Preparation and Some Reactions of Dimeric Isocyanide Complexes of Palladium(I) and Platinum(I)

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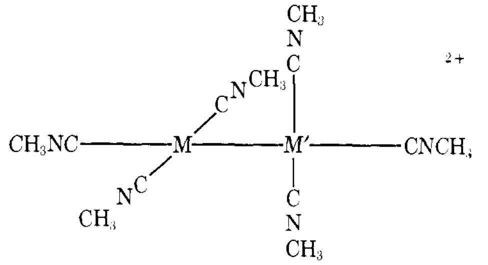
Abstract: The preparations of $[(CH_3NC)_6Pd_2][PF_6]_2$ and $[(CH_3NC)_6Pt_2][X]_2$ ($X = PF_6^-$ or BF_4^-) by the spontaneous reduction of $[(CH_3NC)_4M]^{2+}$ (M = Pd or Pt) in aqueous solutions are described. An alternate route for the preparation of $[(CH_3NC)_6Pd_2]^{2+}$ has been devised by using the reaction of $[(CH_3NC)_4Pd]^{2+}$ with $(CH_3NC)_xPd$. This latter species is generated in solution by the reaction of methyl isocyanide with tris(dibenzylideneacetone)dipalladium. Similarly $(CH_3NC)_xPd$ reacts with $[(CH_3NC)_4Pt][PF_6]_2$ to give $[(CH_3NC)_6PdPt][PF_6]_2$. These new Pd(I) and Pt(I) complexes are characterized by elemental analyses, conductivity data in solution, infrared spectra, and proton magnetic resonance spectra. These dimeric complexes show little tendency to disproportionate into M(0) and M(II) species, and the metal-metal bond resists homolytic cleavage. Halogens react with these dimers to cleave the metal-metal bonds, but otherwise they are surprisingly unreactive.

Complexes of Pd(I) and Pt(I) are not common. The only paramagnetic and hence presumably monomeric Pd(I) or Pt(I) species that have been reported are some electrochemically reduced dithiolene species[1] and species obtained by γ-irradiation of Pd(II) or Pt(II) salts.[2] Most of the known M(I) species for which structural data are available have dimeric structures with direct metal-metal bonds as well as bridging ligands between the two metals.[3] Recently a dimeric Pd(I) complex, **1**, which does not possess bridging ligands has been described.[4] This complex contains two palladium atoms with essentially square-planar coordination. The two coordination planes are nearly perpendicular with a dihedral angle of 86.2° and the two palladium atoms are joined thorough a short metal-metal bond which is 2.531 Å long. A number of other Pd(I) and Pt(I) dimeric complexes have been reported but for these detailed structural data are not available. For most of these, ligand bridged structures have been suggested.[5] However, in the case of $[Pt_2(CO)_2CL_4]^{2-}$, consideration of the infrared spectrum has led to the proposal of a structure free of bridging ligands,[6a] and this has been confirmed by an x-ray structure determination.[6b]



1, M = M′ = Pd
2, M = M′ = Pt
3, M = Pd; M′ = Pt

In addition to its unusual structure, **1** possesses other unusual characteristics. Both palladium atoms in **1** are coordinatively unsaturated. Coordination unsaturation adjacent to a metal-metal bond is rare; a few of the other structurally characterized Pd(I)[3b] or Pt(I)[3a,g,k] dimers possess this feature. Moreover, the palladium dimer **1** is fluxional. Its ^1H NMR spectrum consists of a single methyl resonance at room temperature but on cooling this splits into two singlets of 2:1 intensity.[4] Consequently it appeared worthwhile to explore further the chemistry of **1** and related species. Previous studies of Pd(I) and Pt(I) complexes have been confined to the preparation, usually accidental, and structural characterization of these species. This article describes the preparations of the three dimers **1-3**, presents information relating to their structural properties in solution, and describes certain aspects of their chemical behavior. The substitution reactions of these dimers provide information about the fluxional process available to the Pd(I) dimers and will be described elsewhere.

Experimental Section

Preparation of Compounds. Methyl isocyanide (caution, *toxic*),[7] $[(CH_3NC)_4Pd][PF_6]_2$,[8] $[(CH_3NC)_4Pt][PF_6]_2$,[8] and $(DBA)_3Pd_2\cdot CHCl_3$[9] (DBA = dibenzylideneacetone) were prepared by established procedures.

$[(CH_3NC)_6Pd_2][PF_6]_2$. Method 1. A solution of $PdCl_4^{2-}$ was prepared by dissolving $PdCl_2$ (600 mg, 3.4 mmol) and NaCl (600 mg, 10.4 mmol) in 30 ml of water. Methyl isocyanide (0.8 ml, 13.5 mmol) was added and the brown solution immediately turned colorless. The clear solution was allowed to stand for 18 h during which time bubbles of a gas slowly evolved and a bright yellow color developed. A solution containing 1 g (6 mmol) of ammonium hexafluorophosphate was added and the pale yellow product precipitated immediately. The pure crystalline salt was obtained as an acetone solvate following recrystallization from acetone/2-propanol or from acetone/diethyl ether. Acetone-free material was produced by heating the product under vacuum at 60° for 12 h (yield 70–80%): Anal. Calcd for $C_{12}H_{18}F_{12}N_6P_2Pd_2$: C, 19.24; H, 2.42; N, 11.22. Found: C, 19.17; H, 2.55; N, 11.44.

Method 2. To a solution of 108 mg (0.193 mmol) of $[(CH_3NC)_4Pd][PF_6]_2$ in 10 ml of acetonitrile was added successively 0.25 ml of methyl isocyanide and 100 mg (0.097 mmol) of solid $(DBA)_3Pd_2\cdot CHCl_3$. The mixture was heated for 3 min to give a clear yellow solution. After filtration, the product was obtained by the addition of diethyl ether to the filtrate; yield 94%. The product was identical with that obtained by method 1.

$[(CH_3NC)_6Pt_2][PF_6]_2$. This complex was prepared from aqueous $PtCl_4^{2-}$ and methyl isocyanide in the manner described above for the analogous palladium complex. The crude PF_6^- salt from this reaction (405 mg from 1.0 mmol of $PtCl_4^{2-}$) is more difficult to purify. Pure material was obtained (with considerable loss of product) in the following manner. The crude solids were first extracted with 2 ml of cold acetone. The remaining solids were recrystallized several times from acetonitrile/ether to give a free-flowing white powder (yield: 125 mg, 27%). Anal. Calcd for $C_{12}H_{18}F_{12}N_6P_2Pt_2$: C, 15.56; H, 1.96; N, 9.07. Found: C, 15.83; H, 1.99; N, 8.93.

$[(CH_3NC)_6Pt_2][BF_4]_2$. Potassium tetrachloroplatinate(II) (830 mg, 2 mmol) was added to 10 ml of an aqueous solution saturated with sodium tetrafluoroborate. The mixture was stirred 15 min and filtered to remove the insoluble potassium tetrafluoroborate which formed. The filtrate was treated with methyl isocyanide (0.5 ml, 8.3 mmol) added dropwise with stirring. The pale yellow solution was allowed to stand for 24 h during which time the product formed as white crystals. The mixture was filtered, and the solids were washed with water. The filtrate yielded a smaller second crop of crystals during the following 24 h. The combined crops were recrystallized from acetonitrile/ether (yield: 370 mg, 46%). Anal. Calcd for

$B_2C_{12}H_{18}F_8N_6Pt_2$: C, 17.79; H, 2.24; N, 10.37. Found: C, 17.72; H, 2.03; N, 10.36.

$[(CH_3NC)_6PdPt][PF_6]_2$. To a solution of 125.4 mg (0.193 mmol) of $[(CH_3NC)_4Pt][PF_6]_2$ in 10 ml of acetonitrile was added successively 0.25 ml of methyl isocyanide and 100 mg (0.097 mmol) of solid $Pd_2(DBA)_3{\cdot}CHCl_3$. The mixture was heated briefly until the solid dissolved to give a clear yellow solution. After filtering, the white product was obtained by addition of diethyl ether and purified by dissolution in acetone and reprecipitation with diethyl ether; yield 94%. Anal. Calcd for $C_{12}H_{18}F_{12}N_6P_2PdPt$: C, 17.20; H, 2.17; N, 10.03. Found: C, 17.26; H, 2.23; N, 10.03.

$[(CH_3NC)_3PdCONHCH_3][PF_6]$. The procedure for the preparation of $[(CH_3NC)_6Pd_2][PF_6]_2$ by method 1 was followed except the ammonium hexafluorophosphate was added after 5 h and the precipitate collected immediately. The solid contained both the desired product and $[(CH_3NC)_4Pd][PF_6]_2$ as well as a small amount of $[(CH_3NC)_6Pd_2][PF_6]_2$. The white complex was obtained in low yield (ca. 20%) after four recrystallizations from 2-butanone–diethyl ether. Anal. Calcd for $C_8H_{13}F_6N_4OPPd$: C, 22.21; H, 3.03. Found: C, 21.53; H, 2.74.

Reaction of $[(CH_3NC)_6Pd_2][PF_6]_2$ with Iodine. Iodine (110 mg, 0.42 mmol) was added to a solution containing 150 mg (0.2 mmol) of $[(CH_3NC)_6Pd_2][PF_6]_2$ in 10 ml of acetonitrile. The mixture was heated briefly to give a dark yellow solution which was immediately cooled to room temperature. The volume of the solution was increased to 40 ml by slow addition of diethyl ether. On cooling to −10° white crystals formed and were collected by filtration; yield, 100 mg. These were identified as $[(CH_3NC)_4Pt][PF_6]_2$ by comparison with an authentic sample. Gradual addition of 30 ml of diethyl ether produced a crop of yellow-orange crystals; yield, 80 mg. These were identified as $(CH_3NC)_2PdI_2$ by comparison with an authentic sample. The total yield of palladium complexes was 90%.

Reaction of $[(CH_3NC)_6Pd_2][PF_6]_2$ with Bromine. A solution of 0.011 ml of bromine in 4 ml of acetonitrile was added to a solution of 153 mg of $[(CH_3NC)_6Pd_2][PF_6]_2$ in 2 ml of acetonitrile. Diethyl ether was added to yield 63 mg of a white crystalline solid which was identified as $[(CH_3NC)_4Pd][PF_6]_2$. The mother liquor was evaporated to dryness on a rotory evaporator. The yellow material which remained was dissolved in hot dichloromethane and filtered. Addition of diethyl ether caused the precipitation of pale yellow needles which were contaminated with a yellow amorphous solid. The infrared spectrum of this solid indicated the presence of $(CH_3NC)_2PdBr_2$ (ν_{CN}, 2257 cm^{-1}), which has been prepared independently, and a second substance with ν_{CN} of 2286 cm^{-1}. This latter species is believed to be $[(CH_3NC)_3PdBr][PF_6]$.

$(CH_3NC)_2PdI_2$. Method 1. Methyl isocyanide (1 ml) was added to a solution of 0.42 g (2.4 mmol) of palladium(II) chloride and 0.36 g (4.8 mmol) of potassium chloride in 15 ml of water. The colorless solution was filtered and a saturated aqueous sodium iodide solution was added. The orange precipitate was collected, washed with water, and vacuum dried. Purification was achieved by recrystallization from chloroform/ethanol. Anal. Calcd for $C_4H_6I_2N_2Pd$: C, 10.86; H, 1.37; Pd, 24.06. Found: C, 11.05; H, 1.32; Pd, 24.25.

Method 2. Methyl isocyanide (0.050 ml, 0.91 mmol) and iodine (50 mg, 0.20 mmol) were added successively to a solution of 91 mg (0.088 mmol) of $Pd_2(DBA)_3{\cdot}CHCl_3$ in 20 ml of dichloromethane. The volume of the solid was reduced to 8 ml by distillation and diethyl ether was added to precipitate the product; yield 60 mg, 77%. The product was identical with that produced by method 1.

$(CH_3NC)_2PdBr_2$. Methyl isocyanide was added dropwise to a slurry of 140 mg of palladium(II) bromide suspended in 10 ml of dichloromethane until most of the solid had dissolved. The yellow solution was filtered and diethyl ether was added to the filtrate to give the product as yellow crystals; yield 170 mg, 92%. Anal. Calcd for $Br_2C_4H_6N_2Pd$: C, 13.79, H, 1.74. Found: C, 13.82; H, 1.82.

Reaction of $[(CH_3NC)_6Pt_2][BF_4]_2$ with Iodine. Iodine (26 mg, 0.1 mmol) was added to a suspension of $[(CH_3NC)_6Pt_2][BF_4]_2$ (81 mg, 0.1 mmol) in 10 ml of boiling dichloromethane. Within 2 min all the solids dissolved to give a colorless solution. An equal volume of ethyl acetate was added and the mixture cooled to −10°. The white crystals formed were collected and washed with ether (yield 95 mg, 89%). These were identified as $[(CH_3NC)_3PtI][BF_4]$. Anal. Calcd for $BC_6H_9F_4IN_3Pt$: C, 13.55; H, 1.70; N, 7.90. Found, C, 13.64; H, 1.55; N, 7.81. When this reaction was run on a smaller scale in an NMR tube with acetonitrile-d_3 as solvent, the only product detected by ^1H NMR spectroscopy was $[(CH_3NC)_3PtI][BF_4]$.

Reaction of $[(CH_3NC)_6Pt_2][BF_4]_2$ with Bromine. This reaction was monitored by ^1H NMR spectroscopy. Bromine (one drop) was added to a solution of $[(CH_3NC)_6Pt_2][BF_4]_2$ in acetonitrile-d_3. The ^1H NMR spectrum of the starting material was replaced by the ^1H NMR spectrum of $[(CH_3NC)_3PtBr]^+$. The ^1H NMR spectrum is identical with that of $[(CH_3NC)_3PtBr][PF_6]$, which has been prepared independently.[8]

Physical Measurements. Conductivities were determined in nitromethane solution with an Industrial Instruments conductivity bridge. Infrared spectra were recorded on a Beckman IR-12 spectrophotometer. Proton magnetic resonance spectra were recorded on JEOL-MH-100 spectrometer operating at 100 MHz. The spectra in Figure 1 were recorded on a JEOL PS-100 Fourier transform spectrometer operating at 100 MHz.

Results and Discussion

Preparation and Characterization of $[(CH_3NC)_6M_2]^{2+}$. Addition of methyl isocyanide to an aqueous solution of $[PdCl_4]^{2-}$ or $[PtCl_4]^{2-}$ results in the rapid formation of the colorless ions $[(CH_3NC)_4Pd]^{2+}$ or $[(CH_3NC)_4Pt]^{2+}$. These cations may be precipitated as the hexafluorophosphate salts from aqueous solution by the addition of ammonium hexafluorophosphate.[8] However, if the aqueous solution of $[(CH_3NC)_4Pd]^{2+}$ is allowed to stand for an hour or more before the addition of the precipitating agent, the yield of $[(CH_3NC)_4Pd][PF_6]_2$ is decreased and the solution acquires a yellow color. After 18 h of standing, addition of ammonium hexafluorophosphate to an aqueous solution which initially contained $[(CH_3NC)_4Pd]^{2+}$, produces a pale yellow solid which contains no $[(CH_3NC)_4Pd][PF_6]_2$ but which has been identified as $[(CH_3NC)_6Pd_2][PF_6]_2$.

A number of observations suggest that this reduction occurs via oxidation and hydrolysis of a methyl isocyanide ligand as shown in eq 1–3

$$[(CH_3NC)_4Pd]^{2+} + H_2O = [(CH_3NC)_3PdC({=}O)NHCH_3]^+ + H^+ \quad (1)$$

$$[(CH_3NC)_3PdC({=}O)NHCH_3]^+ + H_2O = [(CH_3NC)_3Pd] + H^+ + CO_2 + CH_3NH_2 \quad (2)$$

$$[(CH_3NC)_3Pd] + [(CH_3NC)_4Pd]^{2+} = [(CH_3NC)_6Pd_2]^{2+} + CH_3NC \quad (3)$$

(one of the products of eq 2 could be formulated as a palladium hydride $[(CH_3NC)_3PdH]^+$). During the course of the reaction the aqueous solution becomes acidic and bubbles of a gas are observed to form. This gas is presumably carbon dioxide. If the reaction mixture is treated with ammonium hexafluorophosphate 5 h after preparation, the precipitate contains, along with $[(CH_3NC)_4Pd][PF_6]_2$ and $[(CH_3NC)_6Pd_2][PF_6]_2$, some $[(CH_3NC)_3PdCONHCH_3][PF_6]$. This carboxamide complex is believed to be an intermediate rather than a by-product, since its yield decreases with increasing reaction time. Other examples of the formation of carboxamide ligands from coordinated isocyanides are known.[10] The reduction reactions of eq 1 and 2 are also closely analogous to the reductions of metal carbonyls that are produced by hydroxide.[11] The discovery of a second route to $[(CH_3NC)_6Pd_2]^{2+}$ through the reaction of a Pd(0) complex with a Pd(II) complex (vide infra) adds credence to the likelihood of reaction 3.

The preparation of the platinum dimer **2** in aqueous solution follows a course that is similar to the palladium reaction. However, the precipitation with hexafluorophosphate produces an impure solid which is difficult to purify. On the other hand, it has been found that tetrafluoroborate is a selective precipitating agent for the dimer, **2**; neither $[(CH_3NC)_4Pt]^{2+}$ nor any intermediates that are formed are precipitated from water by tetrafluoroborate. The preparation of the platinum dimer, **2**, in this manner contrasts with the report[10] that hydroxide reacts

Table I. Infrared and ^{1}H NMR Spectral Data

Compound	Ir (ν_{CN}, fluorocarbon mulls), cm^{-1}	^{1}H NMR ($\Delta\nu$ CH_3NC)		
		τ (intensity)	Coupling	(Solvent)
$[(CH_3NC)_6Pd_2][PF_6]_2$	2240[a]	6.35 (18)	None	$[(CD_3)_2CO]$
$[(CH_3NC)_6Pt_2][PF_6]_2$	2240[a]	6.50 (12)	J_{Pt-H} = 15.8 Hz; J_{Pt-H} = 4.4 Hz	(CD_3CN)
		6.68 (6)	J_{Pt-H} = 12.5 Hz; J_{Pt-H} = 3.5 Hz	
$[(CH_3NC)_6PtPd][PF_6]_2$	2236[a]	6.42 (6)	J_{Pt-H} = 18.0 Hz	(CD_3CN)
		6.54 (9)	None	
		6.61 (3)[a]		
$[(CH_3NC)_3Pd(CONHCH_3)][PF_6]$	2235[b]	6.41 (9)[c]	None	$[(CD_3)_2CO]$
$(CH_3NC)_2PdI_2$	2256	6.43 (6)	None	$(CDCl_3)$
$(CH_3NC)_2PdBr_2$	2261	6.49 (6)	None	$(CDCl_3)$
$[(CH_3NC)_3PtI][BF_4]$	2305, 2280	6.49 (3)	J_{Pt-H} = 8.7 Hz; J_{N-H} = 2.6 Hz	(CD_3CN)
		6.38 (6)	J_{Pt-H} = 8.2 Hz; J_{N-H} = 2.6 Hz	
$[(CH_3NC)_3PtBr][PF_6]$	2286	6.44 (3)	J_{Pt-H} = 8.9 Hz; J_{N-H} = 2.6 Hz	(CD_3CN)
		6.38 (6)	J_{Pt-H} = 7.6 Hz; J_{N-H} = 2.6 Hz	

[a] Unresolved multiplet. [b] Also: ν_{CO}, 1635; ν_{NH}, 3440 cm^{-1}. [c] Also: $\Delta\nu_{NHCH_3}$, 7.27 (3) $^3J_{H-H}$ = 4.5 Hz; $\Delta\nu_{NHCH_3}$, 3.16 (1) unresolved multiplet.

Table II. Conductivity Data[a]

Compound	Λ_0	B	Charge type
$[(CH_3NC)_6Pd_2][PF_6]_2$	111	256	2:1
$[(CH_3NC)_6Pt_2][PF_6]_2$	112	263	2:1
$[(CH_3NC)_6PdPt][PF_6]_2$	111	257	2:1
$[(CH_3NC)_5Ru(C(NHCH_3)_2)][PF_6]_2$[b]	111	259	2:1
$[Au(C(CH_3NH)_2)_2][PF_6]$[c]	103	151	1:1

[a] Λ_0 in cm^2 equiv^{-1} ohm^{-1}; B in cm$^{1/2}$ equiv$^{-1/2}$ ohm^{-1}. [b] D. J. Doonan and A. L. Balch, *Inorg. Chem.*, **13,** 921 (1974). [c] J. E. Parks and A. L. Balch, *J. Organomet. Chem.*, **71,** 456 (1974).

with $[(CH_3NC)_4Pt]^{2+}$ to give the hydroxy complex $[(CH_3NC)_3PtOH]^+$. We have not been able to repeat this preparation and obtain the reported product. The reaction of hydroxide with $[(CH_3NC)_4Pt]^{2+}$, under both the conditions given in ref 10 and under somewhat different conditions, produces in our hands modest yields of $[(CH_3NC)_6Pt_2]^{2+}$. Comparison of the physical data presented herein for $[(CH_3NC)_6Pt_2][BF_4]_2$ with the data reported for the complex formulated as $[(CH_3NC)_3Pt(OH)][BF_4]$[10] suggests that this material may have been an impure sample of $[(CH_3NC)_6Pt_2][BF_4]_2$. The values for the analytical data and ν_{CN} reported in ref 10 for $[(CH_3NC)_3PtOH][BF_4]$ are close to the analogous values for **3**. However, infrared absorptions at 3630, 3420, and 1590 cm^{-1} are not present in **3**. Unfortunately no ^{1}H NMR data for $[(CH_3NC)_3PtOH]^+$ were reported. We have found ^{1}H NMR spectra to be useful in distinguishing between mono- and diplatinum species, since coupling of the methyl isocyanide resonance to both platinum atoms in dimeric platinum species produces a splitting pattern quite different from that found for monoplatinum compounds (vide infra).

An alternate route, which utilizes the reaction of a Pd(0) complex with a M(II) complex has been found to produce these M(I) dimers. The route is basically similar to the reaction between $(t\text{-}BuNC)_2Pd$ and $(t\text{-}BuNC)_2PdX_2$ (X = Cl, Br, I) which produces $(t\text{-}BuNC)_4Pd_2X_2$.[5a] In order to develop this procedure a source of a Pd(0) isocyanide complex was required. However Pd(0) isocyanide complexes generally occur as polymeric materials whose low solubilities reduce their synthetic utility.[12-14] Reduction of $[(CH_3NC)_4Pd]^{2+}$ with hydrazine is not possible since nucleophilic attack of hydrazine to the coordinated isocyanides results in a chelative addition rather than reduction.[15] Reduction of $[(CH_3NC)_4Pd]^{2+}$ with aqueous tetrahydroborate in acetonitrile produces a black solid (ν_{CN}, 2180 cm^{-1}) with low solubility in most common solvents. This material resembles other polymeric Pd(0) isocyanide complexes. The zerovalent palladium complex $(DBA)_3Pd_2\cdot CHCl_3$[9] (DBA = dibenzyladeneacetone) is a useful source of Pd(0). Treatment of $(DBA)_3Pd_2\cdot CHCl_3$ with methyl isocyanide in diethyl ether produces an unstable yellow solid (ν_{CN}, 2165, 1780 cm^{-1}) which appears to be another polymeric isocyanide complex of Pd(0). On drying, this solid turns black but the infrared spectrum shows only minor changes (ν_{CN}, 2160, 1775 cm^{-1}). Neither the yellow nor the black material has been synthetically useful. However, addition of excess methyl isocyanide to solutions of $(DBA)_3Pd_2\cdot CHCl_3$ in acetonitrile, acetone, or dichloromethane produces yellow solutions which are stable in the absence of air and act as sources of $(CH_3NC)_xPd$. We have not determined the exact composition of the species present in solution. Addition of iodine to a solution of $(CH_3NC)_xPd$ gives $(CH_3NC)_2PdI_2$. Evaporation of solutions of $(CH_3NC)_xPd$ in dichloromethane produces a dark brown solid (ν_{CN}, 2185 cm^{-1}) which is similar to that obtained by tetrahydroborate reduction of $[(CH_3NC)_4Pd]^{2+}$. Reaction of a solution of $(DBA)_3Pd_2\cdot CHCl_3$ and methyl isocyanide in acetonitrile with $[(CH_3NC)_4Pd][PF_6]_2$ yields the palladium dimer **1** in good yield, but the best yields and most convenient procedure involves adding solid $(DBA)_3Pd_2\cdot CHCl_3$ to a stirred solution containing $[(CH_3NC)_4Pd]^{2+}$ and an excess of free methyl isocyanide.

Modification of this alternate route to the dimer **1** offers a preparative route for the mixed metal dimer **3**. Addition of $(DBA)_3Pd_2\cdot CHCl_3$ to an acetonitrile solution of $[(CH_3NC)_4Pt][PF_6]_2$ and methyl isocyanide produces **3** in 94% yield. Both the infrared spectrum and the ^{1}H NMR spectrum of **3** indicate that very little of the homonuclear dimers **1** and **2** are present in **3** prepared in this way. The mixed metal dimer **3** is chemically less stable than **1** or **2**. On warming above 40° in solution it decomposes to give a black, presumably metallic residue.

Physical data pertaining to the characterization of the dimeric cations **1**, **2**, and **3** are set out in Table I, and the elemental analytical data are presented in the experimental section. The solid-state structure of the palladium dimer has been established by x-ray crystallography.[5,16] The dimeric nature of **1**, **2**, and **3** is apparent from a study of their conductivities over a range of concentrations in nitromethane solution. These data are contained in Table II. The slopes, B, of linear plots of $\Lambda_0 - \Lambda_e$ vs. $\sqrt{C_e}$, where Λ_e is the equivalent conductance, Λ_0 is the equivalent conductance at infinite dilution, and C_e is the

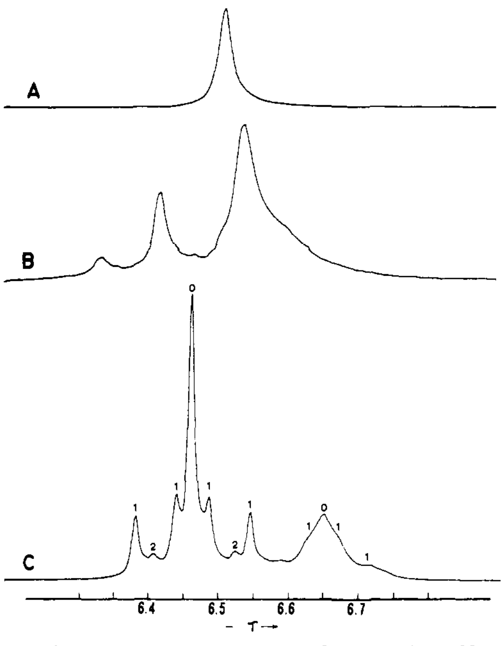


Figure 1. ^{1}H NMR spectra of (A) $[(CH_3NC)_6Pd_2][PF_6]_2$; (B) $[(CH_3NC)_6PdPt][PF_6]_2$; and (C) $[(CH_3NC)_6Pt_2][BF_4]_2$ in acetonitrile-d_3 at 30°. The resonances marked 0, 1, and 2 are assigned, respectively, to platinum dimers containing zero, one, or two ^{195}Pt nuclei.

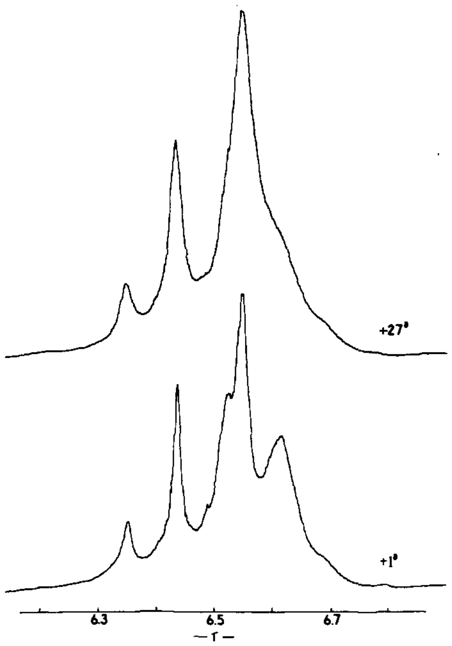


Figure 2. ^{1}H NMR spectra of $[(CH_3NC)_6PdPt][PF_6]_2$ in acetonitrile-d_3 at +27° and +1°.

equivalent concentration, are sensitive to the electrolyte type.[17] The data in Table I indicate that the hexafluorophosphate salts of **1**, **2**, and **3** are each 1:2 electrolytes. The cyanide stretching regions of the infrared spectra of **1**, **2**, and **3** as solids and in acetone solutions indicate that only terminal isocyanide ligands are present. In each case a strong absorption at ca. 2240 cm^{-1} with some poorly resolved structure is observed.

The ^{1}H NMR spectra of these complexes are compared in Figure 1. At 35 °C the spectrum of **1** in acetonitrile or acetone consists of a single resonance. At −30° in acetone solution this resonance is split into two resonances with relative intensities 2:1 at τ 6.22 and 6.31. Obviously **1** is fluxional; the details of this intraionic process which occurs through a nonbridging mechanism will be described elsewhere.[18] The platinum dimer, **2**, appears to have the same structure in solution as the palladium dimer, **1**, but it is not fluxional. The ^{1}H NMR spectrum of **2** consists of two overlapping multiplets which have similar appearances. The more intense, downfield multiplet is assigned to the methyl groups of the four equatorial ligands while the other multiplet is assigned to the methyl groups of the two axial ligands. The multiplet splitting arises from the presence of ^{195}Pt in the complexes. Since naturally occurring platinum is composed of one-third ^{195}Pt ($I = \frac{1}{2}$) and two-thirds of other isotopes with $I = 0$ the statistical distribution of ^{195}Pt labels in a diplatinum dimer is: $\frac{4}{9}$ Pt–Pt nonlabeled, $\frac{4}{9}$ ^{195}Pt–Pt singly labeled, and $\frac{1}{9}$ ^{195}Pt–^{195}Pt doubly labeled. The center line of each multiplet results from the unlabeled dimer. The singly labeled dimer produces two pairs of resonances centered about the single line of the unlabeled dimer. These four lines are of equal intensity and the sum of their intensities equals that of the central line of the multiplet. These four lines arise because of both four bond coupling ($^4J_{Pt-H}$) as well as five bond coupling ($^5J_{Pt-H}$). The spectrum of the doubly labeled compound is of the type $X_6AA'X_6'$ for the equatorial methyl groups and $X_3AA'X_3'$ for the axial methyl groups. For an $X_6AA'X_6'$ spectrum, half of the intensity is expected to reside in a doublet centered about the singlet due to the unlabeled dimer with a spacing equal to the absolute value of the sum of $^4J_{Pt-H}$ and $^5J_{Pt-H}$.[19] The values of these coupling constants are available from the spectrum of the singly labeled compound. If the signs of these two coupling constants are identical this doublet splitting should be 20.2 Hz whereas if the signs are opposite the splitting should be 11.4 Hz. The two weak lines marked 2 in trace C of Figure 1 are assigned as this doublet. Since the splitting between them is 11.4 Hz, $^5J_{Pt-H}$ and $^4J_{Pt-H}$ must have opposite signs. The remainder of the $X_6AA'X_6'$ spectrum is not observed. It is expected to consist of 12 pairs of lines symmetrically disposed about the center line of the equatorial multiplet. The splittings between these lines are dependent upon $^4J_{Pt-H}$, $^5J_{Pt-H}$, and $^1J_{Pt-Pt}$. The last coupling constant is not known. However, most of the intensity of these lines is expected to fall close to the central peak of the equatorial multiplet. We presume that because of their low intensities in comparison to the central peak these lines are not observed. Because of the poorer resolution of the axial multiplet it is not possible to identify the portion of that multiplet due to the doubly labeled dimer. The ^{1}H NMR spectrum of **2** is insensitive to temperature changes over the range +20° to +140° in dimethyl sulfoxide solution.

The ^{1}H NMR spectrum of the mixed dimer **3** is shown in trace B of Figure 1. Comparison of the spectrum of **3** with the spectra of **1** and **2** establishes the unique identity of **3**. The analysis of the spectrum of **3** is made difficult by the overlapping of peaks. Additionally the spectrum is temperature dependent; this effect is shown in Figure 2. The triplet centered at τ 6.42 with J_{Pt-H} = 18.0 Hz comprises one-third of the total intensity. This triplet is assigned to the two equatorial isocyanide ligands on platinum. The resonance position compares favorably with that found for the equatorial ligands in **2**. It is also likely that in **2** $^4J_{Pt-H}$ will be greater than $^5J_{Pt-H}$; thus $^4J_{Pt-H}$ in **2** (15.8 Hz) and in **3** (18.0 Hz) are similar. The broad resonance at higher field is comprised of the methyl groups of the ligands on palladium and the axial ligand on platinum. We suspect that the feature to highest field is one of the ^{195}Pt satellites resulting from the axial platinum ligand. The temperature dependence of the spectrum then arises from splitting of the methyl resonance resulting from the palladium ligands. At room temperature these are nearly coalesced in a line centered at τ 6.54. On cooling this line broadens and separates into two distinct resonances with a 2:1 intensity ratio. These are assigned to the two equatorial and one axial methyl isocyanide ligands on palladium. On cooling, the lines at low field are also observed to narrow. This indicates that an exchange process is occurring with the equatorial platinum ligands. We tentatively suggest that these spectra indicate that the coordination geometry at platinum is more rigid than at platinum in this dimer. Unfortunately two factors limited our ability to characterize this process. The complex decomposes at temperatures above 40° and so the behavior at elevated temperatures cannot be followed. In order to rule out the possibility that adventitious traces of methyl isocyanide are not responsible for causing the observed ligand interchange processes, it would be useful to add palladium(II) chloride to solutions of **3** to scavenge any free methyl isocyanide. Unfortunately palladium(II) chloride also causes solutions of **3** to undergo decomposition.

Reactions of $[(CH_3NC)_6M_2]^{2+}$. Neither heterolytic nor homolytic (eq 4 and 5, respectively) cleavage of the metal-metal bond in these dimers appears to be appreciable in solution or in the solids at room temperature.

$$[(CH_3NC)_6M_2]^{2+} \rightleftharpoons [(CH_3NC)_4M]^{2+} + (CH_3NC)_2M \quad (4)$$

$$[(CH_3NC)_6M_2]^{2+} \rightleftharpoons 2[(CH_3NC)_3M]^{+} \quad (5)$$

The complexes retain their integrity in solution. Numerous attempts to detect other species, especially paramagnetic ones that could arise via eq 5, have been unfruitful. The ^1H NMR spectra of the dimers do not show any line broadening due to the presence of any paramagnetic species. No electron spin resonance signals could be detected in solids or solutions containing these dimers. The isolation and integrity of the mixed-metal dimer **3** also indicates that a facile mechanism for the interchange of metals does not exist. If either eq 4 or 5 occurred appreciably for these complexes, metal interchange should be rapid. Attempts to trap the radicals produced by homolytic cleavage (eq 5) have also been unsuccessful. Nitrosobenzene has been shown to act as a good spin trap for transition-metal-centered radicals[21] but no reaction between nitrosobenzene and **1** has been detected. Similarly no reaction between **1** and pentakis(methyl isocyanide)cobalt(II), which is known to undergo self-association to form a cobalt–cobalt bond in the solid state (eq 6),[22] has been detected.

$$2[(CH_3NC)_5Co]^{2+} \rightleftharpoons [(CH_3NC)_{10}Co_2]^{4+} \quad (6)$$

Despite the low oxidation state of the metals in **1**, **2**, and **3** and the fact that the metals are coordinatively unsaturated, these dimers are surprisingly chemically unreactive. They do undergo some ligand substitution reactions readily and these will be described elsewhere.[18] These dimers have all been prepared and handled under normal atmospheric conditions, and they show no sensitivity to molecular oxygen. Quinones like tetrachloro-1,2-benzoquinone which add to a number of low valent metal complexes[21] do not react with these dimers. The palladium dimer does not react with alkyl halides or with dihydrogen. Both **1** and **2** may be dissolved in trifluoroacetic acid without reaction.

Halogens do react with these dimers to cleave the metal-metal bonds. The products isolated from these reactions are given by eq 7–9.

$$[(CH_3NC)_6Pd_2]^{2+} + I_2 = [(CH_3NC)_4Pd]^{2+} + (CH_3NC)_2PdI_2 \quad (7)$$

$$[(CH_3NC)_6Pd_2]^{2+} + Br_2 \rightarrow [(CH_3NC)_4Pd]^{2+} + [(CH_3NC)_3PdBr]^{+} + (CH_3NC)_2PdBr_2 \quad (8)$$

$$[(CH_3NC)_6Pt_2]^{2+} + X_2 = 2[(CH_3NC)_3PtX]^{+} \qquad X = I, Br \quad (9)$$

The difference in the products obtained in these reactions is probably determined more by the stability of the products than by the nature of the initial oxidation. Thus the platinum complexes of the type $(CH_3NC)_3PtX^+$ are stable in solution and as solids and do not disproportionate into $[(CH_3NC)_4Pt]^{2+}$ and $(CH_3NC)_2PtX_2$. On the other hand, we have not been able to prepare pure samples of $[(CH_3NC)_3PdX]^+$. When equimolar amounts of $[(CH_3NC)_4Pd][PF_6]_2$ and $(CH_3NC)_2PdI_2$ are mixed in acetone, three isocyanide stretching vibrations are observed in the infrared spectrum of the mixture. The vibrations at 2290 and 2256 cm^{-1} are due to $[(CH_3NC)_4Pd]^{2+}$ and $(CH_3NC)_2PdI_2$, respectively; the new vibration at 2274 cm^{-1} is assigned to $[(CH_3NC)_3PdI]^+$. However, when ether is added to this mixture to precipitate the complexes only $[(CH_3NC)_4Pd][PF_6]_2$ and $(CH_3NC)_2PdI_2$ are recovered. Similarily mixing equimolar quantities of $[(CH_3NC)_4Pd][PF_6]_2$ and $(CH_3NC)_2PdBr_2$ in acetone produces three isocyanide stretching vibrations (2290, $[(CH_3NC)_4Pd]^{2+}$; 2280, $[(CH_3NC)_3PdBr]^+$; and 2260, $(CH_3NC)_2PdBr_2$) in the infrared spectrum of the mixture. When solids are isolated from this mixture by the addition of ether some material is precipitated which shows ν_{CN} at 2280 and 2261 cm^{-1}; this solid is believed to contain both $[(CH_3NC)_3PdBr][PF_6]$ and $(CH_3NC)_2PdBr_2$.

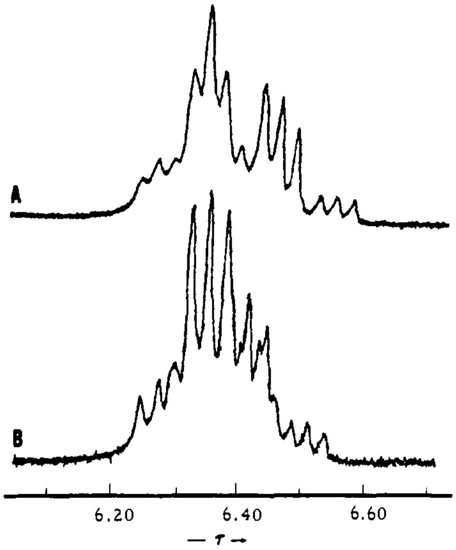


Figure 3. ^1H NMR spectra of (A) $[(CH_3NC)_3PtI][BF_4]$ and (B) $[(CH_3NC)_3PtBr][BF_4]$ in acetonitrile-d_3 at 30°.

The characterization of the products of halogen oxidation is straightforward. Most of the products have been obtained by one or more alternate routes. The ^1H NMR spectra of the complexes $[(CH_3NC)_3PtX]^+$ are shown in Figure 3. These show complications arising from the presence of ^{195}Pt and from coupling of the methyl protons to the isocyanide nitrogen. In each case two multiplets of relative intensities 2:1 arise from the two mutually trans isocyanide ligands and from the unique isocyanide ligand. Each multiplet contains a central feature due to molecules containing no ^{195}Pt and a pair of satellites due to the splitting by the naturally occurring ^{195}Pt. Each line is then further split into a triplet by coupling to the isocyanide nitrogen.

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The Mechanism of the Rearrangement of the Hydrocobalt Carbonyl Catalyzed Isomerization of 3-Phenylpropene

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Abstract: The *trans*-1-phenylpropene produced in the $HCo(CO)_4$ catalyzed rearrangement of 3-phenylpropene-3,3-d_2 was found, by NMR analysis, to contain appreciable deuterium in the 2 position as well as the 1 and 3 positions of the propenyl system. No protium was observed in the 1 position. These results are consistent with the 1,2 addition-elimination mechanism which has previously been postulated to occur in other cobalt carbonyl induced isomerizations of alkenes containing no aryl substituents and are not compatible with the suggestion that intramolecular 1,3-hydrogen shifts are predominant in "activated" systems containing an aryl group.

The isomerization of olefins catalyzed by transition metal complexes has been an important and extensively studied aspect of organometallic chemistry.[1] As has been recently pointed out,[1] there are now two commonly accepted mechanisms, depending on the catalyst system, for such isomerizations. One involves an intramolecular 1,3-hydrogen shift and the other a 1,2 addition-elimination mechanism.

It now seems to be no question but that the isomerization of allylic alcohols with either iron pentacarbonyl or triiron dodecacarbonyl involves an intramolecular 1,3-hydrogen shift.[2] Whether the mechanism proceeds via a π-allyl metal hydride intermediate as initially proposed by Pettit and Emerson,[3] or a concerted mechanism[2b] involving some iron-hydrogen bonding in the transition state, has not been unequivocally established. Recently, Casey and Cyr demonstrated that the triiron dodecacarbonyl-induced rearrangement of 3-ethyl-1-pentene occurred via an intramolecular 1,3-hydrogen shift in which the rate of isomerization of complexed alkene was rapid in comparison with the rate of decomplexation.[1] A π-allyl metal hydride intermediate was postulated to account for the isomerization. In support of this mechanism is the recent report of the first direct observation of a π-allyl–hydride exchange in a π-allyl-molybdenum hydride complex.[4]

The mode of hydrogen transfer in olefin isomerizations with cobalt carbonyls is not so clearly established. Thus it has been shown that olefin isomerizations accompanying the hydroformylation of 3-methyl-1-hexene-3-*d*, initiated by dicobalt octacarbonyl, proceeds by way of a metal hydride addition-elimination mechanism.[5] Similarily, Taylor and Orchin concluded that the $HCo(CO)_4$ catalyzed rearrangement of propene-d_6 proceeded at least in part by the 1,2 addition-elimination of $HCo(CO)_4$.[6] However, in the $DCo(CO)_4$ catalyzed rearrangement of allyl alcohol to propionaldehyde, evidence was obtained for a 1,3 intramolecular hydrogen shift.[7] Also during the isomerization of allylbenzene catalyzed by $DCo(CO)_4$, it was found that the product, β-methylstyrene, contained only about 5% deuterium.[8] These results were stated as not being compatible with an addition-elimination mechanism, and an internal 1,3-hydrogen shift was proposed to account for most of the reaction.[8] To explain the apparent duality of mechanisms, Hubert and Reimlinger have suggested that both types of hydrogen transfer can take place separately or simultaneously.[9] Thus it was proposed that the addition-elimination mechanism would predominate with simple olefins but that with olefins containing an activated allylic hydrogen, e.g., allylbenzene, such hydrogens would be more mobile than the hydrogen bonded to the metal and a 1,3 intramolecular hydrogen transfer would be the preferred mode of isomerization. However, Cramer and Lindsey have questioned the necessity of postulating an internal 1,3-hydrogen shift to explain the small amount of deuterium incorporation accompanying the $DCo(CO)_4$ catalyzed isomerization of allylbenzene and have suggested that the data are completely explicable in terms of an addition-elimination mechanism.[10] While others[5] have concurred with Cramer and Lindsey's interpretation of Orchin's data, experimental verification of this interpretation has not yet been provided.

In an effort to clarify these ambiguities, we have prepared 3-phenylpropene-3,3-d_2 and have studied its rearrangement with $HCo(CO)_4$.

Results

Synthesis. It was necessary to prepare 3-phenylpropene-3,3-d_2 (**1**) with a high degree of isotopic purity and in relatively