increase in temperature. No attempt has been made to correct for effects of ionic strength, which generally were in the range 0.2–2 *M*. Although in many cases the constants for $PtCl_4^{2-}$ have not been distinguished from those of its hydrolysis products, conditions were usually chosen to suppress the concentrations of the latter species. Rate constants reported in ref 4 are for zero ionic strength and very low chloride concentrations and may be somewhat too large in comparison with the others.

Table V shows that bipyridyl and phenanthroline are among the poorest nucleophiles for $PtCl_4^{2-}$, even though their reaction products are very stable. Their reactivities exceed only that of the sterically hindered olefin *trans*-crotylammonium chloride. The unexpected feature of the series is that ammonia, for which steric hindrance is presumably unimportant, is nearly as slow. This parallels the only results[18] available for $PdCl_4^{2-}$. It has a second-order rate constant of 1.7 M^{-1} sec^{-1} (adjusted to 5° using published thermal parameters) compared with 1.2 M^{-1} sec^{-1} for bipyridyl and 0.34 M^{-1} sec^{-1} for phenanthroline.

An interesting aspect of the reactions of $PtCl_4^{2-}$ is that there seems to be no evidence that they obey the two-term rate law (eq 1). Nucleophiles lying below diethylenetriamine in Table V react too rapidly to allow a solvent route to be detected. The remaining reactions from ref 3 do not fit linear plots of k_{obsd} vs.

(18) We believe that the interpretation of the data in ref 13 is not entirely unambiguous. The rates at high chloride concentrations are directly reciprocal to [Cl$^-$]. The nucleophile might not react directly with $PdCl_4^{2-}$ but only with Pd(H$_2$O)Cl$_3^-$. The rate constant of the reaction would then be much larger. A similar situation was observed for the reaction of $PtCl_4^{2-}$ with Cl$^-$.[2]

[nucleophile] well enough to show whether the intercept is k_1 for aquation or zero. Bipyridyl, phenanthroline, and the olefins are strictly second order, and there is no indication that ammonia is otherwise.

The effect of protonation of bipyridyl and phenanthroline is rather difficult to explain. In all systems the reaction proceeds through both the free and the protonated ligand. In the Pt–bipy system, platinum discriminates in favor of the protonated ligand, as shown by the inflection point in the k_{obsd} vs. pH graph (Figure 3) at the pK_a of bipyH$^+$ (4.3 at T = 25°, μ = 0).[19] In the other three systems, however, the metal is insensitive to whether or not the ligand is protonated. The first kind of behavior may be caused by the electrostatic attraction between bipyH$^+$ and the complex anion. bipyH$^+$ still has one free nitrogen, and bond formation may occur through it. The other kind of behavior is more puzzling, for we would have believed that phenH$^+$ should be less reactive than phen. Structural studies suggest that a proton on one phenanthroline nitrogen would partly block the other nitrogen from the metal. This unusual behavior was the principal feature of the phenanthroline reaction that led us to suggest a dissociatively activated mechanism.[14] For the present, the problem remains unsolved. The only alternative explanation we can think of requires some fortuitous combination of reactivity effects causing the protonated and unprotonated chelates to react at the same rate. Since two metals and two ligands show the same behavior, the explanation relies heavily on chance.

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Cationic Organometallic Complexes with Unsaturated Systems. II. Platinum(II)–Isocyanide and –Carbene Complexes

BY H. C. CLARK* AND L. E. MANZER

A variety of cationic platinum(II)–isocyanide complexes of the types *trans*-[PtXL$_2$(CN–R)]Z and *trans*-[Pt(CN–R)$_2$L$_2$]Z$_2$ (where L = P(CH$_3$)$_2$C$_6$H$_5$ or P(CH$_3$)(C$_6$H$_5$)$_2$; X = Cl, I, or CH$_3$; R–NC = alkyl or aryl isocyanide; Z$^-$ = PF$_6^-$, BF$_4^-$, SbF$_6^-$, or B(C$_6$H$_5$)$_4^-$) have been prepared. The isocyanide is shown to be a good σ donor and very weak π acceptor, and the increase in ν(N≡C) on coordination is dependent on the positive charge at the platinum nucleus. One mole of phosphine in *cis*-Pt(CH$_3$)$_2$L$_2$ is readily displaced by *p*-methoxyphenyl isocyanide to give *cis*-Pt(CH$_3$)$_2$L(CN–C$_6$H$_4$–OCH$_3$) which reacts with acetyl chloride to give *cis*-PtCH$_3$ClL(CN–C$_6$H$_4$–OCH$_3$). The nmr spectra of the cationic methylplatinum(II) complexes show very rapid exchange of phosphines at room temperature which may be explained by delocalization of positive charge from platinum to the isocyanide. [Pt(CN–C$_2$H$_5$)$_2$L$_2$](PF$_6$)$_2$ reacts slowly with protic nucleophiles to give a variety of carbene complexes whose mode of formation and stereochemistry are discussed.

Introduction

Previous studies[1–5] have shown that acetylenes and olefins react with methylplatinum(II) compounds to yield a variety of products, depending on the nature of the acetylene or olefin and the reaction conditions.

We have previously reported the preparation and characterization of a wide variety of cationic methylplatinum(II)–nitrile complexes[6,7] and have found that alcohols react with coordinated perfluoroarylnitriles to give imino ether derivatives. The course of the reaction was dependent on the size of the anion as well as the nature of the alcohol.

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TABLE I: Physical and Raman (cm⁻¹) Data[a] for Platinum–Isocyanide Complexes

Compound[b]	Calcd % C	Found % C	Calcd % H	Found % H	Dec pt,[e] °C	Recrystn solvent	ν(N≡C)	Δν(N≡C)[c]
PtCH₃ClQ₂(CNC₆H₄OCH₃)[d]	45.84	45.32	4.92	4.92	78–79	CH₂Cl₂–(C₂H₅)₂O	2181	56
[PtCH₃Q₂(CNC₆H₄OCH₃)](PF₆)	39.27	39.65	4.23	4.26	129–130	CH₂Cl₂–(C₂H₅)₂O	2193	68
[PtCH₃Q₂(CNC₆H₄NO₂)][B(C₆H₅)₄]	60.45	60.23	5.18	4.90	68–71	CH₂Cl₂–CH₃OH	2178	62
[PtCH₃Q₂(CNC₆H₄CH₃)][B(C₆H₅)₄]	63.78	63.75	5.68	5.87	129–132	CH₂Cl₂–CH₃OH	2178	53
[PtCH₃Q₂(CNC₆H₄CH₃)](BF₄)	43.50	43.73	4.67	4.49	91–94	CH₂Cl₂–(C₂H₅)₂O	2192	67
[PtCH₃Q₂(CNC₆H₅)][B(C₆H₅)₄]	67.44	67.20	5.27	4.87	149–151	CH₂Cl₂–(C₂H₅)₂O	2183	66
[PtCH₃L₂(CNC₆H₅)](SbF₆)	34.93	35.16	3.66	3.44	148–149	CH₂Cl₂–(C₂H₅)₂O	2187	80
[PtCH₃Q₂(CNCH₃)](SbF₆)	29.90	30.27	3.70	3.57	118–120	CH₃OH–(C₂H₅)₂O	2242	72
[PtCH₃L₂(CNCH₃)](SbF₆)	39.25	39.02	3.64	3.58	120–123	CH₂Cl₂–(C₂H₅)₂O	2267	97
[PtCH₃L₂(CNC₆H₄CH₃)](SbF₆)	43.63	43.67	3.77	3.53	184–185	Hot CH₃OH	2189	64
[PtCH₃I₂(CNC₆H₄OCH₃)](SbF₆)	42.96	42.92	3.70	3.64	143–145	CH₂Cl₂–(C₂H₅)₂O	2193	68
Pt(CH₃)₂Q(CNC₆H₄OCH₃)	30.90	30.84	3.91	3.80	83–85	(C₂H₅)₂O–n-C₅H₁₂	2234	83
PtCH₃ClQ(CNC₆H₄OCH₃)	43.55	43.30	4.87	4.76	95–96	CH₂Cl₂–n-C₅H₁₂	2149	24
[PtCH₃Q(CNC₆H₄OCH₃)(CNC₆H₄CH₃)](PF₆)	39.50	39.53	4.10	4.05	130–133	CH₂Cl₂–(C₂H₅)₂O	2186	61
[PtClQ₂(CNC₆H₄CH₃)](PF₆)	40.38	40.53	3.80	3.63	160–164	CH₃OH–(C₂H₅)₂O	2217, 2240	92, 115
[PtClQ₂(CNC₆H₄OCH₃)](PF₆)	37.49	37.85	3.80	3.84	225–226	CH₂Cl₂–(C₂H₅)₂O	2250	125
[PtClL₂(CNC₆H₄OCH₃)](PF₆)	36.72	36.73	3.72	3.43	233–235	CH₂Cl₂–(C₂H₅)₂O	2237	112
[PtClL₂(CNC₆H₄CH₃)](PF₆)	45.82	46.06	3.73	3.65	239–240	CH₃OH–(C₂H₅)₂O	2243	118
[PtQ₂(CNCH₂CH₃)₂](PF₆)₂	32.00	32.08	3.74	3.71	114–115	CH₃OH–(C₂H₅)₂O	2267	116
[PtL₂(CNCH₂CH₃)₂](BF₄)₂	27.89	27.85	3.33	3.30	116–117	CH₃OH	2251	100
[PtClQ₂(CNCH₂CH₃)](PF₆)	30.32	30.25	3.70	3.70	275–278	CH₂Cl₂–(C₂H₅)₂O	2294	143
[PtIQ₂(CNCH₂CH₃)](PF₆)	43.81	43.66	4.14	3.98	206–207	CH₃OH–(C₂H₅)₂O	2283	132
[PtClL₂{C(NHC₆H₅)(NHC₆H₅)}](PF₆)₂	34.86	34.71	4.08	4.13	143–146	CH₃OH–(C₂H₅)₂O	…	…
[PtClL₂{C(NHC₆H₅)(NHC₆H₄CH₃)}](PF₆)₂	35.59	35.70	4.22	3.97	151–155	CH₃OH–(C₂H₅)₂O	…	…
[PtQ₂{C(NHC₆H₅)(OC₂H₅)}](PF₆)₂	31.42	31.36	4.06	4.05	>165	CH₂Cl₂–(C₂H₅)₂O	…	…
[PtQ₂{C(NHC₆H₅)(SCH₂C₆H₅)}](PF₆)₂	34.84	34.99	4.05	3.75	>198	CH₃OH–(C₂H₅)₂O	…	…

[a] Values are accurate to ±2 cm⁻¹. [b] Q = P(CH₃)₂C₆H₅; L = P(CH₃)(C₆H₅)₂; all compounds are white except the *p*-nitrophenyl isocyanide complex which is orange. [c] ν(N≡C)(complex) − ν(N≡C)(free ligand). [d] Chloride analysis: calcd, 5.41%; found, 5.73%. [e] Decomposition points are corrected.

TABLE II: ¹H Nuclear Magnetic Resonance Data[a] for Platinum–Isocyanide Complexes

| Compound[d]	Probe temp,[b] °C	Phosphine methyls δ(CH₃)	J(P–H)[c]	J(Pt–H)	Platinum methyls δ(CH₃)	J(P–H)	J(Pt–H)	Isocyanide resonances
PtCH₃ClQ₂(CNC₆H₄OCH₃)	−30	−2.01	7.2	33.0	−0.35	8.0	62.0	δ(OCH₃) −3.99
[PtCH₃Q₂(CNC₆H₄OCH₃)](PF₆)	−30	−1.99	7.2	33.0	−0.39	8.0	62.0	δ(OCH₃) −3.75
[PtCH₃Q₂(CNC₆H₄NO₂)][B(C₆H₅)₄]	31	−1.90	7.4	32.8	−0.69	8.5	61.8	
[PtCH₃Q₂(CNC₆H₄CH₃)][B(C₆H₅)₄]	31	−2.03	7.2	32.6	−0.63	8.1	61.8	δ(CH₃) −2.49
[PtCH₃Q₂(CNC₆H₄CH₃)](BF₄)	0	−2.04	7.5	33.0	−0.43	7.9	63.4	δ(CH₃) −2.37
[PtCH₃L₂(CNC₆H₅)][B(C₆H₅)₄]	31	−2.27	7.0	34.5	−0.44	8.1	62.4	
[PtCH₃Q₂(CNC₆H₅)](SbF₆)	0	−2.04	7.2	33.3	−0.45	8.4	63.0	
[PtCH₃L₂(CNCH₃)](SbF₆)	0	−1.94	7.4	33.3	−0.25	8.2	63.8	δ(CH₃) −3.05[e]
[PtCH₃L₂(CNCH₃)](SbF₆)	−50	−2.26	7.0	34.5	−0.40	7.7	62.5	δ(CH₃) −3.02
[PtClL₂(CNCH₃)](SbF₆)	31	−2.36	7.2	34.5	−0.45	8.1	62.0	δ(CH₃) −2.33
[PtClL₂(CNC₆H₄OCH₃)](SbF₆)	31	−2.36	7.2	34.0	−0.45	8.0	62.0	δ(OCH₃) −3.82
[PtClL₂(CNC₆H₄OCH₃)](SbF₆)	−65	−1.93	7.4	33.2	−0.24	8.1	63.6	δ(CH₂) −3.38, δ(CH₃) −3.82 −1.15[f]
[Pt(CH₃)₂Q(CNC₆H₄OCH₃)]	−20	−2.32	8.4	21.2	−0.71	7.4	62.8	δ(OCH₃) −3.82
	31				−0.39	9.4	68.0	
PtCH₃ClQ(CNC₆H₄OCH₃)	31	−2.01	11.2	49.6	−0.58	4.8	56.6	δ(OCH₃) −3.84
[PtClQ(CNC₆H₄OCH₃)(CNC₆H₄CH₃)](PF₆)	31	−1.73	16.0	52.0	−0.50	6.0	62.5	δ(OCH₃) −3.42, δ(CH₃) −1.93
[PtClQ₂(CNC₆H₄CH₃)](PF₆)	31	−2.10	8.0	29.6				δ(CH₃) −1.88
[PtClQ₂(CNC₆H₄OCH₃)](PF₆)	31	−2.00	8.8	28.8				δ(OCH₃) −3.40
[PtL₂(CNCH₂CH₃)₂](BF₄)₂	−30	−2.64	7.5	31.6				δ(CH₂) −0.79, δ(CH₂) −3.33
[PtClQ₂(CNCH₂CH₃)](PF₆)	31	−2.03	7.2	25.2				δ(CH₃) −0.93, δ(CH₂) −3.74
[PtIQ₂(CNCH₂CH₃)](PF₆)	31	−2.26	7.2	25.6				δ(CH₃) −0.98, δ(CH₂) −3.09

[a] Chemical shifts (δ) in ppm using dichloromethane as internal standard. [PtClL₂(CNC₆H₄CH₃)](PF₆) and [PtQ₂(CNCH₂CH₃)₂](PF₆)₂ are insoluble. [PtIL₂(CNC₆H₄CH₃)](PF₆)₂ is quoted.²⁴ [b] Temperature at which ³¹P–¹H coupling was clearly resolved. [c] ²J(P–H) + ⁴J(P–H) in hertz. [d] L = P(CH₃)(C₆H₅)₂; Q = P(CH₃)₂C₆H₅. [e] J(Pt–H) = 12.8, J(P–H) = 7.5. [f] J(H–H′) = 1.3. Coupling constants (*J*) in hertz.

TABLE III

INFRARED[a] AND ¹H NMR DATA[b] FOR CATIONIC PLATINUM(II)-CARBENE COMPLEXES OF
THE TYPE *trans*-[Pt(CN-C₂H₅){P(CH₃)₂C₆H₅}₂(carbene)](PF₆)₂

Carbene	Phosphine methyls			Ethyl resonances		ν(N—H)	ν(N≡C)	$\Delta\nu$(N≡C)[c]
	δ(CH₃)	J(P—H)	J(Pt—H)	δ(CH₃)	δ(CH₂)			
C$<$ $\genfrac{}{}{0pt}{}{OC_2H_5}{NHC_2H_5}$	2.10	6.0	32.5	1.01	3.05	3382	2271	120
	2.11	6.0	32.5	1.09	3.63			
	2.14	6.4	31.6	1.11				
	2.15	6.4	31.6					
C$<$ $\genfrac{}{}{0pt}{}{NHC_6H_5}{NHC_2H_5}$	1.99	8.2	32.4	1.14	3.51	3341	2265	114
	2.00	8.0	31.6	1.22	3.64	3389		
	2.16	8.0	32.8					
	2.17	8.0	32.8					
C$<$ $\genfrac{}{}{0pt}{}{NHC_6H_5CH_3{}^d}{NHC_2H_5}$	1.91	6.9	32.4	1.12	3.42	3346	2264	113
	1.94	6.9	32.4	1.14	3.57	3393		
	2.07	7.6	31.6					
	2.11	7.6	31.6					
C$<$ $\genfrac{}{}{0pt}{}{SCH_2C_6H_5}{NHC_2H_5}$	2.03[e]	8.0	31.2	1.19	3.52	3342	2257	106
				1.23	3.58			

[a] Estimated to be accurate to ±2 cm⁻¹. [b] Spectra recorded using dichloromethane as solvent and internal standard; chemical shifts in ppm and coupling constants in hertz. [c] ν(N≡C)(complex) − ν(N≡C)(free ligand). [d] δ(CH₃) 2.31. [e] Other resonances were complex and could not be interpreted.

Isocyanides form a wide variety of metal complexes[8] and recently there has been much interest in the chemical reactivity of the coordinated isocyanide. Treichel[9] found that the reaction of pentafluorophenyllithium with coordinated methyl isocyanide gave pentafluorophenylimino derivatives

$$[(\pi\text{-}C_5H_5)Fe(CO)_2(CN\text{-}CH_3)]^+ \xrightarrow{C_6F_5Li}$$
$$[(\pi\text{-}C_5H_5)Fe(CO)_2\{C(C_6F_5)=NCH_3\}]$$
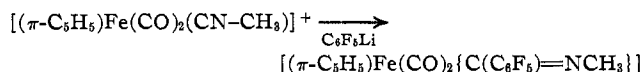
There have also been a variety of insertion reactions of isocyanides into palladium–,[10] nickel–,[11] and platinum–alkyl[12] bonds.

Treichel and Hess[13] have recently reported that dealkylation of methyl isocyanide occurs when [(C₂H₅)₃P]₂Pt(CN–CH₃)Cl⁺Cl⁻ is refluxed in benzene, to give the neutral platinum complex Pt[P(C₂H₅)₃]₂(CN)Cl.

Coordinated isocyanides in palladium(II) and platinum(II) complexes are susceptible to nucleophilic attack by alcohols and amines to give a variety of carbene complexes.[14–19] Unlike the carbenes obtained by reaction of alcohols with cationic methylplatinum(II)–acetylene complexes,[4] which take place instantaneously at room temperature, the formation of carbenes from isocyanides usually requires much more vigorous conditions possibly suggesting a different mechanism for their formation. The apparent chemical reactivity of the coordinated isocyanide prompted us to extend our investigations of CN unsaturated systems to a variety of cationic platinum(II)–isocyanide complexes in order

to determine the relative σ-donor and π-acceptor properties of isocyanides and their carbene derivatives.[20]

Results and Discussion

Preparation of the Complexes.—We have prepared three types of cationic platinum(II)–isocyanide complexes in order to determine how the electron density at platinum affects bonding and reactivity. Physical and spectroscopic data are listed in Tables I–III.

Type I, [PtCH₃L₂(CN–R)]⁺X⁻.—The chloride in *trans*-PtCH₃ClL (where L = P(CH₃)₂(C₆H₅) or P(CH₃)(C₆H₅)₂) is labile[21] due to the strong trans influence of the methyl group. The addition of a silver salt AgX (X⁻ = PF₆⁻ or SbF₆⁻) in methanol to such complexes gives an immediate precipitate of silver chloride and the complex [PtCH₃L₂(CH₃OH)]⁺X⁻. The silver chloride can be removed by centrifugation to give a clear colorless solution. The addition of an isocyanide and subsequent removal of the solvent gives a clear oil which may be dissolved in a polar solvent and induced to crystallize by the addition of diethyl ether or pentane. The complexes were generally quite easy to crystallize using PF₆⁻ or SbF₆⁻ as the anion. However, in several instances where crystallization was difficult, a crystalline product was obtained by exchange of the anion using sodium tetraphenylborate.

The addition of a 1 molar equiv of *p*-methoxyphenyl isocyanide to *trans*-PtCH₃Cl{P(CH₃)₂C₆H₅}₂ in benzene gives an immediate white precipitate of PtCH₃Cl-(CN–C₆H₄–OCH₃){P(CH₃)₂C₆H₅}₂. The complex is soluble in hot benzene and may be a five-coordinate complex in the solid state. However in a polar solvent such as chloroform or dichloromethane it is dissociated·presumably to [PtCH₃{P(CH₃)₂C₆H₅}₂(CN–C₆H₄–OCH₃)]⁺Cl⁻; the proton nmr spectrum in CH₂Cl₂ is identical with that of the analogous PF₆⁻ salt in solution.

Type II, [PtXL₂(CN–R)]⁺PF₆⁻ (X = Cl, I).—Complexes of this type were prepared by cleavage of the cationic halogen-bridged dimers in methanol (eq 1). The reaction proceeds smoothly with precipitation of the isocyanide complexes from the methanol solutions.

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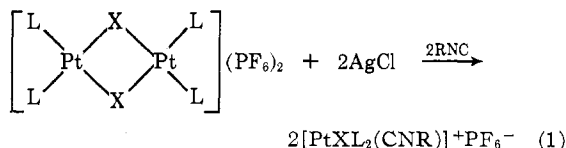(14) E. M. Badley, J. Chatt, R. L. Richards, and G. A. Sims, *ibid.*, 1322 (1969).

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$2cis\text{-}PtX_2L_2 + 2AgPF_6 \longrightarrow$

$$\left[\begin{array}{c} L \diagdown \diagup X \diagdown \diagup L \\ Pt \hspace{1cm} Pt \\ L \diagup \diagdown X \diagdown \diagup L \end{array} \right] (PF_6)_2 + 2AgCl \xrightarrow{\ 2RNC\ }$$
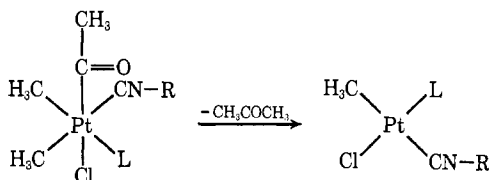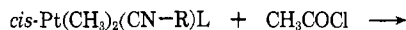
$$2[PtXL_2(CNR)]^+PF_6^- \quad (1)$$

These complexes are generally much less soluble than the corresponding methylplatinum(II) compounds. As for most reactions involving cleavage of the bridged dimer,[22] the phosphines occupy a trans configuration, confirmed by nmr data.

Type III, [PtL₂(CNR)₂]X₂.—The addition of 2 molar equiv of an isocyanide to *cis*-PtCl₂L₂ in methanol gives an immediate, clear, colorless solution, and the subsequent addition of an aqueous solution of Na⁺X⁻ where X = BF_4^- or PF_6^- gives an immediate precipitate of the dipositive cation

$$Cl_2PtL_2 + 2RNC \longrightarrow [PtL_2(CNR)_2]Cl_2 \xrightarrow{\ 2NaX\ } [PtL_2(CNR)_2]X_2$$
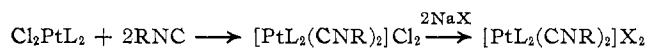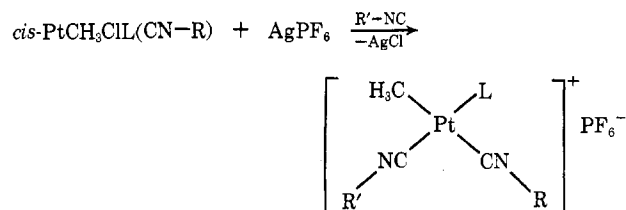
Phosphine Displacement Reaction.—The addition of 1 molar equiv of isocyanide to a benzene solution of *cis*-Pt(CH₃)₂L₂, L = $P(CH_3)_2(C_6H_5)$, causes the ready displacement of one phosphine to give *cis*-Pt-(CH₃)₂(CN–R)L. Such a displacement has previously been observed by Treichel and Hess.[12] The addition of 1 molar equiv of acetyl chloride to this complex gave *cis*-Pt(CH₃)ClL(CN–R)

cis-Pt(CH₃)₂(CN–R)L + CH₃COCl →

$$\begin{array}{c} \underset{|}{CH_3} \\ \underset{|}{C}{=}O \\ H_3C \diagdown \overset{|}{\underset{|}{Pt}} \diagup CN{-}R \\ H_3C \diagup \overset{|}{\underset{|}{Cl}} \diagdown L \end{array} \xrightarrow{\ -CH_3COCH_3\ } \begin{array}{c} H_3C \diagdown \diagup L \\ Pt \\ Cl \diagup \diagdown CN{-}R \end{array}$$

The reaction probably proceeds by way of an unstable platinum(IV) complex, followed presumably by the elimination of acetone. The configuration of the final complex can easily be determined from the nmr coupling constants. The platinum methyl resonance appears as a doublet due to coupling with the ³¹P nucleus with $J(Pt-P-C-H)$ = 4.8 Hz indicating a cis phosphine and platinum satellites of one-fourth the intensity ($J(Pt-C-H)$ = 56.6 Hz for methyl trans to isocyanide). The phosphine methyl resonance appears as a doublet with platinum satellites showing $J(Pt-P-C-H)$ = 49.6 Hz indicating that the phosphine is trans to a weak σ donor such as chloride.[23]

This complex acts as a good starting material for the preparation of a cationic methylplatinum(II)-bis-(isocyanide) complex

cis-PtCH₃ClL(CN–R) + AgPF₆ $\xrightarrow[\ -AgCl\ ]{\ R'-NC\ }$

$$\left[\begin{array}{c} H_3C \diagdown \diagup L \\ Pt \\ NC \diagup \diagdown CN \\ R' \hspace{1cm} R \end{array} \right]^+ PF_6^-$$

(22) W. J. Cherwinski and H. C. Clark, *Can. J. Chem.*, **47**, 2665 (1969).

(23) J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. A*, 2801 (1969).

Raman and Nmr Spectroscopic Data.—The infrared and Raman spectra of the isocyanide complexes show very strong and sharp N≡C stretching absorptions in the region 2300–2100 cm⁻¹. The values of $\Delta\nu$(N≡C) (ν(N≡C)(complex) − ν(N≡C)(free ligand)) are positive and 20–150 cm⁻¹ in magnitude, indicating an increase in bond order on coordination. In a series of cationic methylplatinum(II)–arylnitrile complexes[6] we observed a correlation between the increase in the nitrile stretching frequency and the electronegativity of the para substituent. There does not appear to be any obvious correlation in the analogous isocyanide complexes as $\Delta\nu$(N≡C) decreases in the order CN–C₂H₅ > CN–C₆H₅ > CN–CH₃ > CN–C₆H₄–OCH₃ > CN–C₆H₄–CH₃. However, there is a noticeable increase in $\Delta\nu$ (N≡C) in the order type III > type II > type I and this will be discussed later.

The platinum–methyl stretching vibration appears as a strong and polarizable band in the Raman spectrum[5] yet is very weak in the infrared. The values of ν(Pt–CH₃) are all in the range 530–560 cm⁻¹; although coupling to other vibrational modes is possible, it is unlikely to be a pure mode. For *cis*-Pt(CH₃)₂(CN–C₆H₄–OCH₃){P(CH₃)₂C₆H₅} two bands are observed in the Raman spectrum at 554 and 526 cm⁻¹, as expected.

A significant feature of the proton nmr spectra is the temperature dependence of the coupling constants. At room temperature the methylplatinum(II) complexes show complete loss of phosphorus and platinum coupling to the phosphine methyls and loss of phosphorus coupling to the platinum methyl group. Thus, as shown in Figure 1, at room temperature the phosphine methyl resonance appears only as a sharp singlet, as the temperature is lowered, coupling to platinum and then
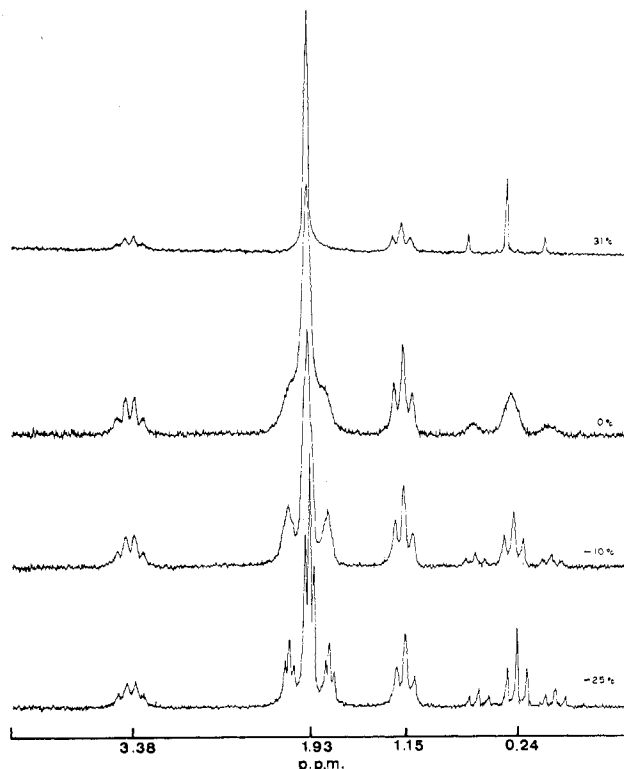

Figure 1.—Variable-temperature nmr spectra of *trans*-[PtCH₃-(CNC₂H₅){P(CH₃)₂C₆H₅}₂]⁺(SbF₆)⁻ recorded on a CH₂Cl₂ solution with an HA100 spectrometer using a 500-Hz sweep width.

to phosphorus appears, and finally at $-20°$ the spectrum is completely resolved into the expected pattern. The phosphine methyls then appear as $1:2:1$ triplets due to strong phosphorus-phosphorus coupling,[24] indicative of virtually coupled trans phosphines. Satellites of one-fourth intensity are also observed due to coupling with ^{195}Pt ($I = {}^1/_2$, natural abundance 34%). The platinum methyl resonances appear as $1:2:1$ triplets due to coupling with two equivalent ^{31}P nuclei, and platinum satellites are also observed. We believe that the temperature dependence results from rapid exchange of phosphines[25] between equivalent sites at room temperature and additional evidence concerning these and related systems will be presented in a future publication.

Assuming that the coupling constant J(Pt-C-H) is governed by the Fermi contact term,[26,27] we have used this value as a relative measure of the σ-donor strength of a ligand (B) trans to the methyl group to form a trans influence series.[21] As the σ-donor strength of B increases, the Pt-B bond gains "s" and "d" character and loses "p" character,[28] resulting in a decrease of "s"-electron density in the platinum-methyl bond and a lower coupling constant. Platinum coupling to the phosphine methyls may be used as a relative measure of the π-acceptor properties of a ligand B, assuming that J(Pt-P-C-H) reflects the total electron density on the platinum nucleus.[5] Thus, isocyanides and tertiary phosphines[21] as ligands show J(Pt-C-H) = $\sim$63 and $\sim$57 Hz and J(Pt-P-C-H) = $\sim$34 and 29 Hz, respectively, which suggests that while both ligands are good σ donors, the phosphine is a better π acceptor. Similarly CO and isocyanide have very similar σ-donor properties but the carbonyl is a better π acceptor. Bancroft, *et al.*,[29] have recently examined a wide variety of complexes of the type [FeHL(depe)$_2$]$^+$[B(C$_6$H$_5$)$_4$]$^-$ (L = neutral ligand, depe = bis(diethylphosphino)ethane) by ^{57}Fe Mössbauer spectroscopy and have calculated the partial quadrupole splitting (pqs) for each ligand[30] (Table IV).

TABLE IV

Ligand	J(Pt-C-H), Hz	J(Pt-P-C-H), Hz	Pqs, mm/sec
CO	$\sim$63	$\sim$33	-0.43
PR$_3$	$\sim$57	$\sim$29	$\sim$$-0.53$
R-NC	$\sim$63	$\sim$34	-0.71

Nmr and Mössbauer Data for Cationic Complexes Containing CO, PR$_3$, and R-NC.—Since the partial quadrupole splitting is a measure of the total π-σ properties of a ligand, it can be seen that both the phosphine and carbonyl are much better π acceptors than isocyanides.

Phosphine exchange occurs in many platinum(0) complexes[31] and labile phosphines have been observed for several neutral platinum(II) complexes[32] with

strongly electron-donating ligands. It is difficult to conceive of labile phosphines in cationic platinum(II) complexes because the positive nuclear charge would hold the electron pairs very tightly to the platinum nucleus. We believe that the isocyanides are very effective in reducing the positive charge on platinum due to the importance of the resonance forms

$$Pt^+\!\leftarrow\!C\!\!=\!\!\ddot{N}\!-\!R \longleftrightarrow Pt\!-\!C\!\!\equiv\!\!\overset{+}{N}\!-\!R$$

Although in *neutral* platinum isocyanide complexes where the CNC bond angle is nonlinear,[33] *i.e.*, *cis*-[PtCl$_2$(CNC$_6$H$_5$)P(C$_2$H$_5$)$_3$] where the CNC bond angle is 165.5°, a more linear CNC bond angle for the *cationic* complexes would be expected due to a greater delocalization of the nitrogen electrons into the p$_z$ orbital of the electron-deficient carbon.

Therefore, in general, the greater the positive charge on the platinum, the greater would be the delocalization and the greater would be the value of $\Delta\nu$(N≡C). This is clearly shown by the fact that $\Delta\nu$(N≡C) increases in the order type III > type II > type I. In the type I complexes, the methyl group is a good electron-donating group and this tends to reduce the effective nuclear charge whereas in type II complexes the chloride is electronegative, tending to increase the positive charge resulting in a greater delocalization of the nitrogen lone pair and a greater increase in $\Delta\nu$(N≡C). Type III compounds exhibit very large positive values for $\Delta\nu$(N≡C) ($\sim$140 cm^{-1}) as would be expected due to the dipositive charge on the cation.

Treichel and Hess[18] reported a mechanism for the dealkylation of cationic methyl isocyanide complexes involving a five-coordinate intermediate. We believe that the mechanism may involve some concentration of the positive charge on nitrogen, followed by elimination of methyl halide

A similar mechanism may also be proposed for the well-known preparation of alkyl isocyanides by alkylation of the nitrogen lone pair in the metal cyanide complexes[8]

$$M\text{-}CN + RX \longrightarrow [M\text{-}CN^+\text{-}R]X^- \xrightarrow{\Delta} M^+X^- + R\text{-}NC$$

Preparation and Spectroscopic Studies of Carbene Complexes.—Carbene formation by the addition of

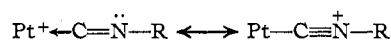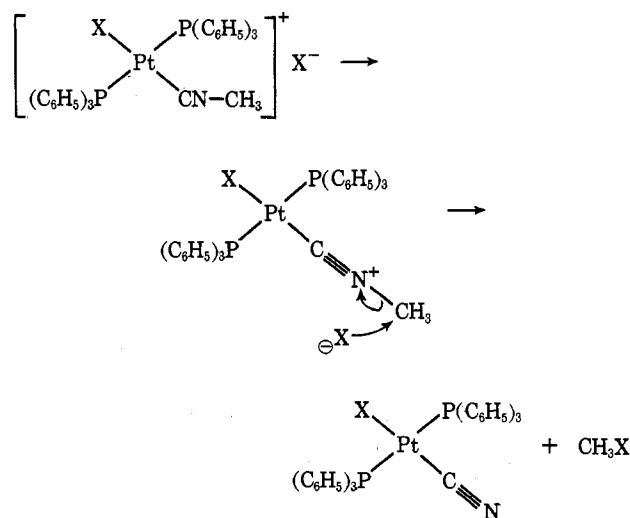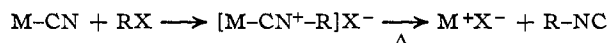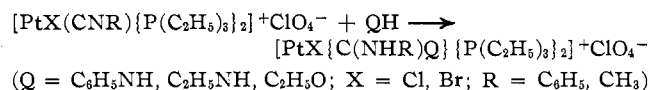(24) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

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(29) G. M. Bancroft, M. J. Mays, and B. E. Prater, *ibid.*, *A*, 956 (1970).

(30) G. M. Bancroft, personal communication.

(31) H. C. Clark and K. Itoh, *Inorg. Chem.*, **10**, 1707 (1971), and references therein.

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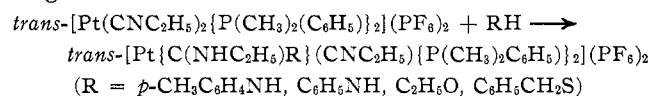(33) E. M. Badley, Ph.D. Thesis, University of Sussex, 1969.

alcohols and amines to coordinated isocyanides requires much more vigorous conditions than carbene formation from reactions involving monosubstituted acetylenes. Methoxy- and ethoxycarbene complexes[4] are obtained instantaneously by the addition of RC≡CH to a solution of *trans*-PtCH₃ClL₂ (L = tertiary phosphine or arsine) and silver hexafluorophosphate in the appropriate alcohol. In contrast neutral arylamino(alkoxy)-carbeneplatinum complexes[15] are obtained only by refluxing the appropriate isocyanide complex in alcohol for long periods of time. Reactions with amines usually proceed smoothly at room temperature within a few hours.

As the positive charge on the platinum increases, so does the difficulty in obtaining carbene complexes. Richards and coworkers[16] have prepared several carbene complexes derived from isocyanide complexes analogous to our type II

$$[PtX(CNR)\{P(C_2H_5)_3\}_2]^+ClO_4^- + QH \longrightarrow$$
$$[PtX\{C(NHR)Q\}\{P(C_2H_5)_3\}_2]^+ClO_4^-$$
$$(Q = C_6H_5NH, C_2H_5NH, C_2H_5O; X = Cl, Br; R = C_6H_5, CH_3)$$

The complexes were more difficult to obtain than the neutral carbene complexes and the ethoxycarbene was not obtained pure but only as a mixture with the parent isocyanide complex.

We have attempted to prepare cationic methylplatinum(II)–carbene complexes by refluxing the appropriate isocyanide complexes in alcohols and amines for long periods of time but unfortunately the methylplatinum compounds are not stable under these vigorous conditions. However, we have found that type III isocyanide complexes are particularly suitable for carbene formation since they are very stable under prolonged reflux conditions

$$trans\text{-}[Pt(CNC_2H_5)_2\{P(CH_3)_2(C_6H_5)\}_2](PF_6)_2 + RH \longrightarrow$$
$$trans\text{-}[Pt\{C(NHC_2H_5)R\}(CNC_2H_5)\{P(CH_3)_2C_6H_5\}_2](PF_6)_2$$
$$(R = p\text{-}CH_3C_6H_4NH, C_6H_5NH, C_2H_5O, C_6H_5CH_2S)$$

The resulting carbene complexes are very soluble in polar solvents and can easily be separated from the unreacted, poorly soluble bis-isocyanide complex by fractional crystallization. The ease of preparation decreases in the order RNH₂ > RSH ≫ ROH, and the ethoxy(amino)carbene was obtained only in 40% yield after refluxing the parent isocyanide complex in ethanol for 10 days.

The phosphine methyl resonances in the nmr appear as 1:2:1 triplets, indicative of mutually trans phosphines, flanked by platinum satellites of one-fourth intensity with J(Pt–P–C–H) ≃ 32 Hz. Elucidation of the stereochemistry comes from the ¹H nuclear magnetic resonance spectra in the phosphine methyl region. Four sets of overlapping triplets are observed (Figure 2) indicating four nonequivalent phosphine methyls caused by the absence of a plane of symmetry along the C–Pt–C axis and restricted rotation of the carbene about the Pt–C bond. The nmr spectra also indicate the presence of only one isomer in solution and the most likely structures are those resulting from a 1,2 cis addition of the nucleophile across the CN triple bond
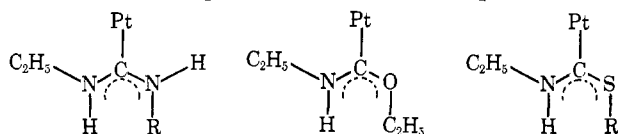

Figure 2.—Phosphine methyl resonances of *trans*-[Pt(CNC₂H₅)-{P(CH₃)₂(C₆H₅)}₂{C(NHC₆H₄CH₃)(NHC₂H₅)}](PF₆)₂ recorded on a CH₂Cl₂ solution at 31° with an HA100 spectrometer using a sweep width of 500 Hz, showing four nonequivalent phosphine methyls and the anilino methyl at δ 2.31. The scheme indicates platinum coupling to the phosphine methyls and phosphorus coupling is omitted for clarity.

The X-ray structure by Richards, *et al.*,[14] indeed shows that such cis addition may occur and that the carbene plane may then be perpendicular to the plane of the complex. It is difficult to predict, *a priori*, whether this is the most stable configuration. In the completely planar structure extensive π bonding involving the carbene carbon $2p_z$ and platinum $5d_{zz}$ orbitals is possible, although there must also be considerable steric interaction between the carbene and the phosphines. That the structure with the carbene perpendicular to the plane of the complex has been observed, in which the carbene carbon $2p_z$ orbital is competing with the phosphines for in-plane π bonding with the Pt $5d_{xy}$ orbitals, suggests that π-bonding possibilities are less important than steric requirements.

Since an increase in the isocyanide stretching frequency, $\Delta\nu$(N≡C), reflects the total positive charge on platinum, the carbene is shown to be a stronger σ donor than the parent isocyanide (Table III). A comparison of J(Pt–C–H) for the complexes *trans*-[PtCH₃L{P-(CH₃)₂C₆H₅}₂]⁺, where L = methoxycarbene[4] and ethyl isocyanide, gives values of 51 and 63 Hz, respectively, again indicating the better σ-donor properties of the carbene. In the methoxy(amino)carbene complex *cis*-PtCl₂(CNR){C(OCH₃)NHR} (R = *p*-tolyl, cyclohexyl) a higher trans influence for the carbene than the isocyanide has been suggested on the evidence of a lower ν(Pt–Cl) frequency than that found in the parent isocyanide complex[17] *cis*-Pt(CNR)₂Cl₂.

Mechanism for Carbene Formation.—The mechanism for carbene formation derived from acetylenic complexes involves nucleophilic attack by the alcohol

at a π-bonded acetylene followed by alkyl or aryl transfer to give the carbene[4]
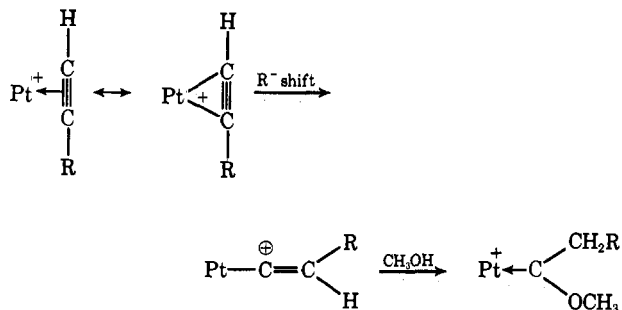
It is very unlikely that the CN triple bond would π bond because the π orbitals are much higher in energy than the carbon σ-bonding orbital. Richards suggested[15] that the nitrogen might be activated toward electrophilic attack by a proton but, clearly, since amines react much faster than alcohols, the rate-determining step must involve nucelophilic attack at the electron-deficient isocyanide carbon of the complex.

Experimental Section

p-Tolyl isocyanide, *p*-nitrophenyl isocyanide, and phenyl isocyanide were prepared by the phosgene method,[34] *p*-methoxyphenyl isocyanide was prepared by the method of Hertler and Corey,[35] and methyl and ethyl isocyanides were prepared by the method of Casanova, Schuster, and Werner.[36]

All reactions were carried out under a nitrogen atmosphere and Spectro Grade solvents were used without further purification. Microanalyses were performed by Chemalytics Inc., Tempe, Ariz. Infrared spectra were recorded on Beckman IR 10 and IR 7 spectrometers as 2.0% by weight KBr disk and were unchanged as Nujol mulls. Raman spectra were obtained from crystalline samples in capillary tubes using a Spex Model 1400 spectrometer with the 6328-Å line of the helium–neon laser. Proton nmr spectra were recorded on Varian T60 and HA100 spectrometers using dichloromethane as solvent as well as internal standard.

trans-PtCH$_3$ClL$_2$, where L = dimethylphenylphosphine or methyldiphenylphosphine, was prepared by the method of Ruddick and Shaw.[23,37]

Many of the complexes were prepared by similar methods so only representative examples are described.

(a) **Preparation of** [PtCH$_3${P(CH$_3$)$_2$(C$_6$H$_5$)}$_2$(CNC$_6$H$_4$OCH$_3$)]$^+$-(PF$_6$)$^-$.—To a suspension of *trans*-PtCH$_3$Cl{ P(CH$_3$)(C$_6$H$_5$)}$_2$ (0.194 g) in 10 ml of methanol was added silver hexafluorophosphate (0.094 g). A flocculent precipitate of silver chloride formed immediately and the solution was magnetically stirred for 10 min to allow complete removal of the chloride and coagulation of the silver chloride. The silver chloride was removed by centrifugation to give a clear, colorless solution. *p*-Methoxyphenyl isocyanide (0.0494 g) was slowly added and a white precipitate formed immediately. The mixture was stirred for 10 min and filtered and then washed with methanol and ether. The product was recrystallized from hot methanol to give white needles of [PtCH$_3$-{ P(CH$_3$)$_2$(C$_6$H$_5$)}(CNC$_6$H$_4$OCH$_3$)]$^+$(PF$_6$)$^-$ (0.165 g).

(b) **Preparation of** PtCH$_3$Cl[P(CH$_3$)$_2$(C$_6$H$_5$)]$_2$(CNC$_6$H$_4$OCH$_3$).—To a solution of *trans*-PtCH$_3$Cl{ P(CH$_3$)$_2$(C$_6$H$_5$)}$_2$ (0.157 g) in 10 ml of benzene was added *p*-methoxyphenyl isocyanide (0.040 g). An oily precipitate formed immediately and the solution was stirred for 15 min. The white solid was filtered, washed with benzene and ether, and then recrystallized from hot benzene to give white crystals of PtCH$_3$Cl{ P(CH$_3$)$_2$(C$_6$H$_5$)}$_2$(CNC$_6$H$_4$OCH$_3$) (0.070 g).

(c) **Preparation of** [PtCH$_3${ P(CH$_3$)$_2$(C$_6$H$_5$)}$_2$(CNC$_6$H$_4$NO$_2$)]$^+$-[B(C$_6$H$_5$)$_4$]$^-$.—To a suspension of *trans*-PtCH$_3$Cl{ P(CH$_3$)$_2$-(C$_6$H$_5$)}$_2$ (0.200 g) in 10 ml of methanol was added silver hexa-

fluorophosphate (0.097 g). The solution was stirred for 10 min and the silver chloride was removed by centrifugation to give a clear solution. A solution of *p*-CNC$_6$H$_4$NO$_2$ (0.057 g) in 5 ml of hot methanol was added to give a clear yellow solution. The methanol was removed on a rotary evaporator to give a yellow oil that could not be crystallized from dichloromethane and ether. Accordingly, it was dissolved in 5 ml of methanol, and sodium tetraphenylborate (0.132 g) in 2 ml of methanol was slowly added to give a yellow solution. The methanol was removed, the complex was extracted from the sodium hexafluorophosphate with dichloromethane, and the solution was then passed through a 1-in. Florisil column. Methanol was added until the solution became cloudy and the flask was then cooled at $-10°$ overnight to yield large orange crystals of *trans*-[PtCH$_3${ P(CH$_3$)$_2$(C$_6$H$_5$)}$_2$(CNC$_6$H$_4$NO$_2$)][B(C$_6$H$_5$)$_4$] (0.233 g).

(d) **Preparation of** *cis*-Pt(CH$_3$)$_2$(CNC$_6$H$_4$OCH$_3$)[P(CH$_3$)$_2$(C$_6$-H$_5$)].—A solution of *cis*-Pt(CH$_3$)$_2$[P(CH$_3$)$_2$(C$_6$H$_5$)]$_2$ (0.146 g) and *p*-methoxyphenyl isocyanide (0.039 g) in 10 ml of benzene was stirred for 3 hr. A strong smell of phosphine was detected. The benzene was then removed under reduced pressure to give a yellow oil which was taken up in 2 ml of diethyl ether and passed through a short Florisil column. Addition of pentane to the ether solution yielded large white needles of *cis*-Pt(CH$_3$)$_2$(CN-C$_6$H$_5$OCH$_3$)[P(CH$_3$)$_2$(C$_6$H$_5$)] (0.120 g).

(e) **Preparation of** *cis*-PtCH$_3$Cl(CNC$_6$H$_4$OCH$_3$)[P(CH$_3$)$_2$(C$_6$-H$_5$)].—*cis*-Pt(CH$_3$)$_2$(CNC$_6$H$_4$OCH$_3$){ P(CH$_3$)$_2$(C$_6$H$_5$)} (0.111 g) was dissolved in 3 ml of diethyl ether and acetyl chloride (0.0174 g) was added. The flask was cooled at $-10°$ for 12 hr and white crystals separated. The ether was removed under reduced pressure and the white crystals were recrystallized from dichloromethane and ether to give *cis*-PtCH$_3$Cl(CNC$_6$H$_4$OCH$_3$){ P(CH$_3$)$_2$-(C$_6$H$_5$)} (0.055 g).

(f) **Preparation of** [PtCH$_3$(CNC$_6$H$_4$OCH$_3$)(CNC$_6$H$_4$CH$_3$){ P-(CH$_3$)$_2$C$_6$H$_5$}]$^+$(PF$_6$)$^-$.—To a solution of PtCH$_3$Cl(CNC$_6$H$_4$-OCH$_3$){ P(CH$_3$)$_2$(C$_6$H$_5$)}$_2$ (0.185 g) and *p*-tolyl isocyanide (0.040 g) in 10 ml of methanol was added AgPF$_6$ (0.095 g). A thick white precipitate formed immediately. The solution was stirred for 10 min, then heated to 60°, and filtered to remove the silver chloride. On cooling, white plates separated which were filtered and washed with ether and then recrystallized from dichloromethane and ether to give [PtCH$_3$(CNC$_6$H$_4$OCH$_3$)-(CNC$_6$H$_4$CH$_3$){ P(CH$_3$)$_2$(C$_6$H$_5$)}]$^+$(PF$_6$)$^-$ (0.082 g).

(g) **Preparation of** [PtCH$_3$(CNC$_6$H$_4$CH$_3$){ P(CH$_3$)$_2$(C$_6$H$_5$)}$_2$]$^+$-(PF$_6$)$^-$.—To a suspension of *cis*-PtCl$_2${ P(CH$_3$)$_2$(C$_6$H$_5$)}$_2$ (0.208 g) in 10 ml of methanol was added AgPF$_6$ (0.095 g) in 2 ml of methanol. The mixture was stirred for 10 min and the silver chloride was removed by centrifugation to give a pale yellow solution. *p*-Tolyl isocyanide (0.044 g) was added and the solution turned colorless and a white precipitate formed. The volume of the solvent was reduced and the solid was filtered, washed with ether, and recrystallized from hot methanol to give [PtCl(CNC$_6$H$_4$CH$_3$){ P(CH$_3$)$_2$(C$_6$H$_5$)}$_2$]$^+$(PF$_6$)$^-$ (0.128 g).

(h) **Preparation of** [Pt(CNC$_2$H$_5$)$_2${ P(CH$_3$)(C$_6$H$_5$)$_2$}$_2$](BF$_4$)$_2$.—Ethyl isocyanide (0.029 g) was added to a suspension of *cis*-Cl$_2$Pt{ P(CH$_3$)(C$_6$H$_5$)$_2$}$_2$ (0.176 g). The resulting clear, colorless solution was stirred for 10 min and NaBF$_4$ (0.058 g) in methanol was added. A slight precipitate formed and the methanol was removed under reduced pressure. The complex was extracted with 10 ml of dichloromethane. The solution was filtered and ether was then added dropwise to give white crystals of [Pt-(CNC$_2$H$_5$)$_2${ P(CH$_3$)(C$_6$H$_5$)$_2$}](BF$_4$)$_2$ (0.187 g).

(i) **Preparation of** [Pt(CNC$_2$H$_5$){ C(NHC$_2$H$_5$)(NHC$_6$H$_5$)}]{ P-(CH$_3$)$_2$C$_6$H$_5$}$_2$](PF$_6$)$_2$.—A suspension of [Pt(CNC$_2$H$_5$)$_2${ P(CH$_3$)$_2$-C$_6$H$_5$}$_2$](PF$_6$)$_2$ (0.350 g) in 10 ml of tetrahydrofuran and 2 ml of aniline was refluxed for 24 hr to give a clear solution. The solvents were removed under vacuum to give a clear yellow oil which was dissolved in dichloromethane and chromatographed through a short Florisil column. The dichloromethane was removed on a rotary evaporator and the clear, colorless oil was dissolved in methanol. Diethyl ether was added until the solution became slightly cloudy; then the flask was placed in a refrigerator at $-10°$ for 2 days to yield white crystals of [Pt(CNC$_2$H$_5$)$_2${ C-(NHC$_2$H$_5$)(NHC$_6$H$_5$){ P(CH$_2$)$_2$C$_6$H$_5$}$_2$] (PF$_6$)$_2$ (0.153 g).

(j) **Preparation of** [Pt(CNC$_2$H$_5$){ C(NHC$_2$H$_5$)(OC$_2$H$_5$)}{ P(CH$_3$)$_2$-C$_6$H$_5$}$_2$] (PF$_6$)$_2$.—A suspension of [Pt(CNC$_2$H$_5$)$_2${ P(CH$_3$)$_2$C$_6$H$_5$}$_2$]-(PF$_6$)$_2$ (0.400 g) was refluxed in ethanol for 10 days to give a dirty yellow solution. The methanol was removed under vacuum and the resulting oil was chromatographed as above with dichloromethane. The solvent was removed on a rotary evaporator and the oil was dissolved in methanol. The addition of

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diethyl ether and subsequent cooling at $-10°$ yielded off-white crystals of $[Pt(CNC_2H_5)\{C(NHC_2H_5)(OC_2H_5)\}\{P(CH_3)_2C_6H_5\}_2]$-$(PF_6)_2$ (0.087 g).

(k) **Preparation of** $[Pt(CNC_2H_5)\{C(NHC_2H_5)(SCH_2C_6H_5)\}$-$\{P(CH_3)_2C_6H_5\}_2](PF_6)_2$.—The above thioalkoxy(amino)carbene complex was prepared by method (i) using 2 ml of the α-toluenethiol. All operations were performed in a fume hood. Yield of the carbene was 40% after purification.

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New Theoretical and Spectral Studies of Uranium(V) Compounds

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The theory of $5f^1$ systems has been extended from O_h symmetry species, such as UX_6^-, to "tetragonally" distorted, more recently prepared species, UOX_5^{2-} ($X^- = F^-$, Cl^-, Br^-). The semiempirical calculation was carried out specifically for $UOCl_5^{2-}$, by beginning with the $5f^1$ energy levels of U^{5+} (in UCl_6^-) split by the O_h crystal field and by the spin-orbit coupling and perturbed by the effects of the lower symmetry field. The results (using the O_h notation) are that (1) the $\Gamma_7 \rightarrow \Gamma_7'$ transition is left nearly unaltered, (2) the Γ_8 and Γ_8' quadruplet levels are significantly split, (3) the Γ_8 level leads to a very low-lying electronic band, (4) the Γ_6 energy is greatly increased, and (5) the average g value is left relatively unchanged. A careful study of the spectrum of $UOCl_5^{2-}$ in the $300–25,000\text{-cm}^{-1}$ range and of the esr spectrum has demonstrated the accuracy of these predictions. We feel there is now an understanding of the electronic and esr spectra of UOX_5^{2-} and other U(V) compounds whose structures are less certain. New complexes of the UO^{3+} entity are reported.

Introduction

There have been relatively few spectral studies for compounds of uranium(V),[1-4] primarily because of the unavailability of compounds and the great instability of most of those which are known. Nevertheless, the electronic simplicity of this chemical system, $[Rn]5f^1$, presents some unusual opportunities for obtaining a deeper understanding of internal 5f electronic transitions generally and specifically the case of *intermediate* ligand fields not perturbed by interelectron repulsion. With the recently published work of Ryan[3] and with our own recent experimental studies, we now have electronic spectral data on the octahedral species, UF_6^-, UCl_6^-, and UBr_6^-, as well as on the series of lower symmetry new monooxo species, UOF_5^{2-}, $UOCl_5^{2-}$, and $UOBr_5^{2-}$. It therefore seemed appropriate to reexamine the theory of the $5f^1$ system in O_h and to then extend this to lower symmetry species. These new theoretical results are reported in this paper. The new results have also made it possible to rationalize the general features of the spectra of other uranium(V) solid compounds and solution species whose structures are unknown. In addition, we report a new route to $UOCl_5^{2-}$, its esr spectrum, and the first preparations of complexes of monooxouranium(V), UO^{3+}, containing ligands other than just halide ions.

Experimental Section

A. Preparation of Compounds. 1. $UCl_5 \cdot TCAC$ (TCAC = Trichloroacryloyl Chloride, $Cl_2C=CClCOCl$).—This was prepared as previously described.[2] Since it, as well as most compounds of uranium(V), is extremely sensitive to both O_2 and H_2O, most

preparative and handling work was carried out in a steel drybox with a nitrogen atmosphere rigorously free of oxygen and moisture.

2. $[(C_2H_5)_4N_2]UOCl_5$, Tetraethylammonium Oxopentachlorouranate(V).—Undried tetraethylammonium chloride was dissolved to approximate saturation in nitromethane. The solution was then diluted 10-fold with undried acetone, filtered, and then poured into a flask containing solid (red-orange) $UCl_5 \cdot$ TCAC (about 50 ml of solution per gram of solid). The blue compound which formed immediately was filtered, washed with dried (using anhydrous $CaSO_4$) acetone, and then dried in a stream of dry nitrogen. It proved in every way to be the same compound prepared by Ryan,[3] who used $(C_2H_5)_4NUCl_6$ as starting material. *Anal.* Calcd for $C_{16}H_{40}N_2UOCl_5$: C, 27.78; H, 5.83; N, 4.05. Found: C, 27.61; H, 5.93; N, 4.06.

3. $[(C_2H_5)_4N]_2UOCl_5 \cdot C_8H_6N_2$, Tetraethylammonium Oxopentachlorouranate(V)–Phthalazine Adduct.[5]—Undried tetraethylammonium chloride was dissolved to approximate saturation in spectroquality nitromethane, diluted 10-fold with undried reagent grade acetone, and filtered. The reagent grade phthalazine (recrystallized from ethyl ether and vacuum sublimed) was dissolved in this solution and the resulting solution was added to a flask containing solid $UCl_5 \cdot TCAC$. (A slight excess over 1:1 mole ratio of the phthalazine was used.) The immediate reaction produced a bright green solid, which was filtered, washed with dry acetone, and dried in a stream of dry nitrogen. The electronic spectrum of the product showed that it contained no more than 1-3% U(IV) and U(VI) species. It was characterized by dta, tga, electronic spectra, and ir spectra. *Anal.* Calcd for $C_{16}H_{40}N_2UOCl_5 \cdot C_8H_6N_2$: C, 35.07; H, 5.64; N, 6.82. Found: C, 33.98; H, 5.61; N, 6.68.

4. $[(C_2H_5)_4N]_2UOCl_5 \cdot 2C_{12}H_8N_2$, Tetraethylammonium Oxopentachlorouranate(V)–Bis(1,10-phenanthroline) Adduct.[5]—Undried $(C_2H_5)_4NCl$ was dissolved to approximate saturation in spectroquality nitromethane, then diluted 10-fold with undried reagent grade acetone, and filtered. To 50 ml of this solution was added 0.831 g (4.61 mmol) of *o*-phenanthroline as purchased from Aldrich Chemical Co. The resulting solution was then

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(5) We cannot name our compound more precisely yet since we do not know for sure, but only surmise, that the organic ligands are bonded directly to the uranium in the UO^{3+} replacing chlorides from the first coordination sphere.