$_5$){(C$_6$H$_5$)$_3$P}$_2$, the above reaction was rerun in benzene at 25° over a 15-min period. The white solid obtained on benzene evaporation was believed to be [PtC$_6$F$_5$(CNCH$_3$){(C$_6$H$_5$)$_3$P}$_2$]Br. Ir: 2240 (m) (C≡N), 1480 (m), 1434 (s), 1308 (w), 1182, 1092 (s), 1057 (m), 1023 (w), 994 (w), 952 (s), 796 (m), 739 (m), 702 (m), 686 (s), 670 (m, sh), 612 (w), 518 (s), 507 (s), 494 (m) cm$^{-1}$. Pmr: $\tau$ 7.16 (s, broad, CNCH$_3$), $\tau$ 2.50 (m, P-C$_6$H$_5$).

Upon recrystallization from chloroform-benzene, however, the isocyanide infrared absorption decreased in intensity. After a second recrystallization the isocyanide absorption had completely disappeared and the infrared spectrum was identical with that of the starting material.

**Isocyanide Insertion Reactions.** Two general procedures are given below.

PtI{C(CH$_3$)=NCH$_3$}{(C$_6$H$_5$)$_3$P}$_2$. **Method A.** This was used primarily in those instances where the ionic intermediate could not be readily isolated in good yield. To a stirred suspension of PtI(CH$_3$){(C$_6$H$_5$)$_3$P}$_2$ (0.80 g, 0.93 mmol) in benzene was added methyl isocyanide (0.04 g, 1.0 mmol) in 15 ml of benzene, the white suspension turning yellow as before. On refluxing for 3 hr, a deep yellow solution formed. The orange oil obtained after evaporation of the solvent was taken up in warm acetonitrile. Cooling at -20° for 12 hr gave the product (0.43 g, 51%) as cubic crystals which could be recrystallized from benzene, mp 193-194°.

*Anal.* Calcd for C$_{39}$H$_{36}$NP$_2$PtI·C$_6$H$_6$: C, 55.2; H, 4.29; N, 1.43; P, 6.33; mol wt 902. Found: C, 55.2; H, 4.08; N, 1.66; P, 6.23; mol wt 880.

Ir: 1621 (s) (C≡N), 1586 (w), 1570 (w), 1477 (s), 1430 (s), 1348 (m), 1306 (w), 1180 (w), 1158 (m), 1139 (m), 1088 (s), 1068 (w), 1024 (w), 994 (m), 900 (m), 746 (s), 740 (s, sh), 695 (s, sh), 686 (s), 677 (s), 570 (w), 516 (s), 508 (s, sh), 493 (s) cm$^{-1}$. Pmr: $\tau$ 8.53 (t*, $J_{Pt-H}$ = 30 Hz, Pt-CCH$_3$), $\tau$ 6.92 (t*, $J_{Pt-H}$ = 13 Hz, Pt-C=NCH$_3$), $\tau$ 2.58 (m), $\tau$ 2.27 (m), P-C$_6$H$_5$).

Evaporation of the acetonitrile filtrate gave a small amount of solid whose infrared spectrum indicated the presence of both terminal -C≡NCH$_3$ and -C≡N but the amount isolated precluded purification and analysis.

**Method B.** The above complex can also be obtained from the ionic intermediate (isolated by the procedure described earlier) on refluxing in benzene for 0.5-2 hr; it can be worked up as described above.

The majority of the other products were isolated in this manner and are listed below.

PtI{C(C$_6$H$_5$)=NCH$_3$}{(C$_6$H$_5$)$_3$P}$_2$: pale yellow crystals; 35% yield; recrystallized from benzene-ethanol; mp 236-238°.

*Anal.* Calcd for C$_{44}$H$_{38}$NP$_2$PtI: C, 54.8; H, 3.84; N, 1.46; P, 6.43; mol wt 964. Found: C, 55.2; H, 3.97; N, 1.52; P, 6.28; mol wt 1030.

Ir: 1597 (sh), 1585 (m) (C≡N), 1570 (m), 1480 (m), 1432 (s), 1295 (w), 1258 (m), 1202 (m), 1180 (m), 1158 (w), 1090 (s), 1018 (m), 992 (m), 880 (m), 763 (w), 737 (m), 698 (m, sh), 682 (s), 643 (w), 607 (m), 516 (s), 505 (s), 493 (m) cm$^{-1}$. Pmr: $\tau$ 6.73 (t*, $J_{Pt-H}$ = 14 Hz, CNCH$_3$), $\tau$ 3.03 (m, C-C$_6$H$_5$), $\tau$ 2.68 (m, P-C$_6$H$_5$).

PtBr{C(C$_6$H$_5$)=NCH$_3$}{(C$_6$H$_5$)$_3$P}$_2$: white; 80% yield; mp 241-243°.

*Anal.* Calcd for C$_{44}$H$_{38}$NP$_2$PtBr·0.5CHCl$_3$: C, 54.7; H, 3.97; N, 1.43; mol wt 917. Found: C, 55.1; H, 4.22; N, 1.92; mol wt 938.

Ir: spectrum identical with that of the iodide. Pmr: $\tau$ 6.80 (t*, $J_{Pt-H}$ = 14 Hz, CNCH$_3$), $\tau$ 3.03 (m, C-C$_6$H$_5$), $\tau$ 2.64 (m, P-C$_6$H$_5$).

PtCl{C(C$_6$H$_5$)=NCH$_3$}{(C$_6$H$_5$)$_3$P}$_2$: white solid; 86% yield; mp 240-242°.

*Anal.* Calcd for C$_{44}$H$_{38}$NP$_2$PtCl·1.5CHCl$_3$: C, 52.0; H, 3.78; N, 1.33. Found: C, 51.0; H, 3.78; N, 1.91.

Ir: 1595 (sh), 1585 (m) (C≡N), 1572 (m), 1482 (m), 1434 (s), 1295 (w), 1204 (w), 1196 (w), 1092 (s), 1068 (w), 1022 (w), 992 (m), 885 (m), 740 (s), 701 (s), 685 (s), 648 (m), 616 (m), 515 (s), 495 (m) cm$^{-1}$. Pmr: $\tau$ 6.83 (t*, $J_{Pt-H}$ = 14 Hz, CNCH$_3$), $\tau$ 3.14 (m, C-C$_6$H$_5$), $\tau$ 2.67 (m, P-C$_6$H$_5$).

PtI{C(CH$_3$)=NCH$_3$}{(C$_6$H$_5$)$_2$(CH$_3$)P}$_2$: colorless prisms; 55% yield; recrystallized from acetone-ethyl ether; mp 98-100°.

*Anal.* Calcd for C$_{29}$H$_{32}$INP$_2$Pt: C, 44.8; H, 4.15; N, 1.80; P, 7.97; mol wt 778. Found: C, 45.30; H, 4.27; N, 1.81; P, 7.77; mol wt 763.

Ir: 1617 (m, br) (C≡N), 3054 (w), 1484 (m, sh), 1436 (vs), 1310 (w), 1189 (w, sh), 1179 (w), 1148 (w), 1102 (s), 1078 (m), 1025 (w), 995 (w), 890 (vs), 738 (vs), 693 (vs), 500 (s), 478 (m), 440 (m), 411 (m) cm$^{-1}$. Pmr: $\tau$ 8.30 (t*, $J_{Pt-H}$ = 30 Hz, Pt-CCH$_3$), $\tau$ 7.72 (t* of t, $J_{Pt-H}$ = 38 Hz, $J_{P-H}$ = 3.5 Hz, P-CH$_3$), $\tau$ 6.86 (t*, $J_{Pt-H}$ = 14 Hz, Pt-C=NCH$_3$), $\tau$ 2.64 (m), 2.40 (m) (P-C$_6$H$_5$).

PtBr{C(CH$_3$)=NCH$_3$}{(C$_6$H$_5$)$_2$(CH$_3$)P}$_2$: pale yellow prisms; 28% yield; recrystallized from acetone-ethyl ether; mp 93-96°.

*Anal.* Calcd for C$_{29}$H$_{32}$BrNP$_2$Pt: C, 47.61; H, 4.41; N, 1.91; P, 8.47; mol wt 732. Found: C, 48.12; H, 4.70; N, 1.82; P, 8.49; mol wt 746.

Ir: identical with that of the iodide. Pmr: $\tau$ 8.29 (t*, $J_{Pt-H}$ = 30 Hz, Pt-CCH$_3$), $\tau$ 7.84 (t* of t, $J_{Pt-H}$ = 34 Hz, $J_{P-H}$ = 3.5 Hz, P-CH$_3$), $\tau$ 6.93 (t*, $J_{Pt-H}$ = 14 Hz, P-C=NCH$_3$), $\tau$ 2.60 (s), 2.33 (m) (P-C$_6$H$_5$).

PtI{C(CH$_3$)=NC$_6$H$_4$Cl}{(C$_6$H$_5$)$_2$(CH$_3$)P}$_2$: pale yellow prisms; 63% yield; recrystallized from acetonitrile; mp 132-135°.

*Anal.* Calcd for C$_{34}$H$_{33}$ClINP$_2$Pt: C, 46.67; H, 3.80; N, 1.60; P,

7.08; mol wt 875. Found: C, 46.59; H, 3.78; N, 1.84; P, 6.98; mol wt 855.

Ir: 1592 (m), 1561 (vs, br) (C=N); 3090 (w), 3065 (m), 1484 (s), 1478 (m), 1439 (m, sh), 1437 (vs), 1424 (m), 1352 (w), 1317 (w), 1302 (vw), 1290 (w), 1214 (w), 1184 (w, sh), 1182 (w), 1163 (w), 1152 (w), 1110 (m, sh), 1100 (vs), 1089 (m), 1029 (w), 1010 (w), 1000 (w), 897 (vs), 886 (s), 850 (w, sh), 839 (m), 818 (w), 800 (w), 748 (s), 731 (s), 694 (s), 683 (m, sh), 677 (m), 638 (w), 618 (w), 550 (w), 542 (m), 505 (vs), 486 (m), 479 (m), 449 (m), 435 (w), 422 (m) cm$^{-1}$. Pmr: $\tau$ 8.04 (t*, $J_{Pt-H}$ = 30 Hz, Pt-CC$H_3$), $\tau$ 7.80 (t* of t, $J_{Pt-H}$ = 36 Hz, $J_{P-H}$ = 3 Hz, P-C$H_3$), $\tau$ 2.60 (AB pattern, $J$ = 9.5 Hz, $J/\Delta\nu$ = 0.18, ClC$_6$H$_4$NC), $\tau$ 2.63 (s), $\tau$ 2.48 (m), P-C$_6$H$_5$.

**PtBr{C(CH$_3$)=NC$_6$H$_4$Cl}{(C$_6$H$_5$)$_2$(CH$_3$)P}$_2$:** pale yellow prisms; 85% yield; recrystallized from acetonitrile; mp 172-173°.

*Anal.* Calcd for C$_{34}$H$_{33}$BrClNP$_2$Pt: C, 49.32; H, 4.02; N, 1.69; P, 7.48; mol wt 828. Found: C, 48.97; H, 3.97; N, 1.80; P, 7.86; mol wt 791.

Ir: identical with that of the iodide. Pmr: $\tau$ 8.06 (t*, $J_{Pt-H}$ = 30 Hz, Pt-CC$H_3$), $\tau$ 7.91 (t* of t, $J_{Pt-H}$ = 36 Hz, $J_{P-H}$ = 3.5 Hz, P-C$H_3$), $\tau$ 2.72 (AB pattern, $J$ = 9.5 Hz, $J/\Delta\nu$ = 0.20, ClC$_6$H$_4$NC), $\tau$ 2.83 (s), 2.45 (m), P-C$_6$H$_5$.

**PtI{C(CH$_3$)=NC$_6$H$_4$Cl}{(C$_2$H$_5$)$_3$P}$_2$:** colorless plates; 76% yield; recrystallized from benzene-hexane; mp 186-189°.

*Anal.* Calcd for C$_{20}$H$_{37}$ClINP$_2$Pt: C, 33.79; H, 5.25; N, 1.97; P, 8.71; mol wt 710. Found: C, 33.93; H, 5.29; N, 1.93; P, 7.59; mol wt 735.

Ir: 1593 (vs), 1580 (vs), 1572 (vs), 1557 (w, sh) (all C=N); 1475 (vs), 1455 (vs), 1422 (m), 1411 (m), 1348 (w), 1257 (w), 1213 (m), 1182 (w), 1160 (w), 1111 (m), 1101 (m), 1094 (s), 1089 (s), 1038 (vs), 1010 (w), 838 (vs), 818 (w), 805 (w), 767 (vs), 761 (vs), 727 (vs), 707 (m), 674 (s), 631 (w, sh), 624 (m), 535 (w), 495 (m), 481 (w) cm$^{-1}$. Pmr: $\tau$ 8.97 (pentet, $|^2J_{P-H} + {}^4J_{P-H}|$ = 7.5 Hz, trans P-CH$_2$C$H_3$), $\tau$ 8.10 (m, P-C$H_2$), $\tau$ 7.54 (t*, $J_{Pt-H}$ = 32 Hz, Pt-CC$H_3$), $\tau$ 2.56 (AB pattern, $J$ = 9 Hz, $J/\Delta\nu$ = 0.25, ClC$_6$H$_4$NC).

**PtBr{C(CH$_3$)=NC$_6$H$_4$Cl}{(C$_2$H$_5$)$_3$P}$_2$:** colorless plates; 78% yield; recrystallized from benzene-hexane; mp 175-176°.

*Anal.* Calcd for C$_{20}$H$_{37}$BrClNP$_2$Pt: C, 36.18; H, 5.62; N, 2.11; mol wt 664. Found: C, 37.00; H, 5.75; N, 2.30; mol wt 633.

Ir and pmr spectra: identical with spectra for the iodide.

**Rearrangement of [PtCH$_3$(CNCH$_3$){(C$_2$H$_5$)$_3$P}$_2$]I.** Dry benzene (20 ml) was added to [PtCH$_3$(CNCH$_3$){(C$_2$H$_5$)$_3$P}$_2$]I (0.50 g, 0.8 mmol) giving a suspension which was refluxed for 1 hr. The resulting solution gave a white solid on evaporation of the solvent. Recrystallization from acetone-ethyl ether-hexane gave the following compound.

**[PtI{C(CH$_3$)=N(CH$_2$)$_2$}{(C$_2$H$_5$)$_3$P}$_2$]I:** 0.08 g, 13% yield; fine white needles, mp 196-198°.

*Anal.* Calcd for C$_{16}$H$_{39}$I$_2$NP$_2$Pt: C, 25.41; H, 5.20; N, 1.85; I, 33.56. Found: C, 25.72; H, 5.68; N, 1.83; I, 33.37.

Ir: 1590 (m, br) (C=N); 1419 (m, sh), 1415 (m), 1352 (m), 1253 (s), 1242 (s), 1179 (m), 1147 (w), 1112 (w), 1087 (m), 1034 (vs), 1010 (m), 987 (w), 970 (w), 766 (vs, sh), 758 (vs), 732 (s), 725 (s), 710 (w), 675 (w), 631 (w), 591 (w), 546 (w, br), 450 (w), 413 (w) cm$^{-1}$. Pmr: $\tau$ 8.85 (pentet, $|^2J_{P-H} + {}^4J_{P-H}|$ = 8 Hz, trans PCH$_2$C$H_3$), $\tau$ 7.90 (m, P-C$H_2$C$H_3$), $\tau$ 6.85 (t*, $J_{Pt-H}$ = 36 Hz, Pt-CC$H_3$), $\tau$ 6.20 (t*, $J_{Pt-H}$ = 4.5 Hz, Pt-C=N-C$H_3$), $\tau$ 5.95 (t*, $J_{Pt-H}$ = 5.5 Hz, Pt-C=N-C$H_3$).

The filtrate, evaporated down to an oil and crystallized from acetone-hexane gave a mixture (0.14 g) of the following two products.

**PtCN(CH$_3$){(C$_2$H$_5$)$_3$P}$_2$:** colorless needles (0.04 g, 10%), obtained by fractional recrystallization from ethyl ether-hexane; mp 84-86°.

*Anal.* Calcd for C$_{16}$H$_{33}$NP$_2$Pt: C, 35.59; H, 7.04; N, 2.96; mol wt 472. Found: C, 35.23; H, 7.03; N, 3.05; mol wt 466.

Ir: 2110 (m) (C≡N); 1412 (m), 1250 (m), 1238 (w), 1178 (vw), 1148 (vw), 1113 (vw), 1035 (vs), 1028 (vw), 1027 (vs, sh), 1011 (m), 1003 (m), 761 (vs), 727 (vs), 710 (m), 685 (vw), 631 (m), 546 (vw), 530 (vw), 445 (m), 408 (m) cm$^{-1}$. Pmr: $\tau$ 9.58 (t* of t, $J_{Pt-H}$ = 50 Hz, $J_{P-H}$ = 6 Hz, Pt-C$H_3$), $\tau$ 8.87 (pentet, $|^2J_{P-H} + {}^4J_{P-H}|$ = 8 Hz, trans PCH$_2$C$H_3$), $\tau$ 8.07 (m, P-C$H_2$).

**PtI{C(CH$_3$)=NCH$_3$}{(C$_2$H$_5$)$_3$P}$_2$:** colorless plates (0.07 g, 14%), obtained by increasing the hexane concentration; melting point data: softens 137°, melts 141-143°.

*Anal.* Calcd for C$_{15}$H$_{36}$INP$_2$Pt: C, 29.4; H, 5.92; N, 2.28; mol wt 614. Found: C, 29.31; H, 6.05; N, 2.27; mol wt 590.

Ir: 1615 (m, sh), 1613 (s) (C=N); 1424 (m), 1411 (m), 1342 (w), 1255 (w), 1242 (w), 1179 (w), 1148 (w), 1129 (w), 1113 (w), 1078 (m), 1030 (is), 1015 (w), 1001 (w), 902 (w), 757 (s), 725 (m), 720 (m, sh), 708 (w), 680 (w), 628 (w), 571 (w), 520 (w), 410 (m) cm$^{-1}$. Pmr: $\tau$ 8.85 (pentet, $|^2J_{P-H} + {}^4J_{P-H}|$ = 8 Hz, trans PCH$_2$-

C$H_3$), $\tau$ 8.04 (m, P-C$H_2$CH$_3$), $\tau$ 7.80 (t*, $J_{Pt-H}$ = 34 Hz, Pt-CC$H_3$), $\tau$ 6.73 (t*, $J_{Pt-H}$ = 7 Hz, Pt-C=NC$H_3$).

**Rearrangement of [PtCH$_3$(CNCH$_3$){(C$_2$H$_5$)$_3$P}$_2$]Br.** The reaction of PtBr(CH$_3$){(C$_2$H$_5$)$_3$P}$_2$ (0.75 g, 1.43 mmol) and methyl isocyanide (1.5 mmol) in refluxing benzene gave initially the ionic intermediate above (verified by ir); after refluxing for 24 hr and removal of the solvent, one obtains an oil which crystallized from ethyl ether-hexane to give the product PtCN(CH$_3$){(C$_2$H$_5$)$_3$P}$_2$ (0.16 g, 24%) as colorless needles, mp 84-86°. Other products, particularly PtBr{C(CH$_3$)=NCH$_3$}{(C$_2$H$_5$)$_3$P}$_2$, were not observed, by ir monitoring.

**Preparation of [PtI{C(CH$_3$)=N(CH$_3$)$_2$}{(C$_6$H$_5$)$_3$P}$_2$]I.** The formation of the analogous triethylphosphine compound above could be rationalized by assuming that methyl iodide had alkylated the imino group of the expected insertion product. We attempted to form this product from methyl iodide and PtI{C(CH$_3$)=NCH$_3$}-{(C$_6$H$_5$)$_3$P}$_2$ to see if this suggestion was reasonable.

To a stirred solution of PtI{C(CH$_3$)=NCH$_3$}{(C$_6$H$_5$)$_3$P}$_2$ (0.25 g, 0.28 mmol) in benzene (10 ml) was added methyl iodide (0.02 ml, 0.32 mmol); a precipitate formed immediately. After an additional 20 min of stirring the mixture was filtered giving the product (0.27 g, 92%) which recrystallized from methanol-ethyl ether-hexane as colorless needles, mp 224-229°.

*Anal.* Calcd for C$_{40}$H$_{39}$I$_2$NP$_2$Pt: C, 45.04; H, 3.76; N, 1.34; I, 24.30. Found: C, 44.13; H, 3.86; N, 1.27; I, 23.14.

Ir: 1594 (m, br) (C=N); 3054 (m), 1478 (s), 1436 (s, sh), 1432 (vs), 1400 (w), 1349 (w), 1309 (w), 1246 (w), 1176 (m), 1156 (w), 1090 (vs), 1068 (w), 1022 (w), 994 (m), 745 (m, sh), 736 (m), 699 (s), 690 (s, sh), 686 (vs), 609 (w), 518 (vs), 511 (w), 493 (s), 459 (w), 429 (w), 419 (w) cm$^{-1}$. Pmr: $\tau$ 8.40 (t*, $J_{Pt-H}$ = 33 Hz, Pt-CC$H_3$), $\tau$ 7.48 (t*, $J_{Pt-H}$ = 10 Hz, Pt-C=N-C$H_3$), $\tau$ 6.33 (t*, $J_{Pt-H}$ = 11 Hz, Pt-C=N-C$H_3$), $\tau$ 2.38 (m, P-C$_6$H$_5$).

**Reaction of PtI{C(C$_6$H$_5$)=NCH$_3$}{(C$_6$H$_5$)$_3$P}$_2$ with NH$_4$PF$_6$.** A solution of NH$_4$PF$_6$ (0.03 g, 0.18 mmol) in acetone was added to PtI{C(C$_6$H$_5$)=NCH$_3$}{(C$_6$H$_5$)$_3$P}$_2$ (0.19 g, 0.2 mmol) in 1:1 chloroform-acetone solution. The sharp odor of ammonia was detected briefly immediately after the addition. After evaporation of the solvent, thorough leaching of the white residue with water, and subsequent drying, the white solid was recrystallized from acetonitrile-ethyl ether to give [PtI{C(C$_6$H$_5$)=NHCH$_3$}{(C$_6$H$_5$)$_3$P}$_2$]PF$_6$ (0.175 g, 88%), mp 280-282° dec.

*Anal.* Calcd for C$_{44}$H$_{39}$NP$_3$PtIF$_6$: C, 47.6; H, 3.54; N, 1.26. Found: C, 47.8; H, 3.72; N, 1.20.

Ir: 1592 (s) (C=N); 3320 (m) ($\nu_{N-H}$), 1480 (s), 1434 (s), 1227 (w), 1182 (w), 1090 (s), 996 (m), 837 (vs), 752 (m, sh), 738 (m), 702 (s), 690 (s), 554 (s), 520 (s), 512 (s), 494 (m) cm$^{-1}$. Pmr (CD$_3$CN): $\tau$ 6.80 (t*, $J_{Pt-C=NCH_3}$ = 12 Hz, CNC$H_3$), $\tau$ 2.50 (m, all phenyl groups together). NH resonance not located.

A solution of 0.08 g of the above protonated compound was dissolved in 10 ml of acetonitrile. To this was added 0.1 g of Na$_2$CO$_3$ dissolved in 3 ml of water and 10 ml of acetonitrile and the resulting mixture was shaken for 5 min at 25°. A white solid precipitated. The solvent was evaporated and the white residue was extracted with chloroform. The chloroform filtrate was evaporated and the resultant solid recrystallized from benzene-ethanol. The infrared spectrum of this complex was identical with that of PtI{C(C$_6$H$_5$)=NCH$_3$}-{(C$_6$H$_5$)$_3$P}$_2$ (70% yield).

**Reaction of *trans*-PtX{C(C$_6$H$_5$)=NCH$_3$}{(C$_6$H$_5$)$_3$P}$_2$ (X = I, Br) with CH$_3$NC.** To a suspension of PtI{C(C$_6$H$_5$)=NCH$_3$}{(C$_6$H$_5$)$_3$P}$_2$ (0.512 g, 0.53 mmol) in 15 ml of benzene was added a solution of CH$_3$NC (0.024 g, 0.6 mmol) in benzene. The suspension rapidly dissolved to a pale yellow solution. Following evaporation of the solvent and drying *in vacuo*, the yellow residue was recrystallized from chloroform-ethyl ether to give [PtCNCH$_3${C(C$_6$H$_5$)=NCH$_3$}-{(C$_6$H$_5$)$_3$P}$_2$]I·1.5CHCl$_3$ (0.50 g, 94%) as pale yellow crystals; melting point data: melts 120-125°, resolidifies 130-140°, remelts 171-174°.

*Anal.* Calcd for C$_{46}$H$_{41}$N$_2$P$_2$PtI·1.5CHCl$_3$: C, 46.9; H, 3.70; N, 2.42. Found: C, 46.6; H, 3.52; N, 2.41.

Ir: 2230 (s) (C≡N); 1597 (sh), 1585 (m) (C=N); 1570 (m), 1477 (s), 1432 (s), 1300 (w), 1237 (m), 1208 (m), 1180 (w), 1160 (w), 1093 (s), 1070 (w), 1018 (w), 993 (m), 947 (w), 886 (w), 744 (s), 703 (s), 687 (s), 655 (m), 612 (m), 515 (s), 498 (s) cm$^{-1}$. Pmr: $\tau$ 7.25 (t*, $J_{Pt-H}$ = 10 Hz, CNC$H_3$), $\tau$ 6.90 (t*, $J_{Pt-C=NCH_3}$ = 13 Hz, Pt-C=NC$H_3$), $\tau$ 2.50 (m, all phenyl groups).

Addition of methyl isocyanide to the corresponding bromide gave **[Pt(CNCH$_3$){C(C$_6$H$_5$)=NCH$_3$}{(C$_6$H$_5$)$_3$P}$_2$]Br·1.0CHCl$_3$:** 84% yield; mp 223-225°; pale yellow crystals from chloroform-ethyl ether.

*Anal.* Calcd for C$_{46}$H$_{41}$N$_2$P$_2$PtBr·1.0CHCl$_3$: C, 52.3; H, 4.00; N, 2.60; P, 5.74. Found: C, 52.0; H, 3.92; N, 3.09; P, 5.60.

Ir: identical with the spectrum of the iodide. Pmr: $\tau$ 7.21 (t*, $J_{Pt-H}$ = 11 Hz, Pt-CNC$H_3$), $\tau$ 6.87 (t*, $J_{Pt-H}$ = 12 Hz, Pt-C=NC$H_3$), $\tau$ 2.51 (m, all phenyl groups).

The above iodide compound was heated in benzene under reflux for 5 hr but infrared spectra of aliquots taken during this period showed no change. A small solid sample was then heated under nitrogen to 150° for 15 min. The resulting sticky brown mass was dissolved in chloroform and filtered. Ethyl ether was added to cloudiness and the solution was cooled to yield a small amount of amorphous white solid. Recrystallization from acetonitrile-ethyl ether gave a cleaner product. The infrared spectrum showed a weak band at 2130 cm$^{-1}$ which indicates probable formation of Pt(CN)-{C(C$_6$H$_5$)=NCH$_3$}{(C$_6$H$_5$)$_3$P}$_2$ although there was not enough of this product for an analysis.

## Discussion

The interposition of a carbonyl group into a transition metal-carbon $\sigma$ bond is a well-known phenomenon in metal carbonyl chemistry. Mechanistic studies have established that such reactions proceed with migration of the organic group to a coordinated carbonyl. In a number of instances these reactions have been used to practical advantage.

In many instances one sees remarkable similarities between carbon monoxide and organic isocyanides and between metal complexes of these species,[16] so it is not unreasonable to expect analogous insertion reactions of isocyanides with metal-alkyl and -aryl complexes.[3] Much work has already appeared documenting this analogy; indeed insertions of various organic isocyanides into alkyl- or aryl-molybdenum,[6] -iron,[17] -nickel,[5,7] -palladium,[7,8a] and -platinum[1,8b] bonds have now been reported. To date, no careful mechanistic studies have been performed; however, assuming this analogy between carbonyl and isocyanide insertion to be valid, one can postulate that the latter reactions will proceed *via* a complex in which isocyanide and an alkyl or aryl group are simultaneously bonded to the metal. In a reaction of a metal-alkyl or -aryl complex and isocyanide such a species might arise either *via* ligand replacement or by direct coordination to the metal with expansion of the metal coordination number. Subsequently, rearrangement of the complex with alkyl or aryl migration would yield the expected insertion product.
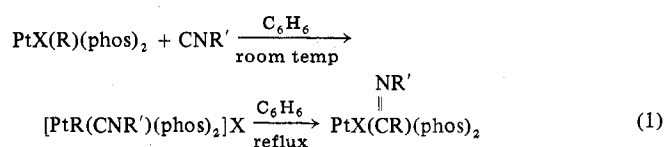
Except for several rather exceptional results which are presented later in this section, the reactions of platinum(II)-methyl and -phenyl complexes with methyl isocyanide and with *p*-chlorophenyl isocyanide proceed in this fashion. When the organoplatinum complex is slurried in benzene and the isocyanide added dropwise at room temperature, a rapid reaction takes place. In the cases involving triphenyl-phosphine complexes the reactions are accompanied by a yellow color. Work-up at this point affords a white or pale yellow crystalline product, which by conventional analyses and spectroscopic data can be identified as a 1:1 adduct of the two reagents. Measurements indicate that these species are electrolytes in solution, and an ionic structure, [PtR-(CNR′)(phos)$_2$]X, may therefore be proposed. One cannot discount the possibility of an equilibrium between four- and five-coordinate species in solution from these data; however such an equilibrium if it exists does seem to favor the four-coordinate formulation.

An extensive compilation of analogous cationic species having noncoordinating anions has appeared.[18] The complex [PtCH$_3$(CNCH$_3$){(C$_6$H$_5$)$_2$(CH$_3$)P}$_2$]$^+$, isolated by us as iodide and bromide salts, was obtained as the SbF$_6$ salt in

this work. In general the spectroscopic data for the three complexes are similar, though small chemical shift differences are evident. These differences might arise from the solvent choice or from the effect of the different anions; with the latter situation there is the implication that some association of ions (to give presumably a five-coordinate uncharged species) could be involved.

The initial intense yellow color of the solution does not appear to be identified with these species. Earlier work in our laboratories[2,19] has indicated that this yellow color is associated with a five-coordinate platinum species, which, in certain instances, may be isolated. In the reactions here, the yellow color is probably associated with the complex [PtR(CNR′)$_2${(C$_6$H$_5$)$_3$P}$_2$]X, formed from the [PtR(CNR′)-{(C$_6$H$_5$)$_3$P}$_2$]X in the presence of excess isocyanide. One would expect these five-coordinate species to lose isocyanide on work-up to give the less intensely colored four-coordinate salts.

The intermediate complexes may be converted to the isocyanide insertion products by returning them to benzene and refluxing the solution or suspension for a period of 1 to several hours. Generally it is worthwhile to monitor the progress of the reactions by infrared spectroscopy, following the decrease of $\nu_{C\equiv N}$ and increase of $\nu_{C=N}$ absorption intensities. As an alternative, one need not actually isolate the intermediate species in these reactions; refluxing of the isocyanide and metal complex in benzene will suffice to convert the reactants directly to the inserted species. The equation below summarizes the data for the reactions carried out here (eq 1).

$$\text{PtX(R)(phos)}_2 + \text{CNR}' \xrightarrow[\text{room temp}]{\text{C}_6\text{H}_6}$$

$$[\text{PtR(CNR}')(\text{phos})_2]\text{X} \xrightarrow[\text{reflux}]{\text{C}_6\text{H}_6} \overset{\overset{\text{NR}'}{\|}}{\text{PtX(CR)(phos)}_2} \quad (1)$$

R = C$_6$H$_5$, phos = (C$_6$H$_5$)$_3$P, R′NC = CH$_3$NC, X = Cl, Br, I
R = CH$_3$, phos = (C$_6$H$_5$)$_3$P, R′NC = CH$_3$NC, X = I
R = CH$_3$, phos = (C$_6$H$_5$)$_2$(CH$_3$)P, R′NC = CH$_3$NC, CNC$_6$H$_4$Cl, X = Br, I
R = CH$_3$, phos = (C$_2$H$_5$)$_3$P, R′NC = CNC$_6$H$_4$Cl, X = Br, I

In this work we attempted to choose a sufficient number of examples to confirm the generality of this reaction; thus we chose to vary the phosphine, isocyanide, and halide ligand groups. In all, ten examples showed a correspondence to this general reaction pattern. Two other examples are cited in the literature.[8b] Difficulty was encountered in isolation of the intermediate complexes derived from the chloride species; although there was spectroscopic evidence for these intermediates they defied attempts at crystallization. We did convert several of these impure species to isolable hexafluorophosphate salts however.

In three instances, these reactions did not follow the anticipated pathway. The complex [PtCH$_3$(CNCH$_3$)-{(C$_2$H$_5$)$_3$P}$_2$]Br, prepared *in situ* from PtBr(CH$_3$){(C$_2$H$_5$)$_3$P}$_2$ and methyl isocyanide (method B), was heated in benzene for 24 hr and only dealkylation of the isocyanide occurred (eq 2), giving the single product PtCN(CH$_3$){(C$_2$H$_5$)$_3$P}$_2$ in poor yield (24%). The reaction was monitored by following infrared absorptions in the usual way; no other products could be identified. We had earlier identified the same type of reaction with other platinum complexes.[2]

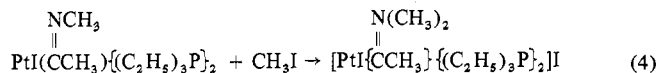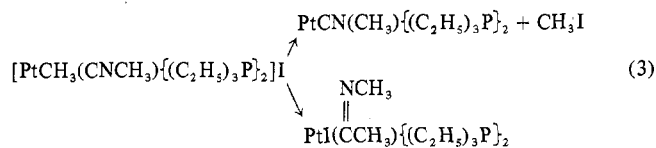(16) P. M. Treichel, *Advan. Organometal. Chem.*, in press.
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(18) H. C. Clark and L. E. Manzer, *Inorg. Chem.*, **11**, 503 (1972).

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$$[PtCH_3(CNCH_3)\{(C_2H_5)_3P\}_2]Br \rightarrow PtCN(CH_3)\{(C_2H_5)_3P\}_2 +$$
$$(24\%)$$
$$CH_3Br \qquad (2)$$
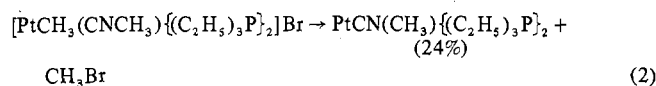
When the complex $[PtCH_3(CNCH_3)\{(C_2H_5)_3P\}_2]I$ was heated in benzene for 1 hr, three products were formed (eq 3, 4).

$$\nearrow PtCN(CH_3)\{(C_2H_5)_3P\}_2 + CH_3I$$
$$[PtCH_3(CNCH_3)\{(C_2H_5)_3P\}_2]I \qquad\qquad (3)$$
$$\searrow\quad \underset{\parallel}{NCH_3}$$
$$PtI(CCH_3)\{(C_2H_5)_3P\}_2$$

$$\underset{\parallel}{NCH_3} \qquad\qquad\qquad \underset{\parallel}{N(CH_3)_2}$$
$$PtI(CCH_3)\{(C_2H_5)_3P\}_2 + CH_3I \rightarrow [PtI\{CCH_3\}\{(C_2H_5)_3P\}_2]I \qquad (4)$$

Apparently dealkylation and insertion occurred at reasonably similar rates. However, the evolved methyl iodide from the dealkylation reaction partially alkylated the nitrogen of the imino group in the inserted product.

Subsequently we carried out the reaction of $PtI\{C(CH_3)=NCH_3\}\{(C_6H_5)_3P\}_2$ and methyl iodide to give $[PtI\{C(CH_3)=N(CH_3)_2\}\{(C_6H_5)_3P\}_2]I$. The result and a previous observation[20] of the reaction of $PtI\{C(CH_3)=NCH_3\}\{(C_6H_5)_3P\}_2$ with ammonium hexafluorophosphate to protonate the imino nitrogen (giving $[PtI\{C(CH_3)=NH(CH_3)\}\{(C_6H_5)_3P\}_2]PF_6$) confirm the substantial basicity of this group.

It is interesting to note that the complexes $[PtCH_3(CN-C_6H_4Cl)\{(C_2H_5)_3P\}_2]X$ (X = Br, I) upon heating in benzene undergo isocyanide insertion only; dealkylation is not observed. One may rationalize the differences between the methyl and *p*-chlorophenyl isocyanide complexes on the basis of relative rates of reaction. It would appear that the rates of insertion (relative to rates of dealkylation) depend on isocyanide ($CNC_6H_4Cl > CNCH_3$) and on halide (I > Br).

The halide ion effect is easy to visualize. The insertion reaction presumably proceeds with nucleophilic attack by halide with simultaneous alkyl migration (Figure 1) and hence the rate would be dependent upon halide nucleophilicity. Such an effect is observed in carbonylation reactions.[21,22] The effect associated with the isocyanide is less easy to rationalize due to lack of definitive evidence on the influence of other ligands. However the result seems in general accord with the postulate that the insertion reaction rate is enhanced by electron-withdrawing ligands;[23] the *p*-chlorophenyl isocyanide is a better electron-withdrawing ligand than methyl isocyanide.

Few data are available on factors influencing rates of insertion reactions with carbonyls, and nothing is yet known about the analogous reactions involving isocyanides. This appears to be a reasonable subject for future study.

A third instance in which anomalous behavior was observed was the reaction of $PtBr(C_6F_5)\{(C_6H_5)_3P\}_2$ and methyl isocyanide. The initial 1:1 adduct $[PtC_6F_5(CNCH_3)\{(C_6H_5)_3P\}_2]Br$ formed was unstable to isocyanide loss, in contrast to other systems described here. Upon heating in benzene dealkylation of the isocyanide occurred giving $PtCN(C_6F_5)\{(C_6H_5)_3P\}_2$. The failure to insert isocyanide in the pentafluorophenyl–platinum bond was not entirely unexpected; no insertion reactions into fluorocarbon–transition metal bonds are yet known.[24]

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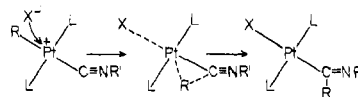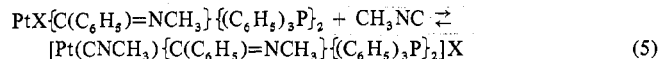(24) P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.*, 1, 146 (1962).

**Figure 1.** Mechanism of the isocyanide insertion reaction.

We found that the insertion products $[PtX\{C(C_6H_5)=NCH_3\}\{(C_6H_5)_3P\}_2$ (X = Br, I) coordinate with additional isocyanide (eq 5), giving another ionic intermediate. How-

$$PtX\{C(C_6H_5)=NCH_3\}\{(C_6H_5)_3P\}_2 + CH_3NC \rightleftarrows$$
$$[Pt(CNCH_3)\{C(C_6H_5)=NCH_3\}\{(C_6H_5)_3P\}_2]X \qquad (5)$$

ever this species does not rearrange with insertion of the additional isocyanide into the metal–carbon bond. The reluctance toward further insertion contrasts with the observed multiple insertions[7,8a] of isocyanides in complexes of nickel and palladium; it is in accord with the lower reactivity of platinum however.

Invariably both the ionic intermediate and the resulting insertion product were found to have trans phosphine groups. Thus the methyl group bonded to platinum in the ionic intermediates appears in the pmr spectrum as a 1:2:1 triplet pattern representing coupling to two phosphorus atoms which appear equivalent through virtual coupling; each absorption was in turn split into a 1:4:1 pattern by coupling to $^{195}Pt$ (spin $^1/_2$, 34% abundance). In addition the diphenylmethylphosphine complexes (for both intermediate ionic and final products) showed the phosphine methyl resonance as a triplet due to virtual coupling between phosphorus atoms, a result ordinarily interpreted for platinum(II) complexes in terms of a trans configuration.[25] The spectrum of the methylene protons for the triethylphosphineplatinum(II) complexes studied is also in accord with this configuration.[26]

When we initiated our work on isocyanide insertion reactions with platinum(II)–methyl and –phenyl complexes, we had as a background the carbonylation work on analogous complexes performed by Booth and Chatt[27] several years earlier. These workers had shown that it was possible to carbonylate various $PtX(R)\{(C_2H_5)_3P\}_2$ species (R = $CH_3$, X = Cl, Br; R = $C_2H_5$, X = I; R = $C_6H_5$, X = Cl, I) under relatively severe conditions utilizing a temperature of 90° and 80 atm of CO pressure; qualitatively these reactions were much less facile than analogous palladium complex reactions, a result attributed to the lesser tendency of platinum to expand its coordination number to 5. Subsequently, there is a report of the carbonylation of $PtCl(CH_3)\{(C_6H_5)(CH_3)_2P\}_2$ at 80° and 5 atm of CO pressure.[10] No mention is made about the possible intermediates of this reaction either, although in the same paper five-coordinate intermediates in the analogous insertion reactions of tetrafluoroethylene and hexafluorobutyne are characterized.

It is clear from our data, however, that the intermediate in the isocyanide insertion reaction is the four-coordinate species. If one is strongly in support of the analogy between this reaction and the carbonylation reaction, then it would be attractive to assume that in the latter reaction the intermediates are the ionic $[PtR(CO)(PR_3)_2]X$ rather than $PtX(R)(CO)(PR_3)_2$ complexes. Perhaps effort should be devoted to the synthesis of the former species. They would no doubt be more unstable than the analogous complexes prepared here, however, since carbon monoxide is an even more effective ligand for electron withdrawal.

Parenthetically, mention should also be made concerning a

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Square-Planar Ni(II) and Cu(II) Complexes

*Inorganic Chemistry, Vol. 12, No. 7, 1973* **1477**

recent paper by Glyde and Mawby.[28] These workers obtained kinetic data for the reaction of $PtCl(C_2H_5)(CO)\{(C_6H_5)_3As\}$ with triphenylarsine, giving $PtCl(COC_2H_5)\{(C_6H_5)_3As\}_2$. From these data they argue for a three-coordinate intermediate, $PtCl(COC_2H_5)\{(C_6H_5)_3As\}$, in the reaction which then adds additional arsine to give the product. In addition, they observed that there is no evidence to support the formation of a 1:1 adduct of initial complex and added ligand. Such an adduct, if isolated, would have been identical to the intermediates proposed in the carbonylation and isocyanide insertion experiments; this would seem to be in contradiction to our conclusions. We are not dismayed by this difference, however, which in a sense may be accommodated by a consideration of the equilibrium reaction

$$PtX(R)L_2 + L' \rightleftarrows [PtR(L')L_2]X \qquad (6)$$

We know[2] that for systems where $L'$ is an isocyanide these equilibria appear strongly to favor the ionic product. However isocyanides appear to be quite unique; it seems reasonable that the complex $[PtCH_3(CO)\{(C_6H_5)_3As\}_2]Cl$ (the other alternative intermediate in the Glyde–Mawby reaction) would be unstable with respect to the reactants. Hence the equilibrium would lie far to the left, ruling out this species as a reasonable intermediate.

**Registry No.** $PtI(CH_3)\{(C_6H_5)_3P\}_2$, 28850-19-3; *trans*-$[PtCH_3(CH_3NC)\{(C_6H_5)_3P\}_2]I$, 27859-00-3; $PtCl(CH_3)\{(C_6H_5)_3P\}_2$, 28850-21-7; $[PtC_6H_5(CNCH_3)\{(C_6H_5)_3P\}_2]I$, 27710-54-9; $[PtC_6H_5(CNCH_3)\{(C_6H_5)_3P\}_2]Br$, 27710-51-6; $[PtC_6H_5(CNCH_3)\{(C_6H_5)_3P\}_2]Cl$, 27710-53-8; $[PtC_6H_5(CNCH_3)\{(C_6H_5)_3P\}_2]PF_6$, 39531-94-7; $[PtCH_3(CNCH_3)\{(C_6H_5)_2(CH_3)P\}_2]I$, 39612-69-6; $[PtCH_3(CNCH_3)\{(C_6H_5)_2(CH_3)P\}_2]Br$, 39531-95-8; $[PtCH_3(CNCH_3)\{(C_2H_5)_3P\}_2]I$, 39531-96-9; $[PtCH_3(CNCH_3)\{(C_2H_5)_3P\}_2]Br$, 39531-97-0; $[PtCH_3(CNC_6H_4Cl)\{(C_6H_5)_2(CH_3)P\}_2]I$, 39531-98-1; $[PtCH_3(CNC_6H_4Cl)\{(C_6H_5)_2(CH_3)P\}_2]Br$, 39531-99-2; $[PtCH_3(CNC_6H_4Cl)\{(C_6H_5)_2(CH_3)P\}_2]PF_6$, 39532-00-8; $[PtCH_3(CNC_6H_4Cl)\{(C_2H_5)_3P\}_2]I$, 39532-01-9; $[PtCH_3(CNC_6H_4Cl)\{(C_2H_5)_3P\}_2]Br$, 39532-02-0; $[PtCH_3(CNC_6H_4Cl)\{(C_2H_5)_3P\}_2]PF_6$, 39532-03-1; $[PtBr(C_6F_5)\{(C_6H_5)_3P\}_2]$, 33915-56-9; $PtCN(C_6F_5)\{(C_6H_5)_3P\}_2$, 27658-81-7; $[PtC_6F_5(CNCH_3)\{(C_6H_5)_3P\}_2]Br$, 27658-80-6; $PtI\{C(CH_3)=NCH_3\}\{(C_6H_5)_3P\}_2$, 27859-01-4; $PtI\{C(C_6H_5)=NCH_3\}\{(C_6H_5)_3P\}_2$, 27710-50-5; $PtBr\{C(C_6H_5)=NCH_3\}\{(C_6H_5)_3P\}_2$, 27710-52-7; $PtCl\{C(C_6H_5)=NCH_3\}\{(C_6H_5)_3P\}_2$, 27858-99-7; $PtI\{C(CH_3)=NCH_3\}\{(C_6H_5)_2(CH_3)P\}_2$, 39532-10-0; $PtBr\{C(CH_3)=NCH_3\}\{(C_6H_5)_2(CH_3)P\}_2$, 39531-83-4; $PtI\{C(CH_3)=NC_6H_4Cl\}\{(C_6H_5)_2(CH_3)P\}_2$, 39531-84-5; $PtBr\{C(CH_3)=NC_6H_4Cl\}\{(C_6H_5)_2(CH_3)P\}_2$, 39531-85-6; $PtI\{C(CH_3)=NC_6H_4Cl\}\{(C_2H_5)_3P\}_2$, 39531-86-7; $PtBr\{C(CH_3)=NC_6H_4Cl\}\{(C_2H_5)_3P\}_2$, 39531-87-8; $PtI\{C(CH_3)=N(CH_3)_2\}\{(C_2H_5)_3P\}_2]I$, 39532-12-2; $PtCN(CH_3)\{(C_2H_5)_3P\}_2$, 22289-45-8; $PtI\{C(CH_3)=NCH_3\}\{(C_2H_5)_3P\}_2$, 39531-89-0; $PtI\{C(CH_3)=N(CH_3)_2\}\{(C_6H_5)_3P\}_2]I$, 39532-13-3; $[PtI\{C(C_6H_5)=NHCH_3\}\{(C_6H_5)_3P\}_2]PF_6$, 39708-57-1; $[PtCNCH_3\{C(C_6H_5)=NCH_3\}\{(C_6H_5)_3P\}_2]I\cdot^3/_2CHCl_3$, 39531-90-3; $[Pt(CNCH_3)\{C(C_6H_5)=NCH_3\}\{(C_6H_5)_3P\}_2]Br\cdot CHCl_3$, 39531-91-4.

**Acknowledgment.** We are pleased to acknowledge support from the National Science Foundation (GP-17,207) and from the University of Wisconsin Graduate School for this work.

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# Square-Planar Nickel(II) and Copper(II) Complexes Containing 14- and 15-Membered Tetraaza Macrocyclic Ligands

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The synthesis of nickel(II) and copper(II) complexes with uninegative and neutral macrocyclic ligands derived from acetylacetone and various linear tetramines has been studied in order to determine the scope of the cyclization reaction and to study the effect of ring size on the acidity of the coordinated neutral ligands. Both nickel(II) and copper(II) complexes containing 14-membered rings have been prepared in both forms I and II; whereas, complexes with a 15-membered ring have been isolated only for nickel(II) and only in form II. No copper(II) complexes with 15-membered rings nor nickel(II) or copper(II) complexes with 16-membered rings have been prepared by these techniques. The $pK_a$ of Ni([14] dieneN$_4$)(PF$_6$)$_2$ is 6.45 while that of Cu([14] dieneN$_4$)I$_2$ is 9.3. These values are of the same order of magnitude as those obtained for the related M([13] dieneN$_4$)X$_2$ systems and it is concluded that the addition of an extra methylene group opposite the diimine ring does not change the steric environment of the proton which is ionized. No $pK_a$ data could be obtained for Ni([15] dieneN$_4$)(PF$_6$)$_2$ in aqueous solution which indicates a marked decrease in ligand acidity in the 15-membered macrocycle. This has been explained in terms of steric crowding due to the positioning of three six-membered chelate rings adjacent to one another, which may prohibit formation of the basic uninegative form of the ligand.

## Introduction

Previously reported studies on the products formed *via* condensation of triethylenetetramine with acetylacetone in the presence of nickel(II)[1-3] and copper(II)[4] ions have identified two types of macrocyclic metal complexes, I and II, where $x = y = 2$. The two forms can be interconverted in solution by adjustment of the pH. Thus, type I complexes which contain the uninegative form of the 13-membered

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