However, it is possible that in these complexes the phosphorus got oxidized resulting in a high-spin nickel(II) five-coordinate complex. Then spin pairing of the essentially metal electron in d_{z^2} with that on the phosphorus would account for the experimental observation that no ligand esr was observed. *Via* resonance or in a three-center MO description (d_{z^2} and two phosphorus σ orbitals), the two phosphorus atoms become equivalent. The unpaired electron is in the near doubly degenerate set, $d_{x^2-y^2}$, d_{xy}, consistent with a higher than spin-only value of 2.1 BM for the complexes. These complexes simply constitute a case where esr does not provide a handle on the molecular orbitals of interest in the complex, because in the three-center MO description of the nickel(II) complex, the electron is in the antibonding mainly metal MO. Whether the phosphine or metal got oxidized depends upon the metal coefficient in the bonding MO of the oxidized species. In view of the *C* property of the phosphines, we prefer to think that there is a substantial increase in the metal contribution to the bonding MO in the oxidized species. (Recall the nonbonding MO has a node at the metal for a true three-center description.) Consequently, we feel the antibonding MO in the complex from which the electron has been removed is composed slightly more of phosphorus than metal so the phosphorus has been oxidized, but this is just speculation on our part.

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Preparation and Reactions of Tetrakis(methyl isocyanide) Complexes of Divalent Nickel, Palladium, and Platinum

BY JOEL STEVEN MILLER AND ALAN L. BALCH*

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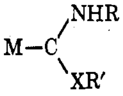
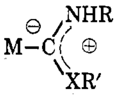
The preparation of the planar complexes $[(CH_3NC)_4M][PF_6]_2$ (M = Ni, Pd, Pt) is reported. Reaction of bromine with the platinum complex yields $[(CH_3NC)_3PtBr][PF_6]$; with iodine no reaction occurs. Methylamine adds to $(CH_3NC)_4M^{2+}$ (M = Pd, Pt) to yield $\{(CH_3NH)_2C\}_4M^{2+}$. The structure and chemical inertness of these complexes, which are the first examples of transition metals coordinated solely by ligands of the resonance-stabilized "carbene" type, are discussed. The structures of the complexes obtained by the addition of hydroxylamine to $(CH_3NC)_4Pt^{2+}$ are discussed. Reaction of chelating dithiols $S_2C_2O_2^{2-}$ and $S_2C_2(CN)_2^{2-}$ with $(CH_3NC)_4M^{2+}$ (M = Pd, Pt) produces $(CH_3NC)_2M$(dithiol) *via* ligand substitution, whereas ethanethiol adds to $(CH_3NC)_4Pt^{2+}$ to yield $(CH_3NC)_2Pt\{C(SC_2H_5)NHCH_3\}_2^{2+}$. The complexes have been characterized by elemental analysis, conductivity, pmr spectra, and infrared spectra.

Introduction

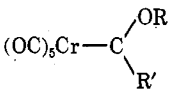
The reactions of coordinated isocyanide ligands, especially their susceptibility to attack by a variety of protic nucleophiles including amines,[1] hydrazines,[2] alcohols,[1b,d,f–i] water,[1h,3] and thiols,[1h] have recently attracted widespread attention. The ligands obtained from these addition reactions may be formulated either as carbenes (with possible resonance stabilization) **1a** or as C-metal-substituted amidinium ions **1b** for X = NH (or the equivalent for X = O, or X = S). These ligands and the complexes containing them are generally characterized by a high degree of stability toward hydrolysis, atmospheric oxidation, and thermal decomposition. Frequently such ligands have been found to undergo reversible deprotonation. Although ligands of this type have only recently been satisfactorily characterized, the first preparation of a complex which has been demonstrated to contain this type of ligand was reported in 1925.[4] A number of early suggestions that such ligands might result from the reaction of nucleophiles with isocyanide complexes remain unconfirmed.[5] It also should be noted that ligands of type **1** are closely related to the resonance-stabilized carbene ligands found in complexes such as **2** which may be prepared from metal carbonyls.[6]



1a, X = NH, O, S



1b



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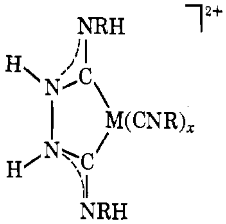
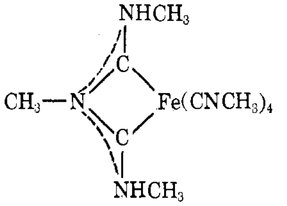
Although the most common ligands produced by the attack of nucleophiles on a coordinated isocyanide are the monodentate ligands **1**, similar reactions with the bifunctional reagent hydrazine lead to the formation of planar chelating ligands (*e.g.*, complexes **3–5**)[2] which



3, M = Pd; x = 2
4, M = Pt; x = 2
5, M = Fe; x = 4

contain two metal-binding sites of the type described above. It has also been observed that similar chelate formation can occur in the reaction of a primary amine with two cis isocyanide ligands; methylamine adds to hexakis(methyl isocyanide)iron(II) to form **6**.[1j]



6

The driving force for chelate formation in this case probably resides in close proximity of the reactive centers.

Herein we report the preparation of the tetrakis(methyl isocyanide) complexes of divalent nickel, palladium, and platinum and the reactions of these complexes with various oxidizing agents and nucleophiles. Isocyanide complexes of both divalent and zerovalent oxidation states of these metals have been reported;[7,8] however, complexes of the type $(\mathrm{RNC})_4\mathrm{M}^{2+}$ have been reported only for platinum.[1d,9]

Experimental Section

Preparation of Compounds.—Methyl isocyanide (*toxic*) was prepared *via* the literature method.[10]

[Pt(CNCH$_3$)$_4$][PF$_6$]$_2$.—Methyl isocyanide (0.32 ml) was added to a filtered solution of 0.313 g of potassium tetrachloroplatinate in 10 ml of water. Immediately a filtered solution of 0.60 g of ammonium hexafluorophosphate in 10 ml of methanol was added. The white precipitate, which rapidly formed, was collected by filtration, washed with water, and vacuum dried. Purification was achieved by recrystallization from acetonitrile, yield 95%: conductivity Λ = 181 cm^2 mol^{-1} ohm^{-1} (nitromethane); ir (cm^{-1}) 3045 w, 2967 w, 2934 w, 2866 w ($\nu_{\mathrm{C-H}}$), 2308 s ($\nu_{\mathrm{C\equiv N}}$), 1401 m; nmr τ 6.32, singlet (deuterioacetonitrile).

Anal. Calcd: C, 14.80; H, 1.86; N, 8.62. Found: C, 15.00; H, 1.65; N, 8.38.

[Pd(CNCH$_3$)$_4$][PF$_6$]$_2$.—This colorless, crystalline complex was prepared from sodium tetrachloropalladate *via* the method described for the platinum analog: conductivity Λ = 180 cm^2 mol^{-1} ohm^{-1}; ir (cm^{-1}) 3044 w, 2969 w, 2932 w, 2864 w ($\nu_{\mathrm{C-H}}$), 2305 s ($\nu_{\mathrm{C\equiv N}}$), 1401 m; nmr τ 6.35, singlet (deuterioacetonitrile).

Anal. Calcd: C, 17.14; H, 2.16; N, 10.00. Found: C, 17.19; H, 2.22; N, 10.04.

[Ni(CNCH$_3$)$_4$][PF$_6$]$_2$.—Methyl isocyanide (0.5 ml) was added to a solution of 0.50 g of bis(tetraethylammonium) tetrachloronickelate dissolved in a minimum of ethanol. A filtered solution of 0.8 g of ammonium hexafluorophosphate in 15 ml of methanol was added to precipitate the microcrystalline, yellow-brown product which was collected by filtration and vacuum dried. Attempts to recrystallize the product led to its decomposition: conductivity Λ = 176 cm^2 mol^{-1} ohm^{-1}; ir (cm^{-1}) 3045 w, 2980 w, 2936 w, 2863 w ($\nu_{\mathrm{C-H}}$), 2300 sh, 2290 s, 2231 w ($\nu_{\mathrm{C\equiv N}}$), 1411 m; nmr τ 6.32, singlet (deuterioacetonitrile).

Anal. Calcd: C, 18.74; H, 2.36; N, 10.93. Found: C, 19.45; H, 2.50; N, 11.37.

[Pt(CNCH$_3$)$_3$Br][PF$_6$].—A solution of 0.089 g (1.11 mmol) of bromine in 2.0 ml of acetonitrile was added dropwise to a solution of 0.723 g (1.11 mmol) of tetrakis(methyl isocyanide)platinum(II) hexafluorophosphate in 25 ml of acetonitrile. The solution, which had a strong odor of free methyl isocyanide, was evaporated to 10 ml under a stream of nitrogen. Ether was slowly added to the concentrated solution to precipitate the colorless, crystalline product, which was collected by filtration, washed with water, and vacuum dried (yield 0.415 g, 70%). Purification was achieved by dissolution in acetonitrile followed by precipitation with ether. This procedure was repeated three times with considerable loss of product: conductivity Λ = 86 cm^2 mol^{-1} ohm^{-1}; ir (cm^{-1}) 3010 ($\nu_{\mathrm{C-H}}$), 2286 ($\nu_{\mathrm{C\equiv N}}$), 1435, 1425.

Anal. Calcd: C, 13.27; H, 1.67; N, 7.74; Br, 14.71. Found: C, 13.21; H, 1.68; N, 7.72; Br, 14.54.

[Pt{C(NHCH$_3$)$_2$}$_4$][PF$_6$]$_2$.—Methyl isocyanide (0.40 ml) and 40% aqueous methylamine (1.0 ml) were added successively to a solution of 0.39 g of potassium tetrachloroplatinate in 15 ml of water. A filtered solution of 0.6 g of ammonium hexafluorophosphate in 10 ml of methanol was added. The colorless mixture was filtered and allowed to stand open to the atmosphere for 1 day during which time white crystals formed as the solvent evaporated. These were collected by filtration, washed with water, and vacuum dried (yield 0.33 g, 45%). The complex may be purified by dissolution in acetonitrile followed by precipitation by slow addition of ether: conductivity Λ = 186 cm^2 mol^{-1} ohm^{-1}; ir (cm^{-1}) 3468 m, 3406 m ($\nu_{\mathrm{N-H}}$), 3010 w, 2947 w, 2878 w, 2827 w ($\nu_{\mathrm{C-H}}$), 1586 m ($\nu_{\mathrm{N}\overset{\cdots}{-}\mathrm{C}\overset{\cdots}{-}\mathrm{N}}$), 1518 m, 1511 m ($\delta_{\mathrm{N-H}}$), 1459 w, 1446 w, 1424 w, 1416 w; nmr, τ 7.32 (rel intensity 3, $J_{\mathrm{H-N-C-H}}$ = 5, $J_{\mathrm{Pt-H}}$ = 3 Hz), 6.81 (3, $J_{\mathrm{H-N-C-H}}$ = 5, $J_{\mathrm{Pt-H}}$ = 3 Hz), 3.38 (2, broad) (deuterioacetonitrile).

Anal. Calcd: C, 18.63; H, 4.17; N, 14.49. Found: C, 18.64; H, 4.23; N, 15.11.

[Pd{C(NHCH$_3$)$_2$}$_4$][PF$_6$]$_2$.—This complex was prepared from potassium tetrachloropalladate by the method described for its platinum analog: conductivity Λ = 178 cm^2 mol^{-1} ohm^{-1}; ir (cm^{-1}) 3471 m, 3399 m ($\nu_{\mathrm{N-H}}$), 3015 w, 2948 w, 2893 w, 2852 w ($\nu_{\mathrm{C-H}}$), 1583 m ($\nu_{\mathrm{N}\overset{\cdots}{-}\mathrm{C}\overset{\cdots}{-}\mathrm{N}}$), 1520 m, 1512 m ($\delta_{\mathrm{N-H}}$), 1461 w, 1449 w, 1411 w, 1418 w; nmr τ 7.31 (rel intensity 3, $J_{\mathrm{H-N-C-H}}$ = 5 Hz), 6.81 (3, $J_{\mathrm{H-N-C-H}}$ = 5 Hz), 3.38 (2, broad) (deuterioacetonitrile).

Anal. Calcd: C, 21.05; H, 4.71; N, 16.36. Found: C, 21.28; H, 5.02; N, 16.54.

[Pt(CH$_3$NHCNOCHNCH$_3$)(CNCH$_3$)$_2$]I·H$_2$O.—Methyl isocyanide (1 ml) was added to a solution of 1.0 g of potassium tetrachloroplatinate in 30 ml of water. A solution containing 1.4 g of hydroxylamine hydrochloride and 1.1 g of potassium hydroxide in 20 ml of water was added to the orange solution to produce an intense red color. A saturated, aqueous, sodium iodide solution was added dropwise to precipitate the product which was collected by filtration and washed with cold water, yield 0.9 g, 70%. The product was purified by recrystallization from warm (50°) water. The complex was obtained as long red needles which became red-brown with a greenish reflectance upon drying: conductivity Λ = 67 cm^2 mol^{-1} ohm^{-1}; ir (cm^{-1}) 3350 m, 3200 m ($\nu_{\mathrm{N-H}}$), 2920 w, 2980 w ($\nu_{\mathrm{C-H}}$), 2240 s ($\nu_{\mathrm{C\equiv N}}$), 1580 s, 1490 s ($\nu_{\mathrm{O}\overset{\cdots}{-}\mathrm{C}\overset{\cdots}{-}\mathrm{N}}$, $\nu_{\mathrm{N}\overset{\cdots}{-}\mathrm{C}\overset{\cdots}{-}\mathrm{N}}$, $\delta_{\mathrm{N-H}}$), 1430 m, 1390 m, 1360 m.

Anal. Calcd: C, 17.92; H, 3.01, N, 12.85; I, 23.66; Pt, 36.38. Found: C, 17.43; H, 2.44; N, 12.85; I, 23.35; Pt, 36.04.

Pt(CH$_3$NHCNHOCHNCH$_3$)Cl$_2$.—Methyl isocyanide (1 ml) and an aqueous solution of hydroxylamine hydrochloride (1.4 g) and potassium hydroxide (1.1 g) in 20 ml of water were added successively to a solution of 1.0 g of potassium tetrachloroplati-

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nate in 30 ml of water. Concentrated hydrochloric acid (10 ml) was added to this solution to produce a pale yellow solution which was heated to boiling. The pale yellow crystals (0.6 g, 65%) which formed as the solution cooled were collected and recrystallized from 100 ml of water containing 3 ml of concentrated hydrochloric acid: ir (cm^{-1}) 3500 m, 3410 sh, 3400 m, 3150 m (ν_{N-H}), 3015 w, 2940 w, 2880 w (ν_{C-H}), 1580 s, br ($\nu_{N\cdots C\cdots N}$, $\nu_{N\cdots C\cdots O}$, δ_{N-H}), 1455 m, 1420 m, 1390 m, 1360 m.

Anal. Calcd: C, 12.60; H, 2.38; N, 11.03; Pt, 51.18. Found: C, 12.43; H, 2.69; N, 10.35; Pt, 50.27.

$(CH_3NC)_2Pd\{S_2C_2(CN)_2\}$.—Methyl isocyanide (2.0 ml) was added to a filtered solution of 3.3 g of potassium tetrachloropalladate in 50 ml of water. A solution of 1.9 g of sodium maleonitriledithiolate in 15 ml of water was added to produce a red-orange precipitate. The product was collected by filtration. washed with water, and vacuum dried, yield 3.7 g, 80%. Purification was achieved by recrystallization from acetone–methanol; mp 227–229° dec: conductivity $\Lambda = 0$; ir (cm^{-1}) 3000 w, 2950 w (ν_{C-H}), 2270 s, 2255 s, 2220 w, 2205 s, 2190 m ($\nu_{C\equiv N-}$, $\nu_{N\equiv C-}$), 1495 m, 1470 m, 1415 m, 1395 m (KBr); nmr τ 6.25, $J_{N-H} = 2.5$ Hz (deuterioacetone).

Anal. Calcd: C, 29.23; H, 1.84; Pd, 32.37. Found: C, 29.39; H, 1.65; Pd, 32.56.

$(CH_3NC)_2Pt\{S_2C_2(CN)_2\}$.—This pink, crystalline complex was prepared from potassium tetrachloroplatinate in the manner described for the palladium analog, mp 267–268° dec: ir (cm^{-1}) 3005 w, 2960 w (ν_{C-H}), 2270 s, 2250 s, 2200 s, 2195 sh ($\nu_{C\equiv N-}$, $\nu_{N\equiv C-}$), 1495 m, 1430 m, 1410 m, 1395 m (KBr); nmr τ 6.28, $J_{Pt-H} = 17$ Hz (deuterioacetone).

Anal. Calcd: C, 23.02; H, 1.45; Pt, 46.74. Found: C, 23.15; H, 1.45; Pt, 46.91.

$(CH_3NC)_2Pt(S_2C_2O_2)$.—Methyl isocyanide (0.5 ml) was added to a solution of 0.42 g of potassium tetrachloroplatinate in 20 ml of water. To this solution was added a solution of 0.20 g of potassium dithiooxalate in 10 ml of water. The orange complex was collected by filtration and vacuum dried, yield 0.30 g, 75%. Purification was effected by recrystallization from acetone–methanol, mp 247° with vigorous gas evolution: ir (cm^{-1}) 2990 w, 2930 w, 2915 w (ν_{C-H}), 2265 s, 2250 s ($\nu_{C\equiv N}$), 1625 s, 1605 s ($\nu_{C=O}$), 1440 m, 1420 m, 1415 m (KBr).

Anal. Calcd: C, 18.14; H, 1.53. Found: C, 18.25; H, 1.52.

$[Pt\{C(SCH_2CH_3)NHCH_3\}_2(CNCH_3)_2][PF_6]_2$.—Methyl isocyanide (0.5 ml) and ethanethiol (1.0 ml) were added successively to a solution of 0.50 g of potassium tetrachloroplatinate in 10 ml of water. A filtered solution of 0.6 g of ammonium hexafluorophosphate in 10 ml of methanol was added to produce an immediate white precipitate which was collected by filtration and vacuum dried, yield 0.40 g, 40%. The complex was recrystallized from acetone–methanol, mp 185–190° dec: conductivity $\Lambda = 193\ cm^2\ mol^{-1}\ ohm^{-1}$; ir ($cm^{-1}$) 3358 m ($\nu_{N-H}$), 3000 w, 2948 w ($\nu_{C-H}$), 2274 s ($\nu_{C\equiv N}$), 1560 m ($\nu_{N\cdots C\cdots S}$, δ_{N-H}), 1446 w, 1429 w, 1415 w, 1382 w; nmr τ 8.53 (rel intensity 3, $J_{H-C-CH} = 7.5$ Hz), 6.73 (3, $J_{H-N-C-H} = 5$, $J_{Pt-H} = 3$), 6.32 (3), 6.25 (2, $J_{H-C-C-H} = 7.5$), −0.40 (1, broad) (deuterioacetonitrile).

Anal. Calcd: C, 18.63; H, 3.13; N, 7.24. Found: C, 18.01; H, 3.47; N, 6.74.

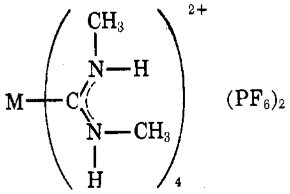
Physical Measurements.—Conductivities were determined by the use of a Serfass conductivity bridge with $\sim 10^{-3}$ M nitromethane solutions of the complexes. Infrared spectra were obtained from fluorocarbon and Nujol mulls unless otherwise specified and recorded on a Beckman IR-12 spectrometer. Varian A-60 and HA-100 spectrometers were utilized for pmr measurements. Electronic spectra were recorded on a Cary 14 spectrophotometer.

Results

Preparation of $(CH_3NC)_4M^{2+}$ (M = Ni, Pd, Pt).—Addition of an excess of methyl isocyanide to aqueous solutions of MCl_4^{2-} (M = Pd, Pt) followed by the addition of ammonium hexafluorophosphate yields the colorless, crystalline salts $[(CH_3NC)_4M][PF_6]_2$. Although nickel ion is reported to cause the polymerization of isocyanides,[11] addition of an excess of methyl isocyanide to an ethanolic solution of $[(C_2H_5)_4N]_2[NiCl_4]$ followed by the addition of ammonium hexafluorophosphate yields yellow-brown, microcrystalline $[(CH_3NC)_4Ni][PF_6]_2$. This latter complex is much less stable in solution than its palladium and platinum analogs, and consequently its chemistry has not been extensively investigated. As expected for square-planar complexes, all of these salts are diamagnetic. Their pmr spectra consist of a single resonance at about τ 6.3; this resonance does not exhibit the long-range $^{14}N-C-H$ coupling which is observed for free methyl isocyanide.[12] In addition to the infrared absorptions in the 4000–1300-cm^{-1} region recorded in the Experimental Section, very strong P–F stretching vibrations were observed in the 860–840-cm^{-1} region for the three salts. Each of the complexes exhibits a C≡N stretching vibration at *ca.* 2300 cm^{-1}. As is generally the case with metals in oxidation states in which insignificant back-donation from the metal to the ligand occurs, this value is higher than that found for free methyl isocyanide.[7]

Oxidation Reactions.—The ability of the Rh(I)–isocyanide complexes $(CH_3NC)_4Rh^+$ and $(CH_3NC)Rh(PPh_3)_2Cl$ to undergo oxidative addition has been demonstrated.[3] Similar reactions were anticipated for the $[(CH_3NC)_4M]^{2+}$ complexes, especially in the case of platinum where the IV oxidation state is reasonably stable. However, stable oxidized forms of these complexes have not been obtained. Treatment of $[(CH_3NC)_4Pt][PF_6]_2$ with 2 equiv of bromine results in the isolation of the Pt(II) complex $[(CH_3NC)_3PtBr][PF_6]$. The formation of this complex may be rationalized by assuming an initial oxidative addition to give $[(CH_3NC)_4PtBr_2][PF_6]_2$ followed by reduction to give the product, free methyl isocyanide, and free bromide ion. The reducing agent may be either coordinated methyl isocyanide, the solvent (acetonitrile), or possible traces of impurities in the solvent. Numerous cases in which metal ions are reduced by isocyanides have been recorded.[7] After treatment of $[(CH_3NC)_4Pt][PF_6]_2$ with iodine (under the same conditions used for the bromine oxidation) the starting complex may be recovered unchanged. In view of the failure to isolate stable Pt(IV)–isocyanide complexes, no attempts at oxidizing the palladium or nickel complexes were made.

Methylamine Addition.—Methylamine reacts with an aqueous solution of $[(CH_3NC)_4M]^{2+}$ (M = Pd, Pt)



7a, M = Pd
b, M = Pt

to give products **7** in which 4 mol of the amine has added to the cation. These complexes have been isolated as the colorless, crystalline, air-stable hexafluorophosphate salts. In nitromethane solution **7a** and **7b** have conductivities consistent with their formulation as 1:2 electrolytes. The infrared spectra of these salts exhibit no bands in the region (2300–2000 cm^{-1}) characteristic of coordinated isocyanide. The infrared spectrum of

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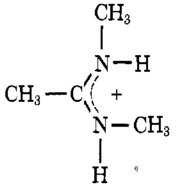
(11) Reference 9, p 159.

(12) I. D. Kuntz, Jr., P. v. R. Schleyer, and A. Allerhand, *J. Chem. Phys.*, **35**, 1533 (1961).

7a exhibits absorptions at 3471 and 3399 cm^{-1} due to N–H stretching, at 3015, 2948, 2893, and 2852 due to C–H stretching, at 1583 due to stretching of the $\mathrm{N \overset{\cdots}{-} C \overset{\cdots}{-} N}$ unit, and at 1520 and 1512 due to N–H bending motion. The infrared spectrum of a deuterated form of **7a**, $\mathrm{Pd(C(NDCH_3)_2)_4^{2+}}$, prepared from $\mathrm{[(CH_3NC)_4Pd]^{2+}}$ and $\mathrm{CH_3ND_2}$ in deuterium oxide, confirms these assignments. In the deuterated complex the N–D stretching vibrations occur at 2580 and 2517 cm^{-1}, the N–D bending mode occurs at 1172 cm^{-1}, while the vibration ascribed principally to stretching of the $\mathrm{N \overset{\cdots}{-} C \overset{\cdots}{-} N}$ unit has undergone only a slight shift to 1551 cm^{-1}. The infrared spectrum of the platinum complex **7b** is virtually identical with that of its palladium analog **7a**.

The pmr spectrum of the palladium complex **7a** in deuterioacetonitrile consists of two methyl doublets at τ 7.31 (J_{HNCH} = 5.0 Hz) and 6.81 (J_{HNCH} = 5.0 Hz) of equal intensity and a broad resonance at τ 3.43 with an intensity two-thirds that of either methyl resonance due to the nitrogen-bound protons. The spectrum of **7b** is similar except that Pt–H coupling of 3 Hz is present on each of the two methyl doublets. The H–N–C–H coupling constants are consistent with the values observed for *N*-methylacetamide[13] and *N,N'*-dimethylacetamidinium ion[14] and for metal complexes containing similar functions.[2] In addition the couplings between each of the methyl doublets and the broad N–H resonance have been confirmed by double resonance experiments. These experiments also indicate that the broad absorption at τ 3.43 consists of two superimposed resonances with an estimated chemical shift difference of about 0.05 ppm, since irradiation of the methyl doublet at τ 6.81 causes the N–H resonance to become assymetrical with narrowing on the high-field side while irradiation of the other methyl doublet causes narrowing on the low-field portion of the N–H resonance. The pmr spectrum of **7a** is invariant over the temperature range −50 to 90°. At higher temperatures each of the methyl doublets collapses into a singlet; this is indicative of the onset of rapid proton exchange similar to that observed for *N,N'*-dimethylacetamidinium ion at elevated temperatures.[14]

The structure of the complexes **7** is probably closely related to that of the *N,N'*-dimethylacetamidinium ion **8**.[14] In solution this ion exists in the amphi configuration with one proton and one methyl group on the "inside" positions. The simplest and most reasonable model of the complexes **7a** and **7b** in view of the available spectral data consists of a metal ion coordinated by four equivalent ligands with each ligand in amphi configuration as shown. The invariance of the pmr data over the temperature range −50 to 90° indicates that there is appreciable multiple bond character to the N–C–N bonds; however, the extent of multiple bonding between the central metal and its carbon neighbors cannot be ascertained. Inspection of molecular models indicates that the four ligands, which must be planar because of the partial double bond character of the N–C–N unit, cannot lie in the same plane as the metal ion and its four carbon donors. However, the ligands may be arranged so that they lie in planes approximately perpendicular to the Pt–$\mathrm{C_4}$ plane; this arrangement with idealized D_{2d} symmetry is shown in Figure 1. Another sterically reasonable arrangement with C_{2h} symmetry can be derived from that shown in Figure 1 by rotation of one ligand in plane *a* of the drawing by 180° and rotation of a ligand in plane *b* by 180°. It is also possible that the ligand planes are arranged to form a propeller-like, chiral structure.


$$\mathrm{CH_3{-}C(NHCH_3)_2^{+}}$$

8

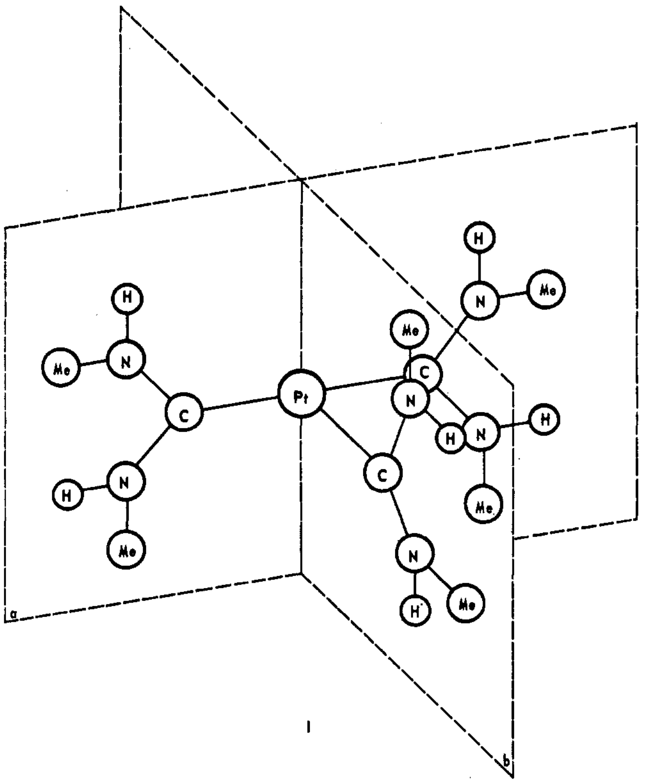
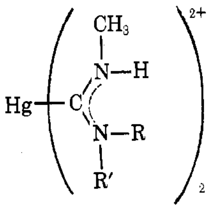


Figure 1.—A proposed idealized structure for $\mathrm{M[C(NHCH_3)_2]_4^{2+}}$ (M = Pd, Pt). For clarity only three of the four ligands are shown. Planes *a* and *b* are mirror planes.

Complexes **7a** and **7b** are unusual since they are the first transition metal complexes in which the metal is coordinated solely by ligands of the resonance-stabilized "carbene" type. In fact, few complexes containing more than one ligand of this type are known. However the mercury complex **9**[1a] does involve a nontransition metal coordinated wholly by this type of ligand.


$$\mathrm{Hg[C(CH_3NH)(NRR')]_2^{2+}}$$

9

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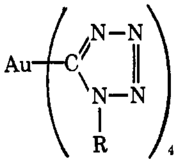
(13) G. Fraenkel and C. Franconi, *J. Amer. Chem. Soc.*, **82**, 4478 (1960).

(14) G. S. Hammond and R. C. Neuman, Jr., *J. Phys. Chem.*, **67**, 1655, 1659 (1963).

Of relevance to the structure of **7a** and **7b** is the recent report of the isolation of the tetrazolatogold(III) complex **10**, prepared by the addition of isocyanide to

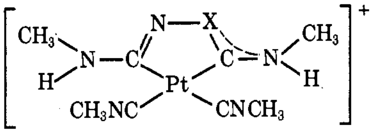


10

Au(N$_3$)$_4^-$.[15] An X-ray crystallographic study of this ion reveals that the tetrazolato ligands lie in planes approximately perpendicular to the Au–C$_4$ coordination plane.[16]

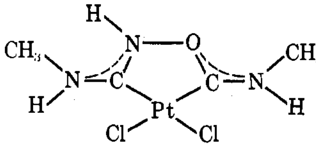
The complexes **7a** and **7b** are quite stable. They are unreactive toward atmospheric oxygen both in the solid state and in solution. Their preparation in aqueous media attests to their hydrolytic stability. Refluxing solutions of these complexes with an excess of α,α'-bipyridyl or triphenylphosphine in acetonitrile does not result in any ligand substitution. The complexes are not oxidized by iodine. At least some of the stability of these complexes may come from the shielding of the vacant coordination sites on the metal by the bulky, planar ligands.

Addition of Hydroxylamine.—Addition of hydroxylamine to an aqueous solution of (CH$_3$NC)$_4$Pt^{2+} produces a red-brown complex which has been isolated as the iodide salt. This complex, which is a 1:1 electrolyte in solution, is assigned the structure **11** on the basis of spectroscopic and chemical information outlined below and on the basis of its similarity to the complexes **12** and **13** which are formed by the addition of hydrazine and methylhydrazine to (CH$_3$NC)$_4$Pt^{2+}.[2] The structure of **13** has been established from an X-ray study.[2d] The infrared spectrum of **11** indicates the presence of N–H, C–H, C≡N, and C$\overset{...}{-}$Y (Y = O, N) functions in the molecule. The inability to prepare an analogous compound from methoxyamine indicates the oxygen of hydroxylamine has been involved in attack on coordinated isocyanide. An analogous compound could not be prepared from *N*-methylhydroxylamine; this suggests that **11** lacks a proton on the inner nitrogen. The failure of *N*-methylhydroxylamine to yield a complex analogous to **11** cannot be reasonably ascribed to steric interactions since methylhydrazine has been successfully added to two isocyanide ligands of (CH$_3$NC)$_4$Pt^{2+},[2a,e] to yield **13**. Finally the electronic spectra of **11** and **12** are very similar. In dimethyl sulfoxide solution **11** exhibits a broad absorption at 357 nm (ϵ 2100) and a narrow absorption at 318 (ϵ 3300) whereas **12** shows a broad band at 410 (ϵ 1900) and a narrow peak at 323 (ϵ 2000).



11, X = O
12, X = NH
13, X = NCH$_3$

Treatment of **11** with refluxing hydrochloric acid yields the pale yellow crystalline complex **14** which is the result of protonation of the chelating ligand in **11** and substitution of chloride for the isocyanide ligands. Under less vigorous conditions, protonation of the chelating ligand occurs rapidly, but substitution of chloride for coordinated methyl isocyanide occurs more slowly. Similar behavior for **12** has previously been demonstrated.[2a] The infrared spectrum of **14** exhibits no absorptions in the region characteristic of coordinated isocyanide; however, absorptions due to N—H, C—H, and C$\overset{...}{-}$Y (Y = O, N) functions are observed. The solubility of **14** is insufficient to allow pmr observation.

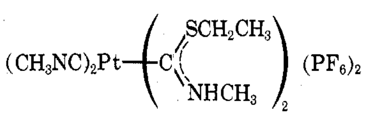


14

Although the addition of hydroxylamine to (CH$_3$NC)$_4$Pd^{2+} produced a yellow, crystalline complex presumably analogous to **11**, attempts to isolate and dry this material always led to its decomposition. Similarly the presumed palladium analog of **14** underwent decomposition before it could be characterized.

Reactions with Thiols.—The chelating dithiols dithiooxalate and maleonitriledithiolate react with (CH$_3$NC)$_4$M^{2+} (M = Pd, Pt) to yield the substitution products (CH$_3$NC)$_2$M(S$_2$C$_2$X$_2$) (X = O, CN). These nonelectrolytes are simple, square-planar complexes. However the pmr spectrum of (CH$_3$NC)$_2$PdS$_2$C$_2$(CN)$_2$ exhibits the unusual feature of the N–C–H coupling. Although such coupling is characteristic of free isocyanides with appropriate protons,[12] this is apparently the first case of a metal complex in which this coupling has been resolved.

In contrast to the chelating dithiols, ethanethiol adds to (CH$_3$NC)$_4$Pt^{2+} to yield the white, crystalline complex **15**. The infrared spectrum of **15** exhibits



$$(CH_3NC)_2Pt\left(C\begin{matrix}SCH_2CH_3\\NHCH_3\end{matrix}\right)_2(PF_6)_2$$

15

an absorption at 2274 cm^{-1} due to $\nu_{(C\equiv N)}$ of the unreacted isocyanide ligands and absorptions in regions diagnostic for the presence of N–H, C–H, C$\overset{...}{-}$N, and P—F functions. The pmr spectrum consists of a triplet at τ 8.53 (J_{H-H} = 7.5 Hz, rel intensity 6) which is assigned to the terminal methyl group of the ethyl group, a quartet at 6.25 (J_{H-H} = 7.5 Hz, 4) due to the methylene unit, a doublet at 6.73 (J = 5.0 Hz, 6) due to the nitrogen bond methyl group of the newly formed ligand, a singlet at 6.32 (6) due to the methyl group of the unreacted methyl isocyanide ligands, and a broad resonance at −0.40 (2) due to the two nitrogen bound protons. The couplings between the methyl and methylene resonances at τ 8.53 and 6.25, respectively, and between the methyl group at τ 6.73 and the N–H at −0.40 have been confirmed by double resonance experiments. These observations are consistent with the structure **3** and indicate equivalence

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[15] W. Beck, K. Burger, and W. P. Fehlhammer, *Chem. Ber.*, **104**, 1816 (1971).

[16] P. Fehlhammer and L. F. Dahl, *J. Amer. Chem. Soc.*, **94**, 3370 (1972).

of the carbene-like ligands but do not allow a determination of the configuration of the presumably planar ligands. Preliminary X-ray results[17] indicate that the complex has a trans arrangement of ligands about platinum.

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[17] J. H. Enemark, personal communication.

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Reactions of 3,3,3-Trifluoropropyne with Methylplatinum(II) Complexes

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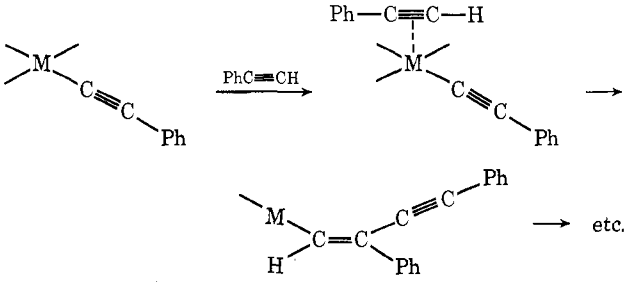
3,3,3-Trifluoropropyne, $CF_3C\equiv CH$, reacts with complexes of the types *cis*-$Pt(CH_3)_2L_2$ and *trans*-$PtCl(CH_3)L_2$, where L = $P(CH_3)_2(C_6H_5)$ (Q), $As(CH_3)_3$, or $As(CH_3)_2(C_6H_5)$, to give varying amounts of polymer and organoplatinum products. Polymerization occurs by an ionic mechanism. Major products from the reaction of $PtCl(CH_3)Q_2$ with $CF_3C\equiv CH$ in benzene are *trans*-$PtCl(-C\equiv CCF_3)Q_2$, *trans*-$PtCl\{C(CF_3)=CHCl\}Q_2$, *trans*-$Pt(-C\equiv CCF_3)_2Q_2$, and $PtCl_2(CH_3)_2Q_2$. In alcohols, ROH, $PtCl(CH_3)Q_2$ reacts with $CF_3C\equiv CH$ to give complexes of the type *trans*-$PtCl\{C(CF_3)=CH(OR)\}Q_2$.

Introduction

Continuing our studies[1-3] on the reactions of unsaturated compounds with methylplatinum(II) complexes, we have investigated the reactions of 3,3,3-trifluoropropyne, $CF_3C\equiv CH$, with complexes *trans*-$PtCl(CH_3)L_2$ and *cis*-$Pt(CH_3)_2L_2$, where L = $P(CH_3)_2(C_6H_5)$, $As(CH_3)_3$, or $As(CH_3)_2(C_6H_5)$; Q will be substituted for $P(CH_3)_2(C_6H_5)$. The reactions of this acetylene with a variety of metal complexes have been reported.[4-7] We have found that $CF_3C\equiv CH$ is polymerized by methylplatinum(II) complexes. Our results suggest that this polymerization does not occur by the mechanism which has been proposed[8-10] for the polymerization of phenylacetylene by complexes of platinum group metals

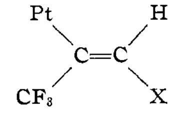


Rather, polymerization is anionic, initiated by the electron-rich organoplatinum complex, either directly or *via* a five-coordinate intermediate.

Results

Characterization of Reaction Products.—When the polymer was obtained, it formed as a white precipitate in the reaction mixture. A typical polymeric product decomposed slowly above 115°, gave infrared bands at 1610 and 1670 cm^{-1} arising from C=C groupings, and was insoluble or very sparingly soluble in common organic solvents. These properties suggest that the polymer is cross-linked, since linear polyacetylenes are usually highly colored, and soluble in organic solvents,[11] although X-ray powder photographs show an unexpectedly large degree of crystallinity.

The filtrate after removal of polymer usually contained a fairly complex mixture of organoplatinum complexes. In some cases the major products could be isolated using column chromatography. Otherwise, the products were identified, or their natures ascertained, from nmr spectra (especially ^{19}F nmr) of crude of partially separated reaction mixtures. Major products in most reactions contained 3,3,3-trifluoropropynylplatinum groups, $Pt—C\equiv CCF_3$, or substituted vinylplatinum groups of the type



The spectroscopic features of these groups, used to characterize the complexes, are described below.

The 3,3,3-trifluoropropynylplatinum complexes[12] show a strong infrared absorption in the region 2100–2150 cm^{-1} corresponding to C≡C stretching. Their ^{19}F nmr spectra show sharp peaks in the region 46–48 ppm upfield from $CFCl_3$ with coupling (19–35 Hz) to ^{195}Pt ($I = {}^1/_2$, 34% abundant). For phosphine complexes, coupling with ^{31}P nuclei is also observed.

The complexes containing vinylplatinum groups, $PtC(CF_3)=CH(X)$ (X = OR, Cl), show a moderately

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