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REACTIONS OF DIMETHYL- AND DIPHENYL-PLATINUM(II) COMPLEXES AND ISOCYANIDES

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SUMMARY

Reactions of PtR_2L_2 species ($R=CH_3$, C_6H_5; L = several phosphines) with methyl and *p*-chlorophenyl isocyanides were found to proceed either with ligand substitution or isocyanide insertion into the carbon–metal bond; the type of reaction was dependent on the nature of the phosphine and isocyanide. Substitution yielding $PtR_2(CNR')(Phos)$, occurred for Phos = PPh_3 with both isocyanides and for PPh_2Me, with *p*-chlorophenyl isocyanide; insertion occurred for Phos = PEt_3 for both isocyanides and for $PPhMe_2$ with *p*-chlorophenyl isocyanide. Interestingly, no product was isolated in the reactions of PtR_2Phos_2 (Phos = PPh_2Me and $PPhMe_2$) with methyl isocyanide, a result attributed to the unfavorable position of an equilibrium, $PtR_2Phos_2 + CNMe \rightleftarrows PtR_2(CNMe)Phos + Phos$, in these systems. If methyl iodide is added to these reaction systems two possible reactions can occur. A deficiency of methyl iodide can quaternize the free phosphine allowing the isocyanide substitution reaction product to be isolated (Phos = PPh_2Me only). Alternatively, excess methyl iodide will add oxidatively to give the platinum(IV) species $PtIMe_3(L)Phos$ (L = Phos or CNMe).

INTRODUCTION

A preliminary report of our work on reactions of $PtXR(PPh_3)_2$* and $PtR_2(PPh_3)_2$ (X = halogen, R = Me, Ph) with methyl isocyanide has appeared[1]. Subsequently we have extended the work on reactions of other platinum(II) species having the stoichiometry $PtXR(Phos)_2$ with methyl- and *p*-chlorophenyl isocyanide[2]. A general pattern of reactivity emerges from this study, wherein these platinum(II) complexes are shown to give, initially, stable 1/1 adducts with isocyanides having the formula, $[PtR(CNR')(Phos)_2]X$. The ionic formulation of these species in solution is supported by conductivity data. Upon heating, these adducts may rearrange with insertion of the isocyanide into the carbon–metal bond**; alternatively dealkylation

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* Common abbreviations will be used throughout (Phos = a phosphine; $Ph=C_6H_5-$, $Me=CH_3-$; $Et=C_2H_5-$).

** For a recent review on isocyanide insertion reactions see ref. 3.

occurs in several instances. The product of isocyanide insertion may add an additional mole of isocyanide. However the reaction does not proceed past this point; in particular subsequent insertion reactions are not observed, in contrast to multiple insertion reactions which occur with analogous nickel[4] and palladium[4,5] systems, and which are believed to occur in polymerizations of isocyanides by various metal species[6] including nickel alkyls[4].

In contrast to these apparently general and relatively facile insertion reactions, the reaction of $PtR_2(PPh_3)_2$ (R = Me, Ph) and methyl isocyanide gave only ligand replacement, yielding $PtR_2(CNMe)PPh_3$[1]. Failure to accomplish an isocyanide insertion was also noted in the reaction of $PtMe_2(PPhMe_2)_2$ and *p*-methoxyphenyl isocyanide[7]; the product $PtMe_2(CNC_6H_4OCH_3)(PPhMe_2)$ was obtained instead.

A further search of the literature reveals that insertion reactions with PtR_2L_2 species are in fact quite rare, whereas insertion reactions involving the carbon–metal bond in $PtXRL_2$ have been extensively documented. In one instance carbonylation was demonstrated by the isolation of $Pt(COMe)(Me)(Et_2PCH_2CH_2PEt_2)$ from the reaction of $PtMe_2(Et_2PCH_2CH_2PEt_2)$ and carbon monoxide. However attempted carbonylation of analogous complexes PtR_2L_2 (R = Me, Ph, L = PEt_3; R = Me, L = PPh_3) gave either a polynuclear platinum(0) complex or degradation. As biacetyl was a second product in one of these reactions the suggestion was made that carbonylation precedes reduction[8]. More recently Clark and Puddephatt[9] were able to insert tetrafluoroethylene into one or both carbon–platinum bonds in $PtMe_2L_2$ (L = $AsPhMe_2$, $PPhMe_2$). A similar reaction with $HC{\equiv}CCF_3$ gave $Pt(CH_3)(C{\equiv}CCF_3)L_2$ or $Pt(C{\equiv}CCF_3)_2L_2$ species, though, presumably via an intermediate acetylene–metal complex from which methane was eliminated[10].

We now report on efforts to follow up our earlier work involving isocyanide and PtR_2L_2 species. This study led to results which were not anticipated from the earlier work: we have found that ligand substitution or insertion may result depending on the choice of ligand L in this starting complex, and on the chosen isocyanide.

EXPERIMENTAL

All reactions were carried out under a nitrogen atmosphere. Melting points were taken on a Kofler hot-stage and are uncorrected. Infrared spectra using Nujol and Fluorolube mulls were recorded on a Beckman IR-10 spectrometer. High resolution data was obtained on a Perkin–Elmer Model 457 grating spectrometer using suitable scale expansion. Molecular weight determinations were made on chloroform solutions using a Mechrolab Osmometer, Model 301A. PMR spectra were recorded on a Varian A-60A and JEOL-NM-MH-100 instruments; data on new compounds are given in Tables 1 and 2. Analyses were performed by Meade Microanalytical Laboratories, Amherst, Mass. and by Galbraith Laboratories, Knoxville, Tenn.

Starting materials

Methyl[11] and *p*-chlorophenyl[12] isocyanides were prepared by the literature methods. The platinum(II) complexes PtR_2L_2 (R = Me, Ph; L = PPh_3, PPh_2Me, $PPhMe_2$, PEt_3) were prepared from the appropriate $PtCl_2L_2$ complex and methyl or phenyl Grignard reagents, according to the method of Chatt and Shaw[13]. Two complexes $PtPh_2(PPh_2Me)_2$ and *cis*-$PtPh_2(PPhMe_2)_2$ appear not to be described before; data of these complexes is given below.

$PtPh_2(PPh_2Me)_2$: *cis*- and *trans*-isomers co-precipitate as white prisms (recrystallized from benzene/ethanol), m.p. 150–152°, obtained in 74% yield. (Found: C, 60.06; H, 4.79. $C_{38}H_{36}P_2Pt$ calcd.: C, 60.88; H, 4.84%.)

Infrared: 3050 w, 1570 m, 1435 s, 1310 w, 1179 m, 1148 w, 1100 m, 1070 w, 1018 m, 995 w, 895 m(sh), 890 s, 880 s, 747 m, 735 s(sh), 727 vs, 700 s(sh), 690 vs, 510 m, 497 s, 487 s, 447 m, 420 m cm^{-1}.

PMR ($CDCl_3$). τ 8.75 ppm (t* of d), $^3J(^{195}Pt\text{–}H) = 29$ Hz, $^2J(P\text{–}H) = 8$ Hz, P–Me (*cis* isomer); τ 8.59 ppm (t* of t), $^3J(^{195}Pt\text{–}H) = 34$ Hz, $|^2J(P\text{–}H) + {}^4J(P\text{–}H)| = 4$ Hz, P–Me, (*trans* isomer); τ 3.43 ppm (m), Pt–C_6H_5; τ 2.72 ppm (m), P–C_6H_5.

*cis-$PtPh_2(PPhMe_2)_2$**. White prisms (recrystallized from benzene/ethanol), m.p. 125–127°, were obtained in 82% yield. (Found: C, 53.51, H, 5.54. $C_{28}H_{32}P_2Pt$ calcd.: C, 53.76; H, 5.16%.)

Infrared: 2050 m, 1570 s, 1490 m, 1435 s, 1422 m, 1410 m, 1323 w, 1293 m, 1280 m, 1180 w, 1146 w, 1102 m, 1070 w, 1062 w, 1055 w, 1020 s, 1000 w, 940 vs, 912 vs, 900 vs, 860 w, 841 m(sh), 831 s, 731 vs, 721 s(sh), 701 s, 690 vs, 675 m, 653 w, 490 vs, 423 m cm^{-1}.

PMR ($CDCl_3$). τ 8.80 (t* of d), $^3J(^{195}Pt\text{–}H) = 21$ Hz, $^2J(P\text{–}H) = 8$ Hz, P–Me; τ 3.22 and 3.10 (m), Pt–C_6H_5; τ 2.72 (m), P–C_6H_5.

Substitution reactions

A. Direct substitution

The reactions of $PtR_2(Phos)_2$ ($R = CH_3, C_6H_5$; Phos $= PPh_3$) with methyl and *p*-chlorophenyl isocyanide, and of $PtR_2(PPh_2Me)_2$ with the latter isocyanide, gave only $PtR_2(CNR')(Phos)$ species arising from ligand substitution. The following general procedure was followed.

The starting platinum complex, generally in about one millimolar quantity was slurried in 10 ml benzene. An equimolar quantity of the isocyanide in about 10 ml of benzene was added dropwise with stirring. At this time a yellow color was occasionally observed (in the case of the PPh_3 complexes). In some instances, usually using *p*-chlorophenyl isocyanide, the slurry dissolved. After stirring at room temperature for a short time (≈ 1 h) the solvent was evaporated off, and the residue crystallized using an appropriate solvent combination. Obtained in this manner were the following compounds:

cis-$PtPh_2(CNMe)(PPh_3)$. Obtained as white crystals, 90% yield, from benzene/hexane, m.p. 175–177°d. (Found: C, 58.9; H, 4.23; N, 2.21; P, 4.70. Mol. wt. 653. $C_{32}H_{28}NPPt$ calcd.: C, 58.9; H, 4.32; N, 2.15; P, 4.75%. Mol. wt. 652.)

Infrared: 2195 s (C≡N); 1568 m, 1477 m, 1432 s, 1401 m, 1155 w, 1175 w, 1091 m, 1073 w, 1018 m, 992 w, 750 m(sh), 727 s, 695 s(sh), 685 s, 522 s, 508 s, 492 m cm^{-1}.

cis-$PtMe_2(CNMe)(PPh_3)$. Obtained as a white solid, 93% yield, from methanol, m.p. 160–161°. (Found: C, 50.28; H, 4.65; N, 2.57. Mol. wt. 546. $C_{22}H_{24}NPPt$ calcd.: C, 50.00; H, 4.58; N, 2.65%. Mol. wt. 528.)

Infrared: 2195 s (C≡N); 1479 s, 1435 s, 1412 s, 1310 w, 1179 m, 1173 m, 1092 s, 1067 w, 1022 w, 997 w, 752 s, 742 s, 698 s(sh), 691 s, 542 m(sh), 529 s, 510 s, 496 s, 459 m, 423 m cm^{-1}.

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* *trans*-$PtPh_2(PPhMe_2)_2$ has been described however: see Ref. 14.

TABLE 1

PMR DATA FOR PLATINUM(II) INSERTION AND SUBSTITUTION PRODUCTS[a,b]

Compound	*Pt–R and PtC(R)=N* [*mult.; J(Pt–H), J(P–H)*]	*C≡NR and* $>$*C=NR* [*mult.; J(Pt–H), J(P–H)*]	*Phosphine ligand(s)* [*mult.; J(Pt–H), J(P–H)*]
cis-$PtPh_2(CNMe)(PPh_3)$	3.66(m) Ph *trans* to P 3.10(m) Ph *cis* to P	7.40 (t*, 12 Hz)	2.70(m)
cis-$PtMe_2(CNMe)(PPh_3)$	9.68(t* of d; 69 Hz, 8.7 Hz) Me *trans* to P 9.23(t* of d; 74 Hz, 7.5 Hz) Me *cis* to P	7.28(t* of d; 12 Hz, 1.5 Hz)	2.68(m), 2.50(m)
cis-$PtPh_2(CNC_6H_4Cl)(PPh_3)$	3.43(m) Ph *trans* to P 3.10(m) Ph *cis* to P	3.10(AB pattern; *J* 9 Hz; *J*/Δν 0.27)	2.67(m)
cis-$PtMe_2(CNC_6H_4Cl)(PPh_3)$	9.56(t* of d, 68 Hz, 9 Hz) Me *trans* to P 9.07(t* of d, 73 Hz, 6.5 Hz) Me *cis* to P	3.00(AB pattern; *J* 9.5 Hz; *J*/Δν 0.26)	2.58(m), 2.43(m)
cis-$PtPh_2(CNC_6H_4Cl)(PPh_2Me)$	3.40(m) Ph *trans* to P 2.78(m) not resolved from PPh_2	3.17(AB pattern, *J* 13 Hz; *J*/Δν = 0.38)	8.45(t* of d; 22 Hz, 9 Hz) P–Me 2.78(m)
cis-$PtMe_2(CNC_6H_4Cl)(PPh_2Me)$	9.54(t* of d; 69 Hz, 10 Hz) Me *trans* to P 9·14(t* of d; 72 Hz, 8 Hz) Me *cis* to P	3.05(AB pattern, *J* 8.5 Hz; *J*/Δν 0.21)	7.83(t* of d, 22 Hz, 8 Hz) P–Me 2.66(m), 2.46(m)
cis-$PtPh_2(CNMe)(PPh_2Me)$	3.30(m) Ph *trans* to P 3.18(m) P *cis* to P	7.33(t* of d; 11 Hz, 1.5 Hz)	8.44(t* of d; 22 Hz, 9 Hz) 2.60(m)
cis-$PtMe_2(CNMe)(PPh_2Me)$	9.70(t* of d, 72 Hz, 9 Hz) Me *trans* to P 9.31(t* of d, 72 Hz, 7.5 Hz) Me *cis* to P	7.28(t*, 11.5 Hz)	7.98(t* of d; 21 Hz, 7.5 Hz) PMe 2.68(m), PPh
cis-$PtPh(CPh{=}NMe)(PEt_3)_2$	3.30, 2.85, 2.35, 1.88 (multiplets) both PtPh and Pt(CPh=N) groups	6.22(t*, 12 Hz)	8.93(m) $PCH_2C\underline{H}_3$ 8.45(m) $PC\underline{H}_2CH_3$
cis-$PtMe(CMe{=}NMe)(PEt_3)_2$	10.01(t*, each peak split into d of d, 60 Hz, 7.5 Hz *trans* P, 2.0 Hz *cis* P) PtMe	6.90(t*, 12 Hz)	9.18 [two overlapping triplets, 1/2/2/2/1 intensities; ^3J(PCCH) 15.5 Hz, ^3J(HCCH) 7.5 Hz]

	7.88(t* of d, 34 Hz, 2 Hz) Pt(CMe=N)		$PCH_2C\underline{H}_3$ 8.49 [two overlapping quartets, 1/3/4/3/1 intensities; $^3J(PCCH)$ 7.5 Hz, $^3J(HCCH)$ 7.5 Hz] $PC\underline{H}_2CH_3$
trans-$PtPh(CPh{=}NC_6H_4Cl)(PEt_3)_2$	3.15, 2.70, 2.23, 1.82 (multiplets) both PtPh and Pt(CPh=N)	2.75(AB pattern, *J* 8 Hz, $J/\Delta\nu$ 0.09)	9.17[p, $\lvert {}^2J(PH)+{}^4J(PH)\rvert$ 8 Hz] *trans* $PCH_2C\underline{H}_3$ 8.67(m) $PC\underline{H}_2CH_3$
cis-$PtMe(CMe{=}NC_6H_4Cl)(PEt_3)_2$	9.71(t*, each peak split into d of d, 64 Hz, 7.5 Hz *trans* P, 2 Hz *cis* P), PtMe 7.85(t* of d, 28 Hz, 2 Hz) Pt(CMe=N)	3.15(AB pattern, *J* 8 Hz, $J/\Delta\nu$ 0.45)	9.14(m) $PCH_2C\underline{H}_3$ 8.43[two overlapping quartets, $^3J(PCCH)$ 2 Hz, $^3J(HCCH)$ 7.5 Hz] $PC\underline{H}_2CH_3$
trans-$PtPh(CPh{=}NC_6H_4Cl)(PPhMe_2)_2$	2.97 mult. PtPh, Pt(CPh=N) and CNC_6H_4Cl protons unresolved	(2.97, mult.)	8.92(t* of t, 22 Hz, 3 Hz) 2.63(m) PPh 7.93(s) CH_3CN of recrystallization
cis-$PtMe(CMe{=}NC_6H_4Cl)(PPhMe_2)_2$	9.56(t* each peak split into d of d, 67 Hz, 10 Hz *trans* P, 6.5 Hz *cis* P), PtMe 7.58(t* of d, 33 Hz, 3.5 Hz), Pt(CMe=N–)		8.84, 8.65(t* of d, 19.5 Hz, 8.0 Hz) PMe_2 *trans* to PtMe 8.81, 8.50(t* of d, 25.5 Hz, 8.5 Hz) PMe_2 *cis* to PtMe 2.89, 2.73, 2.69, 2.30 multiplets unresolved PPh and CNC_6H_4Cl

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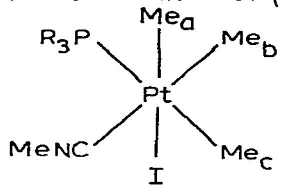
[a] All spectra were run in $CDCl_3$, using TMS ($\tau = 10.0$ ppm) as an internal or external standard. Data are reported in τ units; values of *J* are accurate to ± 0.5 Hz.

[b] t* refers to a 1/4/1 triplet pattern arising from proton coupling to $^{195}Pt(S = 1/2, 34\,\%$ abundance)

TABLE 2

PMR DATA FOR PLATINUM(IV) SPECIES[a,b]



fac-$PtIMe_3(CNMe)PR_3$

Compound (R_3P =)	*Pt–Me*[J(*Pt–H*), J(*P–H*)]	*CNMe*[J(*Pt–H*)]	*Phosphine*
PPh_3	9.22(t* of d, 70, 7.5) Me_a 8.95(t* of d, 61.5, 8.3) Me_b 8.47(t* of d, 58.5, 7.5) Me_c	6.68(t*, 5.0)	2.28(m), 2.61(m)
PPh_2Me	9.10(t* of d, 70, 8.0) Me_a 9.06(t* of d, 61, 10) Me_b 8.72(t* of d, 59Hz, 8 Hz) Me_c	6.78(t*, 8.0)	7.72[t* of d, $^3J(^{195}PtH)$ 11, ^2J(PH) 9.0] PMe 2.26(m), 2.60(m) PPh
$PPhMe_2$	9.16(t* of d, 70, 7) Me_a 9.00(t* of d, 60, 8.5) Me_b 8.57(t* of d, 60,7.0) Me_c	6.85(t*, 8.0)	8.21[t* of d, $^3J(^{195}PtH)$ 12, ^2J(PH) 9.5] PMe 7.83[t* of d, $^3J(^{195}PtH)$ 10.5, ^2J(PH) 9.0] PMe′ 2.56(m) PPh
PEt_3	8.92(m) $Me_{a,b,c}$	6.52(t*, 8.0)	8.92(m) $PCH_2C\underline{H}_3$ 7.98(m) $PC\underline{H}_2CH_3$

[a] All spectra were measured using $CDCl_3$ solvent, with TMS as internal standard. J in Hz.

[b] t* refers to a "1/4/1" triplet pattern arising from proton coupling to ^{195}Pt(S = 1/2, 34% abundance)

cis-$PtPh_2(CNC_6H_4Cl)(PPh_3)$. Obtained as pale yellow prisms from benzene/hexane, 93% yield, m.p. 147–148°. (Found: C, 59.46; H, 4.05; N, 1.63. Mol. wt. 737. $C_{37}H_{29}ClNPPt$ calcd.: C, 59.32; H, 3.90; N, 1.87%. Mol. wt. 749.)

Infrared: 2150 s (C≡N); 1573 m, 1484 s, 1432 s, 1405 w, 1175 w, 1150 w, 1091 m, 1073 w, 1018 m, 1011 w, 887 w, 830 w(sh), 820 m, 748 w(sh), 737 m, 730 m, 725 m, 687 s, 525 s, 505 m, 492 m cm^{-1}.

cis-$PtMe_2(CNC_6H_4Cl)(PPh_3)$. Obtained as pale yellow prisms from ethyl ether/hexane, 65% yield, m.p. 125–127°. (Found: C, 51.96; H, 4.31; N, 2.16. Mol. wt. 624. $C_{27}H_{25}ClNPPt$ calcd.: C, 51.89; H, 4.03; N, 2.24%. Mol. wt., 625.)

Infrared: 2136 s (C≡N); 3075 w, 3055 w, 2805 m, 1590 w, 1575 w, 1485 s, 1435 s, 1405 m, 1295 w, 1209 w, 1190 m, 1180 m, 1158 w, 1150 w, 1111 m, 1095 vs, 1027 m, 1012 s, 997 m, 833 vs, 806 w, 753 m, 747 m, 740 m, 702 vs, 690 vs, 560 m, 527 vs, 515 s, 495 s, 461 m, 413 m cm^{-1}.

cis-$PtPh_2(CNC_6H_4Cl)(PPh_2Me)$. Obtained as white needles from benzene/ethanol, 47% yield, m.p. 133–135°. (Found: C, 56.45; H, 4.32; N, 1.77; Mol. wt. 692. $C_{32}H_{27}ClNPPt$ calcd.: C, 55.94; H, 3.96; N, 2.04%. Mol. wt. 687.)

Infrared: 2150 vs (C≡N); 3050 m, 1540 m, 1485 s, 1435 s, 1310 w(br), 1287 w, 1180 w, 1150 w, 1105 m, 1096 m, 1083 w, 1020 m, 995 w, 888 s, 882 s(sh), 829 m, 812 w, 745 m, 735 vs, 726 s, 700 s, 690 vs, 508 s, 488 m, 455 m, 414 m cm^{-1}.

cis-$PtMe_2(CNC_6H_4Cl)(PPh_2Me)$. Obtained as colorless needles from benzene/ethanol, 45% yield. m.p. 105–107°. (Found: C, 47.94; H, 4.38; N, 2.38. Too little pure sample available for mol. wt. determination. $C_{22}H_{23}ClNPPt$ calcd.: C, 46.94; H, 4.12; N, 2.49%. Mol. wt. 563.)

Infrared: 2134 vs (C≡N); 3060 w, 2904 w, 1482 vs, 1435 s, 1404 w, 1309 w, 1287 w, 1181 m, 1149 w, 1100 m, 1091 vs, 1012 m, 940 w, 892 s, 885 s, 828 vs, 817 w, 807 w, 745 s, 727 s, 695 vs, 543 w(sh), 530 m, 510 s, 485 m, 448 m, 412 m cm^{-1}.

No product could be isolated from other reactions of PtR_2Phos_2 with methyl or *p*-chlorophenyl isocyanides, when these reactions were carried out at room temperature and worked up in the same way; in general the starting materials could be isolated. Some variation in conditions, up to 2 × excess of isocyanide, reaction times up to 24 h, also gave no product. However in each instance the infrared spectrum run on the solution of reactants (in benzene) showed the presence of a coordinated isocyanide, implying the presence of the substituted complexes. The following data were recorded. [Note the absorptions of the free isocyanides in benzene: CNC_6H_4Cl, $\nu(CN)$ 2116 cm^{-1}; CNMe, $\nu(CN)$ 2156 cm^{-1}].

Reaction	$\nu(CN)(cm^{-1})$
$PtPh_2(PPhMe_2)_2+CNC_6H_4Cl$*	2133
$PtMe_2(PPhMe_2)_2+CNC_6H_4Cl$*	2120
$PtPh_2(PEt_3)_2+CNC_6H_4Cl$*	2138
$PtMe_2(PEt_3)_2+CNC_6H_4Cl$*	2120
$PtPh_2(PPh_2Me)_2+CNMe$	2210
$PtMe_2(PPh_2Me)_2+CNMe$	2178
$PtPh_2(PPhMe_2)_2+CNMe$	2200
$PtMe_2(PPhMe_2)_2+CNMe$	2180
$PtPh_2(PEt_3)_2+CNMe$*	2195
$PtMe_2(PEt_3)_2+CNMe$*	2170

Those reactions designated with an asterisk (*) proceeded on heating with insertion of the isocyanide into the metal–carbon bond (*vide infra*).

Attempts to accomplish a further substitution were unsuccessful. Addition of an excess of methyl isocyanide to $PtMe_2(CNMe)(PPh_3)$ in benzene gave a deep red solution from which a red-orange amorphous solid was separated. This solid showed new $\nu(C{\equiv}N)$ absorptions at 2245 s and 2190 w cm^{-1}. On recrystallization, or on heating the color faded rapidly and the starting material [$\nu(CN)=2195$ cm^{-1}] was obtained.

B. Substitution reactions in the presence of methyl iodide

The above data suggested that in the systems $PtR_2(Phos)_2+CNMe$ (Phos = PPh_2Me and $PPhMe_2$; R = Me, Ph) an equilibrium might exist in solution between the reactants and substituted product and free phosphine. On this assumption methyl iodide was added to quaternize the phosphine and shift the equilibrium to the products allowing isolation of $PtR_2(CNMe)(Phos)$ species not obtained otherwise.

Although this reaction was successful a second observation was noted at this point, namely that oxidative-addition of methyl iodide also occurred giving platinum(IV) complexes. This development complicated the application of this reaction for general usage.

Oxidative addition reactions are discussed later in this section.

Preparation of cis-$PtPh_2(CNCH_3)(PPh_2Me)$. To a solution of $PtPh_2(PPh_2Me)_2$ (0.25 g, 0.34 mmol) in benzene (10 ml) was added methyl iodide (0.04 ml, 0.58 mmol). A solution of methyl isocyanide (0.02 ml, 4 mmol) in 8 ml benzene was added dropwise while stirring under nitrogen at room temperature, and a white precipitate of $[PPh_2Me_2]I$ (0.08 g, 66%) appeared. Stirring was continued for 14 h; then the phosphonium iodide was filtered and the solvent removed, giving a pale yellow oil. Crystallization from methanol gave the product (0.075 g, 38%) as very pale yellow prisms, m.p. 155–158°(d). (Found: C, 55.08; H, 4.56; N, 2.23. Mol. wt. 594. $C_{27}H_{26}NPPt$ calcd.: C, 54.91; H, 4.44; N, 2.37%. Mol. wt. 590.)

Infrared: 2212 vs (C≡N); 3045 m, 1571 m(sh), 1568 m, 1482 m(sh), 1437 m, 1432 m, 1421 m, 1411 m, 1309 w, 1177 w, 1148 w, 1100 w, 1090 w, 1071 w, 1052 w, 1020 m, 1018 m, 912 w, 887 s, 879 m, 737 s, 728 s, 704 m, 696 m(sh), 689 s, 650 w, 646 w, 510 m, 488 w, 454 w, 447 w, 420 w cm^{-1}.

cis-$PtMe_2(CNMe)(PPh_2Me)$. This was prepared similarly from $PtMe_2(PPh_2Me)_2$ (0.30 g, 0.48 mmol), methyl isocyanide (0.025 ml, 0.5 mmol) and 0.04 ml methyl iodide. The phosphonium salt $[PPh_2Me_2]I$ (0.176 g, 100%) was obtained as before, the filtrate giving a pale yellow oil which crystallized from a methanol/diethyl ether/pentane mixture giving the product (0.07 g, 30%) as colorless prisms which were recrystallized with some difficulty from the same solvent mixture. M.p. 103–104°. (Found: C, 42.97; H, 4.58; N, 2.78. Mol. wt., 492. $C_{17}H_{22}NPPt$ calcd.: C, 43.78; H, 4.75; N, 3.00%. Mol. wt., 466.)

Infrared: 2178 s (C≡N, benzene): 1588 w, 1572 w, 1482 m, 1433 s, 1409 m, 1306 w, 1282 w, 1252 w, 1220 w, 1207 w, 1178 w, 1158 w, 1096 m, 1077 w, 1067 w, 1025 w, 995 w, 958 w, 940 w, 897 m, 888 s, 882 m, 750 s, 740 m, 690 vs, 615 w(br), 528 m, 522 m, 515 m, 510 m, 480 m, 470 w, 442 m, 433 m cm^{-1}.

Isocyanide insertion reactions

Isocyanide insertion into one metal–carbon bond was observed in reactions of $PtR_2(PEt_3)_2$ (R = Me, Ph) with methyl and *p*-chlorophenyl isocyanides and of $PtR_2(PPhMe_2)_2$ with the latter isocyanide.

The preparation of *cis*-$PtPh(CPh{=}NMe)(PEt_3)_2$ illustrates the general procedure used.

Reaction of $PtPh_2(PEt_3)_2$ *and methyl isocyanide.* To a suspension of *cis*-$PtPh_2(PEt_3)_2$ (0.47 g, 0.8 mmol) in benzene (20 ml) was added methyl isocyanide (0.06 ml, 1.2 mmol) in benzene (10 ml). At this time an isocyanide complex $PtPh_2(CNMe)(PEt_3)$ was apparently formed, as the infrared spectrum showed a strong peak at 2195 cm^{-1}. The mixture was refluxed for 27 h under nitrogen, the reaction mixture being monitored until the 2195 cm^{-1} absorption was absent. Evaporation of the solvent gave a pale yellow oil which was taken up in acetonitrile and filtered. Removal of the solvent gave a clear oil which slowly solidified on standing. Crystallization from benzene/hexane gave the product, $PtPh(CPh{=}NMe)(PEt_3)_2$, (0.10 g, 21%) as very pale yellow crystals, m.p. 165–167°. (Found: C, 50.69; H, 7.15; N, 1.86; mol. wt.,

606. $C_{26}H_{43}NP_2Pt$ calcd.: C, 49.83; H, 6.92; N, 2.23%. Mol. wt., 626.)

Infrared: 1596 m, 1582 s, 1572 vs, 1566 vs (C=N); 3055 m, 3035 m(sh), 2730 w, 1435 s(sh), 1421 m, 1295 w, 1260 w, 1245 w, 1208 w(sh), 1200 m, 1180 w, 1160 m, 1148 w(sh), 1110 w, 1065 w, 1037 s(sh), 1030 vs, 1020 vs, 1004 s, 995 s, 882 m(br), 760 vs, 750 s, 730 vs, 715 vs, 701 vs, 693 vs, 649 w, 644 w, 625 m, 601 s, 485 w, 405 m cm^{-1}.

Other compounds prepared in this way included:

cis-PtMe(CMe=NMe)(PEt$_3$)$_2$. A two-fold excess of isocyanide was used to compensate for its loss due to volatility at reflux temperatures over the longer reaction time needed (24 h). The oily residue after removal of the solvent was crystallized from hexane, giving the product (18%) as very pale yellow prisms, m.p. 136–139°. (Found: C, 38.42; H, 7.72; N, 2.87; P, 11.48. Mol. wt. not determined as too little sample was available. $C_{16}H_{39}NP_2Pt$ calcd.: C, 38.23; H, 7.82; N, 2.79; P, 12.33%. Mol. wt. 502.)

Infrared: 1594 vs (C=N); 1435 m(sh), 1421 m, 1337 w, 1259 w, 1250 w, 1198 vw, 1180 w, 1150 w(sh), 1136 w, 1080 w, 1037 s, 1021 m, 1001 w(sh), 996 w, 901 w, 762 m, 755 m(sh), 718 vs, 704 w(sh), 665 w, 636 w, 628 w, 505 w, 495 w.

trans-PtPh(CPh=NC$_6$H$_4$Cl)(PEt$_3$)$_2$. Obtained using much shorter reaction time (0.5 h); recyrstallized from acetonitrile giving yellow prisms, 18%, m.p. 200–203°. (Found: C, 50.88; H, 6.67; N, 1.84. Mol. wt. 719. $C_{31}H_{44}ClNP_2Pt$ calcd.: C, 51.49; H, 6.13; N, 1.94%. Mol. wt., 723.)

Infrared: 1525 vs (C=N); 3070 w, 3055 w, 1590 w, 1575 w, 1435 m, 1412 m, 1296 w, 1260 w, 1216 w, 1173 m, 1151 s, 1087 m(sh), 1079 m, 1032 s, 1002 m, 928 w, 902 s, 830 m, 791 m, 764 s, 751 s, 694 vs, 681 s, 631 m, 619 m, 609 m, 550 w, 515 m, 433 m cm^{-1}.

cis-PtMe(CMe=NC$_6$H$_4$Cl)(PEt$_3$)$_2$. Reaction time 5.5 h; the product was obtained as white prisms (57%) from ethyl acetate, m.p. 153–154°. (Found: C, 41.89; H, 6.60; N, 2.63. Mol. wt., 583. $C_{21}H_{40}ClNP_2Pt$ calcd.: C, 42.10; H, 6.73; N, 2.34%. Mol. wt., 599.)

Infrared: 1554 vs(br), (C=N); 1477 s(sh), 1468 s(sh), 1454 s(sh), 1434 m, 1423 m, 1397 w, 1346 m, 1292 w, 1261 w, 1241 w, 1216 w, 1165 w, 1110 m, 1091 m, 1042 s, 1031 m(sh), 1003 m(sh), 1000 m, 965 w, 835 s, 815 w, 805 w, 765 vs, 720 vs, 712 m(sh), 705 w(sh), 678 m, 668 w(sh), 638 w(sh), 632 m, 535 w, 495 m cm^{-1}.

trans-PtPh(CPh=NC$_6$H$_4$Cl) (PPhMe$_2$)$_2$. Reaction time 2.5 h; the oil crystallized upon addition of acetonitrile giving the product, 34%, as pale yellow prisms, which were washed with ethyl ether and dried, m.p. 199–202°. The product retained some CH_3CN of solvation. (Found: C, 55.34; H, 4.68; N, 2.98. Mol. wt. 828. $C_{35}H_{36}ClNP_2Pt \cdot 0.5\ CH_3CN$ calcd.: C, 55.17; H, 4.82; N, 2.68%. Mol. wt. 784.)

Infrared: 1596 s, 1582 s, 1568 vs, 1532 w(C=N); 3080 w, 3075 w, 2165 w, 2155 w (CH_3CN); 1475 vs, 1440 s, 1424 w, 1300 m, 1283 m, 1225 w, 1180 s, 1155 vs, 1110 m, 1085 s, 1027 w, 1010 m, 960 s, 920 s(sh), 904 vs, 870 w, 843 m(sh), 826 s, 809 m, 765 s, 760 s, 750 s, 740 m, 732 m, 710 s, 690 vs, 687 vs(sh), 643 w, 628 w, 614 m, 601 w, 591 w, 555 w, 530 w, 490 s, 448 m, 424 s(br) cm^{-1}.

cis-PtMe(CMe=NC$_6$H$_4$Cl)(PPhMe$_2$)$_2$. Reaction time 15 h, recrystallized from ethyl ether/hexane as off-white plates 42%, m.p. 146–149°. (Found: C, 46.50; H, 5.38; N, 2.35. Mol. wt., 615. $C_{25}H_{32}ClNP_2Pt$ calcd.: C, 46.99; H, 5.05; N, 2.19%. Mol. wt., 639.)

Infrared: 1574 s(sh), 1541 vs(br)(C=N); 3082 w, 3068 w, 3050 w, 1474 vs, 1434 vs, 1347 m, 1310 m, 1294 w, 1282 m, 1212 m(br), 1180 w, 1175 w, 1164 w, 1158 w, 1111 s, 1102 vs, 1084 s, 1073 w, 1021 w(br), 1008 w, 1000 w, 950 s, 939 s, 906 vs, 900 vs, 870 w, 838 s(sh), 832 vs, 802 m, 743 s, 730 m, 714 w, 704 m, 697 m, 690 m, 679 w(sh), 673 m, 630 w, 547 w, 539 m, 503 m, 495 w, 482 m, 432 m, 425 m cm^{-1}.

Attempts to accomplish isocyanide insertion reactions of methyl isocyanide with $PtR_2(PPhMe_2)_2$, and of both methyl and *p*-chlorophenyl isocyanide with $PtR_2(PPh_2Me)_2$ utilizing reflux conditions were unsuccessful. In the former reactions starting material was recovered; in the latter (with the PPh_2Me complexes) eventual degradation was observed.

We also noted that heating of the reaction of $PtMe_2(PPhMe_2)_2$ and *p*-methoxyphenyl isocyanide (which is known to give a substitution product[7] at room temperature) gave only degradation.

Oxidative addition reactions with methyl iodide

The observation of an oxidative addition reaction in earlier experiments prompted us to study the reaction of methyl iodide with the platinum(II) isocyanide species $PtR_2(CNR')(Phos)$.

Reaction of $PtMe_2(CNMe)PPh_3$) and CH_3I. To a solution of $PtMe_2(CNMe)(PPh_3)$ (0.36 g, 0.68 mmol) in dry benzene (20 ml) was added MeI (2.5 ml, excess) and the mixture stirred at room temperature for 54 h. The volume of the pale yellow solution was reduced to 5 ml, white crystals of the product $PtIMe_3(CNMe)(PPh_3)$ (0.25 g, 55 %) precipitated on standing. M.p. 103–108°. (Found: C, 42.32; H, 3.96; N, 1.79; P, 4.65. Mol. wt. 681. $C_{23}H_{27}INPPt$ calcd.: C, 41.20; H, 4.06; N, 2.09; P, 4.62 %. Mol. wt. 670.)

Infrared: 2228 s (C≡N), 3055 w, 3040 w, 1588 w, 1574 w, 1480 w, 1441 (sh), 1440 s, 1432 vs, 1415 w, 1338 w, 1265 m, 1238 w, 1220 m, 1212 m, 1182 w, 1176 w, 1152 w, 1148 w, 1110 m, 1087 s, 1025 w(br), 991 w, 954 w, 910 m, 900 m, 851 w, 782 w, 751 (sh), 743 s, 738 s, 715 w, 710 m, 697 s, 690 (sh), 685 s, 676 (sh), 668 w, 542 w, 520 s, 509 m, 500 s, 449 m cm^{-1}.

This product was also obtained in low yield (9 %) from the reaction of $PtMe_2(PPh_3)_2$ (0.50 g, 0.67 mmol) with MeI (0.6 ml, ≈ 10 mmol) and CNMe (0.04 ml, 0.8 mmol) in dry benzene, and identified by its infrared spectrum and melting point. The main product isolated here was $PtMe_2(CNMe)(PPh_3)$ (40 %).

Preparation of $PtIMe_3(CNMe)$ (PPh_2Me). To a solution of $PtMe_2(PPh_2Me)_2$ (0.40 g, 0.64 mmol) in dry benzene (20 ml) was added 0.6 ml (excess) MeI and a solution of CNMe (0.035 ml, 0.7 mmol) in 10 ml benzene. The mixture was stirred at room temperature for 6 h. The white precipitate of $[PPh_2Me_2]I$ (0.207 g, 93 %) which separated, was filtered off, and its identity verified by comparison of the infrared spectrum with that of an authentic sample. All solvent was removed from the filtrate, giving an oil which crystallized from methanol giving the product (0.14 g, 28 %) as pale yellow prisms, m.p. 128–129°. (Found: C, 35.59; H, 4.14; N, 2.26; P, 5.54. Mol. wt. 616. $C_{18}H_{25}INPPt$ calcd.: C, 35.42; H, 4.13; N, 2.29; P, 5.07 %. Mol. wt. 610.)

Infrared: 2220 vs (C≡N); 3055 w, 3038 w, 1587 w, 1573 w, 1486 m, 1433 vs, 1408 m, 1339 w, 1328 w, 1308 w, 1290 w, 1253 m, 1224 s, 1206 m, 1190 w, 1180 w, 1160 w, 1148 w, 1096 m, 1071 w, 1026 w, 996 w, 973 w, 950 m, 896 vs, 888 s, 746 vs, 733 vs, 694 vs, 614 w, 527 m, 511 s, 483 s, 444 m, 435 m, 423 m cm^{-1}.

Reaction of $PtMe_2(PPhMe_2)_2$, CNMe, and MeI. This reaction was carried out in the manner described above, giving two products. The unsubstituted platinum-

(IV) species *PtIMe$_3$(PPhMe$_2$)$_2$* was obtained as pale yellow prisms crystallizing first from a benzene/pentane mixture, 14% yield, m.p. 144–146° (lit.[14] m.p. 155–160°). (Found: C, 35.85; H, 4.64. Mol. wt. 639. $C_{19}H_{31}IP_2Pt$ calcd.: C, 35.47; H, 4.86%. Mol. wt. 643.)

Infrared: 1572 w, 1481 m, 1435 s, 1401 m, 1301 m, 1297 m, 1285 m, 1280 w, 1247 m, 1210 s, 1203 s, 1177 m, 1147 m, 1106 m(br), 1075 w(br), 992 w, 940 s, 911 s, 902 vs, 841 m(br),749 s, 740 vs, 709 m, 695 s(sh), 690 s, 674 w, 612 w(br), 541 w(sh), 530 m, 520 m, 494 s(sh), 490 s, 483 m(sh), 419 s(sh), 412 s cm^{-1}.

The species *PtIMe$_3$(CNMe)(PPhMe$_2$)* was obtained as colorless needles in 58% yield, from the filtrate of the above crystallization by increasing the pentane concentration. It was recrystallized from benzene/pentane, m.p. 141–142°. (Found: C, 28.81; H, 4.18; N, 2.53; P, 5.60. Mol. wt. 542. $C_{13}H_{22}INPPt$ calcd.: C, 28.58; H, H, 4.06; N, 2.56; P, 5.67%. Mol. wt. 546.)

Infrared: 2236 (sh), 2227 vs (C≡N); 3058 w, 1433 s, 1408 m, 1403 m, 1332 m, 1300 m, 1281 m, 1256 m, 1224 s, 1208 m, 1178 m, 1155 w, 1147 w, 1109 w(br), 1075 w, 1020 w, 994 w, 969 w, 942 s, 919 s, 911 s, 871 w, 849 w, 841 w, 742 vs, 716 m, 693 s, 523 m, 494 m, 436 m, 417 m cm^{-1}.

Reaction of PtMe$_2$(PEt$_3$)$_2$, CNMe, and MeI. By an analogous reaction the complex PtIMe$_3$(CNMe)(PEt$_3$) was obtained as a white micro-crystalline material in 27% yield; it was recrystallized from hot n-heptane; m.p. 93–95°. (Found: C, 25.11; H, 5.36; N, 2.73; P, 5.96. Mol. wt. 535. $C_{11}H_{27}INPPt$ calcd.: C, 25.10; H, 5.17; N, 2.66; P, 5.89%. Mol. wt. 526.)

Infrared: 2228 vs, 2216 s(sh) (C≡N); 1412 m, 1396 m, 1280 w, 1250 m, 1218 m, 1207 m, 1179 m, 1148 m, 1112 m(br), 1078 w, 1051 w(sh), 1039 s, 1027 m, 1005 w, 981 w, 948 m, 758 s, 721 s, 701 m, 661 w, 630 w, 612 w, 550 w, 539 w, 527 m, 479 w, 431 m, 410 m cm^{-1}.

DISCUSSION

Reactions of the complexes PtR$_2$(Phos)$_2$ (R = Me, Ph) with *p*-chlorophenyl isocyanide may be considered using the data in Table 3 below. When the platinum(II) species was slurried in benzene and isocyanide added, at 25°, a rapid reaction occurred. This reaction was monitored by infrared spectroscopy, noting the appearance of an absorption associated with a coordinated *p*-chlorophenyl isocyanide at 2130–2150 cm^{-1} for the phenyl–platinum or at 2130–2135 cm^{-1} for the methyl–platinum systems, [compared to ν(CN) for free isocyanide at 2116 cm^{-1}]. Only for the triphenylphosphine and diphenylmethylphosphine complexes could an isocyanide substituted species, PtR$_2$(CNC$_6$H$_4$Cl)(Phos), be isolated however. From the other reactions, with Phos = PPhMe$_2$ and PEt$_3$, starting material was recovered when the solvent was evaporated and the residue crystallized. These data may be accommodated within the hypothesis that an equilibrium is established in benzene [eqn. (1)], which favors the product formation sufficiently to allow its isolation only for the two less basic phosphines.

$$\mathrm{PtR_2(Phos)_2 + CNC_6H_4Cl \rightleftharpoons PtR_2(CNC_6H_4Cl)(Phos) + Phos} \qquad (1)$$

The same rationale may be used in reactions of the methyl and phenyl-platinum(II) compounds with methyl isocyanide. However, the positions of these

TABLE 3

PRODUCTS FROM $PtR_2(Phos)_2+R'NC$ (R=Me, Ph)[a]

R'NC	*Phos*	*Product, 25° reaction*	*Product, 80°[b] reaction*
CNC_6H_4Cl	PPh_3	$PtR_2(CNC_6H_4Cl)(PPh_3)$ 2150 cm^{-1} (Ph); 2136 cm^{-1} (Me)	
CNC_6H_4Cl	PPh_2Me	$PtR_2(CNC_6H_4Cl)(PPh_2Me)$ 2150 cm^{-1} (Ph); 2136 cm^{-1} (Me)	Decomposition
CNC_6H_4Cl	$PPhMe_2$	$PtR_2(CNC_6H_4Cl)(PPhMe_2)$ Not isolable; IR evidence: 2133 cm^{-1} (Ph), 2120 cm^{-1} (Me)	$PtR(CR{=}NC_6H_4Cl)(PPhMe_2)_2$
CNC_6H_4Cl	PEt_3	$PtR_2(CNC_6H_4Cl)(PEt_3)$ Not isolable; IR evidence: 2138 cm^{-1} (Ph); 2120 cm^{-1} (Me)	$PtR(CR{=}NC_6H_4Cl)(PEt_3)_2$
CNMe	PPh_3	$PtR_2(CNMe)(PPh_3)$ 2195 cm^{-1} (Ph and Me)	
CNMe	PPh_2Me	$PtR_2(CNMe)(PPh_2Me)$ Not isolable; IR evidence: 2210 cm^{-1} (Ph), 2178 cm^{-1} (Me)	Decomposition
CNMe	$PPhMe_2$	$PtR_2(CNMe)(PPhMe_2)$ Not isolable; IR evidence: 2200 cm^{-1} (Ph), 2180 cm^{-1} (Me)	Decomposition
CNMe	PEt_3	$PtR_2(CNMe)(PEt_3)$ Not isolable; IR evidence: 2195 cm^{-1} (Ph), 2170 cm^{-1} (Me)	$PtR(CR{=}NMe)(PEt_3)_2$

[a] Infrared data for complexes not isolated was obtained on the Beckman IR-10 (low resolution) and are accurate to ±5 cm^{-1}. For comparison *p*-chlorophenyl isocyanide in benzene has $\nu(CN)=2116\ cm^{-1}$; methyl isocyanide has $\nu(CN)=2156\ cm^{-1}$ in benzene (high resolution). [b] Benzene reflux.

equilibria are such that only the triphenylphosphine complexes, $PtR_2(CNMe)(PPh_3)$, can be isolated, whereas the other species are not isolable, being unstable relative to the starting materials.

It is difficult to rationalize why some reactions will yield products while others do not, but the results can be correlated with donor and acceptor characteristics for the ligands. Specifically the ability to isolate an isocyanide-substituted species PtR_2-(CNR')(Phos) is related to the electron withdrawing power of the isocyanide and phosphine ligands. The series of phosphines chosen differ in donor ability, *i.e.*, the ability to transfer negative charge to the metal[15], in the order $PEt_3 > PPhMe_2 > PPh_2Me > PPh_3$ although one would expect the differences not to be large. Aryl isocyanides are known to be considerably better electron acceptors than alkyl isocyanides. Our results show that isolation of a substituted product is favored for $Phos = PPh_3 > PPh_2Me > \cdots$, and for $p\text{-}CNC_6H_4Cl > CNMe$; this is the same order seen for ligand donor abilities. The values of $\nu(CN)$ for each series of complexes generally corroborate this idea. Thus, there is a shift of $\nu(CN)$ to lower wavenumbers in the series $PtR_2(CNR')(Phos)$ for $Phos = PPh_3 > PPh_2Me > PPhMe_2 > PEt_3$.

The substituted platinum(II) products should be obtained from these reactions if the free phosphine could be removed from the equilibrium mixture. An apparently ideal experiment to test this proposal involves inclusion of methyl iodide in the reaction mixture; this, it was assumed, would react with any free phosphine to give an insoluble phosphonium salt, removing one component of the equilibrium system. Indeed, this proved to be the case [eqn. (2)]; however only in two instances did this

$$\mathrm{PtR_2(PPh_2Me)+CNMe+MeI \rightarrow PtR_2(CNMe)(PPh_2Me)+[PPh_2Me_2]I} \quad (\mathrm{R=Me,\ Ph}) \tag{2}$$

reaction prove to be a viable synthetic technique. One has also to contend with a second possible reaction, oxidative addition of methyl iodide to these platinum(II) complexes [eqn.(3)]. Thus mixtures are often obtained, for which separation is quite

$$\begin{tikzcd}
\mathrm{PtMe_2(Phos)_2+CNR'+MeI} \arrow[r] \arrow[d, "(+\mathrm{MeI})"] & \mathrm{PtMe_2(CNR')(Phos)+[PhosMe]I} \arrow[d, "(+\mathrm{MeI})"] \\
\mathrm{PtIMe_3(Phos)_2} & \mathrm{PtIMe_3(CNR')(Phos)}
\end{tikzcd} \tag{3}$$

difficult. Nevertheless, this observation did seem to offer further justification for the assumed equilibrium and the unexpected results opened an opportunity for further study of the oxidative addition reaction (*vide infra*).

Addition of an excess of methyl isocyanide to the $\mathrm{PtR_2(PPh_3)_2}$ complexes resulted in a deepening of color and the appearance of a new ν(CN) absorption at considerably higher frequency. We suspect that this is the consequence of the coordination of a fifth ligand. This type of species could not be isolated however. We have recently commented on other instances of five-coordination in platinum(II) chemistry[16].

When the $\mathrm{PtR_2(Phos)_2+R'NC}$ systems were heated in benzene (reflux), two possible reactions were noted. In some instances decomposition occurred with diminishing recovery of the isolable platinum(II) species, either $\mathrm{PtR_2(Phos)_2}$ or $\mathrm{PtR_2(CNR')(Phos)}$. Generally decomposition proceeded slowly, with partial recovery of the metal complex being possible even after 24 h. No attempt to determine the mechanism of this decomposition was made here; a suggestion that these decompositions proceed with reductive elimination was offered earlier[8].

The more interesting observation, in our opinion, was that insertion of the isocyanide into one carbon–metal bond of the complex occurred in certain instances [eqn. (4)]. In all six examples of this type of reaction were recorded. It is worth noting

$$\begin{tikzcd}
\mathrm{PtR_2(Phos)_2+R'NC} \arrow[r, shift left] & \mathrm{[PtR_2(CNR')(Phos)]+Phos} \arrow[l, shift left] \arrow[d, "\Delta"] \\
 & \mathrm{PtR(CR{=}NR')(Phos)_2}
\end{tikzcd}$$

$$(\mathrm{R=Me,\ Ph;\ Phos=PEt_3;\ CNR'=CNMe,\ CNC_6H_4Cl})$$

$$(\mathrm{R=Me,\ Ph,\ Phos=PPhMe_2;\ CNR'=CNC_6H_4Cl})$$

that these reactions occurred only for those complexes $\mathrm{PtR_2(Phos)_2}$, in which Phos = $\mathrm{PEt_3}$ and $\mathrm{PPhMe_2}$; these are of course the phosphines designated earlier as better donors of negative charge to the metal. Interestingly, though perhaps coincidentally, the reactions which gave insertion products were also among those for which a substitution product, $\mathrm{PtR_2(CNR')(Phos)}$, was not isolated.

The observation of an insertion reaction here is particularly noteworthy, in view of the lack of known examples of similar reactions. Moreover, the occurrence or not of this reaction in an apparently predictable manner based on ligand characteristics seems a desirable result.

Elaborate comment on the observation of insertion in these systems would be premature, but certainly a tentatively offered hypothesis to serve as a catalyst for further work has some merit. Our inclination, at the moment, is to view this phenomenon in kinetic rather than thermodynamic terms. Herein we make the assumption that insertion is observed because the rate of this reaction is enhanced in some systems over others. In turn this allows consideration of factors influencing this rate.

There is a general consensus that most insertion reactions into metal–carbon bonds are promoted by a lower electron density on the metal[7,17,18]. This could be reflected by a net positive charge on a complex, formalistically residing on the metal; thus Clark and co-workers[7,10] observed an enhancement of insertion reactions in cationic platinum complexes relative to analogous uncharged species. One can also apply this same argument in a comparison of effects of ancilliary ligands within metal complexes[17]. Ligands which are poorer electron donors have been observed to enhance insertion rates[7,17,18]. Regrettably little evidence is yet available on this subject however.

Nonetheless, it is clear that our results are in variance with this presumed trend, for our data seem to indicate the preference for insertion with the electron-donating ligands. We would like to reconcile this apparent difference within a mechanistic postulate for this reaction.

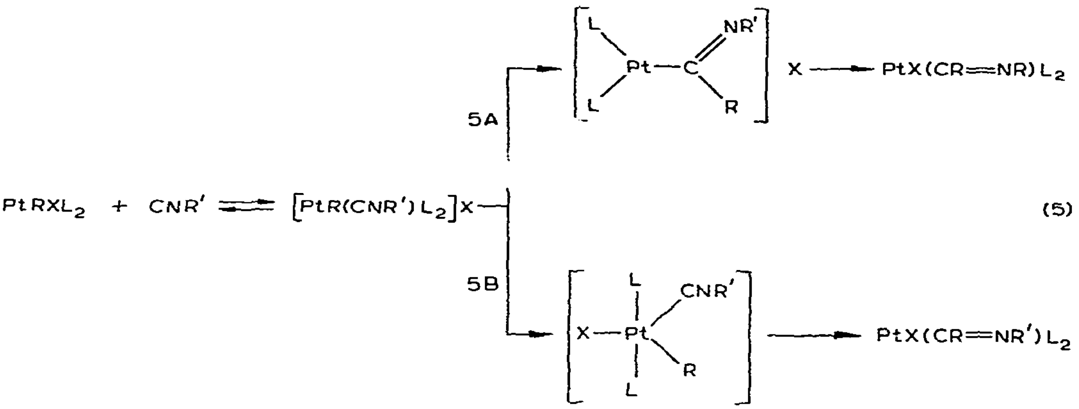
We suggested earlier[1,2] that the rearrangement of the complexes [PtR(CNR')(Phos)$_2$]X proceeded via a five-coordinate intermediate, [PtRX(CNR)(Phos)$_2$], as the halide ion reentered the metal coordination sphere [eqn. (5B)]. The same mechanism might well apply to the insertions with PtR$_2$(Phos)$_2$ [eqn. (6B)]. A second mechanism could be considered for both systems however, involving three coordinate intermediates (5A, 6A). The postulation of a three-coordinate intermediate is not without merit; Whitesides *et al.*[19] have recently observed that a three-coordinate intermediate is involved in dialkylplatinum(II) thermal decompositions. In a sense the insertion reaction data for PtR$_2$L$_2$ species is better accommodated within this latter mechanism. One would expect the first step to be rate determining, and that this reaction would be promoted by a higher electron density on platinum[19].

If on the other hand one chooses to argue for a five-coordinate intermediate in these reactions [eqn. (6B)], then the data can be rationalized by assuming the rate of the reaction is dependent on the nucleophilicity of the attacking phosphine. In other instances this type of effect is noted[20].

Clearly further work needs yet to be completed before the right answers are established. Some studies are underway here.

The several platinum(IV) species PtIMe$_3$(CNR)(Phos) prepared by oxidative additions of methyl iodide are of interest only insofar as they are new species. Oxidative addition reactions involving PtR$_2$L$_2$ species were known prior to this work[14], and platinum(IV) isocyanides have recently been described[21]. One might note parenthetically that the oxidative addition reactions involving PtR$_2$(CNR')(Phos) species appear to be more facile than those for PtR$_2$(Phos)$_2$. This comparison can be made from reaction conditions; also one notes that methyl iodide could have reacted with either component of the equilibrium system defined by [eqn. (1)].

PMR spectra were generally useful in establishing the stereochemistry for



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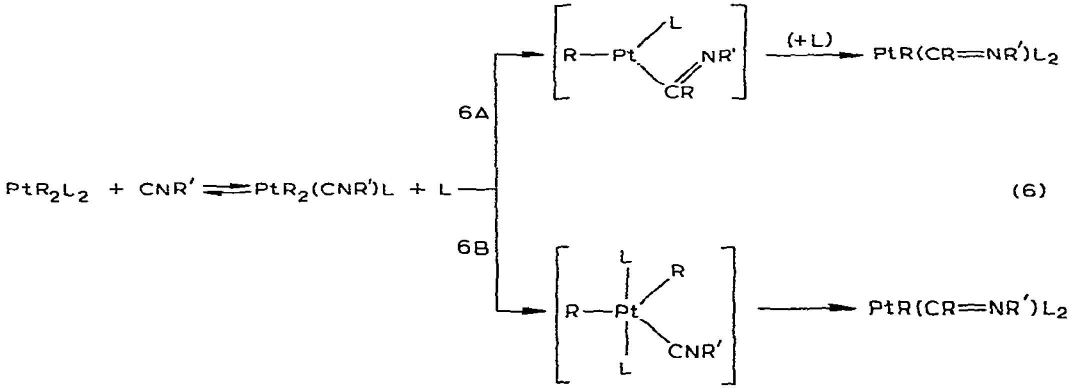

(6)

compounds of each type described above. These data are presented in Tables 1 and 2.

The species $PtR_2(CNR')(Phos)$, without exception, gave PMR spectra characteristic of a *cis* configuration around the metal. Thus two resonances associated with the R groups (methyl or phenyl) could be distinguished. Although phenyl resonances were unresolved multiplets, the platinum–methyl proton resonances in the complexes $PtMe_2(CNR')(Phos)$ each appeared as doublets, arising due to $^3J(P\text{–}H)$, with additional resonances of about one-fourth the intensity flanking these peaks due to coupling with the platinum(195) nucleus ($S = 1/2$, 34% abundance). The latter coupling constants, around 60–70 Hz, are typical of platinum(II)–methyl coupling constants observed in many other instances[14]. A tentative assignment of resonances as due to methyl groups either *cis* and *trans* to the phosphine ligand was made, based on the assumption that the coupling of methyl protons to a *trans*-phosphine is usually greater than that to a *cis*-phosphine[22,23,*]. Here we assigned $^3J(P\text{–}H)$ values of 8.7–10 Hz to a coupling with a *trans* phosphine, and 6.5–8.0 Hz to a coupling with the *cis* phosphine.

The phosphine and isocyanide resonances were not unusual. The PMR spectra of the methyl isocyanide complexes had the 1/4/1 "triplet" pattern near τ 6.5 ppm,

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[*] Earlier work proposed that the coupling to a *trans* phosphine was always greater than coupling to a *cis* phosphine. However, recent work[24,27] has defined at least two instances where this is not so.

the outer peaks arising from a $^2J(^{195}Pt-H)$ coupling of 11–12 Hz. The *p*-chlorophenyl isocyanide protons gave a simple AB pattern with $J/\Delta\nu$ ranging from 0.21 to 0.38 at 60 MHz. The phosphine methyl proton resonances in the diphenylmethylphosphine complexes occurred as 1/1 doublets, $^2J(P-H) = 7.5-9$ Hz, with coupling to platinum-(195) of 21–22 Hz.

With two notable exceptions all of the platinum(II) imino complexes had a *cis* configuration. The insertion products *cis*-$PtMe(CMe{=}NR')(PEt_3)_2$ ($R' = Me$, C_6H_4Cl) each gave well resolved spectra with the protons of the methyl group bonded to platinum appearing as a 1/4/1 "triplet" of doublets [$^2J(^{195}Pt-H) = 60$ and 64 Hz for the $R' = Me$ and C_6H_4Cl complexes above] with each peak further split into a doublet. The doublet of doublet pattern arises from coupling of methyl protons to *trans* phosphine (7.5 Hz) and *cis* phosphine (2.0 Hz) respectively. The ethyl groups on the two different phosphines show separate sets of resonances as well. Although there is considerable overlapping one can identify the methyl and methylene resonances of each phosphine. The methyl groups in each phosphine appear as 1/2/2/2/1 patterns, a result of the overlap of two triplets [$^3J(P-C-C-H) = 15.5$ Hz, $^3J(H-C-C-H) = 7.5$ Hz]. Each set of methylene protons occur as two overlapping quartets giving a 1/4/6/4/1 pattern with $^2J(P-C-H) = {}^3J(H-C-C-H) = 7.5$ Hz.

Similarly, the compound *cis*-$PtMe(CMe{=}NC_6H_4Cl)(PPhMe_2)_2$ shows resonances due to the platinum methyl group, with splitting arising from coupling to *trans* (10 Hz) and *cis* (6.5 Hz) phosphines, and to platinum(195) (67 Hz). The phosphine groups are non-equivalent, being *trans* or *cis* to the methyl group. In addition, the two methyls on each dimethylphenylphosphine ligand are also non-equivalent, each appearing as a doublet [$^2J(P-H)$] of "triplets" [$^3J(^{195}Pt-H)$]. The net effect is four overlapping resonances for the phosphine methyl groups. Analogous results on other dimethylphenylphosphine complexes have been reported by Yamamoto and Yamazaki[25]. These workers chose to interpret this non-equivalence as due to asymmetry introduced by coordination of the lone pair of electrons on the imino-nitrogen to platinum, proposing a five-coordinate platinum structure. This postulate is unnecessary, however, as any restriction in rotation of the platinum–imino-carbon bond would lead to the same observation.

Although the three products discussed above have *cis* configurations, this is apparently not the situation for two other imino complexes, *trans*-$PtPh(CPh{=}NC_6H_4Cl)(PPhMe_2)_2$ and *trans*-$PtPh(CPh{=}NC_6H_4Cl)(PEt_3)_2$. The latter complex gives a typical pentet for the methyl groups on phosphorus, with $|^2J(P-H) + {}^4J(P-H)| = 8$ Hz, and the dimethylphenylphosphine analog gives a 1/4/1 "triplet" of triplets with $^3J(Pt-H) = 22$ Hz, $^2J(P-H) = 3$ Hz; both patterns are indicative of *trans*-phosphine atoms[22]. Steric factors may be responsible for this different configuration, both the two phenyl groups and the *p*-chlorophenyl group contributing to crowding within this system.

The *fac* geometry proposed here for the new species, $PtIMe_3(CNMe)(Phos)$, is similar to the *fac* geometry suggested for various $PtIMe_3(Phos)_2$[14], $[PtIMe_2(CF_3)(Phos)_2]$[26], and $[PtMe_3L(Phos)_2]^+$[27] complexes. For this geometry the three methyl groups bonded to platinum are dissimilar, each being *trans* to different groups, phosphine, isocyanide and iodide. The observation of three individual methyl resonances, possible only for the *fac*-isomer, confirms the overall geometry.

Specific assignment of each resonance to the appropriate methyl group is difficult, but may be made tentatively (see Table 2) based on comparisons with other data. We have assigned the three resonances [each a doublet due to ^3J(P–H) with additional peaks arising from ^2J(^{195}Pt–H)], in order of decreasing τ value, to methyl groups *trans* to iodide (Me$_a$), isocyanide (Me$_b$), and phosphine (Me$_c$) respectively.

The high field resonance has by far the highest platinum(195)–hydrogen coupling constant, $^2J(^{195}\text{Pt–H}) = 70$ Hz; by comparison the other methyl proton resonances in these compounds have values of approximately 60 Hz. The value of 70 Hz is identical to that observed for protons of the methyl group *trans* to iodide in the complex $PtIMe_3(PPhMe_2)_2$[14] for which the identification of this resonance is known with certainty; also the coupling constants, ^2J(^{195}Pt–H), for methyl protons *trans* to phosphines in these species is 57 Hz, in agreement with our data. Moreover in a variety of complexes $PtXMe_3(PPhMe_2)_2$ (X = Cl, Br, I) the resonance for the protons in the methyl group *trans* to the halogen is invariably at higher field than the resonance for those methyl protons *trans* to a phosphine.

A decision on the assignment of the other two methyl proton resonances is more tenuous. We prefer to make this assignment based on the values of ^2J(^{195}Pt–H) assigning the resonance with the higher value to the protons of the methyl group *trans* to the isocyanide. This assignment would be in accord with the *trans* influence correlation observed by Clark *et al.*[21,27] which should hold even if the compounds are dissimilar. On this basis the resonance at the intermediate τ value is assigned to H$_b$, *trans* to the isocyanide ligand, leaving H$_c$, the low field resonance, to the protons of the methyl group *trans* to the phosphine.

One consequence of this assignment is that the values of ^3J(P–H), the coupling constant between methyl group protons and phosphorus of the phosphine in a *cis* configuration, are greater than the value of ^3J(P–H) between similar groups in a *trans* configuration. Though this is somewhat unusual there is apparently some precedent for this in other platinum(IV) species[27].

One may make comparisons of PMR chemical shift data for $PtIMe_3(PPhMe_2)_2$[14], $PtIMe_3(CNMe)(PPhMe_2)$ and $PtIMe_3(CNC_6H_4CH_3)_2$[26]. Within this series the chemical shift (τ) of the protons of the methyl group *trans* to iodine (*cis* to the two ligands) decreases, reflecting presumably the decreased shielding resulting from greater charge delocalization from platinum to the isocyanide relative to the phosphine. Also the τ values for the resonances of the protons in the methyl groups *trans* to the phosphine decrease between the first and second compound, as do the τ values for the resonances of the methyl protons *trans* to the isocyanides in the second and third species. If the assignments of H$_b$ and H$_c$ were reversed this would not be the case.

According to our data, the three phosphines PPh_3, PPh_2Me, and $PPhMe_2$ all have a *trans* influence greater than the *trans* influence of methyl isocyanide. Within this series, the *trans* influence is found to be $PPhMe_2 > PPh_2Me > PPh_3$ although the difference is clearly small. This order is to be expected, paralleling the order of decreasing basicity of these ligands.

Finally, it is interesting to consider the ratio $^2J(\text{Pt}^{\text{IV}}\text{–CH}_3)/^2J(\text{Pt}^{\text{II}}\text{–CH}_3)$, for which a theoretical value of 0.67 has been calculated[28] on the assumption that the platinum 6*s* character is equally distributed over all bonds. In our work, comparison of data for $PtMe_2(CNMe)PR_3$ and $PtIMe_3(CNMe)PR_3$ ($PR_3 = PPh_3$ and PPh_2Me) gave an average value of 0.90. This is higher than the typical value of 0.77 reported[14] for related Pt$^{\text{II}}$ and Pt$^{\text{IV}}$ complexes not containing isocyanide but, interestingly, very similar to the range of 0.88–0.92 recently reported[21] for some cationic Pt^{IV} isocyanide complexes. On the assumption therefore, that the theoretical arguments are valid, both neutral and cationic Pt^{IV} isocyanide complexes appear to retain 10–15% more of the *s* character of their related Pt^{II} analogs than do those complexes containing no isocyanide. This would imply that there is more net change in the bond hybridization around platinum for the latter than for the isocyanide substituted compounds.

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