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Synthesis of New Platinum Isocyanide Complexes from $[Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$ by Facile Replacement of Acetonitrile by Anionic and Uncharged Ligands

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The acetonitrile ligand group in $[Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$ is extraordinarily labile and may be replaced by a variety of molecular ligands ($(CH_3)_3N$, pyridine, $(C_6H_5)_3P$, $(C_2H_5)_3P$, $(CH_3O)_3P$, $(CH_3)_2S$, CH_3NC) and anionic groups (I^-, Cl^-, CN^-, N_3^-, NO_2^-, OH^-). Infrared spectra for the series of compounds $[PtX(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$ and $[Pt(L)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$ have been recorded and a correlation attempted between ν_{CN} and various parameters related to the groups L or X.

Introduction

The synthesis of *trans*-$[Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$, described in the previous paper, was accomplished by protonation of $[Pt(CONHCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$ in acetonitrile according to the sequence[1]

$$[Pt(CONHCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4 + HBF_4 \xrightarrow[25°]{\text{aq } CH_3CN}$$

$$[[Pt(CO)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2] \xrightarrow[-CO]{+CH_3CN}$$

$$[Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$$

This compound proved to be particularly useful in the synthesis of a wide variety of other platinum compounds, due to the high degree of lability of the acetonitrile ligand. This paper describes reactions of this complex with various neutral ligands and with a number of anionic nucleophiles.

Results and Discussion

We investigated the reaction of *trans*-$[Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$ with seven neutral ligand molecules: $(CH_3)_3N$, pyridine, $(C_6H_5)_3P$, $(C_2H_5)_3P$, $(CH_3O)_3P$, $(CH_3)_2S$, CH_3NC. This choice encompasses a relatively broad spectrum of ligands from those of "hard" character,[2] the nitrogen bases, to the "soft" ligands such as phosphines and methyl isocyanide. In each case the reaction proceeded rapidly to give a nearly quantitative yield of the appropriate *trans*-$[Pt(L)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$ complex, in which the ligand L has replaced acetonitrile. It is reasonable to assume that the list of ligands which are capable of substitution could have been expanded considerably further.

We were particularly interested in the facile synthesis of the trimethylamine complex by this route. Although platinum(II) complexes of nitrogen bases are not uncommon, trialkylamineplatinum(II) species are somewhat rare. We were also pleased to accomplish the synthesis of $[Pt(CNCH_3)\{P(C_6H_5)_3\}_3](BF_4)_2$, a compound for which we had unsuccessfully searched previously,[3] since it fit into the series $[Pt(CNCH_3)_4]^{2+}$, $[Pt(CNCH_3)_3\{P(C_6H_5)_3\}]^{2+}$ (yet unknown), $[Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2]^{2+}$, and $[Pt(CNCH_3)\{P(C_6H_5)_3\}_3]^{2+}$. Obvious routes to this compound, such as the reaction of $[Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2](BF_4)_2$ and triphenylphosphine, are not successful.

Reactions of $[Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$ with anionic reagents X^- (X = I, Cl, CN, N_3, NO_2, OH) were also carried out and in each case the appropriate complex *trans*-$[PtX(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$ was obtained in good yield.[4,5] Again there appears to be considerable versatility in the reactions that can be carried out, and so we sought primarily to establish the scope of this synthetic route by the specific choice of anions. Several of the complexes synthesized by this method, specifically those where X = Cl or CN in the above formulation, had been synthesized by us earlier,[3] in reactions of $[Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2](BF_4)_2$ with chloride and cyanide anions. However, the synthesis of nitro-[6,7] and hydroxoplatinum complexes from nitrite and hydroxide ion substitution contrasts with the additions of these groups to the isocyanide ligand in $[Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2](BF_4)_2$.[3]

In addition, the synthesis of the iodide complex $[PtI(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$ should be noted. In previous work[3] we had found that the reaction of $[Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2](BF_4)_2$ and iodide ion led to the five-coordinate $[PtI(CNCH_3)_2\{P(C_6H_5)_3\}_2]BF_4$, stable in contrast to other halide analogs. The availability of the complexes $[PtI(CNCH_3)\{phos\}_2]BF_4$ allowed us to study the equilibrium between this complex and various ligands and the five-coordinate species in more detail:[8] $[PtI(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4 + L \rightleftharpoons [PtI(L)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$.

Substitution of azide ion for acetonitrile occurs in preference to cyclization of this group with isocyanide or nitrile ligands to give a σ-bonded tetrazole group. The latter cyclization reactions are rather common; we had observed this phenomenon in the reaction of [Pt-

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(1) P. M. Treichel and W. J. Knebel, *Inorg. Chem.*, **11**, 1285 (1972).

(2) S. Ahrland, J. Chatt, N. R. Davies, *Quart. Rev., Chem. Soc.*, **12**, 265 (1958); R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

(3) P. M. Treichel, R. W. Hess, and W. J. Knebel, *ibid.*, **93**, 5424 (1971).

(4) Other known $[PtX(CNCH_3)\{phos\}_2]Y$ complexes are reviewed in ref 3.

(5) The assignment of a trans configuration of both series of compounds is made on the basis that the phenyl proton resonances in the nmr spectrum appeared as one relatively narrow multiplet, indicating one type of phosphine ligand. A cis configuration would have dissimilar phosphines and would presumably give two multiplets in different positions (as was observed for $[Pt(CNCH_3)\{P(C_6H_5)_3\}_3](BF_4)_2$). In addition it may be noted that if a phosphine is trans to methyl isocyanide, the CH_3 resonance is often a doublet, due to a $J_{P-Pt-CNCH_3}$ coupling of several hertz. In these compounds the CH_3 resonance does not show this splitting.

(6) This linkage isomer was identified from its infrared spectrum, which showed four bands (1410 (s), 1340 (m), 861 (w), 583 (w) cm^{-1}), attributed to the NO_2 group.[7]

(7) H. Elliot, B. J. Hathaway, and R. C. Slade, *Inorg. Chem.*, **5**, 669 (1966).

(8) P. M. Treichel and W. J. Knebel, *J. Coord. Chem.*, in press.

$(CNCH_3)_2\{P(C_6H_5)_3\}_2](BF_4)_2$ and azide, giving $[Pt(CN_4CH_3)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$[3] (in this reaction CN_4CH_3 = 5 methyl-1-tetrazolato, *i.e.*, carbon bonded to platinum).

It is interesting to note that $[Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2](BF_4)_2$ and $[Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$ are linkage isomers.

The ease of substitution of acetonitrile in $[Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$ is quite remarkable, prompting us to look for other examples of this phenomenon. Indeed there are several fairly obvious examples, in particular, the use of $Cr(NCCH_3)_3(CO)_3$ as an intermediate in the syntheses of various $L_3Cr(CO)_3$ or (arene)$Cr(CO)_3$ species.[9] Of course the use of bis(benzonitrile)palladium dichloride[10] as an intermediate in a wide range of synthetic applications is well known. Remarkably, however, only a few bis(organonitrile)platinum(II) halides have been made.[11] No particular use has been made of these species in syntheses, and no studies have been undertaken with these or other platinum complexes to elaborate on the facile replacement of nitriles that we observe here. Very recently Clark and Manzer have reported platinum complexes of several perfluoroorganonitriles, in which they suggested that the nitrile is bonding through the π electrons of the CN group.[12]

Infrared Studies

Because of the availability of a large number of $[PtX(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$ and $[Pt(L)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$ complexes made during this and in previous work,[3,13] we decided to look at the values of ν_{CN} to ascertain whether correlations with appropriate substituent parameters are possible. We were particularly interested in the degree to which varying electronic properties of L were transmitted through the platinum atom to the isocyanide group and the sensitivity of the latter group to these effects as reflected in frequency shifts of C≡N group. The high-resolution $\nu_{C\equiv N}$ data obtained in this study are given in Table I.

TABLE I

ν_{CN} VALUES FOR PLATINUM ISOCYANIDE COMPLEXES[a]

	Ref[c]	Solvent	ν_{CN}, cm^{-1}
$[PtX(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$			
X = CN	*b*	$CHCl_3$	2273
SCN	3	$CHCl_3$	2270
NO_2	*b*	$CHCl_3$	2268
Cl	*b*	$CHCl_3$	2264
N_3	*b*	$CHCl_3$	2263
I	*b*	$CHCl_3$	2262
CN_4CH_3		$CHCl_3$	2260
C_6F_5		$CHCl_3$	2254
OH	*b*	$CHCl_3$	2251
$C(OCH_3)=NCH_3$	3, *b*	$CHCl_3$	2245
$C(OCH_2CH=CH_2)=NCH_3$	3, *b*	$CHCl_3$	2245
$C(NHC_6H_4NO_2)=NCH_3$	1	$CHCl_3$	2245
$C(NHC_6H_4CH_3)=NCH_3$	1	$CHCl_3$	2242
C_6H_5 (as PF_6^- salt)	13	$CHCl_3$	2240
CH_3 (as PF_6^- salt)		$CHCl_3$	2236
$[Pt(L)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$			
L = $(C_6H_5)_3P$	*b*	CH_2Cl_2	2280
CH_3CN	*b*	CH_2Cl_2	2279
$(CH_3O)_3P$	*b*	CH_2Cl_2	2278
$(CH_3)_2S$	*b*	CH_2Cl_2	2277
C_5H_5N	*b*	CH_2Cl_2	2277
$(C_2H_5)_3P$	*b*	CH_2Cl_2	2276
CH_3NC	*b*	CH_2Cl_2	2274
$C(OCH_2CH=CH_2)=NHCH_3$		CH_2Cl_2	2268
$C(NHC_6H_4CH_3)=NHCH_3$	1	CH_2Cl_2	2265
$(CH_3)_3N$	*b*	CH_2Cl_2	2263

[a] Perkin-Elmer 421 spectrometer; values accurate to ±1 cm^{-1}. [b] This work. [c] No citation indicates compounds are from unpublished work of P. M. Treichel and W. J. Knebel.

In the series *trans*-$[PtX(CNCH_3)\{P(C_6H_5)_3\}_2]^+$, $\nu_{C\equiv N}$ values were observed in the range 2273–2236 cm^{-1} and decreased with changes in substituent (X^-) in the order $CN^- > SCN^- > NO_2^- > Cl^- > N_3^- > I^- > CN_4CH_3^- \gg C_6F_5^- > OH^- \gg C(OCH_3)NCH_3^- \approx C(OCH_2CH=CH_2)NCH_3^- \approx C(NHC_6H_4NO_2)NCH_3^- > C(NHC_6H_4CH_3)NCH_3^- > C_6H_5^- > CH_3^-$. This total range is fairly small, of course, especially so when considered in contrast to the ranges of ν_{CO} in metal carbonyls. Furthermore, one is at a disadvantage in not having force constants rather than frequencies in a comparison of this type. Nonetheless, a general trend of the values is expected; presumably this trend relates to the total electronic charge on platinum which arises as a result of contributions of the various ligands. This net charge will influence both σ and π bonding to the isocyanide ligand, with an increase in σ donation by this ligand giving an increase in $\nu_{C\equiv N}$, and an increase in π-accepting capacity, a decrease in the frequency. We observe a good linear correlation between $\nu_{C\equiv N}$ values and the inductive parameter, σ_I,[14] for the substituents X^-. The least-squares treatment gave the empirical equation $\nu_{C\equiv N} = 56\sigma_I + 2238$. We also noted a linear correlation between $\nu_{C\equiv N}$ and pK_a values for the protonated substituents HX.[15] A least-squares fit gave the empirical equation $\nu_{C\equiv N} = -0.63pK_a + 2265$. However, appreciable deviations by the substituents CN^- and I^- from this relationship are noted; perhaps this reflects the importance of some π-bonding capability (I^-, π donor; CN^-, π acceptor) of these ligands to platinum(II).

The relationship of ν_{CN} and σ-bonding parameters is not totally unexpected of course, as other studies noted these correlations.[16] It does not deny the existence of π bonding to the isocyanide ligand in these complexes although it appears to minimize the importance of this contribution. This would be in accord with the ideas suggested by Venanzi, *et al.*, on platinum(II) complexes.[17]

In the dicationic complexes $\nu_{C\equiv N}$ values were observed in the range 2280–2263 cm^{-1} and decreased in magnitude with changes in substituent L in the following order: $(C_6H_5)_3P \gtrsim CH_3CN \gtrsim (CH_3O)_3P \gtrsim (CH_3)_2S \approx C_5H_5N \gtrsim (C_2H_5)_3P > CH_3NC \gg C(OCH_2CH=CH_2)NHCH_3 > C(NHC_6H_4CH_3)NHCH_3 > (CH_3)_3N$. It is first appropriate to note that there is really a very small difference in $\nu_{C\equiv N}$ for this series of compounds, with only the last three being particularly different from the others. In view of this it is perhaps not surprising that a correlation of these values with

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

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(15) R. G. Pearson, H. Sobel, and J. Songstod, *J. Amer. Chem. Soc.*, **90**, 319 (1968).

(16) R. P. Stewart and P. M. Treichel, *ibid.*, **92**, 2710 (1970).

(17) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.*, 1707 (1966).

appropriate σ and/or π parameters is not successful. Only the most general differentiation between the soft polarizable ligands—phosphines, sulfides, and isocyanides—and the hard ligands, like trimethylamine, is clearly made in this series.

Experimental Section

The preparation of the starting complex, $[\mathrm{Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2}$, was described in the previous paper.[1] Methyl isocyanide was prepared by the literature method.[18] Other reagents and solvents were commercial samples and were used without further purification.

Routine infrared spectra were run on a Beckman IR-10; high-resolution infrared data were obtained on a Perkin-Elmer 421 spectrometer. Proton nmr data were obtained using Varian A-60A and T-60 instruments. Melting points were determined on a Kofler hot stage and are uncorrected. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The high-resolution infrared data are given in Table I.

Reactions of $[\mathrm{Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2}$ with Neutral Molecules. Reaction of $[\mathrm{Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2}$ and Trimethylamine.—A solution of the above complex (0.400 g, 0.410 mmol) in dichloromethane (20 ml) was treated with trimethylamine (0.06 ml, 0.62 mmol) and the colorless solution was stirred for 3 hr. The reaction mixture was evaporated to dryness and the white residue was redissolved in dichloromethane. After filtering and concentrating the resulting solution, pale pink crystals of $[\mathrm{Pt(CNCH_3)\{P(C_6H_5)_3\}_2\{N(CH_3)_3\}](BF_4)_2}$ (0.305 g, 75% yield) were precipitated on addition of ethyl ether. This product was recrystallized from dichloromethane–ethyl ether; mp 104–105°. *Anal.* Calcd for $\mathrm{C_{42}H_{42}B_2F_8N_2P_2Pt \cdot 0.2C_4H_{10}O}$:[19] C, 49.8; H, 4.16; N, 2.64; P, 6.17. Found: C, 49.8; H, 3.91; N, 2.32; P, 6.50. Infrared spectrum (cm^{-1}): $\nu_{\mathrm{C{\equiv}N}}$: 2263 (s); other bands: 3190 (w), 3140 (vw), 3060 (w, sh), 1587 (vw), 1280 (vw), 1185 (w), 1160 (vw), 1090 (s, sh), 1050 (vs), 993 (w), 743 (s), 706 (m), 686 (vs), 518 (vs), 508 (vs), 496 (w, sh), 470 (w), 420 (vw). Nmr spectrum (dichloromethane-d_2): τ 2.36 (multiplet), $\mathrm{C_6}H_5$; 6.5–7.5 (multiplet), $\mathrm{N(C}H_3)_3$; 7.38 (1:4:1 "triplet";[20] $J_{\mathrm{Pt-H}}$ = 19 Hz), $\mathrm{CNC}H_3$.

Reaction of $[\mathrm{Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2}$ and Pyridine.—Using a similar procedure the acetonitrile complex (0.120 g, 0.123 mmol) and pyridine (0.013 ml, 0.16 mmol) in dichloromethane (20 ml) gave white crystals of $[\mathrm{Pt(CNCH_3)(C_5H_5N)\{P(C_6H_5)_3\}_2](BF_4)_2}$ (0.115 g, 93% yield). These crystals were purified by recrystallization from dichloromethane–ethyl ether; mp 259–262°. *Anal.* Calcd for $\mathrm{C_{43}H_{38}B_2F_8N_2P_2Pt \cdot 0.2C_4H_{10}O}$: C, 51.3; H, 3.91; N, 2.71. Found: C, 51.5; H, 3.68; N, 2.42. Infrared spectrum (cm^{-1}): $\nu_{\mathrm{C{\equiv}N}}$: 2277 (s); other bands: 3661 (w), 3570 (vw), 3060 (w), 1615 (m), 1585 (w), 1575 (vw), 1480 (m), 1455 (m), 1435 (s), 1310 (w), 1285 (w), 1215 (vw), 1180 (w), 1160 (w), 1095 (s, sh), 1055 (vs), 995 (w, sh), 940 (vw), 750 (s), 710 (m, sh), 690 (vs), 525 (vs), 510 (vs), 495 (m, sh), 460 (vs), 435 (vs), 420 (vs). Nmr spectrum (acetonitrile-d_3): τ 2.37 (multiplet), $\mathrm{C_6}H_5$; 7.38 (1:4:1 "triplet"; $J_{\mathrm{Pt-H}}$ = 19 Hz), $\mathrm{CHC}H_3$.

Reaction of $[\mathrm{Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2}$ and Triphenylphosphine.—Using a similar procedure the acetonitrile complex (0.120 g, 0.123 mmol) and triphenylphosphine (0.042 g, 0.160 mmol) in acetonitrile (30 ml) gave white crystals of $[\mathrm{Pt(CNCH_3)\{P(C_6H_5)_3\}_3](BF_4)_2}$ (0.130 g, 88% yield). This product was purified by recrystallization from dichloromethane–hexane; mp 222–225°. *Anal.* Calcd for $\mathrm{C_{56}H_{48}B_2F_8NP_3Pt \cdot 0.1CH_2Cl_2}$: C, 55.9; H, 4.02; N, 1.16; P, 7.72. Found: C, 56.0; H, 3.77; N, 1.07; P, 7.07. Infrared spectrum (cm^{-1}): $\nu_{\mathrm{C{\equiv}N}}$: 2280 (s); other bands: 3060 (w, sh), 1587 (w), 1574 (vw), 1483 (m, sh), 1437 (s), 1310 (w), 1280 (vw), 1180 (w), 1160 (vw), 1090 (s, sh), 1055 (vs), 995 (w), 740 (s), 690 (vs), 540 (w, sh), 520 (vs), 510 (vs), 495 (w, sh), 425 (vw), 460 (w). Nmr spectrum (dichloromethane-d_2): τ 2.53 (multiplet), $\mathrm{(C_6H_5)_3P}$ cis to $\mathrm{CNCH_3}$; 2.93 (multiplet), $\mathrm{(C_6}H_5)_3\mathrm{P}$ trans to $\mathrm{CNCH_3}$; 7.87 (1:4:1 triplet; $J_{\mathrm{Pt-H}}$ = 15 Hz), $\mathrm{CNC}H_3$.

Reaction of $[\mathrm{Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2}$ and Triethylphosphine.—Using a similar procedure the acetonitrile complex (0.230 g, 0.236 mmol) and triethylphosphine (0.040 ml, 0.27 mmol) in dichloromethane (20 ml) gave white crystals of $[\mathrm{Pt(CNCH_3)\{P(C_2H_5)_3\}\{P(C_6H_5)_3\}_2](BF_4)_2}$ (0.179 g, 69% yield), precipitated from acetone–water; mp 178–180°. *Anal.* Calcd for $\mathrm{C_{44}H_{48}B_2F_8NP_3Pt}$: C, 52.9; H, 4.36; N, 1.25; P, 8.36. Found: C, 53.4; H, 4.70; N, 0.95; P, 8.30. Infrared spectra (cm^{-1}): $\nu_{\mathrm{C{\equiv}N}}$: 2276 (s); other bands: 3060 (w), 1585 (w), 1574 (vw), 1483 (m, sh), 1437 (s), 1310 (w), 1280 (vw), 1185 (w), 1160 (vw), 1090 (s, sh), 1050 (vs), 995 (w), 735 (s), 690 (vs), 540 (w, sh), 515 (vs), 508 (vs), 495 (w, sh), 460 (vw), 420 (vw). Nmr spectrum (dichloromethane-d_2): τ 2.63 (multiplet), $\mathrm{C_6}H_5$; 7.13 (1:4:1 triplet; $J_{\mathrm{Pt-H}}$ = 18 Hz), $\mathrm{CNC}H_3$; 8.23 (multiplet), $\mathrm{C}H_2$; 8.93 (multiplet), $\mathrm{CH_3}$ ($J_{\mathrm{C}H_2\mathrm{-C}H_3}$ = 8 Hz; other values not determinable.

Reaction of $[\mathrm{Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2}$ and Trimethyl Phosphite.—Using a similar procedure the acetonitrile complex (0.230 g, 0.236 mmol) and trimethyl phosphite (0.032 ml, 0.271 mmol) in dichloromethane (20 ml) gave white crystals of $[\mathrm{Pt(CNCH_3)\{P(OCH_3)_3\}\{P(C_6H_5)_3\}_2](BF_4)_2}$ (0.210 g, 84% yield). This product was recrystallized from dichloromethane–ethyl ether; mp 211–213°. *Anal.* Calcd for $\mathrm{C_{41}H_{42}B_2F_8NO_3P_3Pt}$: C, 45.3; H, 4.01; N, 1.33; P, 8.37. Found: C, 45.1; H, 4.02; N, 1.44; P, 7.98. Infrared spectrum (cm^{-1}): $\nu_{\mathrm{C{\equiv}N}}$: 2278 (s); other bands: 3060 (vs, sh), 1585 (vw), 1574 (vw), 1480 (m, sh), 1435 (s), 1308 (w), 1280 (w), 1170 (m), 1090 (s, sh), 1050 (vs), 990 (w, sh), 810 (m), 740 (s), 700 (w), 685 (vs), 567 (w), 515 (vs), 506 (vs), 495 (w, sh), 445, 420 (w). Nmr spectrum (dichloromethane-d_2): τ 2.29 (multiplet), $\mathrm{C_6}H_5$; 6.85 (doublet; $J_{\mathrm{P-OC}H_3}$ = 12 Hz), $\mathrm{P(OC}H_3)_3$; 7.70 (1:4:1 triplet; $J_{\mathrm{Pt-H}}$ = 14 Hz), $\mathrm{CNC}H_3$.

Reaction of $[\mathrm{Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2}$ and Dimethyl Sulfide.—Using a similar procedure the acetonitrile complex (0.200 g, 0.205 mmol) and dimethyl sulfide (0.100 ml, 1.36 mmol) in dichloromethane (20 ml) gave white crystals of $[\mathrm{Pt(CNCH_3)\{S(CH_3)_2\}\{P(C_6H_5)_3\}_2](BF_4)_2}$ (0.178 g, 87% yield), which were recrystallized from dichloromethane–ethyl ether; mp 230–232°. *Anal.* Calcd for $\mathrm{C_{40}H_{39}B_2F_8NP_2PtS \cdot 0.3CH_2Cl_2}$: C, 47.4; H, 3.89; N, 1.38; S, 3.13. Found: C, 47.4; H, 3.84; N, 1.71; S, 3.00. Infrared spectrum (cm^{-1}): $\nu_{\mathrm{C{\equiv}N}}$: 2277 (s); other bands: 3650 (w), 3560 (vw), 3130 (w), 3060 (vw, sh), 1587 (vw), 1573 (vw), 1510 (vw), 1482 (m, sh), 1436 (s), 1335 (vw), 1310 (vw), 1282 (vw), 1190 (w), 1163 (vw), 1095 (s, sh), 1055 (vs), 994 (w), 897 (vw), 747 (s), 704 (w, sh), 690 (vs), 538 (w, sh), 522 (vs), 510 (vs), 497 (w, sh), 460 (vw), 415 (vw). Nmr spectrum (dichloromethane-d_2): τ 2.43 (multiplet), $\mathrm{C_6}H_5$; 7.03 (1:4:1 triplet; $J_{\mathrm{Pt-H}}$ = 20 Hz), $\mathrm{CNCH_3}$; 7.42 (multiplet), $\mathrm{S(C}H_3)_2$.

Reaction of $[\mathrm{Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2}$ and Methyl Isocyanide.—To a solution of the acetonitrile complex (0.100 g, 0.103 mmol) in acetonitrile (10 ml) was added methyl isocyanide (0.007 ml, 0.124 mmol) and the reaction mixture was stirred for 15 min. Addition of ethyl acetate to the resulting system gave white needles of $[\mathrm{Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2](BF_4)_2}$ (0.096 g, 95% yield), which was identified from its spectral properties and melting point (269–271°).

Reactions of $[\mathrm{Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2}$ with Anionic Nucleophiles. Reaction of $[\mathrm{Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2}$ and Iodide Ion.—A solution of the acetonitrile complex (0.857 g, 0.878 mmol) in dichloromethane (20 ml) was treated with $[(n\text{-}\mathrm{C_4H_9})_4\mathrm{N}]\mathrm{I}$ (0.421 g, 1.14 mmol) in dichloromethane (10 ml) and the reaction mixture was stirred for 20 min. After filtering and concentrating the reaction system, white plates of $[\mathrm{PtI(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4}$ (0.796 g, 93% yield) separated from the solution on addition of excess methanol. This product was purified by recrystallization from dichloromethane–methanol; mp 213–216°. Its molar conductivity in acetonitrile was 141 ohm^{-1} cm^2 mol^{-1} and representative of a 1:1 electrolyte. *Anal.* Calcd for $\mathrm{C_{38}H_{33}BF_4INP_2Pt}$: C, 46.8; H, 3.42; N, 144; I, 13.1. Found: C, 46.5; H, 3.45; N, 1.68; I, 13.6. Infrared spectrum (cm^{-1}): $\nu_{\mathrm{C{\equiv}N}}$: 2262 (s); other bands: 3060 (w, sh), 1587 (vw), 1573 (vw), 1480 (m, sh), 1436 (s), 1310 (vw), 1280 (vw), 1180 (w), 1156 (vw), 1093 (s), 1050 (vs), 993 (w), 740 (s), 703 (m), 687 (vs), 520 (vs), 508 (vs), 498 (vw, sh), 460 (w), 420 (vw). Nmr spectrum (chloroform-d_1): τ 2.42 (multiplet), $\mathrm{C_6}H_5$; 7.67 (1:4:1 triplet; $J_{\mathrm{Pt-H}}$ = 19 Hz), $\mathrm{CNC}H_3$.

Reaction of $[\mathrm{Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2}$ and Chloride Ion.—A solution of the acetonitrile complex (0.150 g,

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[18] R. E. Schuster, J. E. Scott, and J. Casanova, *Org. Syn.*, **46**, 75 (1968).

[19] It was difficult to remove solvents of recrystallization completely. In some instances analytical samples retained a small amount of solvent. The presence of the solvents and approximate quantity were verified by nmr.

[20] The two peaks flanking the center absorption arise due to coupling with platinum-195, spin $^1/_2$ (relative abundance 33.8%).

0.154 mmol) in dichloromethane (20 ml) was treated with $[(C_2H_5)_4N]Cl$ (0.028 g, 0.170 mmol) in dichloromethane (10 ml) and the reaction mixture was stirred for 2 hr. After filtering and concentrating the resulting solution, addition of excess NH_4PF_6 in methanol (30 ml) gave the white crystalline $[PtCl(CNCH_3)\{P(C_6H_5)_3\}_2]PF_6$ (0.107 g, 74% yield), which was identified by spectral properties and its melting point (231–233°).[3]

Reaction of $[Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$ and Cyanide Ion.—A solution of this complex (0.150 g, 0.154 mmol) in acetonitrile (30 ml) was treated with potassium cyanide (0.011 g, 0.170 mmol) in water (5 ml) and the reaction mixture was stirred for 2 hr. The system was evaporated to dryness and the residue was redissolved in chloroform. After filtering and concentrating the resulting solution, the addition of ethyl ether gave the white crystalline $[Pt(CN)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$ (0.128 g, 83% yield), which was identified by spectral properties and its melting point (236–239°).[3]

Reaction of $[Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$ and Azide Ion.—Using a similar procedure the addition of sodium azide (0.048 g, 0.738 mmol) in water (5 ml) to the acetonitrile complex (0.600 g, 0.615 mmol) in acetone (30 ml) gave the yellow crystalline $[PtN_3(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$ (0.459 g, 84% yield). This product was recrystallized from chloroform–ethyl ether; mp 108–110°. *Anal.* Calcd for $C_{38}H_{33}BF_4N_4P_2Pt \cdot 1.0CHCl_3$: C, 46.3; H, 3.41; N, 5.54. Found: C, 46.3; H, 3.56; N, 5.41. Infrared spectrum (cm^{-1}): $\nu_{C\equiv N}$, 2263 (s); other bands: 3060 (w, sh), 2058 (vs), 1587 (vw), 1573 (vw), 1480 (m, sh), 1433 (s), 1330 (vw), 1310 (vw), 1278 (vw), 1180 (w), 1154 (vw), 1093 (s), 1050 (vs), 990 (w), 740 (s), 703 (m), 685 (vs), 517 (vs), 506 (vs), 496 (w, sh), 470 (vw), 440 (vw). Nmr spectrum (chloroform-d_1): τ 2.40 (multiplet), C_6H_5; 7.45 (1:4:1 "triplet"; J_{Pt-H} = 19 Hz), $CNCH_3$.

Reaction of $[Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$ and Nitrite Ion.—Using a similar procedure the addition of sodium nitrite (0.032 g, 0.462 mmol) in water (10 ml) to the acetonitrile complex (0.300 g, 0.308 mmol) in acetonitrile (30 ml) gave pale yellow crystals of $[Pt(NO_2)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$ (0.218 g, 79% yield), which were purified by recrystallization from dichloromethane–ethyl ether; mp 202–204°. Infrared spectral data indicated this product was the nitro derivative.[6] *Anal.* Calcd for $C_{38}H_{33}BF_4N_2O_2P_2Pt$: C, 51.0; H, 3.73; N, 3.14. Found: C, 50.8; H, 3.75; N, 3.10. Infrared spectrum (cm^{-1}): $\nu_{C\equiv N}$: 2268 (s); other bands: 3060 (w, sh), 1587 (vw), 1577 (vw), 1486 (m, sh), 1438 (s), 1410 (s), 1340 (m), 1310 (vw), 1280 (vw), 1190 (w), 1162 (vw), 1096 (s), 1053 (vs), 996 (w), 816 (w), 746 (m), 708 (w), 690 (s), 583 (w), 520 (vs), 510 (vs), 498 (vw, sh), 450 (vw), 420 (vw). Nmr spectrum (chloroform-d_1): τ 2.36 (multiplet), C_6H_5; 7.27 (1:4:1 "triplet"; J_{Pt-H} = 16 Hz), $CNCH_3$.

Reaction of $[Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$ and Hydroxide Ion.—Using a similar procedure the addition of potassium hydroxide (0.018 g, 0.324 mmol) in water (8 ml) to the acetonitrile complex (0.301 g, 0.309 mmol) in acetonitrile (20 ml) gave pale yellow microcrystals of $[Pt(OH)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$ (0.219 g, 82% yield), which were precipitated from acetone–water; mp 104–105°. *Anal.* Calcd for $C_{38}H_{34}BF_4NOP_2Pt$: C, 52.8; H, 3.97; N, 1.62. Found: C, 52.8; H, 4.06; N, 1.73. Infrared spectrum (cm^{-1}): $\nu_{C\equiv N}$: 2251 (s); other bands: 3610 (w), 3060 (w, sh), 1436 (s), 1305 (vw), 1278 (vw), 1185 (w), 1158 (vw), 1095 (s) 1055 (vs), 996 (w), 745 (m), 708 (m), 690 (s), 550 (w), 520 (s), 510 (s), 498 (vw, sh), 450 (vw), 418 (vw). Nmr spectrum (chloroform-d_1): τ 2.40 (multiplet), C_6H_5; 7.40 (1:4:1 "triplet"; J_{Pt-H} = 18 Hz), $CNCH_3$.

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Kinetics of Nucleophilic Attacks on Palladium(II) Isocyanide Complexes

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Kinetic data on reactions of the type *cis*-$[Pd(p\text{-}YC_6H_4NC)LX]$ + *p*-$ZC_6H_4NH_2 \rightarrow$ *cis*-$[Pd\{C(NHC_6H_4Y)NHC_6H_4Z\}LX_2]$ ($Y = CH_3O, CH_3, H, NO_2$; $Z = CH_3O, CH_3, H, Cl, NO_2$; $L = P(C_6H_5)_3, As(C_6H_5)_3$; $X = Cl, Br$) in 1,2-dichloroethane at 30° are reported. The reactions occur according to the rate law: $k_{obsd} = k[\text{amine}]$. The proposed reaction mechanism implies a direct attack of the entering para-substituted amine on the carbon atom of the isocyanide linked to the central metal. For the phenyl isocyanide complex, the reactivity order of the amine is $CH_3OC_6H_4NH_2 > CH_3C_6H_4NH_2 > C_6H_5NH_2 > ClC_6H_4NH_2 \gg O_2NC_6H_4NH_2$. For the entering *p*-toluidine, the reactivity order of coordinated isocyanides is $O_2NC_6H_4NC \gg C_6H_5NC > CH_3C_6H_4NC > CH_3OC_6H_4NC$. These reactivity trends are interpreted in terms of electronic effects of para substituents Y and Z. The activation parameters for the reaction of *cis*-$[Pd(C_6H_5NC)(P(C_6H_5)_3)Cl_2]$ with *p*-toluidine in 1,2-dichloroethane are $\Delta H^* = 9.4 \pm 0.1$ kcal/mol and $\Delta S^* = -35.1 \pm 1.7$ eu. The largely negative value of ΔS^* suggests a transition state the formation of which involves a considerable reduction of degrees of freedom leading to a rigid activated structure.

Introduction

Coordinated ligands containing unsaturated carbon atoms such as carbon monoxide,[1-7] olefins[8] or acetylenes,[9] and isocyanides[10-16] readily undergo nucleophilic attack. In particular, the isocyanide group linked to a transition metal ion exhibits a pronounced tendency to react with amines or alcohols to give carbene complexes.[10-16]

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