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Carboxamidoplatinum Complexes Derived from Hydroxide Addition to Platinum(II) Isocyanide Complexes and Their Protonation in Polar Solvents

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Hydroxide ion adds to $[Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2](BF_4)_2$, giving the carboxamido complex $[Pt(CONHCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$. Upon treatment of this complex with acid in aqueous acetonitrile one obtains $[Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$, *via* the unstable platinum(II) carbonyl species $[Pt(CO)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$. Addition of SH^- to $[Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2](BF_4)_2$ gives the thiocarboxamido complex $[Pt(CSNHCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$ and additions of NHR^- ($R = C_6H_5$, $p\text{-}CH_3C_6H_4$, $p\text{-}O_2NC_6H_4$) give the amidinium complexes $[Pt(C\{NR\}NHCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$. Protonation of the thiocarboxamide complex was not successful, but a proton could be added reversibly to the amidinium species. Hydroxide ion does not add to $[Pt(CNCH_3)_4](BF_4)_2$ and $[Pt(CNCH_3)\{P(C_6H_5)_3\}_3](BF_4)_2$ but instead replaces one isocyanide ligand.

Introduction

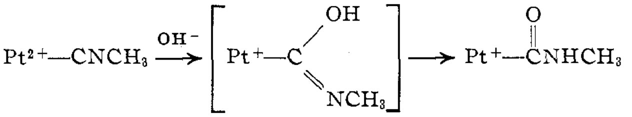
In earlier work[1] on platinum(II) isocyanide complexes we investigated the reaction of nitrite anion with *trans*-$[Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2](BF_4)_2$. Remarkably, this reaction gave the product $[Pt(CONHCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$, in which the net change accomplished was the addition of OH^- to a coordinated isocyanide ligand. In turn this observation suggested that addition of hydroxide ion to this complex should be attempted; preliminary success in this reaction was observed.[2] Here we report fully on this work, on related studies, involving analogous SH^- and NHR^- additions to coordinated isocyanides, and on protonation studies of the resulting complexes.

Results and Discussion

To gain some perspective for this work, it is important to realize that the most common mode of reaction for square-planar d^8 complexes, like $[Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2](BF_4)_2$, is ligand substitution.[3] Indeed we have verified this in earlier studies; reactions of X^- (Cl^-, Br^-, CN^-, SCN^-) occur to give $[PtX(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$.[1] Apparently these reactions proceed through a five-coordinate adduct of cation and anionic reagent from which one ligand is lost. In certain instances, the five-coordinate adduct is stable to ligand loss.

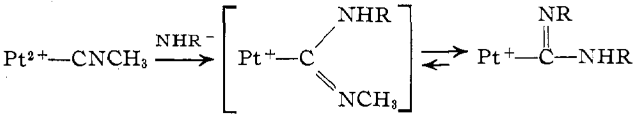
Interestingly, reactions of alkoxide anions (OR^-) and $[Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2](BF_4)_2$ do not follow the general pattern; instead the nucleophile adds to the carbon atom of the coordinated isocyanide.[1] For example, $[Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2](BF_4)_2$ and methoxide ion react to give $[Pt\{C(OR){=}NCH_3\}(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$ rather than $[Pt(OR)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$. Alkoxide ion addition to an isocyanide ligand is not particularly unusual, since analogous reactions are known for carbonyls;[4] however its occurrence here instead of the expected ligand replacement seems noteworthy. An explanation of this result may rely on thermodynamics rather than kinetics: the affinity of the soft acid (platinum atom) for the hard base (alkoxide) is low, and as a result the product from substitution is less stable than the observed product.

In view of the attack of alkoxide at the coordinated isocyanide in this complex the hydroxide ion reaction is less surprising. The formation of the carboxamido complex can occur by hydroxide ion attack on the carbon of the isocyanide, followed by hydrogen migration from oxygen to nitrogen



$$\mathrm{Pt^{2+}{-}CNCH_3} \xrightarrow{\mathrm{OH^-}} \left[\mathrm{Pt^{+}{-}C}\begin{matrix}\diagup\mathrm{OH}\\ \diagdown\!\!\diagdown\mathrm{NCH_3}\end{matrix}\right] \longrightarrow \mathrm{Pt^{+}{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{NHCH_3}$$

The same route to amidinium complexes can be envisioned. The hard base NHR^- attacks the coordinated isocyanide ligand, and then hydrogen migrates to the more basic nitrogen atom



$$\mathrm{Pt^{2+}{-}CNCH_3} \xrightarrow{\mathrm{NHR^-}} \left[\mathrm{Pt^{+}{-}C}\begin{matrix}\diagup\mathrm{NHR}\\ \diagdown\!\!\diagdown\mathrm{NCH_3}\end{matrix}\right] \rightleftarrows \mathrm{Pt^{+}{-}}\overset{\overset{\mathrm{NR}}{\|}}{\mathrm{C}}\mathrm{{-}NHR}$$

($R = C_6H_5$, $p\text{-}CH_3C_6H_4$, $p\text{-}O_2NC_6H_4$)

The position of the hydrogen ($-N\mathit{H}CH_3$) is confirmed for $R = p\text{-}O_2NC_6H_4$ and $R = C_6H_5$ by the observation that the methyl proton nmr resonance occurs as a doublet, due to J_{H-NCH_3} coupling. For $R = p\text{-}CH_3C_6H_4$ the overlap of the CH_3 resonances obscures this coupling.

The addition of SH^- to $[Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2](BF_4)_2$ occurs in a manner analogous to the above reactions. The product isolated in this reaction is the thiocarboxamidoplatinum complex $[Pt(CSNHCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$. Although SH^- is a softer base than OH^- this addition reaction takes precedence over ligand displacment.

Elemental analyses for the complexes described above are in accord with these formulations. Conductance measurement show each species to be a 1:1 electrolyte. Infrared spectra have appropriate peaks associated with $\nu_{C\equiv N}$, $\nu_{C=N}$, $\nu_{C=O}$, $\nu_{C=S}$, and ν_{NH}; these assignments are noted in the Experimental Section. The proton nmr spectra also present absorptions appropriate to these overall formulations.

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

[2] Preliminary communication: W. J. Knebel and P. M. Treichel, *J. Chem. Soc. D*, 516 (1971).

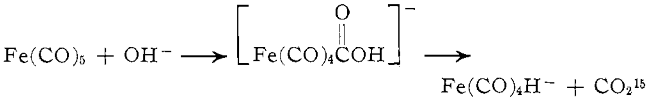
[3] F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 1 (1961).

[4] T. Kruck and M. Noack, *Chem. Ber.*, **97**, 1693 (1964).

Carboxamido-[5–10] and thiocarboxamidometal[11] complexes were known prior to this work, of course. These complexes were prepared either from reactions of dialkylcarbamoyl halides with metal carbonyl anions or by reactions of amines with cationic metal carbonyl or thiocarbonyl complexes. However, our work represents the first conversion of a complexed isocyanide to such a ligand group and in this sense is particularly interesting.

Unfortunately, the reaction of hydroxide ion with a coordinated isocyanide may be unique to a small group of metal complexes. We have not yet achieved such a reaction with any other systems. With a closely related complex such as $[Pt(CNCH_3)_4](BF_4)_2$ ligand displacement occurs giving $[Pt(OH)(CNCH_3)_3]BF_4$; with $[Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$ the nitrile ligand is displaced to give $[Pt(OH)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$.[12] With hydroxide ion and $[Pt(CNCH_3)\{P(C_6H_5)_3\}_3](BF_4)_2$, the complex $[Pt(CONHCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$ arises, but its formation may well have occurred after preliminary ligand redistribution. Finally the reactions of $[C_5H_5Fe(CO)(CNCH_3)_2]^+$ or $[C_5H_5Fe(CO)_2(CNCH_3)]^+$ and hydroxide lead only to formation of the dimeric species $(C_5H_5Fe)_2(CO)_{4-x}(CNCH_3)_x$ ($x = 1, 2$)[13] by reduction; and both the complexes $[Mn(CNCH_3)_6]^+$ and $[C_5H_5Fe(CNCH_3)_3]^+$ do not react with hydroxide ion and may be recovered unchanged.[14]

Our studies in this area are not complete, but even from these data some observations may be put forward. It appears that hydroxide addition to a coordinated isocyanide may be a rather unique phenomenon, limited to a few specially chosen reaction systems. Reduction seems to be a reasonable alternative; indeed such reactions with metal carbonyls have long been known, for example



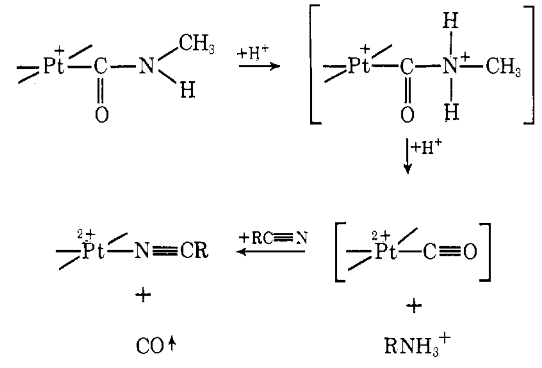
$$\mathrm{Fe(CO)_5 + OH^- \longrightarrow \left[Fe(CO)_4\overset{\overset{\displaystyle O}{\|}}{C}OH\right]^- \longrightarrow Fe(CO)_4H^- + CO_2}$$[15]

Low-valent isocyanide complexes will react in a similar fashion, provided that a stable lower oxidation state complex can arise. In a few instances ligand replacement would seem to be a reasonable alternative. In particular labile complexes such as d^8 square-planar complexes seem likely to proceed in this fashion.

Reaction may not occur when the isocyanide complex is both inert to substitution and not favorably disposed to reduction or addition on thermodynamic grounds. With respect to this, it may be noted that isocyanide complexes of the lower valence states of metals are fairly uncommon. Thus, complexes like $Mn(CNR)_6^+$ are not reducible under any conditions; they eventually decomposed before reduction occurs.

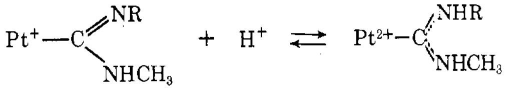
Protonation of the complex $[Pt(CONHCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$ was attempted in aqueous acetonitrile solution using the strong acid HBF_4. (This choice was made primarily on the basis that this was a strong acid and the anion would not coordinate with platinum.) During the course of the reaction a gas was evolved; this was identified as carbon monoxide by its mass spectrum. The solid product isolated from the reaction mixture was identified as $[Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$ by analyses and spectral data. Using other nitrile solvents (benzonitrile, *tert*-butylnitrile) analogous complexes were obtained.

A plausible reaction mechanism for this acidification involves the nonisolable intermediate $[Pt(CO)(CNCH_3)\{P(C_6H_5)_3\}_2]^{2+}$, *i.e.*



Analogous conversions of carboxamido complexes of iron,[6] manganese,[7] rhenium,[8,9] and ruthenium[10] to the appropriate carbonyl complexes have been reported. These reactions are generally accomplished using nonaqueous conditions, with hydrogen chloride in benzene or ether. The only reported aqueous hydrolysis, run in neutral solution,[5] appears contradictory to our observations. This work, predating the other studies, indicated the facile aqueous hydrolysis of $C_5H_5Fe(CO)_2CONR_2$ to $[C_5H_5Fe(CO)_2]_2$; it is suggested that this perhaps occurs *via* $C_5H_5Fe(CO)_2COOH$ which would decompose to $C_5H_5Fe(CO)_2H$ and CO_2.[16] Because of this possibly contradictory observation it was particularly important that we verified the gas evolved as CO rather than CO_2.[17]

It is of interest to note that the amidinium complexes can be reversibly protonated by acids



Unfortunately, the product does not rearrange, with amine loss, giving an isocyanide complex, even under forcing conditions.

The attempted acidification of $[Pt(CSNHCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2]^+$ under similar conditions as described in the above system gave no net change and nearly quantitative recovery of starting material. The inability of this thiocarboxamido complex to undergo protonation with subsequent splitting off of an amine group from the main substrate is unique and is in direct contrast with the analogous reaction of carboxamido

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(5) R. B. King, *J. Amer. Chem. Soc.*, **85**, 1918 (1963).

(6) L. Busetto and R. J. Angelici, *Inorg. Chim. Acta*, **2**, 391 (1968).

(7) R. J. Angelici and D. L. Denton, *ibid.*, **2**, 3 (1968).

(8) H. Behrens, E. Lindner, and P. Pässler, *Z. Anorg. Allg. Chem.*, **365**, 137 (1969).

(9) R. J. Angelici and A. E. Kruse, *J. Organometal. Chem.*, **22**, 461 (1970).

(10) A. E. Kruse and R. J. Angelici, *ibid.*, **24**, 231 (1970).

(11) L. Busetto, M. Graziani, and U. Belluco, *Inorg. Chem.*, **10**, 78 (1971).

(12) P. M. Treichel and W. J. Knebel, *ibid.*, **11**, 1289 (1972).

(13) J. P. Stenson, Ph.D. Thesis, University of Wisconsin, 1970.

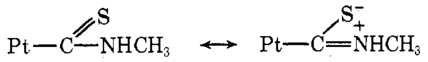
(14) P. M. Treichel, unpublished observation.

(15) See review by F. Calderazzo on metal carbonyls in I. Wender and P. Pino, "Metal Carbonyls in Organic Synthesis," Interscience, New York, N. Y., 1968.

(16) R. B. King, M. B. Bisnette, and A. Fronzaglia, *J. Organometal. Chem.*, **5**, 341 (1966).

(17) It may also be possible that the initial product in the hydrolysis of $C_5H_5Fe(CO)_2CONR_2$ is $C_5H_5Fe(CO)_3^+$ which decomposes under basic conditions; *i.e.*, $C_5H_5Fe(CO)_3^+ + OH^- \rightarrow [C_5H_5Fe(CO)_2COOH] \rightarrow [C_5H_5Fe(CO)_2]_2$.

derivatives. It is also in contrast to the nonaqueous reaction of $C_5H_5Fe(CO)_2CSNR_2$ and HCl which gives $C_5H_5Fe(CO)_2CS^+$.[11] One possible explanation is that the sulfur atom in $[Pt(CSNHCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$ has considerable negative charge and is protonated reversibly in strong acid rather than nitrogen. This idea has some merit since the value of ν_{CS} is considerably lower than expected in this system, falling at 915 cm^{-1} *vs.* ν_{CS} of 1150–1250 cm^{-1} in $C_5H_5Fe(CO)_2CSNR_2$. The lower frequency would be the result of negative charge delocalization to sulfur.



$$Pt{-}C({=}S){-}NHCH_3 \longleftrightarrow Pt{-}C(S^-){=}\overset{+}{N}HCH_3$$

Experimental Section

The preparations of *trans*-$[Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2](BF_4)_2$ and $[Pt(CNCH_3)_4](BF_4)_2$ were described earlier.[1] The preparation of $[Pt(CNCH_3)\{P(C_6H_5)_3\}_3](BF_4)_2$ is fully described in the subsequent paper.[12] Amines were purified by established procedures. Acetonitrile was dried over CaH_2, distilled onto P_2O_5, and then redistilled for use as a solvent for conductivity measurements. Tetrahydrofuran was dried over $LiAlH_4$. All other reagents and solvents (reagent grade) were used without further purification.

Routine infared spectra were recorded by a Beckman IR-10 spectrometer using Nujol mulls; high-resolution infrared data were obtained on a Perkin-Elmer 421 spectrometer using chloroform solutions (except as noted). Proton nmr data were obtained using Varian A-60A and T-60 instruments. Mass spectra were obtained from a MS-902 spectrometer. Conductivity measurements were made on $\sim 5 \times 10^{-4}$ *M* acetonitrile solutions with a Beckman conductivity bridge, Model RC-18A, with an associated cell of constant $k = 0.20$. 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.

Reaction of *trans*-$[Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2](BF_4)_2$ and Hydroxide Ion.—Treatment of *trans*-$[Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2](BF_4)_2$ (1.20 g, 1.23 mmol) in acetonitrile (50 ml) with KOH (0.090 g, 1.60 mmol) in water (20 ml) gave a colorless solution which became pale yellow on stirring for 8 hr at 25°. After solvent removal the solid residue was taken up in dichloromethane and filtered. Partial solvent removal and addition of hexane to the filtrate gave $[Pt(CONHCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$ (1.08 g, 97% yield) as pale yellow crystals. This product was recrystallized from dichloromethane–hexane; mp 184–186°. Its molar conductance in acetonitrile was 141 ohm^{-1} cm^2 mol^{-1} which is representative of a 1:1 electrolyte. *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. Infrared and nmr data for this compound were reported earlier.[1]

Reaction of $[Pt(CNCH_3)_4](BF_4)_2$ and Hydroxide Ion.—A solution of the above complex (0.315 g, 0.592 mmol) in acetonitrile (20 ml) was treated with potassium hydroxide (0.040 g, 0.710 mmol) in water (7 ml) and the resulting pale yellow solution was stirred at 25° for 12 hr. The reaction system was evaporated to dryness and the residue was redissolved in acetone. After the resulting solution was filtered and concentrated, addition of ethyl ether and cooling (−21°) slowly gave pale yellow crystals of $[Pt(OH)(CNCH_3)_3]BF_4$ (0.188 g, 76% yield), which were recrystallized from acetone–ethyl ether; mp 213–217° dec. This product appears unstable and decomposes slowly under normal room conditions. *Anal.* Calcd for $C_6H_{10}BF_4N_3OPt$: C, 17.2; H, 2.39; N, 9.93. Found: C, 17.5; H, 2.38; N, 9.41. Infrared spectrum (cm^{-1}): $\nu_{C\equiv N}$: 2240 (vs) (Nujol, low resolution); other bands: 3630 (w), 3420 (w), 1590 (m), 1410 (m), 1283 (w), 1220 (vw), 1055 (vs), 940 (w), 760 (vw), 720 (w), 690 (vw), 516 (m), 462 (s), 445 (w, sh).

Reaction of $[Pt(CNCH_3)\{P(C_6H_5)_3\}_3](BF_4)_2$ and Hydroxide Ion.—A solution of the above complex (0.600 g, 0.502 mmol) in acetonitrile (30 ml) was treated with potassium hydroxide (0.0366 g, 0.652 mmol) in water (9 ml) and the resulting pale yellow suspension, which eventually gave a clear solution, was stirred for 24 hr. The reaction mixture was evaporated to dryness and the residue was redissolved in dichloromethane. After the resulting solution was filtered and concentrated, products were precipitated on addition of ethyl ether as a gummy red oil (first crop) and an off-white solid (second crop). The red oil was intractable and could not be characterized further. The white solid was recrystallized several times from dichloromethane–ethyl ether and identified as $[Pt(CONHCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$ (0.214 g, 47% yield) from its spectral properties and its melting point, 183–185° dec. From the ether filtrate of the original separation, a white crystalline solid, $(C_6H_5)_3PO$ (0.103 g, 0.370 mmol), was precipitated on addition of excess hexane. This latter product was identified from its infrared spectrum and its melting point, 152–154°.

Reaction of *trans*-$[Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2](BF_4)_2$ and Hydrosulfide Ion.—Treatment of $[Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2](BF_4)_2$ (1.00 g, 1.02 mmol) in acetonitrile (50 ml) with $Na_2S \cdot 9H_2O$ (0.320 g, 1.33 mmol) in water (10 ml), to which was added 6 drops of aqueous fluoroboric acid (48–50%), gave a yellow solution which was stirred for 6 hr at 25°. Using a similar work-up procedure as was described in the previous synthesis, $[Pt(CSNHCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$ (0.76 g, 81% yield) was obtained. It was purified by crystallization from dichloromethane–ethyl ether; mp 117–118°. Its molar conductance in acetonitrile was 148 ohm^{-1} cm^2 mol^{-1}. *Anal.* Calcd for $C_{40}H_{37}BF_4N_2P_2PtS \cdot 0.3C_4H_{10}O$:[18] C, 52.4; H, 4.26; N, 2.96; S, 3.41. Found: C, 52.7; H, 4.14; N, 2.57; S, 3.71. Infrared spectrum (cm^{-1}): $\nu_{C\equiv N}$: 2230 (s) (Nujol, low resolution); other bands: 3340 (m), 3050 (w, sh), 1587 (vw), 1574 (vw), 1525 (m), 1480 (m), 1435 (s), 1355 (m), 1335 (w, sh), 1310 (vw), 1285 (w), 1185 (w), 1155 (w), 1095 (s, sh), 995 (w, sh), 915 (m), 745 (s), 704 (m, sh), 685 (vs), 620 (w), 570 (vw), 520 (vs), 510 (vs), 495 (w, sh), 440 (vw), 415 (vw). Nmr spectrum (dichloromethane solution): τ 2.46 (multiplet), C_6H_5; 7.66 (1:4:1 triplet, $J_{Pt-H} = 11$ Hz), $C{\equiv}NCH_3$; 7.92 (multiplet, $J_{Pt-H} = 5$ Hz, $J_{HNCH_3} = 5$ Hz), $CSN(H)CH_3$.

Reactions of *trans*-$[Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2(BF_4)_2$ and Amide Ions.—Treatment of $[Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2](BF_4)_2$ (0.809 g, 0.828 mmol) with sodium *p*-toluidide (1.24 mmol, from 0.029 g of sodium and 1.0 g of *p*-toluidine) in tetrahydrofuran (40 ml) gave a pale brown suspension which was stirred vigorously at reflux temperature for 3 days under a nitrogen atmosphere. After solvent removal the residue was redissolved in dichloromethane (30 ml) and the resulting solution was filtered. Addition of excess ethyl ether precipitated $[Pt\{C(NC_6H_4CH_3)NHCH_3\}(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$ (0.628 g, 76% yield) as brownish yellow crystals. This product was recrystallized from dichloromethane–ethyl ether; mp 199–200°. Its molar conductance in acetonitrile was 143 ohm^{-1} cm^2 mol^{-1}. *Anal.* Calcd for $C_{47}H_{44}BF_4N_3P_2Pt \cdot 0.2CH_2Cl_2$:[18] C, 56.0; H, 4.42; N, 4.15; P, 6.14. Found: C, 56.2; H, 4.31; N, 4.15; P, 6.26. Infrared spectrum (cm^{-1}): $\nu_{C\equiv N}$: 2242 (s); $\nu_{C=N}$: 1590 (vw, sh), 1575 (vs, sh), 1550 (vs), 1490 (s); other bands: 3430 (s), 3060 (w, sh), 1483 (s), 1435 (s), 1400 (w), 1335 (vw), 1310 (w), 1300 (vw), 1280 (w), 1210 (w, sh), 1196 (m), 1190 (w, sh), 1157 (w), 1130 (w, sh), 1095 (s, sh), 1050 (vs), 995 (w, sh), 880 (w), 828 (m), 812 (w), 743 (s), 703 (m), 686 (s), 536 (w, sh), 517 (vs), 506 (vs), 495 (w, sh), 447 (vw), 415 (vw). Nmr spectrum (chloroform-d_1): τ 2.55 (multiplet), C_6H_5; 3.43 (multiplet), C_6H_4; 7.70 (multiplet), composite of $CNCH_3$, $=N \cdot CH_3$, and $C_6H_4CH_3$.

Using a similar procedure $[Pt\{C(NC_6H_5)NHCH_3\}(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$ (65% yield) was prepared from $[Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2](BF_4)_2$ and sodium anilide as light brown microcrystals. It was purified by recrystallization from chloroform–ethyl ether; mp 188–191°. *Anal.* Calcd for $C_{46}H_{42}BF_4N_3P_2Pt$: C, 56.4; H, 4.31; N, 4.28. Found: C, 56.2; H, 4.59; N, 4.06. Infrared spectrum (cm^{-1}): $\nu_{C\equiv N}$: 2240 (m); $\nu_{C=N}$: 1595 (m), 1560 (s) (Nujol, low resolution); other bands: 3430 (w), 3300 (w), 3060 (w, sh), 1620 (w, sh), 1495 (w, sh), 1483 (m), 1435 (s), 1310 (vw), 1280 (w), 1180 (w), 1160 (w), 1095 (s), 1055 (vs), 995 (w, sh), 835 (vw), 825 (vw), 745 (m), 690 (s), 535 (w, sh), 520 (s), 510 (s), 495 (vw, sh), 450 (vw), 415 (vw). Nmr spectrum: τ 2.47 (multiplet), $(C_6H_5)_3P$ and $C_6H_5N{=}$; 7.72 (1:4:1 triplet, $J_{Pt-H} = 12$ Hz), $CNCH_3$; 7.87 (doublet, $J_{H-NCH_3} = 2$ Hz), $NHCH_3$.

Using a similar procedure $[Pt\{C(NC_6H_4NO_2)NHCH_3\}(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$ (0.884 g, 85% yield) was prepared as

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[18] The complete solvent removal on drying was difficult, and in some cases small amounts of solvent were retained in the analytical sample. In such cases their presence was confirmed by nmr, in which the appropriate solvent resonances could be observed.

yellow-orange crystals from the reaction of $[\mathrm{Pt(CNCH_3)_2\{P(C_6H_5)_3\}_2}](\mathrm{BF_4})_2$ (1.00 g, 1.02 mmol) and sodium *p*-nitroanilide (1.23 mmol, from 0.052 g of NaH dispersion (57%) and 1.0 g of *p*-nitroaniline). It was purified by repeated crystallization from dichloromethane–ethyl ether; mp 216–218°. *Anal.* Calcd for $\mathrm{C_{46}H_{41}BF_4N_4O_2P_2Pt\cdot 0.2CH_2Cl_2}$: C, 53.2; H, 4.01; N, 5.24. Found: C, 53.2; H, 4.02; N, 5.12. Infrared spectrum ($\mathrm{cm^{-1}}$): $\nu_{\mathrm{C\equiv N}}$: 2245 (s); $\nu_{\mathrm{C=N}}$: 1585 (m), 1510 (s, sh), 1490 (vs); other bands: 3420 (m), 3060 (w, sh), 1435 (s), 1395 (w), 1310 (vs), 1205 (w), 1165 (w), 1105 (w, sh), 1095 (s), 1055 (s), 995 (w, sh), 885 (w), 840 (m), 740 (m), 705 (w, sh), 685 (s), 515 (vs), 510 (s, sh), 500 (w, sh), 485 (vs, sh), 445 (vw), 410 (vw). Nmr spectrum (dichloromethane): τ 2.50 (multiplet), $\mathrm{C_6}H_5$; 7.77 (1:4:1 triplet, $J_{\mathrm{Pt-H}} = 12$ Hz), $\mathrm{CNC}H_3$; 7.90 (doublet, $J_{\mathrm{NHCH_3}} = 4$ Hz), $\mathrm{NHC}H_3$.

Acidification of $[\mathrm{Pt(CONHCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2}]\mathrm{BF_4}$.—The addition of concentrated fluoroboric acid in aqueous solution (8 ml) to the above complex (0.240 g, 0.265 mmol) in acetonitrile (10 ml) was accompanied by considerable heat evolution and rapid escape of carbon monoxide. This gaseous product was collected and identified by mass spectrometric measurements on the gas using a specially prepared reaction system which had been deaerated thoroughly by standard vacuum-line techniques prior to the reaction. After stirring for 1 hr at 25° the reaction mixture was evaporated to a small volume, at which time a white crystalline solid began to separate from the solution. The resulting mixture was treated with 10 ml of water and extracted several times with dichloromethane. The dichloromethane solution was filtered and evaporated to dryness; the residue was redissolved in a small volume of dichloromethane, and the product precipitated on addition of ethyl ether. Final purification of the sample by crystallization from acetonitrile–ethyl acetate gave $[\mathrm{Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2}](\mathrm{BF_4})_2$ (0.236 g, 91% yield); mp 246–248° dec. Its molar conductivity in acetonitrile was 325 $\mathrm{ohm^{-1}\,cm^2\,mol^{-1}}$ and representative of a 2:1 electrolyte. *Anal.* Calcd for $\mathrm{C_{40}H_{36}B_2F_8N_2P_2Pt}$: C, 49.2; H, 3.72; N, 2.87; P, 6.36. Found: C, 48.5; H, 3.93; N, 2.95; P, 6.34. Infrared spectrum ($\mathrm{cm^{-1}}$): $\nu_{\mathrm{N\equiv CCH_3}}$: 2330 (w), 2305 (vw, sh); $\nu_{\mathrm{C\equiv NCH_3}}$: 2279 (s); other bands: 3660 (w), 3550 (w), 3060 (w, sh), 1620 (w), 1587 (vw), 1573 (vw), 1483 (m, sh), 1437 (s), 1340 (vw), 1310 (w), 1280 (vw), 1187 (w), 1163 (vw), 1060 (vs), 994 (w), 750 (s), 710 (m), 690 (vs), 520 (vs), 512 (vs), 500 (s), 488 (vw, sh), 455 (vw), 420 (vw). Nmr spectrum (dichloromethane-d_2): τ 2.32 (multiplet), $\mathrm{C_6}H_5$; 7.27 (1:4:1 triplet, $J_{\mathrm{Pt-CNCH_3}} = 20$ Hz), $\mathrm{CNC}H_3$; 8.32 (1:4:1 "triplet," $J_{\mathrm{Pt-NCCH_3}} = 12$ Hz), $\mathrm{NCC}H_3$.

Using a similar procedure other nitrile complexes were prepared by an appropriate choice of solvent. Treatment of $[\mathrm{Pt(CONHCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2}]\mathrm{BF_4}$ (0.250 g, 0.276 mmol) in trimethylacetonitrile (10 ml) with excess fluoroboric acid (10 ml) gave $[\mathrm{Pt\{NCC(CH_3)_3\}(CNCH_3)\{P(C_6H_5)_3\}_2}](\mathrm{BF_4})_2$ (0.260 g, 94% yield) on precipitation from dichloromethane–ethyl ether. This product was purified by recrystallization from dichloromethane–ethyl ether; mp <235° dec. *Anal.* Calcd for $\mathrm{C_{43}H_{42}B_2F_8N_2P_2Pt\cdot 0.9CH_2Cl_2}$: C, 47.6; H, 4.08; N, 2.59; P, 5.73. Found: C, 47.6; H, 4.10; N, 2.57; P, 5.71. Infrared spectrum ($\mathrm{cm^{-1}}$): $\nu_{\mathrm{C\equiv N}}$: 2290 (s), 2270 (w, sh) (Nujol, low resolution); other bands: 3060 (w, sh), 1587 (vw), 1575 (vw), 1483 (m, sh), 1437 (s), 1310 (vw), 1282 (vw), 1270 (w), 1235 (w), 1180 (w), 1160 (vw), 1090 (s), 1050 (vs), 992 (w), 745 (s), 725 (w), 705 (s), 688 (vs), 520 (vs), 510 (vs), 502 (s, sh), 476 (w), 450 (vw), 425 (vw). Nmr spectrum (acetonitrile-d_3): τ 2.30 (multiplet), $\mathrm{C_6}H_5$; 7.33 (1:4:1 "triplet," $J_{\mathrm{Pt-CNCH_3}} = 19$ Hz), $\mathrm{CNC}H_3$; 8.67 (singlet), $\mathrm{C(C}H_3)_3$.

Treatment of $[\mathrm{Pt(CONHCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2}]\mathrm{BF_4}$ (0.170 g, 0.188 mmol) in benzonitrile (10 ml) with excess fluoroboric acid (10 ml) gave a two-phase mixture which was stirred vigorously for 16 hr. Addition of ethyl ether–hexane (v/v 1:1) to the benzonitrile layer gave pale violet crystals of $[\mathrm{Pt(NCC_6H_5)(CNCH_3)\{P(C_6H_5)_3\}_2}](\mathrm{BF_4})_2$ (0.168 g, 86% yield). This product was purified by recrystallization from dichloromethane–hexane; mp 189–191°. *Anal.* Calcd for $\mathrm{C_{45}H_{38}B_2F_8N_2P_2Pt\cdot 1.2CH_2Cl_2}$: C, 48.6; H, 3.57; N, 2.46; P, 5.46. Found: C, 48.6; H, 3.55; N, 2.48; P, 5.82. Infrared spectrum ($\mathrm{cm^{-1}}$): $\nu_{\mathrm{C\equiv N}}$: 2280 (s) (Nujol, low resolution); other bands: 3060 (w, sh), 1595 (w), 1587 (w), 1575 (vw), 1483 (m, sh), 1437 (s), 1335 (vw), 1310 (w), 1280 (w), 1185 (w), 1160 (vw), 1095 (s), 1050 (vs), 995 (m), 765 (vw, sh), 755 (vw, sh), 745 (s), 725 (w), 710 (w), 690 (vs), 680 (vw, sh), 555 (w), 520 (vs), 510 (vs), 480 (w), 450 (vw). Nmr spectrum (acetonitrile-d_3): 2.30 (multiplet), $(\mathrm{C_6}H_5)_3\mathrm{P}$ and $\mathrm{C_6}H_5\mathrm{CN}$; 7.33 (1:4:1 triplet, $J_{\mathrm{Pt-CNCH_3}} = 20$ Hz), $\mathrm{CNC}H_3$.

Attempted Acidification of $[\mathrm{Pt(CSNHCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2}]\mathrm{BF_4}$.—The starting complex (0.350 g, 0.378 mmol) in acetonitrile (10 ml) was treated with excess fluoroboric acid solution (10 ml) and the resulting pale yellow suspension was stirred for 2 hr. Although a very faint odor of hydrogen sulfide was detected initially, very little change was apparent in the system during the allowed stirring time. Using a work-up procedure similar to that described previously, a pale yellow solid was precipitated from acetone–ethyl ether and was identified by spectral data as the starting complex (85% recovery).

Acidification of $[\mathrm{Pt\{C(NC_6H_4CH_3)NHCH_3\}(CNCH_3)\{P(C_6H_5)_3\}_2}]\mathrm{BF_4}$.—To this starting complex (0.220 g, 0.221 mmol) in acetonitrile (10 ml) was added excess fluoroboric acid solution (10 ml). The bright yellow solution of the starting complex faded rapidly on introduction of the acid solution, and the resulting system became colorless after stirring for 15 min. Using a similar work-up procedure as described in prior acidification reactions, ivory needles of $[\mathrm{Pt\{C(NHC_6H_4CH_3)NHCH_3\}(CNCH_3)\{P(C_6H_5)_3\}_2}](\mathrm{BF_4})_2$ (0.213 g, 89% yield) were precipitated and purified by recrystallization from acetonitrile–ethanol; mp 262–263°. *Anal.* Calcd for $\mathrm{C_{47}H_{45}B_2F_8N_3P_2Pt}$: C, 52.2; H, 4.19; N, 3.88; P, 5.72. Found: C, 52.3; H, 4.08; N, 3.91; P, 5.60. Infrared spectrum ($\mathrm{cm^{-1}}$): $\nu_{\mathrm{C\equiv N}}$: 2265 (s); $\nu_{\mathrm{C=N}}$: 1610 (m), 1573 (m), 1517 (m); other bands: 3370 (m), 3300 (m), 3060 (w, sh), 1483 (m, sh), 1438 (s), 1315 (w), 1287 (vw, sh), 1187 (w), 1163 (vw), 1093 (s), 1065 (vs), 1010 (vs), 830 (w), 808 (m), 750 (s), 710 (m), 690 (vs), 520 (vs), 510 (vs), 495 (w, sh), 440 (vw), 420 (vw). Nmr spectrum (acetonitrile-d_3 solution): τ 2.42 (multiplet), $\mathrm{C_6}H_5$; 3.03 (multiplet), $\mathrm{C_6}H_4$; 7.67 (multiplet), $\mathrm{CNC}H_3$ and $\mathrm{C_6H_4C}H_3$; 8.20 (doublet, $J_{\mathrm{H-NCH_3}} = 4$ Hz), $=\!\mathrm{NHC}H_3$.

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