New Isocyanide–Platinum Complexes

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Abstract: A number of studies of platinum(II)–isocyanide complexes have been carried out including (1) the synthesis of $[Pt(CNCH_3)_4][BF_4]_2$ and $[(phos)_2Pt(CNCH_3)_2][BF_4]_2$ by alkylation of $K_2Pt(CN)_4$ and $(phos)_2Pt(CN)_2$ with $[(CH_3)_3O][BF_4]$; (2) the reactions of L_2PtX_2 and CH_3NC (L = several phosphines, $(C_6H_5)_3As$, $(C_6H_5O)_3P$; X = Cl, Br, I) to give $LPt(CNCH_3)X_2$, $(CH_3NC)_2PtX_2$, $[L_2Pt(CNCH_3)X][X]$, or $[L_2Pt(CNCH_3)_2X][X]$, depending on L and X and on the conditions of the reaction (the complexes $[(phos)_2Pt(CNCH_3)X][X]$ (X = Br, Cl) on heating in benzene slowly lose CH_3X to give $(phos)_2Pt(CN)X$); (3) the reactions of $[(phos)_2Pt(CNCH_3)_2][A]$ and various anions X^- to give $[(phos)_2Pt(CNCH_3)X][A]$ and/or $(phos)_2PtX_2$ [$(phos)_2$ = diphos only; X = Cl, SCN, CN] and $[(phos)_2Pt(CNCH_3)_2X][A]$ (X = I), with azide ion to give $[(phos)_2Pt(CNCH_3)CN_4CH_3][A]$ or $(phos)_2Pt(CN_4CH_3)_2$ [$(phos)_2$ = diphos only], with nitrite ion to give $[(phos)_2Pt(CNCH_3)CONHCH_3][A]$, with C_6F_5Li or CH_3Li to give $(phos)_2PtR_2$ and $phosPt(CNCH_3)R_2$, and with alkoxide ion to give $[(phos)_2Pt(CNCH_3)C(OR){=}NCH_3][A]$ or $(phos)_2Pt\{C(OR){=}NCH_3\}_2$ [$(phos)_2$ = diphos only]. The former compound can be alkylated by $[(CH_3)_3O][BF_4]$, then treated again with alkoxide ion to give $[(phos)_2Pt\{C(OR){=}NHCH_3\}\{C(OR){=}N(CH_3)_2\}][BF_4]_2$. The new compounds reported here are characterized fully by analyses, and infrared and nmr spectroscopic studies are reported. Conductivities in acetonitrile have been run on appropriate ionic complexes.

Most of the early work on platinum–isocyanide complexes[1] dealt with complexes of the general formulas $(RNC)_2PtX_2$ and $[(RNC)_4Pt][A]_2$ (A = noncoordinating anion), and since these stoichiometries are quite typical for this metal in the divalent state, such complexes would not attract much attention. However, with a general resurgence of research on metal isocyanide complexes in recent months, it is not surprising that new and interesting work has appeared. In particular, two outstanding observations have been made in studies on these complexes. The first, that small molecules such as alcohols and primary and secondary amines add to the carbon–nitrogen multiple bond in a coordinated isocyanide ligand, was accomplished initially using the complex $\{(C_2H_5)_3P\}Pt(CNC_6H_5)Cl_2$.[2] However, this work just preceded two reports[3,4] describing the structural characterization of related complexes derived from $[Pt(CNR)_4][PtCl_4]$ and hydrazine which had been incorrectly identified by Chugaev;[5] these complexes apparently originate from additions of N–H units to two coordinated isocyanides. Subsequent to these studies, additions of alcohol to isocyanide ligands in $(RNC)_2PtCl_2$ complexes,[6] and in isocyanide complexes of palladium,[7] have been reported. The second observation concerned isolation of complexes of the formula $[(phos)_2Pt(CNCH_3)R][X]$ and their subsequent rearrangement to imino complexes, $(phos)_2Pt(CR{=}NCH_3)X$.[8] This work, reminiscent of carbonylation reactions, has been shown to occur with several other metals,[9,10] and clearly emphasizes the analogy between carbonyl and isocyanide ligand groups.

In addition to these papers there have also appeared the syntheses of several complexes, $[\{(C_2H_5)_3P\}_2Pt(CNR)X][ClO_4]$, included in a more general study on $\{(C_2H_5)_3P\}_2Pt(L)X][ClO_4]$ complexes,[11] and the description of several trichlorostannatoisocyanideplatinum(II) complexes.[6]

We began the work described in this paper with a successful synthesis of several new platinum(II)–isocyanide complexes from cyanoplatinum(II) species by alkylation reactions, and continued in a study of their reactions with various nucleophiles (X^-). Because products such as $[(phos)_2Pt(CNR)X][A]$ arise in these reactions, we decided to investigate reactions of $(phos)_2PtX_2$ complexes with isocyanides; this work also fit in with our studies on reactions of platinum alkyls and aryls[8] and methyl isocyanide, which give initially $[(phos)_2Pt(CNCH_3)R][X]$. One aspect of the present work, the dealkylation of methyl isocyanide, was published in preliminary form.[12] We now wish to present a detailed description of our work on platinum(II) isocyanide chemistry.

Experimental Section

Infrared spectra (4000–400 cm^{-1}) were recorded on a Beckman IR-10 spectrometer, using Nujol mulls and KBr plates; high-resolution data on $\nu_{C\equiv N}$ were obtained on a Perkin-Elmer Model 421 spectrometer using chloroform solutions. Proton nmr spectra were obtained on Varian A-60 and T-60 spectrometers using tetramethylsilane, τ 10.0, as an internal standard. Conductivity measurements were made on $\sim 5 \times 10^{-4}$ *M* dichloromethane and acetonitrile solutions with a Beckman conductivity bridge, Model RC-18A, and a Beckman conductivity cell with cell constant k = 0.20. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Conductivity data are summarized in Table I.

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Table I. Conductivity Data on Ionic Complexes

	Λ_M, ohm^{-1} cm^2 mol^{-1} [a]	
Compound	CH_2Cl_2 [b]	CH_3CN [c]
$[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$		320
$[\{(C_6H_5)_3P\}_2Pt(CNCH_3)Br][Br$	41	128
$[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2I][I]$	46	142
$[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2I][BF_4]$	52	145
$[\{(C_2H_5)_3P\}_2Pt(CNCH_3)Cl][Cl]$	32	145
$[\{(C_2H_5)_3P\}_2Pt(CNCH_3)Br][Br]$	33	
$[\{(C_2H_5)_3P\}_2Pt(CNCH_3)I][I]$	34	

[a] All solution concentrations were ~5×10^{-4} *M*. [b] In dichloromethane, Λ_M for a 1×10^{-4} *M* solution of $(C_2H_5)_4NClO_4$ was 53. [c] In acetonitrile, Λ_M for a 5×10^{-4} *M* solution of $(n\text{-}C_4H_9)_4NI$ was 151.

The starting platinum complexes, $[(n\text{-}C_4H_9)_4N]_2[Pt(CN)_4]$,[13] *cis*-$\{(C_6H_5)_3P\}_2PtCl_2$,[14] $\{(C_6H_5)_3As\}_2PtX_2$ (X = Cl, I),[14] *cis*-$\{(C_6H_5)_2PCH_3\}_2PtCl_2$,[15] *cis*-$\{(C_2H_5)_3P\}_2PtCl_2$,[16] *trans*-$\{(C_2H_5)_3P\}_2PtCl_2$,[17] diphosPtCl$_2$ (diphos = 1,2-bisdiphenylphosphinoethane),[18] and $\{(C_6H_5O)_3P\}_2PtI_2$,[14] were synthesized by the literature procedures; $\{(C_6H_5)_3P\}_2PtX_2$, $\{(C_2H_5)_3P\}_2PtX_2$ (X = Br, I), and diphosPtI$_2$ were prepared from the appropriate (phos)$_2$PtCl$_2$ with either lithium bromide in acetone or sodium iodide in methanol.[19] The preparations of $\{(C_6H_5)_3P\}_2Pt(CN)_2$, $\{(C_6H_5)_2PCH_3\}_2Pt(CN)_2$, and diphosPt(CN)$_2$ from the corresponding dichlorides and potassium cyanide were accomplished by the literature method,[20] except that these reactions were carried out in refluxing dichloromethane, with a somewhat better yield than reported. Trimethyloxonium tetrafluoroborate[21] and methyl isocyanide[22] were prepared by literature methods. Pentafluorophenyllithium was prepared from approximately equimolar quantities of bromopentafluorobenzene and *n*-butyllithium in dry, freshly distilled tetrahydrofuran at −78°.[23]

Acetonitrile was dried over calcium hydride, distilled onto P_2O_5, and then redistilled for use as a solvent for conductivity measurements. Manipulations were carried out routinely under nitrogen.

Preparation of Platinum(II)–Isocyanide Complexes by Alkylation Reactions Using Trialkyloxonium Salts. The preparation of $[Pt(CNCH_3)_4][BF_4]_2$ from $[(n\text{-}C_4H_9)_4N]_2[Pt(CN)_4]$ and trimethyloxonium tetrafluoroborate illustrates the general procedure for these alkylation reactions.

Tetrakis(methyl isocyanide)platinum(II) Tetrafluoroborate, $[Pt(CNCH_3)_4][BF_4]_2$. To a solution of $[(n\text{-}C_4H_9)_4N]_2[Pt(CN)_4]$ (2.5 g, 3.2 mmol) in anhydrous dichloromethane (80 ml) was added excess $[(CH_3)_3O][BF_4]$ (2.8 g, 19 mmol). The initial pale green suspension became colorless over a 4-hr reflux period. The solvent was evaporated and the resulting residue was dissolved in a small volume of acetonitrile. The solution was filtered and, on addition of ethyl acetate, crystallization occurred. Two crops of white crystalline $[Pt(CNCH_3)_4][BF_4]_2$ (1.6 g, 94% yield) were collected. The compound could be recrystallized from acetonitrile–ethyl acetate; mp 224–227°. *Anal.* Calcd for $C_8H_{12}B_2F_8N_4Pt \cdot 0.7C_4H_8O_2$: C, 22.0; H, 2.99; N, 9.56. Found: C, 22.4; H, 3.00; N, 10.0. The infrared spectrum shows a band at 2300 cm^{-1} (s) (Nujol mull) for C≡N stretching frequency, and other bands at 1333 (w), 1299 (w), 1060 (vs), 795 (w), 716 (w), 520 (m), and 497 cm^{-1} (m). The pmr spectrum (CD_3CN) shows a methyl proton multiplet (1:4:1 triplet due to ^{195}Pt coupling) at τ 6.32 with *J*(Pt–CNCH$_3$) = 16 Hz.

Using an identical procedure the following compounds were prepared.

$[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$, white crystals, mp 269–272°, was prepared from $\{(C_6H_5)_3P\}_2Pt(CN)_2$ and $[(CH_3)_3O][BF_4]$: 77% yield; ir ($CHCl_3$) 2275 cm^{-1} (s, C≡N) and other bands (Nujol mull) 1587 (vw), 1574 (vw), 1484 (m), 1437 (s), 1313 (w), 1187 (w), 1163 (vw), 1095 (s), 1055 (vs), 993 (m), 750 (s), 713 (s), 692 (s), 528 (s), and 500 cm^{-1} (s); pmr (CD_3CN) τ 7.29 (t, *J*(Pt–CH$_3$) = 16 Hz, CNCH_3) and 2.30 (m, P(C$_6\mathit{H}_5$)$_3$). *Anal.* Calcd for $C_{40}H_{36}B_2N_2P_2Pt$: C, 49.4; H, 3.70; N, 2.87; P, 6.36. Found: C, 49.8; H, 4.06; N, 3.13; P, 6.45.

$[\{(C_6H_5)_3P\}_2Pt(CNC_2H_5)_2][BF_4]_2$, white crystals, mp 255–258°, was prepared from $\{(C_6H_5)_3P\}_2Pt(CN)_2$ and $[(C_2H_5)_3O][BF_4]$: 42% yield; ir (Nujol mull) 2260 cm^{-1} (s) (C≡N) and other bands 1593 (vw), 1580 (vw), 1488 (m), 1437 (s), 1340 (w), 1317 (vw), 1290 (vw), 1188 (w), 1167 (vw), 1090 (s), 1050 (vs), 992 (w), 747 (s), 710 (s), 690 (s), and 510 cm^{-1} (s); pmr (CD_3CN) τ 9.47 (t, *J*(CH$_2$CH$_3$) = 7 Hz, CNCH_2CH$_3$), 6.92 (m, *J*(CH$_2$CH$_3$) = 7 Hz, CNCH_2CH$_3$], and 2.25 (m, P(C$_6$H$_5$)$_3$). *Anal.* Calcd for $C_{42}H_{40}B_2F_8N_2P_2Pt$: C, 50.2; H, 4.02; N, 2.79; P, 6.17. Found: C, 50.2; H, 4.15; N, 2.68; P, 5.88.

trans-$[\{(C_6H_5)_2PCH_3\}_2Pt(CNCH_3)_2][BF_4]$, white crystals, mp 228–230°, was prepared from $\{(C_6H_5)_2PCH_3\}_2Pt(CN)_2$ and $[(CH_3)_3O][BF_4]$: 82% yield; ir (Nujol mull) 2264 cm^{-1} (s) (C≡N) and other bands 1588 (vw), 1577 (vw), 1483 (m), 1440 (s), 1318 (w), 1287 (vw), 1190 (w), 1168 (w), 1060 vs), 996 (w), 896 (s), 743 (s), 708 (w), 693 (s), 497 (s), 453 (w), and 428 cm^{-1} (vw); pmr (CD_3CN) τ 7.38 (m, *J*(Pt–PCH$_3$) = 32 Hz, *J*(P–CH$_3$) = 4 Hz, P–CH_3), 7.07 (t, *J*(Pt–NCH$_3$) = 16 Hz, CNCH_3), and 2.31 (m, P(C$_6\mathit{H}_5$)$_3$). *Anal.* Calcd for $C_{30}H_{32}B_2F_8N_2P_2Pt \cdot 0.2C_4H_8O_2$: C, 42.6; H, 3.90; N, 3.62. Found: C, 42.7; H, 3.97; N, 3.26.

[diphosPt(CNCH$_3$)$_2$][PF$_6$]$_2$, white crystals, mp 188–191°, was prepared from reaction of diphosPt(CN)$_2$ and $[(CH_3)_3O][BF_4]$, followed by addition of NH_4PF_6 solution in acetonitrile–water to convert it to hexafluorophosphate salt: 75% yield; ir (Nujol mull) 2291 (s) and 2284 cm^{-1} (s) (C≡N) and other bands 1590 (vw), 1578 (vw), 1484 (m), 1439 (s), 1413 (w), 1337 (vw), 1314 (vw), 1187 (vw), 1161 (vw), 1104 (s), 997 (w), 830 (vs), 750 (w), 714 (s), 687 (s), 553 (s), 533 (s), and 487 cm^{-1} (m); pmr (CD_3CN) τ 6.60 (t, *J*(Pt–CH$_3$) = 15 Hz, CNCH_3), 7.38 (m, –CH_2P), and 2.31 (m, –P(C$_6\mathit{H}_5$)$_2$). *Anal.* Calcd for $C_{30}H_{30}F_{12}N_2P_4Pt$: C, 37.4; H, 3.14; N, 2.90; P, 12.0. Found: C, 37.7; H, 3.30; N, 2.99; P, 12.9.

Reactions of Bisphosphine-, Bisphosphite-, and Bisarsineplatinum Dihalides with Methyl Isocyanide. Reaction of $\{(C_6H_5)_3P\}_2PtCl_2$ with CH_3NC. A solution of 0.08 ml (1.5 mmol) of methyl isocyanide in 15 ml of benzene was added dropwise to a benzene suspension of 1.13 g (1.42 mmol) of $\{(C_6H_5)_3P\}_2PtCl_2$ at 25°. A yellow coloring formed around each drop as it reached the benzene suspension which then rapidly faded. After 30 min the benzene was evaporated and the white solid which remained was recrystallized from benzene to give $\{(C_6H_5)_3P\}Pt(CNCH_3)Cl_2 \cdot 0.5C_6H_6$: 0.70 g, 70% yield; mp 264–267°; ir ($CHCl_3$) 2259 (s) and 2243 cm^{-1} (sh) (C≡N) and other bands (Nujol mull) 1587 (vw), 1572 (vw), 1480 (s), 1435 (s), 1410 (vw), 1313 (vw), 1180 (w), 1155 (vw), 1095 (s), 1070 (vw), 1025 (vw), 995 (vw), 820 (vw), 747 (s), 742 (s), 703 (s), 687 (vs), 610 (vw), 540 (vs), 507 (vs), 473 (w), 452 (w), and 425 cm^{-1} (vw); pmr ($CDCl_3$) τ 7.22 (t, *J*(Pt–CH$_3$) = 19 Hz, CNCH_3) and 2.46 (m, P(C$_6\mathit{H}_5$)$_3$). *Anal.* Calcd for $C_{20}H_{18}Cl_2NPPt \cdot 0.5C_6H_6$: C, 45.4; H, 3.46; N, 2.30; P, 5.10. Found: C, 46.0; H, 3.05; N, 2.49; P, 5.11.

In acetone, this reaction took a different course. An acetone solution of 0.06 ml (1.2 mmol) of methyl isocyanide was added dropwise to a suspension of 1.00 g (1.27 mmol) of $\{(C_6H_5)_3P\}_2PtCl_2$ in 30 ml of acetone. No transient color formation was noted as in benzene solution. The suspension dissolved over a 5-min period; then acetone was evaporated until crystals began to form. The white solid was recrystallized from acetone–ethyl ether to give $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)Cl][Cl]$: 0.95 g, 90% yield; mp 325–335° dec; ir ($CHCl_3$) 2264 cm^{-1} (s) (C≡N) and other bands (Nujol mull) 1588 (vw), 1574 (vw), 1482 (m), 1436 (vs), 1310 (vw), 1175 (w), 1157 (vw), 1097 (s), 1025 (vw), 998 (w), 762 (m, sh), 742 (s), 710 (s), 688 (vs), 630 (vw), 522 (vs), 510 (vs), 502 (s, sh), 487 (w), and 455 cm^{-1} (vw); pmr (CD_3CN) τ 7.73 (t, CNCH_3) and 2.38 (m, P(C$_6\mathit{H}_5$)$_3$). *Anal.* Calcd for $C_{38}H_{33}Cl_2NP_2Pt$: C, 54.9; H, 4.00; N, 1.85. Found: C, 53.8; H, 4.38; N, 2.41.

When $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)Cl][Cl]$ (0.95 g, 1.10 mmol) was dissolved in a chloroform–benzene mixture, and the mixture was worked up as above, $\{(C_6H_5)_3P\}Pt(CNCH_3)Cl_2$ (0.58 g, 80% yield) was obtained. Likewise, when a suspension of 0.55 g (0.83 mmol) of $\{(C_6H_5)_3P\}Pt(CNCH_3)Cl_2$ was added to a solution of 0.30 g (1.15 mmol) of triphenylphosphine in acetone, and the mixture was stirred for 15 min, $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)Cl][Cl]$ was formed (0.48 g, 70% yield). Both products obtained in these interconversions were shown to be identical with the sample obtained in the direct reaction in benzene by comparison of infrared and nmr spectra and melting point.

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Reaction of $\{(C_6H_5)_3P\}_2PtBr_2$ with CH_3NC. A benzene solution of 0.90 ml (1.7 mmol) of methyl isocyanide was added dropwise to a suspension of $\{(C_6H_5)_3P\}_2PtBr_2$ (1.20 g, 1.39 mmol) in benzene at 25° with no perceptible color change. The pale orange solid left on evaporation of the benzene was dissolved in chloroform to give a deep orange solution. Yellow needle-shaped crystals (0.13 g) were obtained on addition of ethyl ether. Proton nmr indicated a phosphine-to-isocyanide ratio of 1:1; analysis confirmed the identity of the complex as $[\{C_6H_5)_3P\}_2Pt(CNCH_3)_2Br][Br]$ (13% yield). The compound melted at 100° turning yellow-green, resolidified ~120°, and began to remelt with decomposition above 300°: ir ($CHCl_3$) 2258 cm^{-1} (s) ($C{\equiv}N$) and other bands (Nujol mull) 1590 (vw), 1572 (vw), 1481 (m), 1437 (m), 1413 (w), 1308 (vw), 1247 (vw), 1232 (vw), 1181 (vw), 1155 (vw), 1095 (s) 1070 (vw), 1023 (vw), 996 (w), 750 (vs), 740 (vs), 708 (m), 690 (s), 654 (w), 523 (s), 512 (s), and 496 cm^{-1} (s); pmr ($CDCl_3$) τ 7.20 (t, $CNC\mathit{H}_3$) and 2.39 (m, $P(C_6\mathit{H}_5)_3$). *Anal.* Calcd for $C_{40}H_{36}Br_2N_2P_2Pt \cdot 2.5CHCl_3$: C, 40.0; H, 3.12; N, 2.22; P, 4.92. Found: C, 39.9; H, 3.13; N, 2.34; P, 4.97.

Repeated recrystallization from chloroform–ethyl ether resulted in slow loss of methyl isocyanide, giving eventually $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)Br][Br]$. This loss was followed by the increasing phosphine-to-isocyanide intensity ratio in the nmr.

Additional ethyl ether was added to the mother liquor from which the bisisocyanide adduct was originally obtained. After 2 days at 0° an orange oil separated from this solution which solidified after 2 more days at 0°. Crystallization from acetonitrile–ethyl ether and two recrystallizations from chloroform– ethyl ether gave 0.50 g of pale yellow crystals identified as $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)Br][Br] \cdot 0.5CHCl_3$ (37% yield), mp >335° dec. This compound has infrared and nmr spectra identical with those of the complex formed by isocyanide loss from $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2Br][Br]$: ir ($CHCl_3$) 2261 cm^{-1} (s) ($C{\equiv}N$) and other bands (Nujol mull) 1590 (vw), 1574 (vw), 1483 (m), 1434 (s), 1409 (vw), 1310 (vw), 1186 (w), 1155 (vw), 1098 (s), 1070 (w), 1022 (vw) 992 (w), 750 (s), 740 (s), 705 (s, sh), 698 (s, sh), 688 (s), 523 (s), 512 (s), 492 (s), 470 (w), and 453 cm^{-1} (w); pmr ($CDCl_3$) τ 7.35 (t, $J(Pt{-}CH_3)$ = 20 Hz, $CNC\mathit{H}_3$) and 2.39 (m, $P(C_6H_5)_3$). *Anal.* Calcd for $C_{38}H_{33}Br_2NP_2Pt \cdot 0.5CHCl_3$: C, 47.2; H, 3.45; N, 1.43; P, 6.32. Found: C, 47.3; H, 3.58; N, 1.73; P, 6.41.

Reaction of $\{(C_6H_5)_3P\}_2PtI_2$ with CH_3NC. A benzene solution of 0.80 ml (1.5 mmol) of methyl isocyanide was added dropwise to a benzene suspension of 1.08 g (1.12 mmol) of $\{(C_6H_5)_3P\}_2PtI_2$ at 25°. The yellow-orange color of the suspension changed to bright yellow. After 10 min the benzene was evaporated and the remaining yellow solid was recrystallized from chloroform–ethyl ether to give 0.43 g of bright yellow needles identified as $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2I][I]$ (55% yield based on methyl isocyanide): mp 127–128°; ir ($CHCl_3$) 2252 cm^{-1} (s) ($C{\equiv}N$) and other bands (Nujol mull) 1620 (vw), 1587 (vw), 1572 (vw), 1482 (m), 1435 (s), 1410 (vw), 1400 (vw), 1312 (vw), 1183 (w), 1158 (vw), 1095 (s), 1024 (vw), 995 (w), 853 (vw), 754 (m), 640 (m), 707 (m), 685 (s), 522 (s), 510 (s), and 497 cm^{-1} (s); pmr ($CDCl_3$) τ 7.22 (s, $CNC\mathit{H}_3$) and 2.38 (m, $P(C_6\mathit{H}_5)_3$). *Anal.* Calcd for $C_{40}H_{36}I_2N_2P_2Pt$: C, 45.4; H, 3.41; N, 2.62; P, 5.88. Found: C, 45.2; H, 3.13; N, 2.82; P, 5.76.

Reaction of $\{(C_2H_5)_3P\}_2PtX_2$ (X = Cl, Br, I) with CH_3NC. Solutions of 0.40 ml (0.75 mmol) of methyl isocyanide in 10 ml of benzene were added dropwise to benzene solutions of *cis*-$\{(C_2H_5)_3P\}_2PtX_2$ (0.5 mmol, X = Cl, Br, I) at 25°. Colorless solutions of the dichloride and the dibromide grew cloudy and a white solid formed over a 5-min addition period. The bright yellow diiodide solution more rapidly faded on addition of methyl isocyanide and a white solid settled out. The benzene suspensions were filtered and the white solids recrystallized from acetone–ethyl ether. The dichloride adduct $[\{(C_2H_5)_3P\}_2Pt(CNCH_3)Cl][Cl]$ (0.26 g, 96% yield, mp 139–140.5°) and the dibromide adduct $[\{(C_2H_5)_3P\}_2Pt(CNCH_3)Br][Br]$ (0.29 g, 92% yield, mp 141.5–142.5°) thus obtained both gave proton nmr spectra in which coupling between the methyl protons on the methyl isocyanide ligand and platinum were observable. The diiodide adduct $[\{(C_2H_5)_3P\}_2Pt(CNCH_3)_x$i]-[I] gave, after one recrystallization from acetone–ethyl ether, an extremely sharp methyl resonance which showed no platinum coupling; integration of the spectrum gave a phosphine-to-isocyanide ratio of 1:1. Subsequent recrystallizations resulted in loss of methyl isocyanide giving eventually pure $[\{(C_2H_5)_3P\}_2Pt(CNCH_3)I][I]$ (0.25 g, 70% yield, mp 139–140°). For the dichloride adduct, the following were observed: ir ($CHCl_3$) 2252 cm^{-1} (s) ($C{\equiv}N$) and other bands (Nujol mull) 1418 (s), 1262 (m), 1145 (w), 1030 (vs), 1005 (m), 970 (vw), 763 (vs), 732 (vs), 720 (s, sh), 678 (vw), 630 (w), 473 (m), and 413 cm^{-1} (w); pmr ($CDCl_3$) τ 6.05 (t, $J(Pt{-}NCH_3)$ = 20 Hz, $CNC\mathit{H}_3$), 7.70 (m, $J(CH_2CH_3)$ = 7 Hz, $PC\mathit{H}_2CH_3$), and 8.80 (m, $J(CH_2CH_3)$ = 7 Hz, $J(P{-}CH_3)$ = 8 Hz, $PCH_2C\mathit{H}_3$). *Anal.* Calcd for $C_{14}H_{33}Cl_2NP_2Pt$: C, 30.9; H, 6.12; N, 2.5. Found: C, 30.8; H, 6.64; N, 2.44.

For the dibromide adduct, the following were observed: ir ($CHCl_3$) 2251 cm^{-1} (s) ($C{\equiv}N$) and other bands (Nujol mull) 1420 (s), 1263 (m), 1238 (w), 1140 (vw), 1030 (s), 1005 (m), 763 vs), 733 (vs), 720 (s, sh), 678 (vw), 628 (w), 472 (m), and 413 cm^{-1} (m); pmr ($CDCl_3$) τ 6.05 (t, $J(Pt{-}NCH_3)$ = 20 Hz, $CNC\mathit{H}_3$), 7.70 (m, $J(CH_2CH_3)$ = 7 Hz, $PC\mathit{H}_2CH_3$), and 8.80 (m, $J(CH_2CH_3)$ = 7 Hz, $J(P{-}CH_3)$ = 8 Hz, $PCH_2C\mathit{H}_3$). *Anal.* Calcd for $C_{14}H_{33}Br_2NP_2Pt$: C, 26.6; H, 5.26; N, 2.21. Found: C, 26.8; H, 5.41; N, 2.16.

For the diiodide adduct, the following were observed: ir (Nujol mull) 2230 cm^{-1} (vs) ($C{\equiv}N$) and other bands 1410 (s), 1260 (w), 1030 (s), 980 (vw), 765 (m), 750 (m, sh), 735 (s), 715 (m, sh), 625 (vw), 497 (m), and 410 cm^{-1} (w); pmr ($CDCl_3$) τ 6.13 (s, $CNC\mathit{H}_3$), 7.67 (m, $J(CH_2CH_3)$ = 7 Hz, $PC\mathit{H}_2CH_3$), and 8.75 (m, $J(CH_2CH_3)$ = 7 Hz, $J(P{-}CH_3)$ = 8 Hz, $PCH_2C\mathit{H}_3$). *Anal.* Calcd for $C_{14}H_{33}I_2NP_2Pt$: C, 23.2; H, 4.58; N, 1.93. Found: C, 24.0; H, 4.80; N, 2.66.

The reaction of *trans*-$\{(C_2H_5)_3P\}_2PtCl_2$ with methyl isocyanide gave a 90% yield of $[\{(C_2H_5)_3P\}_2Pt(CNCH_3)Cl][Cl]$ which was identical with the product obtained from the cis dichloride.

Reactions of $\{(C_6H_5)_3As\}_2PtX_2$ (X = Cl, I) with Methyl Isocyanide. To a suspension of $\{(C_6H_5)_3As\}_2PtCl_2$ (0.314 g, 0.357 mmol) in 20 ml of dichloromethane was added methyl isocyanide (0.0146 g, 0.357 mmol). The resulting solution was stirred for 1 hr at 25°, then evaporated to dryness, and the residue was taken up in excess dichloromethane and filtered. After concentrating the solution to a small volume, addition of excess ethyl ether gave the white crystalline $\{(C_6H_5)_3As\}Pt(CNCH_3)Cl_2$ (0.204 g, 96% yield), which was recrystallized from dichloromethane–ethyl ether: mp 247–248°; ir ($CHCl_3$) 2255 (s) and 2241 cm^{-1} (sh) ($C{\equiv}N$) and other bands (Nujol mull) 1580 (vw), 1480 (m), 1436 (s), 1308 (w), 1184 (vw), 1156 (vw), 1077 (m), 1022 (w), 997 (w), 740 (s), 687 (s), 477 (s), and 463 cm^{-1} (w); pmr ($CDCl_3$) τ 7.17 (t, $J(Pt{-}CH_3)$ = 18 Hz, $CNC\mathit{H}_3$) and 2.47 (m, $As(C_6\mathit{H}_5)_3$). *Anal.* Calcd for $C_{20}H_{18}AsCl_2NPt$: C, 39.1; H, 2.94; Cl, 11.6; N, 2.28. Found: C, 38.8; H, 2.93; Cl, 12.0; N, 2.27.

Utilizing the same procedure, $\{(C_6H_5)_3As\}_2PtCl_2$ (0.500 g, 0.570 mmol) and excess methyl isocyanide (0.0584 g, 1.42 mmol) gave known *cis*-$(CH_3NC)_2PtCl_2$[24] (0.153 g, 75% yield), which was purified by recrystallization from dichloromethane–methanol, mp 229–231° dec.

Utilizing the same procedure, $\{(C_6H_5)_3As\}_2PtI_2$ (0.478 g, 0.450 mmol) and methyl isocyanide (0.0184 g, 0.450 mmol) gave the yellow crystalline $\{(C_6H_5)_3As\}Pt(CNCH_3)I_2$ (0.307 g, 86% yield), which was recrystallized from dichloromethane–ethyl ether, mp 226–228°; and $\{(C_6H_5)_3As\}_2PtI_2$ (0.600 g, 0.565 mmol) and excess methyl isocyanide (0.0533 g, 1.30 mmol) gave the yellow crystalline $(CH_3NC)_2PtI_2$ (0.272 g, 91% yield), which was recrystallized from dichloromethane–ethyl ether; turns white without melting at 203–205°: ir ($CHCl_3$) 2247 (s) and 2239 cm^{-1} (s) ($C{\equiv}N$) and other bands (Nujol mull) 1582 (vw), 1483 (m), 1437 (s), 1408 (w), 1313 (vw), 1183 (vw), 1154 (vw), 1076 (w), 1022 (vw), 997 (w), 738 (s), 992 (m), 484 (w), 470 (w), and 460 cm^{-1} (w); pmr ($CDCl_3$) τ 6.27 (t, $J(Pt{-}CH_3)$ = 19 Hz, $CNC\mathit{H}_3$) and 2.46 (m, $As(C_6\mathit{H}_5)_3$). *Anal.* Calcd for $C_{20}H_{18}AsI_2NPt$: C, 30.2; H, 2.27; I, 31.8; N, 1.76. Found: C, 30.3; H, 2.25; I, 31.3; N, 1.69.

Reaction of $\{(C_6H_5O)_3P\}_2PtI_2$ with Methyl Isocyanide. To a solution of $\{(C_6H_5O)_3P\}_2PtI_2$ (1.07 g, 1.00 mmol) in 30 ml of chloroform was added methyl isocyanide (0.0902 g, 2.20 mmol). A yellow suspension immediately formed and the solution phase turned yellow-orange. After 1 hr at 25°, the solvent was evaporated and the residue dried *in vacuo* overnight. The oily residue was taken up in excess chloroform, filtered, and concentrated. Addition of excess hexane gave the yellow crystalline product $(CH_3NC)_2PtI_2$ (0.332 g, 68% yield), which was recrystallized from chloroform–ether.

Attempted Reaction of diphosPtX_2 with $CNCH_3$. When a drop of methyl isocyanide was added to a chloroform suspension of diphosPtX_2 (X = Cl, I) the solids dissolved gave a bright yellow solution. The nmr of this solution showed a sharp singlet due to methyl isocyanide which is shifted 0.2 ppm downfield from the

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(24) L. Chugaev and P. Teearu, *Chem. Ber.*, **47**, 568 (1914).

position for free ligand (3.08 ppm). However, attempts at crystallization led only to recovery of starting material.

Dealkylation of the Isocyanide Ligand in Platinum–Isocyanide Complexes. Demethylation of $[(phos)_2Pt(CNCH_3)X][X]$. The reaction using $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)Cl][Cl]$ was typical. A suspension of this complex (0.18 g, 0.22 mmol) in 50 ml of heptane was refluxed for 1.5 hr. The solvent was evaporated and the remaining white solid was washed thoroughly with acetone and recrystallized from chloroform–benzene to give $[\{(C_6H_5)_3P\}_2Pt(CN)Cl$: 0.60 g, 36% yield; mp 325–330°; ir (Nujol mull) 2125 cm^{-1} (m) ($C\equiv N$) and other bands 1587 (vw), 1572 (vw), 1480 (m), 1434 (vs), 1330 (vw), 1305 (vw), 1182 (vw), 1155 (vw), 1095 (s), 1023 (vw), 995 (w), 742 (s), 704 (s), 687 (vs), 520 (vs), 508 (s), 502 (s), 472 (vw), 452 (vw), and 436 cm^{-1} (vw).

$\{(C_6H_5)_3P\}_2Pt(CN)Br$ was obtained from $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)Br][Br]$ in an analogous reaction except using benzene reflux for 3.5 hr: yield 82%; mp >340°; ir (Nujol mull) 2125 cm^{-1} (m) ($C\equiv N$) and other bands 1588 (vw), 1570 (vw), 1468 (m), 1433 (s), 1308 (w), 1182 (w), 1156 (vw), 1095 (s), 1068 (vw), 1025 (w), 995 (w), 756 (vs), 737 (m, sh), 702 (m), 688 (s), 660 (vw), 520 (vs), 510 (vs), 498 (m), 452 (w), and 428 cm^{-1} (w). *Anal.* Calcd for $C_{37}H_{30}BrNP_2Pt \cdot 1.75CHCl_3$: C, 45.0; H, 3.09; N, 1.35. Found: C, 44.9; H, 3.04; N, 1.49.

$\{(C_2H_5)_3P\}_2Pt(CN)Cl$ was obtained from $[\{(C_2H_5)_2Pt(CNCH_3)Cl][Cl]$ on benzene reflux for 2 hr: yield 50%; mp 146–149°; ir (Nujol mull) 2120 cm^{-1} (s) ($C\equiv N$) and other bands 1415 (m), 1265 (w), 1240 (w, sh), 1155 (vw), 1035 (s), 1005 (m), 762 (vs), 730 (vs), 708 (m), 628 (m), 458 (m), and 412 cm^{-1} (w).

Demethylation of $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2I][I]$. A benzene suspension of 0.2 g (0.19 mmol) of this complex was refluxed for 4 hr. The yellow solid remaining on filtration was dissolved in acetone and filtered. A small amount of white solid insoluble in acetone as well as a small amount which crystallized out of the acetone on cooling to 0° (~20 mg total) were identified as $\{(C_6H_5)_3P\}_2Pt(CN)_2$,[20] mp 332–335°. Addition of ethyl ether to the acetone filtrate gave an additional 0.12 g of an approximate 1:2 mixture of $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2I][I]$ and $\{(C_6H_5)_3P\}_2Pt(CN)_2$ which was not separated further (identified by infrared spectra).

Attempted Demethylation of $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2I][BF_4]$. The above compound (0.20 g, 0.20 mmol) was refluxed in benzene. Little demethylation occurred after 8 hr; however, the desired change became significant after 24 hr. The solvent was then removed and the resulting residue was dissolved in chloroform. The product, $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)CN][BF_4]$ (0.084 g, 50% yield), was obtained on addition of hexane: mp 240–242°; ir ($CHCl_3$) 2273 (m) and 2152 cm^{-1} (m) ($C\equiv N$) and other bands (Nujol mull) 1590 (vw), 1578 (vw), 1484 (m), 1435 (s), 1310 (vw), 1185 (vw), 1160 (vw), 1096 (s), 1050 (vs), 997 (w), 740 (s), 708 (m), 687 (s), and 510 cm^{-1} (s); pmr ($CDCl_3$) τ 7.47 (t, $J(Pt\text{–}CH_3)$ = 15 Hz, $CNC\mathit{H}_3$) and 2.41 (s, $P(C_6\mathit{H}_5)_3$). *Anal.* Calcd for $C_{39}H_{33}BF_4N_2P_2Pt \cdot 1.0CHCl_3$: C, 48.4; H, 3.46; N, 2.84. Found: C, 48.4; H, 3.32; N, 2.97.

Analogous results were obtained from refluxing in acetonitrile.

Reactions of $[(phos)_2Pt(CNCH_3)_2][BF_4]_2$ and Organolithium Reagents. Reaction of $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$ and C_6F_5Li. Pentafluorophenyllithium (2.97 mmol) and $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$ (1.45 g, 1.49 mmol) were stirred at −78° for 1 hr, then warmed to 0 and 25° and stirred for 5 and 10 hr, respectively. The resulting pale yellow solution was evaporated to dryness and the residue extracted with benzene. Addition of methanol gave several crops of impure $\{(C_6H_5)_3P\}_2Pt(C_6H_5)_2$[25] (0.22 g, 14% yield), which was purified by recrystallization from benzene–methanol, mp 305–308°. The filtrate from the reaction mixture was evaporated to dryness and the residue dissolved in chloroform. Addition of hexane gave several crops of $\{(C_6H_5)_3P\}Pt(CNCH_3)(C_6F_5)_2$ (0.61 g, 50% yield), which were recrystallized from chloroform–hexane: mp 242–243°; ir ($CHCl_3$) 2244 (sh) and 2234 cm^{-1} (s) ($C\equiv N$) and other bands (Nujol mull) 1636 (w), 1607 (w), 1500 (s), 1482 (vw), 1458 (s), 1440 (s), 1417 (w), 1363 (m), 1184 (vw), 1160 (vw), 1095 (s), 1056 (s), 955 (s), 793 (m), 785 (m), 702 (m), 690 (s), 533 (m), 514 (m), 490 (w), and 468 cm^{-1} (vw); pmr ($CHCl_2$) τ 7.17 (m, $J(Pt\text{–}CH_3)$ = 15 Hz, $CNC\mathit{H}_3$) and 2.56 (m, $P(C_6\mathit{H}_5)_3$). *Anal.* Calcd for $C_{32}H_{18}F_{10}NPPt$: C, 46.1; H, 2.21; N, 1.80; P, 3.72. Found: C, 45.9; H, 2.01; N, 1.64; P, 3.80.

Reaction of $[diphosPt(CNCH_3)_2][PF_6]_2$ and C_6F_5Li. To pentafluorophenyllithium in dry, freshly distilled tetrahydrofuran (50 ml) at −78° was added $[diphosPt(CNCH_3)_2][PF_6]_2$ (0.76 g, 0.79 mmol). The initial red-brown suspension changed rapidly to a pale yellow solution. No further apparent change occurred as the system was stirred continuously at −78° for 1 hr and at 0° for 4 hr. After solvent removal, the residue was dissolved in benzene and filtered. A white crystalline solid, $diphosPt(C_6F_5)_2$ (0.70 g, 94% yield), precipitated upon the addition of excess methanol; it was identified by infrared and melting point data,[25] mp 265–267°.

Reaction of $[diphosPt(CNCH_3)_2][PF_6]_2$ and CH_3Li. To a suspension of $[diphosPt(CNCH_3)_2][PF_6]_2$ (0.60 g, 0.62 mmol) in dry, freshly distilled tetrahydrofuran (50 ml) was added methyllithium (1.43 mmol) in ethyl ether. The pale yellow solution was allowed to stir for 7 hr at 25°. After solvent removal, the residue was washed with water and dried. Recrystallization from acetone gave colorless needles of $diphosPt(CH_3)_2$ (0.29 g, 76% yield), which were identified by infrared and nmr spectroscopy, mp 260° dec.

Reactions of $[(phos)_2Pt(CNCH_3)_2][A]_2$ with Alkoxide Ion and with Alcohols. Reaction of $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$ and Methoxide. A solution of $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$ (0.37 g, 0.38 mmol) and sodium methoxide (0.48 mmol, from 0.011 g of sodium) in methanol (40 ml) was stirred for 3 hr at 25°. The mixture was then evaporated to dryness. The white residue was dissolved in chloroform and filtered and the filtrate was evaporated to a small volume. A white crystalline product, $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)C(OCH_3){=}NCH_3][BF_4]$ (0.29 g, 84% yield), precipitated upon the addition of excess ethyl ether; it was purified by recrystallization from chloroform–ethyl ether: mp 172–174°; ir ($CHCl_3$) 2245 (m) ($C\equiv N$), 1626 cm^{-1} (m) ($C{=}N$), and other bands (Nujol mull) 1483 (m), 1437 (s), 1387 (w), 1183 (vw), 1139 (w), 1097 (s), 1053 (vs), 996 (w), 744 (m), 707 (w), 687 (m), 612 (w), and 510 cm^{-1} (s); pmr ($CDCl_3$) τ 7.42 (t, $J(Pt\text{–}C\equiv NCH_3)$ = 12 Hz, $CNC\mathit{H}_3$), 7.25 (t, $J(Pt\text{–}C{=}NCH_3)$ = 8 Hz, $>C{=}NC\mathit{H}_3$), 7.30 (s, $OC\mathit{H}_3$), and 2.45 (m, $P(C_6\mathit{H}_5)_3$). *Anal.* Calcd for $C_{41}H_{39}BF_4N_2OP_2Pt \cdot 0.2CHCl_3$: C, 52.5; H, 4.19; N, 2.97. Found: C, 52.7; H, 4.25; N, 3.16.

A reaction was run utilizing the same procedure but using excess sodium methoxide (2.05 mmol, formed from 0.047 g of sodium) in methanol (30 ml) and $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]$ (0.40 g, 0.41 mmol). The only product isolated from this reaction was $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)C(OCH_3){=}NCH_3][BF_4]$ (0.33 g, 90% yield).

Using the same procedure the following reactions were carried out.

Reaction of $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$ and ethoxide gave white crystalline $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)C(OC_2H_5){=}NCH_3][BF_4]$ (74% yield), which was purified by recrystallization from chloroform–hexane: mp 192–193°; ir (Nujol mull) 2240 (m) ($C\equiv N$), 1620 cm^{-1} (s) ($C{=}N$), and other bands 1483 (m), 1437 (s), 1310 (vw), 1280 (vw), 1185 (w), 1152 (w), 1093 (s), 1050 (vs), 996 (w), 747 (s), 705 (w), 692 (s), 610 (w), and 518 cm^{-1} (s); pmr ($CDCl_3$) τ 7.43 (t, $J(Pt\text{–}C\equiv N\text{—}CH_3)$ = 12 Hz, $CNC\mathit{H}_3$), 7.25 (t, $J(Pt\text{–}C{=}NCH_3)$ = 8 Hz, $<C{=}NCH_3$), 6.8–7.3 (m, $J(CH_2CH_3)$ = 7 Hz, $\text{–}OC\mathit{H}_2CH_3$), 9.38 (m, $\text{–}OCH_2C\mathit{H}_3$), and 2.42 (m, $P(C_6\mathit{H}_5)_3$). *Anal.* Calcd for $C_{42}H_{41}BF_4N_2OP_2Pt \cdot 0.9CHCl_3$: C, 49.6; H, 4.07; N, 2.69. Found: C, 49.7; H, 4.19; N, 2.92.

Reaction of $[diphosPt(CNCH_3)_2][PF_6]_2$ and methoxide gave the white crystalline product $diphosPt\{C(OCH_3){=}NCH_3\}_2$ (83% yield), recrystallizable from chloroform–ethyl ether–hexane: mp 192–195°; ir (Nujol mull) 1597 cm^{-1} (vs) ($C\equiv N$) and other bands 1482 (w), 1434 (m), 1398 (w), 1374 (w), 1307 (vw), 1180 (w), 1136 (m), 1100 (m), 1083 (m), 1066 (s), 1040 (m), 1023 (w), 994 (vw), 944 (vw), 874 (vw), 833 (w), 820 (m), 750 (m), 744 (m), 732 (m), 700 (s), 686 (s), 677 (s), 652 (w), 597 (w), 563 (w), 524 (s), 486 (m), 463 (vw), and 444 cm^{-1} (vw); pmr ($CDCl_3$) τ 7.08 (t, $J(Pt\text{–}C{=}NCH_3)$ = 10 Hz, $=NC\mathit{H}_3$), 6.53 (t, $J(Pt\text{–}C\text{—}OCH_3)$ = 5 Hz, $\text{–}OC\mathit{H}_3$), 7.2–8.3 (m, $\text{–}C\mathit{H}_2P$), and 2.53 (m, $\text{–}P(C_6\mathit{H}_5)_2$). *Anal.* Calcd for $C_{32}H_{36}F_2N_2O_2P_2Pt$: C, 51.6; H, 5.12; N, 3.74; P, 8.27. Found: C, 51.8; H, 5.12; N, 3.75; P, 8.20.

Methylation of $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)C(OCH_3){=}NCH_3][BF_4]$ and Subsequent Reaction with Ethoxide. To a solution of the above compound (0.47 g, 0.51 mmol) in 40 ml of dichloromethane was added excess $[(CH_3)_3O][BF_4]$ (0.23 g, 1.52 mmol). After refluxing the solution for 4 hr, the solvent was removed and the residue dissolved in acetonitrile and filtered. Upon addition of ethyl acetate a white crystalline solid $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)C(OCH_3){=}N(CH_3)_2][BF_4]_2$ was formed (0.43 g, 84% yield), which could be further recrystallized from acetonitrile–ethyl acetate: mp 258–259°; ir (Nujol mull) 2260 cm^{-1} (m) ($C\equiv N$), 1588 cm^{-1} (m) ($C{=}N$), and other bands 1483 (m), 1437 (s), 1376 (w), 1297 (w), 1248 (vw), 1187 (vw), 1163 (vw), 1097 (s), 1053 (vs), 996 (w), 752 (m), 712 (m), 693 (s), 624 (w), 525 (s), 513 (s), and 497 cm^{-1} (m); pmr (CD_3CN) τ 7.50 (t, $J(Pt\text{–}C\equiv N\text{—}CH_3)$ = 14 Hz,

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$\equiv NCH_3$), 7.67 (m, *J*($Pt{-}C{=}NCH_3$) ≈ 0 Hz, $=NCH_3$ (cis to Pt)), 7.22 (m, *J*($Pt{-}C{=}NCH_3$) = 8 Hz, $=NCH_3$ (trans to Pt)), 6.10 (m, *J*($Pt{-}COCH_3$] = 5 Hz, $-OCH_3$), and 2.33 (m, $P(C_6H_5)_3$). *Anal.* Calcd for $C_{42}H_{42}B_2F_8N_2OP_2Pt$: C, 49.3; H, 4.14; N, 2.75. Found: C, 49.3; H, 4.24; N, 3.17.

This product (0.29 g, 0.28 mmol) and sodium ethoxide (1.34 mmol, from 0.031 g of sodium metal) in 40 ml of ethanol were stirred for 8 hr at 25°, during which time a colorless solution developed. After solvent removal and chloroform extraction, the material was dissolved in dichloromethane and a methanolic solution containing excess NH_4PF_6 was added. A pale yellow microcrystalline material, $[\{(C_6H_5)_3P\}_2Pt\{C(OCH_3){=}N(CH_3)_2\}{-}C(OC_2H_5){=}NHCH_3][PF_6]_2$ (0.22 g, 67% yield), was recrystallized from dichloromethane–methanol: mp 234–238° dec; ir (Nujol mull) 1574 cm^{-1} (s) ($C{=}N$) and other bands 1483 (m), 1437 (s), 1377 (w), 1314 (w), 1290 (m), 1252 (s), 1166 (vw), 1096 (m), 1042 (vw), 1000 (w), 835 (vs), 752 (m), 707 (w), 697 (s), 557 (s), 522 (s), 496 (m), 460 (vw), and 418 cm^{-1} (vw); pmr (CD_3CN) τ 9.00 (m, $-OCH_2CH_3$), 5.9–8.0 (m, $-OCH_3$, $=NCH_3$, $-OCH_2$), and 2.40 (m, $P(C_6H_5)_3$). *Anal.* Calcd for $C_{44}H_{48}F_{12}N_2O_2P_4Pt$: C, 45.0; H, 4.47; N, 2.37; P, 10.4. Found: C, 45.3; H, 4.49; N, 2.42; P, 9.95.

Addition of Methanol to $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$. $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$ (0.60 g, 0.62 mmol) was refluxed in anhydrous methanol (25 ml) for 9 hr. The reaction mixture was filtered and the methanolic solution was concentrated to 5 ml, whereupon white crystals began to separate. After cooling, the product $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)C(OCH_3){=}NHCH_3][BF_4]_2$ (0.60 g, 98% yield) was collected, dried, and recrystallized from methanol: mp 233–236°; ir (Nujol mull) 2254 cm^{-1} (m) ($C{\equiv}N$), 1592 cm^{-1} (m) ($C{=}N$), and other bands 3317 (w), 1480 (m), 1437 (s), 1308 (vw), 1278 (vw), 1257 (m), 1094 (s), 1055 (vs), 993 (w), 747 (m), 708 (m), 690 (s), 634 (w), and 510 cm^{-1} (s); pmr (CD_3CN) τ 7.2–7.8 (m, $\equiv NCH_3$ and $=NCH_3$), 6.08 (m, $-OCH_3$), and 2.33 (m, $P(C_6H_5)_3$). *Anal.* Calcd for $C_{41}H_{40}B_2N_2OP_2Pt$: C, 48.9; H, 4.00; N, 2.78. Found: C, 49.1; H, 3.68; N, 3.05.

Addition of a molecule of alcohol across the second isocyanide group in this complex was unsuccessful, even after prolonged reflux (7 days).

Addition of Ethanol to $[diphosPt(CNCH_3)_2][PF_6]_2$. By a similar method, $[diphosPt(CNCH_3)_2][PF_6]_2$ (0.20 g, 0.207 mmol), when refluxed in 20 ml of anhydrous ethanol for 8 hr, gave $[diphosPt\{C(OC_2H_5){=}NHCH_3\}_2][PF_6]_2$ (0.21 g, 100% yield). This compound was recrystallized from ethanol–ethyl ether: mp 136° dec; ir (Nujol mull) 1587 cm^{-1} (vs) ($C{=}N$) and other bands 3390 (w), 3340 (w), 1480 (w), 1436 (m), 1250 (s), 1163 (w), 1142 (w), 1100 (m), 1036 (w), 1023 (w), 997 (w), 835 (vs), 740 (m), 710 (s), 690 (s), 654 (vw), 615 (vw), 552 (s), 526 (s), 487 (w), and 420 cm^{-1} (vw); pmr (CD_3CN) τ 7.38 (m, $=NCH_3$), 5.4–6.2 (m, $-OCH_2CH_3$), 8.6–9.2 (m, $-OCH_2CH_3$), and 2.33 (m, $P(C_6H_5)_2$).

Reactions of $[(phos)_2Pt(CNCH_3)_2][BF_4]_2$ with Halides, Pseudohalides, and Other Nucleophilic Reagents. The procedure used in the following reaction is typical (except as noted below).

Reaction of $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$ and Chloride Ion. A solution of $[(C_2H_5)_4N][Cl]$ (0.26 g, 1.5 mmol) in chloroform (10 ml) was added to a suspension of $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$ (0.50 g, 0.51 mmol) in 40 ml of chloroform. The reaction system became a pale yellow solution with the release of methyl isocyanide. After 2 hr of stirring at 25°, the solvent was removed and the residue was dissolved in acetonitrile. Excess NH_4PF_6 dissolved in acetonitrile was added and the resulting system was evaporated to dryness, washed well with water, and dried. The resulting solid, $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)Cl][PF_6]$ (0.45 g, 94% yield), was recrystallized from dichloromethane–methanol: mp 235–236°; ir ($CHCl_3$) 2265 cm^{-1} (s) ($C{\equiv}N$) and other bands (Nujol mull) 1584 (vw), 1570 (vw), 1480 (m), 1436 (m), 1374 (w), 1180 (vw), 1354 (vw), 1093 (m), 1020 (vw), 993 (vw), 834 (vs), 757 (m), 734 (m), 704 (m), 684 (s), 553 (m), 517 (s), 498 (m), and 470 cm^{-1} (vw); pmr (CH_2Cl_2) τ 7.67 (t, *J*($Pt{-}CH_3$) = 20 Hz, $CNCH_3$) and 2.42 (m, $P(C_6H_5)_3$). *Anal.* Calcd for $C_{38}H_{33}ClF_6NP_3Pt$: C, 48.6; H, 3.54; N, 1.55; P, 9.90. Found: C, 48.7; H, 3.55; N, 2.23; P, 10.2.

$[\{(C_6H_5)_3P\}_2Pt(CNCH_3)SCN][BF_4]$, a white solid, was obtained in the reaction of KSCN and $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$ in acetonitrile: yield 78%; mp 216–218°; ir ($CHCl_3$) 2272 cm^{-1} (m) ($C{\equiv}N$), 2102 cm^{-1} (s) ($SC{\equiv}N$), and other bands (Nujol mull) 1587 (vw), 1573 (vw), 1483 (m), 1438 (s), 1303 (vw), 1287 (vw), 1184 (vw), 1157 (vw), 1097 (s), 1053 (vs), 996 (w), 743 (m), 708 (m), 690 (s), and 513 cm^{-1} (s); pmr ($CDCl_3$) τ 7.34 (m, $CNCH_3$) and 2.38 (m, $P(C_6H_5)_3$). *Anal.* Calcd for $C_{39}H_{33}BF_4N_2P_2PtS\cdot 0.7CHCl_3$: C, 48.2; H, 3.44; N, 2.83. Found: C, 47.9; H, 3.61; N, 3.16.

$[\{(C_6H_5)_3P\}_2Pt(CNCH_3)CN][BF_4]$ (white crystals, mp 240–242°, 60% yield) and $\{(C_6H_5)_3P\}_2Pt(CN)_2$ (34% yield) were obtained in the reaction of KCN and $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$ in acetonitrile.

$[\{(C_6H_5)_3P\}_2Pt(CNCH_3)CONHCH_3][BF_4]$ as pale yellow crystals; mp 184–186° (89% yield), was obtained in the reaction of $NaNO_2$ and $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$ in aqueous acetonitrile. This product was also formed in the reaction of KOH and $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$ in aqueous acetonitrile (97% yield). It was recrystallized from dichloromethane–hexane: ir (Nujol mull) 2235 cm^{-1} (s) ($C{\equiv}N$), 1598 cm^{-1} (s) ($C{=}O$), and other bands 3410 (w), 1508 (w), 1484 (m), 1436 (s), 1403 (w), 1377 (m), 1333 (vw), 1310 (vw), 1206 (m), 1150 (vw), 1096 (s), 1055 (vs), 1020 (s), 996 (w), 750 (s), 707 (m), 690 (s), 524 (s), 510 (s), and 500 cm^{-1} (m); pmr ($CDCl_3$) τ 7.49 (m, *J*($Pt{-}C{\equiv}NCH_3$) = 11 Hz, $C{\equiv}NCH_3$), 8.30 (m, $-NCH_3$), and 2.45 (m, $P(C_6H_5)_3$). *Anal.* Calcd for $C_{40}H_{37}BF_4N_2OP_2Pt$: C, 53.0; H, 4.12; N, 3.09; P, 6.84. Found: C, 52.4; H, 4.20; N, 3.11; P, 6.79.

Reaction of $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$ and Iodide Ion. A solution of $[(n\text{-}C_4H_9)_4N][I]$ (0.71 g, 1.9 mmol) in chloroform (8 ml) was added to a white suspension of $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$ (0.86 g, 0.88 mmol) in benzene (40 ml). Immediately upon introduction of the iodide solution, the reaction system became a bright yellow solution with no further change during 1 hr of stirring at 25°. After solvent removal, the resulting residue was dissolved in chloroform and the solution filtered. From the solution a yellow crystalline solid was precipitated by the addition of excess ethyl ether. The product, $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2I][BF_4]$ (0.71 g, 80% yield), was collected, washed with ethyl ether, and recrystallized from chloroform–ethyl ether: mp 118–120°; ir ($CHCl_3$) 2252 cm^{-1} (s) ($C{\equiv}N$) and other bands (Nujol mull) 1592 (vw), 1573 (vw), 1484 (m), 1438 (s), 1230 (vw), 1183 (vw), 1160 (vw), 1096 (s), 1058 (s), 996 (w), 750 (m), 710 (m), 692 (s), and 510 cm^{-1} (s); pmr ($CDCl_3$) τ 7.28 (s, $CNCH_3$) and 2.46 (m, $P(C_6H_5)_3$). *Anal.* Calcd for $C_{40}H_{36}BF_4IN_2P_2Pt\cdot 1.0CHCl_3$: C, 43.3; H, 3.29; I, 11.3; N, 2.48. Found: C, 43.2; H, 3.28; I, 12.6; N, 2.82.

Reaction of $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$ and Azide Ion. A solution of NaN_3 (0.056 g, 0.86 mmol) in water (20 ml) was added to a solution of $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$ (0.70 g, 0.72 mmol) in acetonitrile (30 ml). The reaction mixture was stirred at 25° for 6 hr, during which time a yellow suspension developed from an intensely colored orange solution. After the solvent was evaporated to 10 ml, the resulting system was extracted with chloroform. The chloroform solution was concentrated and filtered. From the filtrate, a pale yellow microcrystalline solid was precipitated by the addition of excess ethyl ether. The product, $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)(CN_4CH_3)][BF_4]$ (0.52 g, 78% yield), was collected, washed with ethyl ether, and recrystallized from chloroform–ethyl ether: mp 210–212°; ir ($CHCl_3$) 2261 cm^{-1} (m) ($C{\equiv}N$) and other bands (Nujol mull) 1588 (vw), 1577 (vw), 1484 (m), 1434 (s), 1267 (w), 1188 (w), 1144 (w), 1094 (s), 1060 (vs), 996 (w), 747 (m), 707 (w), 694 (s), and 510 cm^{-1} (s); pmr ($CDCl_3$) τ 7.52 (m, *J*($Pt{-}C{\equiv}NCH_3$) = 13 Hz, $CNCH_3$), 7.26 (m, $>C{=}NCH_3$), and 2.48 (m, $P(C_6H_5)_3$). *Anal.* Calcd for $C_{40}H_{36}BF_4N_5P_2Pt\cdot 0.5C_4H_{10}O$: C, 52.2; H, 4.29; N, 7.24; P, 6.41. Found: C, 52.4; H, 4.42; N, 7.24; P, 6.40.

Reaction of $[diphosPt(CNCH_3)_2][PF_6]_2$ and Iodide Ion. A solution of NaI (0.14 g, 0.91 mmol) in water (10 ml) was added to a solution of $[diphosPt(CNCH_3)_2][PF_6]_2$ (0.40 g, 0.41 mmol) in acetone (30 ml). The homogeneous mixture was stirred at 25° for 1 hr, during which time a pale yellow coloration persisted and methyl isocyanide was released. After solvent evaporation, the residue was extracted with chloroform and the chloroform phase evaporated to dryness. The residue was taken up in dichloromethane and filtered, and the resulting solution was evaporated to a low level. Addition of excess methanol gave the yellow crystalline $diphosPtI_2$ (0.12 g, 34% yield), which was identified by its infrared spectrum, mp >340°.

After separation of the above species, the resulting filtrate was evaporated to dryness. The residue was taken up in methanol (5 ml) and filtered, and the product, $[diphosPt(CNCH_3)I][PF_6]$ (0.17 g, 46% yield), was precipitated by water. The crude product was washed with water and purified from methanol–water: mp 112–116°; ir (Nujol mull) 2254 cm^{-1} (s) ($C{\equiv}N$) and other bands 1587 (w), 1575 (w), 1484 (m), 1436 (s), 1409 (w), 1377 (m), 1310 (vw), 1186 (w), 1160 (vw), 1102 (s), 1024 (w), 997 (m), 873 (m), 835 (vs), 746 (m), 710 (s), 686 (s), 653 (w), 556 (s), 532 (s), 482 (m), and 438 cm^{-1} (w); pmr ($CDCl_3$) τ 6.70 (m, *J*($Pt{-}CH_3$) = 13 Hz, $CNCH_3$), 6.8–8.0 (m, $-CH_2P$), and 2.43 (m, $P(C_6H_5)_3$). *Anal.*

Calcd for $C_{26}H_{27}F_6INP_3Pt$: C, 37.1; H, 3.00; I, 10.4; N, 1.54. Found: C, 37.1; H, 3.12; I, 10.2; N, 1.52.

Reaction of [diphosPt($CNCH_3$)$_2$][PF_6]$_2$ and Azide Ion. A solution of NaN_3 (0.056 g, 0.86 mmol) in water (10 ml) was added to a solution of [diphosPt($CNCH_3$)$_2$][PF_6]$_2$ (0.40 g, 0.41 mmol) in acetone (20 ml). The solution remained orange throughout the course of the reaction, Utilizing similar reaction conditions and work-up, the white crystalline product, diphosPt(CN_4CH_3)$_2$ (0.29 g, 90% yield) was precipitated and recrystallized from dichloromethane–methanol: mp 176–177°; ir (Nujol mull) 1588 (vw) 1573 (vw), 1487 (m), 1436 (s), 1409 (vw), 1376 (w), 1353 (m), 1260 (s), 1210 (w), 1133 (m), 1103 (s), 1060 (w), 1027 (vw), 997 (w), 950 (w), 877 (w), 820 (m), 751 (m), 743 (s), 711 (m), 690 (s), 646 (w) 531 (s), 482 (m), and 432 cm^{-1} (vw); pmr ($CDCl_3$) τ 6.57 (m, $J(Pt\text{–}CH_3)$ = 4 Hz, –C*H*$_3$), 7.0–8.0 (m, –C*H*$_2$P), and 2.56 (m, P(C_6*H*$_5$)$_2$). *Anal.* Calcd for $C_{30}H_{30}N_8P_2Pt$: C, 47.3; H, 4.00; N, 14.7; P, 8.08. Found: C, 47.1; H, 4.07; N, 14.1; P, 7.80.

Results and Discussion

The Alkylation of Platinum–Cyanide Complexes. Two general methods are used in the synthesis of metal–isocyanide complexes. The direct reaction of a compound of the metal with the free isocyanide, with or without ligand displacement, has been extensively pursued.[1] Though there are some aspects of this work which are unique to this ligand, such as the polymerization of the isocyanide catalyzed by metals (such as Ni^{2+})[1] and the reduction of the oxidation state of the metal either through disproportionation (Cr^{2+} + excess RNC → $Cr(CNR)_6$ + Cr^{3+})[26] or by a reduction by the anion (MnI_2 + excess RNC → $Mn(CNR)_6{}^+I_3{}^-$),[27] most of these studies are basically straightforward. For platinum, reactions of PtX_2 and isocyanides give two types of complexes, $(RNC)_2PtX_2$ and $[(RNC)_4Pt][PtX_4]$;[23] these formulas are typical for platinum(II) complexes, and the reactions leading to these products are the expected ones. The second general synthetic method for the preparation of metal–isocyanide complexes is by alkylation of a metal cyanide, usually accomplished with alkyl iodides or sulfates. A considerable effort had been expended in this area, centering especially on elements in group VIb, Ib, and IIb, on iron, and to a lesser extent on other metals including platinum.[1] The reaction of methyl iodide and either $K_2Pt(CN)_4$ or $Ag_2[Pt(CN)_4]$ has been shown to give $(CH_3NC)_2Pt(CN)_2$.[28] This is a particularly stable complex and cannot be further alkylated by methyl iodide, nor can the cyanide ion be displaced by addition of free isocyanide, in contrast to the facile reaction of $(RNC)_2PtX_2$ (X = halogen) and RNC to give $[(RNC)_4Pt][X]_2$.[23]

Initially in our work we looked at the reaction of methyl iodide and $(phos)_2Pt(CN)_2$ (phos represents several common phosphines), and found that in accord with the above observations it is not possible to form $[(phos_2)Pt(CNCH_3)_2][X]_2$ complexes by this route. However, the reaction of $(phos)_2Pt(CN)_2$ and the stronger alkylating agent $[R_3O][BF_4]$ (R = CH_3, C_2H_5) does give the complexes $[(phos)_2Pt(CNCH_3)_2][BF_4]_2$. The tetracyanoplatinate(II) ion can also be converted to tetrakis(methyl isocyanide)platinum(II) tetrafluoroborate using this reagent.

The $[(phos)_2Pt(CNCH_3)_2][BF_4]_2$ complexes are diamagnetic and square planar. The phosphine methyl proton resonance in the nmr of $[\{(C_6H_5)_2PCH_3\}_2Pt(CNCH_3)_2][BF_4]_2$ occurs as a 1:2:1 triplet, with equivalent coupling of these protons to both phosphorus atoms, which suggests a trans geometry.[29] From infrared evidence, the trans configuration appears appropriate for the other complexes prepared in this reaction except, of course, the complex [diphosPt($CNCH_3$)$_2$][PF_6]$_2$. The diphos complex shows the anticipated $\nu_{C\equiv N}$ bands at 2284 and 2191 cm^{-1}, whereas other $[(phos)_2Pt(CNR)_2][BF_4]_2$ complexes have a single sharp band in their infrared spectra, at approximately 2260 cm^{-1}.

The Reactions of Bis(phosphine)platinum Dihalides and Methyl Isocyanide. Replacement of either a single phosphine ligand or chloride ion by isocyanide would be expected to yield complexes of the types phosPt(CNR)X_2 and ([phos)$_2$Pt($CNCH_3$)X][X], respectively. Examples of each type of complex have been reported previously, though not from the direct reaction; in fact, attempts have not been made to study this substitution reaction in any detail. Compounds having the general formula phosPt(CNR)X_2 were prepared by the reaction of $(phos)_2Pt_2X_4$ and the free isocyanide;[2] this reaction, involving cleavage of the Pt–X–Pt bridging groups by a donor ligand such as an isocyanide can be considered to be typical behavior. In addition, the bis(phosphine)platinum dihalides and isocyanides are reported to react in the presence of $NaClO_4$ to form $[(phos)_2Pt(CNR)X][ClO_4]$.[11] Such reactions, run in the presence of a sodium salt of a noncoordinating anion, NaA (A = $ClO_4{}^-$, $B(C_6H_5)_4{}^-$, $PF_6{}^-$), are directly applicable to the synthesis in good yield of a number of $[(phos)_2Pt(L)R][A]$ (where L can be a variety of ligands and R can be halide,[11,30,31] hydride,[32] alkyl, or aryl[33,34]). In such a reaction the addition of the salt NaA is critical, since the driving force to product formation is linked, at least in part, to the precipitation of insoluble NaX from the reaction system.

The basic reaction system with which we are concerned in this work, involving the equilibrium

$$(phos)_2Pt(R)X + L \rightleftharpoons [(phos)_2Pt(L)R][X]$$

where R = alkyl, aryl, halide, hydride, was recognized some time ago by Basolo, *et al.*[33] These authors determined equilibrium constants from conductivity data for reactions of seven $\{(C_6H_5)_3P\}_2Pt(R)Cl$ (R = H, CH_3, aryl) species with pyridine in ethanol; they found that the equilibrium generally favored the reactants and suggested that this was the reason that the ionic product was not isolated. Equilibrium indices determined by the same conductometric method were reported more recently by Belluco and coworkers for reactions of $\{(C_2H_5)_3P\}_2PtHCl$ with eleven bases in 1,2-dichloroethane solvent.[32] Although several of these values were rather high, indicating that the ionic species was favored, these complexes were reported to be isolated only as perchlorates following addition of

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$NaClO_4$. No attempt appears to have been made to isolate the ionic complexes directly as halide salts.

In fact, successful isolation of the ionic complexes $[(phos)_2Pt(L)R][X]$ (X = halide) in direct reactions of a ligand L with $(phos)_2Pt(R)X$ (R = alkyl, aryl, H, halogen, etc.) has been accomplished in only a very few instances. The series of complexes $[(phos)_2Pt(CNCH_3)R][X]$ ($R = CH_3, C_6H_5$) was isolated in reactions of methyl isocyanide and $(phos)_2Pt(R)X$; formulation as 1:1 electrolytes was verified by conductivity data.[8] When $\{(C_2H_5)_3P\}_2Pt(R)X$ (R = alkyl, aryl,[35,36] hydride[37]) complexes were treated with diphos, 1 mol of triethylphosphine was lost, giving $[diphos\{(C_2H_5)_3P\}PtR][X]$. One other example of an ionic complex, $[\{C_6H_5)_2PCH_3\}_3PtCl][Cl]$, is reported to precipitate from benzene on addition of diphenylmethylphosphine to the bis(phosphine)platinum dihalide.[31] This complex and also $[diphos\{(C_2H_5)_3P\}PtH][X]$ (X = Cl, Br)[37] are probably isolable only by virtue of their insolubility in the solvent; attempts to dissolve these species for recrystallization leads only to decomposition to unidentified products. On the other hand, the complexes $[(phos)_2Pt(CNCH_3)R][X]$[8] and $[diphos\{(C_2H_5)_3P\}PtR][X]$[35,36] are stable in solution in polar solvents.

In the light of the unencouraging equilibrium constants and the relatively few ionic complexes, $[(phos)_2Pt(L)R][X]$, isolated in direct ligand + $(phos)_2Pt(R)X$ reactions, our results are particularly interesting. The isolation of stable ionic complexes, usually having the formula $[(phos)_2Pt(CNCH_3)X][X]$, from the reaction of $(phos)_2PtX_2$ and methyl isocyanide in our work seems to be the general rule.

We studied the reaction of $\{(C_6H_5)_3P\}_2PtCl_2$ with methyl isocyanide in most detail. Results of these studies are summarized in the equations below.

$$\begin{tikzcd}
\{(C_6H_5)_3P\}_2PtCl_2 \arrow[r, "C_6H_6,\ 25°", "CNCH_3"'] \arrow[d, "\substack{CNCH_3\\ acetone,\ 25°}"'] & \{(C_6H_5)_3P\}Pt(CNCH_3)Cl_2 \arrow[dl, shift left, "\substack{acetone,\ 25°\\ +(C_6H_5)_3P}"] \\
{[\{(C_6H_5)_3P\}_2Pt(CNCH_3)Cl][Cl]} \arrow[ur, shift left, "\substack{C_6H_6,\ 25°\\ -(C_6H_5)_3P}"] &
\end{tikzcd}$$

The reaction is dependent on the choice of solvent. In the polar solvent acetone, $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)Cl][Cl]$ is the only product. This is stable and isolable, and is recrystallizable from acetone on slow addition of ether. However, when it is dissolved in a less polar solvent chloroform, and benzene is added, it converts completely to $\{(C_6H_5)_3P\}Pt(CNCH_3)Cl_2$ with phosphine loss. The reverse reaction may be carried in acetone if an equivalent of phosphine is present.

The reaction of $\{(C_6H_5)_3P\}_2PtCl_2$ suspended in benzene and methyl isocyanide proceeds with formation of a transient yellow color directly to white $\{(C_6H_5)_3P\}Pt(CNCH_3)Cl_2$, soluble in the solvent. The product is anticipated from the above conversion of $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)Cl][Cl]$ to $\{(C_6H_5)_3P\}Pt(CNCH_3)Cl_2$ on dissolution in chloroform. The transient yellow color may be associated with an unstable intermediate such as $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2Cl][Cl]$; the analogous five-coordinate bromide complex is isolable in the same reaction and is rather intensely colored; it readily loses one isocyanide to give the pale-yellow-colored $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)Br][Br]$, which is also isolable. The yellow iodide complex, $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2I][I]$, is the only product isolable in the reaction of $\{(C_6H_5)_3P\}_2PtI_2$ and methyl isocyanide under the same conditions. It does not lose isocyanide.

The stoichiometry of these complexes has been determined by elemental analyses and also by nmr, since integration of relative intensity of phosphine and isocyanide proton resonances is possible. Measurements on the conductivity of these complexes in acetonitrile and dichloromethane leaves no doubt of the uniunivalent electrolyte formulation of the ionic complexes (see Table I). It is particularly interesting to note that conductivity data on $[(phos)_2Pt(CNCH_3)_2I][I]$ suggests this to be a 1:1 electrolyte and not a 1:2 electrolyte, for this demands that platinum be five-coordinate.

Logically one concludes that it is the character of the solvent which is controlling the isolation of $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)Cl][Cl]$. This assistance could be due to solvation of the ions, which stabilizes the charged species in solution and makes phosphine loss an unfavorable process. In the absence of a polar solvent, this added stabilization is not gained and this complex reverts to the uncharged species. The reaction can be reversed by the addition of acetone.

The reaction of the complexes $\{(C_6H_5)_3P\}_2PtX_2$ and methyl isocyanide in benzene can be summarized.

$$(phos)_2PtI_2(s) + CNCH_3 \xrightarrow{C_6H_6} \underset{\text{(isolated)}}{(phos)_2Pt(CNCH_3)_2I^+I^-} \tag{1}$$

$$(phos)_2PtBr_2(s) + CNCH_3 \xrightarrow{C_6H_6} \underset{\text{(isolated)}}{[(phos)_2Pt(CNCH_3)_2Br][Br]} \xrightarrow[\substack{\text{crystallization}\\ -1CNCH_3}]{\text{repeated}} \underset{\text{(isolated)}}{[(phos)_2Pt(CNCH_3)Br][Br]} \tag{2}$$

$$\begin{tikzcd}
 & {[(phos)_2Pt(CNCH_3)Cl][Cl]} \\
(phos)_2PtCl_2(s) + CNCH_3 \arrow[r] & \underset{\text{(transient, postulated)}}{[(phos)_2Pt(CNCH_3)_2Cl][Cl]} \arrow[u, "\text{in acetone}"'] \arrow[d, "\substack{(CNCH_3,\\ phos)}"', "\text{in } C_6H_6"] \\
 & \underset{\text{(isolated)}}{phosPt(CNCH_3)Cl_2} \quad (3)
\end{tikzcd}$$

The analogous reactions with $\{(C_2H_5)_3P\}_2PtX_2$ and methyl isocyanide appear mostly complementary to the reactions above. In each case (X = Cl, Br, I) the isolated product (using benzene) is $[\{(C_2H_5)_3P\}_2Pt(CNCH_3)X][X]$. The reaction for X = I appears to proceed *via* $[\{(C_2H_5)_3P\}_2Pt(CNCH_3)_2I][I]$ which cannot be isolated, readily losing 1 equiv of methyl isocyanide. So it appears that these reactions to the ionic species are rather general. The exceptional reaction would seem to be that of $\{(C_6H_5)_3P\}_2PtCl_2$ and methyl isocyanide in benzene to give $\{(C_6H_5)_3P\}Pt(CNCH_3)Cl_2$.

The reactions of $\{(C_6H_5)_3As\}_2PtX_2$ (X = Cl, I) with methyl isocyanide (1:1) give $\{(C_6H_5)_3As\}Pt(CNCH_3)X_2$; with excess methyl isocyanide, $(CH_3NC)_2PtX_2$ is the isolated product. Replacement of both ligands in $\{(C_6H_5O)_3P\}_2PtI_2$ by excess isocyanide is also

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(35) F. Glockling and K. A. Hooton, *J. Chem. Soc. A*, 826 (1968).
(36) K. A. Hooton, *ibid.*, *A*, 1896 (1970).
(37) M. Guistiniani, G. Dolcetti, and U. Belluco, *ibid.*, *A*, 2047 (1969).

observed. These results are anticipated from lower phosphite- and arsine–platinum bond strengths.

An interesting fringe benefit in this work is derived from the isolation of the five-coordinate platinum(II) species $[(\mathrm{phos})_2\mathrm{Pt(CNCH_3)_2X}][\mathrm{X}]$. Five-coordination for platinum(II) is not new, but it is nonetheless a rare phenomenon for complexes with unidentate ligands. In fact, the only well-known example of a five-coordinate platinum(II) species is the anion $\mathrm{Pt(SnCl_3)_5}^{3-}$. The existence of the species $[\{(\mathrm{C_6H_5})_3\mathrm{P}\}_2\mathrm{Pt(CNCH_3)_2I}][\mathrm{I}]$ is no doubt related to several factors. The platinum–iodide bond strength is high. In addition, iodide is not a strongly polarizing ligand; this leaves a lower net positive charge on the metal and may mean that back-bonding to the isocyanide ligand is more favorable, stabilizing the platinum–isocyanide and platinum–phosphine bonds in $[(\mathrm{phos})_2\mathrm{Pt(CNCH_3)_2I}][\mathrm{I}]$ against dissociation. However, we can see no way to avoid the conclusion that the two phosphine ligands, and specifically triphenylphosphine ligands, play an integral part in this stabilization. Even the analogous triethylphosphine complex is apparently not stable.

One other observation was made in this work which appears most remarkable. When a benzene suspension of $[\{(\mathrm{C_6H_5})_3\mathrm{P}\}_2\mathrm{Pt(CNCH_3)X}][\mathrm{X}]$ ($\mathrm{X} = \mathrm{Cl, Br}$) or $[\{(\mathrm{C_2H_5})_3\mathrm{P}\}_2\mathrm{Pt(CNCH_3)Cl}][\mathrm{Cl}]$ was refluxed, an elimination of the elements $\mathrm{CH_3{-}X}$ occurred. The resulting platinum complex, $(\mathrm{phos})_2\mathrm{Pt(CN)X}$, was isolable in good yield in each case. Quite frankly, we had expected to find the compounds $\mathrm{phosPt(CNCH_3)X_2}$ in these reactions; only in the thermal reaction of $[\{(\mathrm{C_6H_5})_3\mathrm{P}\}_2\mathrm{Pt(CNCH_3)Cl}][\mathrm{Cl}]$ was $\{(\mathrm{C_6H_5})_3\mathrm{P}\}\mathrm{Pt(CNCH_3)Cl_2}$ observed as a secondary product.

This dealkylation reaction is, in principle, the opposite of the general synthetic methods for isocyanide formation involving alkylation of a metal cyanide. It had been observed, but not fully appreciated, twice before in our group. Once we observed $\mathrm{C_5H_5Fe(CO)_2CN}$ as a minor though reproducible product, in the reaction of $[\mathrm{C_5H_5Fe(CO)_2CNCH_3}][\mathrm{X}]$[38] and pentafluorophenyllithium. Subsequently we prepared in the reaction of $\{(\mathrm{C_6H_5})_3\mathrm{P}\}_2\mathrm{Pt(C_6F_5)Br}$ and methyl isocyanide a weak 1:1 adduct which at benzene reflux was converted to $\{(\mathrm{C_6H_5})_3\mathrm{P}\}_2\mathrm{Pt(C_6F_5)CN}$.[8] Interestingly, there is also an old reference to an analogous reaction.[39]

The significance of the dealkylation reaction in both the mechanistic sense and also the thermodynamic sense is not yet clear, and some additional information is needed. We prefer to visualize this reaction as involving halide attack at the metal followed by $\mathrm{CH_3X}$ elimination (figure of ref 12). Such a route is analogous to most reactions of square-planar platinum(II) species.[40] The driving force in our systems may be the volatility (and loss) of $\mathrm{CH_3X}$.

Reactions of Isocyanide–Platinum(II) Complexes and Various Nucleophilic Reagents. Platinum(II) complexes, like most complexes of metals having a d^8 configuration, possess square-planar geometry. One of the typical properties of this geometry is ligand lability. Both the phenomenon of ligand exchange and the facile substitution of one ligand for another are common for square-planar complexes; there is substantial documentation for this in platinum(II) complex chemistry because of extensive work on the trans-effect phenomenon. Most ligand substitution reactions follow a common pathway involving ligand approach along the least hindered axis, with formation of a five-coordinate intermediate which is generally not isolated; this in turn loses a ligand group to return to the square-planar geometry. On occasion, the intermediate may undergo intramolecular rearrangement with the same net effect.

In view of this particularly strong precedent, it is anticipated that most nucleophilic reactions of $[(\mathrm{phos})_2\mathrm{Pt(CNCH_3)_2}][\mathrm{X}]_2$ will lead simply to ligand substitution. Indeed, in this study, this seems to be the reaction type of primary importance; it is observed here for a variety of reactions with simple nucleophiles such as chloride, bromide, iodide, cyanide, and thiocyanate. Choosing mild conditions (room temperature, several hours), only a single substitution of anion for isocyanide was observed for $[(\mathrm{phos})_2\mathrm{Pt(CNCH_3)_2}][\mathrm{A}]_2$ complexes of triphenylphosphine. Utilizing the same conditions, complexes of the chelating 1,2-bisdiphenylphosphinoethane (diphos) proceed to disubstituted products.

It is possible to isolate the five-coordinate complex $[\{(\mathrm{C_6H_5})_3\mathrm{P}\}_2\mathrm{Pt(CNCH_3)_2I}][\mathrm{BF_4}]$ from iodide addition to $[\{(\mathrm{C_6H_5})_3\mathrm{P}\}_2\mathrm{Pt(CNCH_3)_2}][\mathrm{BF_4}]_2$. The same complex, as the iodide salt, had been obtained from $\{(\mathrm{C_6H_5})_3\mathrm{P}\}_2\mathrm{PtI_2}$ and methyl isocyanide. Both iodide and tetrafluoroborate salts showed similar conductivity values, supporting our postulated five-coordinate structure.

The reactions of azide ion and $[(\mathrm{phos})_2\mathrm{Pt(CNCH_3)_2}][\mathrm{A}]_2$ also served to differentiate the behavior of the diphos complex from that of the nonchelated phosphine complexes. Here the reactions observed were

$$\{(\mathrm{C_6H_5})_3\mathrm{P}\}_2\mathrm{Pt(CNCH_3)_2}][\mathrm{A}]_2 + \mathrm{N_3}^- \longrightarrow [\{(\mathrm{C_6H_5})_3\mathrm{P}\}_2\mathrm{Pt(CNCH_3)(CN_4CH_3)}][\mathrm{A}$$

$$[\mathrm{diphosPt(CNCH_3)_2}][\mathrm{PF_6}]_2 + 2\mathrm{N_3}^- \longrightarrow \mathrm{diphosPt(CN_4CH_3)_2}$$

The $-\mathrm{CN_4CH_3}$ group arises from addition of methyl isocyanide and azide ion to give a cyclic tetrazole-like ligand. The reaction probably proceeds by attack of azide ion on the square-planar complex to give an intermediate five-coordinate species containing the metal bonded both to isocyanide and azide groups which then undergoes a facile intramolecular rearrangement. Attack at the metal seems reasonable in view of the precedent established with other nucleophiles listed above; however, we cannot rule out attack at a coordinated isocyanide by the azide ion on the basis of our data since such a reaction would obviously lead to the same product. Beck and coworkers have previously studied reactions involving cyclization of azide with various ligands (RCN,[41] $\mathrm{CS_2}$, $\mathrm{CF_3CN}$, $\mathrm{C_6H_{11}NC}$[42]) when the ligand was added to a metal–azide complex; presumably, such reactions proceed by an analogous azido–ligand–metal complex.

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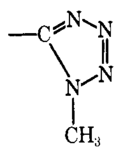
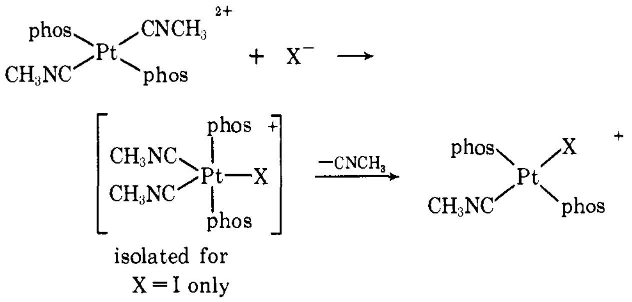
The most likely structure for the $-CH_4CH_3$ ligand group is shown below.

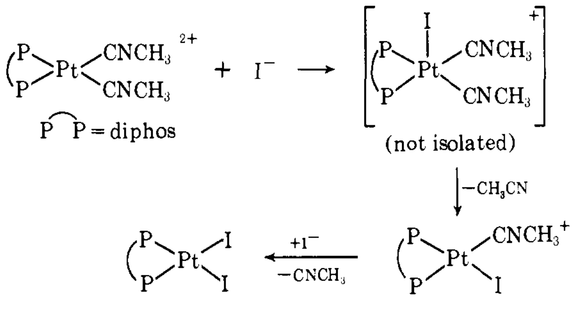


The ligand group is formally one of the two possible isomers of a tetrazole (5-metalo-1-methyl-1,2,3,4-tetrazole), and its structure from the combination of isocyanide and azide can be easily seen. Any other structure would require substantial rearrangement, such as alkyl migration.

Summarizing, the general pathway for reactions of $[(phos)_2Pt(CNCH_3)_2][X]_2$ and anions using mild conditions appears to be



where phos = $(C_6H_5)_3P$, X = Cl, SCN, CN, I; and



The reaction of pentafluorophenyllithium and $[(phos)_2Pt(CNCH_3)_2][A]_2$ complexes gives pentafluorophenyl complexes of platinum. From $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$ two compounds, the known $\{(C_6H_5)_3P\}_2Pt(C_6F_5)_2$[25] and $\{(C_6H_5)_3\}(CH_3NC)Pt(C_6F_5)_2$, are observed. The complex diphosPt$(C_6F_5)_2$ was formed from [diphosPt$(CNCH_3)_2$][PF_6]$_2$; the analogous methyl compound was formed from methyllithium. Although one can visualize possible ligand addition to the isocyanide group to give pentafluorobenzimino complexes (as observed for $[C_5H_5Fe(CO)_{3-x}(CNCH_3)_x][A]$ and organolithium reagents[38]), this did not occur. It is true, however, that the ligands in the six-coordinate iron systems are considerably less readily replaced than are ligands in d^8 square-planar platinum complexes. The very rapid substitution reactions for platinum presumably could preempt the alternative of ligand attack.

Ligand attack does occur, however, with alkoxide ion. With $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$, alkoxide ion adds to one isocyanide giving $[\{C_6H_5)_3P\}_2Pt(CNCH_3)C(OR){=}NCH_3][BF_4]$ (R = CH_3, C_2H_5), whereas with the diphos complex addition of two methoxide groups occurs giving diphosPt$\{C(OCH_3){=}NCH_3\}_2$. Alcohols also add to one isocyanide in the triphenylphosphine complex and to two in the diphos complex. The addition of alcohols to coordinated isocyanides has been observed before.[2-4] The addition of an alkoxide to the coordinated isocyanide is not unexpected in view of the known addition of alkoxide ion to carbonyls in complexes of several metals.[43-45]

Strictly speaking, the behavior of the two complexes $[\{C_6H_5)_3P\}_2Pt(CO)X][A]$ and $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][A]_2$ are not comparable, but there ought to be some interesting analogies. Work on the former system, by Clark and coworkers,[46,47] showed that alcohols (ROH) add to this system with concurrent loss of H^+, presumably to the solvent ($\rightarrow ROH_2^+$), and formation of $\{(C_6H_5)_3P\}_2Pt(COOR)X$. Addition of aqueous HBF_4 causes the reverse reaction to proceed, and at higher temperature, water causes degradation to $\{(C_6H_5)_3P\}_2PtHX$, carbon dioxide, and the alcohol. Regrettably, no work with addition of alkoxide ion is reported, but presumably this reagent and $[\{(C_6H_5)_3P\}_2Pt(CO)X][A]$ should also generate $\{(C_6H_5)_3P\}_2Pt(COOR)X$. In our work, the complex $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$ adds one molecule of methanol to give $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)C(OCH_3){=}NHCH_3][BF_4]_2$ which, even though more highly charged than hypothetical $[\{(C_6H_5)_3P\}_2Pt\{C(OCH_3){=}OH\}X][A]$, does not give up its acidic proton. This clearly indicates the stronger acceptor properties of the nitrogen atom in the *m*-C(OR)=NR system *vs.* the acceptor capabilities of *m*-C(OR)=O (*i.e.*, *m*-COOR), a phenomenon on which we have commented before.[48] The complex $[\{(C_6H_5)_3P\}_2Pt(CNCH)_3C(OR){=}NCH_3][BF_4]$ is stable to water, although we have not carried out studies using forcing conditions analogous to those described by Clark and Jacobs.[47]

The fact that alkoxides (and alcohols) do not react with ligand displacement is noteworthy since virtually all other nucleophiles do react in this fashion. Perhaps this reflects a low affinity of oxygen ligands for platinum.

The reaction of nitrite ion with $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$ was unusual; the product characterized from this reaction is $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)CONHCH_3][BF_4]$. We had some doubts about the identity of this compounds, until its synthesis was accomplished by addition of hydroxide ion to this complex. Several mechanisms can be suggested for the formation of this complex from nitrite ion. One possibility involves nitrite attack at a coordinated isocyanide. The resulting product could then pick up a proton from the solvent and split off NO^+; the latter would immediately react with the solvent.

The differences in behavior between $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2][BF_4]_2$ and [diphosPt$(CNCH_3)_2$][PF_6]$_2$ observed throughout this work are interesting. One notes first that there are no isolated five-coordinate intermediates in reactions of nucleophiles with the diphos complex. This seems to be in accord with the feeling, ex-

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pressed earlier, that there are rather subtle criteria for stability of these complexes. The only stable complex (stable to loss of one ligand) is $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2I][BF_4]$; we suspect that this has a trigonal-bipyramidal structure with phosphines in trans (axial) positions. Diphos, which chelates cis positions, could not give an analogous complex. Not so clear, however, is an explanation for the reaction of two nucleophilic groups with the diphos complex, leading to an uncharged complex. No disubstitution products were found in the reaction of the triphenylphosphine complexes except with organolithium compounds. In view of the relatively facile nature of these reactions, it is somewhat hard to picture this as a kinetic phenomenon, and one cannot make a strong case using trans-effect arguments. Presumably, for reactions of complexes of triethyl- and triphenylphosphine, several thermodynamic effects (including heat of solvation) control how many groups substitute.

Acknowledgments. We are pleased to acknowledge support from the National Science Foundation through Grants No. GP-8140 and GP-17207, and from the University of Wisconsin Graduate School.

Polarized Crystal Absorption Spectra for Dichloro(ethylenediamine)platinum(II). Evidence for Ionic Exciton States[1]

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Received December 14, 1970

Abstract: In $Pt(en)Cl_2$ crystals, flat molecules stack in chains along an orthorhombic *c* axis. Crystal absorption spectra at 300 and 77°K with light polarized in the *b* and *c* directions are reported for the region 18,000–42,000 cm^{-1}. These spectra indicate pronounced crystal effects from comparisons with the solution spectrum. A one-dimensional exciton theory is applied which accounts for the observed features. A dipole-allowed transition, $d_{xy} \leftarrow L(\pi)$, has been shifted from $\sim$49,000 to 37,500 cm^{-1} with *c* polarization by crystal perturbations. In *b* polarization the temperature dependence indicates some allowed character to two weak bands at 33,100 and 39,100 cm^{-1}. These two bands have been assigned as unusual transitions to ionized exciton states based on the excitation of an electron into a d_{xy} (σ antibonding orbital) from the d_{z^2} and $L(\pi)$ orbitals on adjacent molecules, respectively.

In a recent X-ray diffraction study, Jacobson and Benson[2] have shown that crystals of $Pt(en)Cl_2$ belong to the orthorhombic system, space group $C222_1$, $a:b:c$ = 12.44:8.12:6.78 Å with four molecules per unit cell. The nearly planar molecules stack in a nearly linear array as shown in Figure 1 along the *c* axis. The crystal symmetry requires a uniform spacing between adjacent platinum atoms of 3.39 Å. These chains of stacked molecules are arranged in approximately a close-packed manner, so each molecule is surrounded by six neighbors in a plane with the Pt–Pt distances in the range of 7.5–8.1 Å. Each molecule in a 001 plane has the same orientation in space. The crystals have an exceptionally ideal orientation for spectral studies since the chains are directed along the orthorhombic *c* axis, and the symmetry axis and dipole moment of every molecule are in the $\pm b$ direction. It is possible to obtain directly, therefore, the absorption spectra with polarizations in these two important molecular directions.

A preliminary note concerning the crystal spectra was published earlier.[3] In that work the existence of an absorption peak with *b* polarization was noted which becomes narrower but higher at lower temperatures. Such behavior is not characteristic of vibronic excitation. A band theory in which the platinum d electrons were delocalized along the chains was proposed to account for this behavior. However, certain features of the crystal spectra did not appear consistent with such a delocalization. Consequently, exciton theory, which has proved so effective with aromatic organic molecular crystals,[4] has been applied to the interpretation of these spectra. The alignment of the molecules with respect to orthorhombic axes and the close approach of the platinum atoms provided some effects which are not usually encountered in the aromatic crystals. However, the fine structure which is commonly encountered with organic molecules does not occur with this coordination compound.

The present work includes crystal spectra of considerably higher quality than the earlier report, as thinner crystals have been obtained. It has been possible to extend the spectral range to shorter wavelengths and, in addition, certain limitations of the instrumenta-

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(1) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission; Contribution No. 2822.

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