

halogen. As Figures 8–11 indicate, this is in full accord with the expectation based on the pes spectra.

Thermodynamic Threshold. The thermodynamic thresholds for the observed photodissociation processes (calculated from reported heats of formation)¹⁰ are listed in Table I and marked (vertical slash) in each ion spectrum. For most of the ions examined there was only one heat of formation available¹⁰ for the photodissociation product ion of the observed (substituted benzene) empirical formula. It was necessarily assumed that the product ion of the photodissociation process was of the same isomeric configuration as that observed in the literature.¹⁰ With one exception (*N,N*-dimethylaniline) no photodissociation peaks were observed below the calculated thresholds.

In the case of *N,N*-dimethylaniline the only available heat of formation for the observed ($P - 1$) photodissociation product is 217 kcal mol⁻¹ (obtained by photoionization).¹¹ This yields a heat of dissociation of 3.69 eV, which is ~ 1.4 eV above the onset of the lowest observed pds peak. This implies that the reported heats of formation are incorrect by approximately 32 kcal mol⁻¹ or that the ions of the observed photodissociation (parent or product) are of a different isomeric form than that obtained by the photoionization process.¹¹ Rearrangement of the observed parent ion seems unlikely in view of the strong correspondence of the pds and pes peaks for *N,N*-dimethylaniline as seen in Figure 14.

The heat of dissociation can be calculated for alterna-

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tive dissociation pathways for most of the ions examined. In each case the alternative path is more endothermic by at least 0.5 eV. Even though this alternative threshold may be within the energy range of excitation (<6 eV), the ion essentially always dissociates along the lower energy path. This is in accord with the predictions of the quasiequilibrium theory of unimolecular decay and is also in accord with the observed most probable fragmentation process for all of these ions from mass spectroscopy.¹²

Conclusion

The present results represent the first extensive series of photodissociation spectra reported for the wide range of energies used. The striking and distinctive spectral peaks found for these ions have potential value in understanding the electronic properties of the ions. The degree of correspondence found between the photodissociation results and the pes spectra is sufficient to give confidence that the two techniques are indeed comparable in the expected way and that the ions examined by the two techniques are structurally similar. The substantial differences in the spectra produced by the two techniques clearly provide opportunities for fruitful comparison.

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Platinum and Palladium Complexes Formed by Chelative Addition of Amines to Isocyanides

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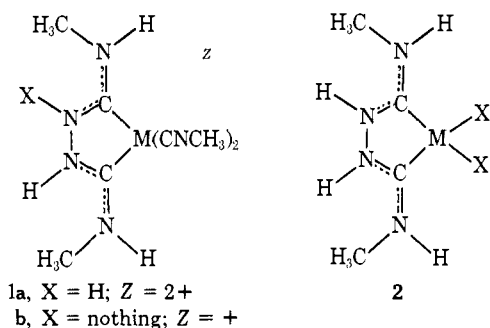
Abstract: The addition of amines to coordinated isocyanides has been explored as a method of preparing new chelating ligands. The reaction of amidines and 2-aminopyridine with $\text{Pt}(\text{CNCH}_3)_4^{2+}$ produces complexes of the type (chelate) $\text{Pt}(\text{CNCH}_3)_2^{2+}$ containing bidentate ligands which utilize one imine nitrogen donor and one trigonal carbon donor. Biacetyldihydrazone reacts with $\text{M}(\text{CNCH}_3)_4^{2+}$ ($\text{M} = \text{Pd}, \text{Pt}$) to produce a bidentate ligand which contains two trigonal carbon donors, one of which is incorporated into an imidazole ring. The addition of 2,6-diaminopyridine to $\text{M}(\text{CNCH}_3)_4^{2+}$ produces a tridentate ligand with one pyridine nitrogen donor and two trigonal carbon donors. These new complexes have been isolated and characterized by elemental analysis, conductivities, and infrared and proton magnetic resonance spectra. The properties of these complexes and the related cations obtained by the addition of hydrazine to $\text{M}(\text{CNCH}_3)_4^{2+}$ are compared. The new chelating ligands undergo reversible loss (or gain) of protons and the sites of these reactions have been elucidated. The electronic spectra of these complexes in solution are sensitive to the site of the proton transfer. In the solid state certain of these complexes exhibit electronic absorptions which are not found in their solutions. It is suspected that these additional absorptions result from the formation of stacks of complexes in the solid state so that chains of metal atoms result. In general the new chelating ligands and their complexes are very stable to acidic and oxidizing conditions, and it has been possible to oxidize some Pt(II) complexes to Pt(IV) species by the addition of halogens.

Although considerable effort has been expended on the design and synthesis of chelating ligands,¹ the

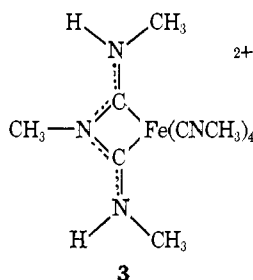
(1) For examples see D. St. C. Black and A. J. Hartshorn, *Coord. Chem. Rev.*, **9**, 219 (1973).

number of chelating ligands involving simple carbon donors (excluding, that is, π -complexes) is relatively small. In this report we develop the use of the reaction between isocyanide ligands and nitrogen bases for the

construction of chelating ligands. It has been shown that bifunctional nucleophiles such as hydrazine and hydroxylamine will add to a pair of cis isocyanide ligands to produce compounds such as **1** and **2** ($M = \text{Pt}, \text{Pd}$;



X = halide)²⁻⁶ as well as analogous six-coordinate iron⁷ and ruthenium⁸ complexes. In a related but so far unique reaction primary amines react with $\text{Fe}(\text{CNCH}_3)_6^{2+}$ to give the four-membered chelate ring present in **3**;^{9,10}



more generally primary and secondary amines simply add to a single isocyanide ligand. The ligands formed in these reactions belong to the class of the so-called carbene donors.¹¹

The chemical behavior of chelates of this type, the range of ligands which may be constructed, and the properties which those ligands confer on the metals they bind have not been extensively investigated. This work on the scope of chelate ring formation has utilized palladium and platinum as metals because, in addition to generally exhibiting well-defined square-planar geometry, these metals form stable metal-ligand bonds, especially with carbon, but at the same time the metal ligand bonds are sufficiently labile to allow other donors to enter the coordination sphere.

It should also be noted that two other types of chelate ligands have been prepared from isocyanides. One group has been obtained through the multiple insertion of isocyanides into metal-alkyl bonds¹² and the second

from the addition of tetrahydroborate to coordinated isocyanides.^{13,14}

Experimental Section

Preparation of Compounds. Methyl isocyanide¹⁵ (*toxic*), *N,N'*-dimethylformamide,¹⁶ biacetyldihydrazone,¹⁷ and the complexes **1** and **2**⁵⁻⁶ were obtained through established procedures; all other chemicals were obtained through commercial sources.

$[(\text{C}_6\text{H}_5\text{N}_3)\text{Pt}(\text{CNCH}_3)_2]\text{BF}_4 \cdot \text{H}_2\text{O}$ (**4b**). The following procedure was utilized for the preparation of most complexes. Methyl isocyanide (0.5 ml) was added to a solution of 0.5 g of potassium tetrachloroplatinate(II) in 7 ml of water. After the addition of 3 ml of a saturated aqueous solution of sodium tetrafluoroborate, the mixture was filtered and a solution containing 0.5 g of acetamide hydrochloride and 0.2 g of sodium hydroxide in 5 ml of water was added. The orange crystalline product which formed was collected after the mixture had stood for 1 hr. After washing with water and vacuum drying, the product was recrystallized from acetone-methanol to produce the red modification of the complex. The yellow form of the salt was obtained by adding ether slowly to a warm (40°) nitromethane solution of the complex. The two forms are readily interconvertible and dissolve to give solutions with identical properties. The yield was 0.47 g. Conductivity, $\Lambda = 100 \text{ cm}^2 \text{ mol}^{-1} \text{ ohm}^{-1}$.

Anal. Calcd: C, 20.01; H, 3.36; N, 14.59. Found: C, 19.80; H, 2.75; N, 15.04.

$[(\text{C}_5\text{H}_9\text{N}_3)\text{Pt}(\text{CNCH}_3)_2]\text{BF}_4$ (**5b**). This complex was prepared from *N,N'*-dimethylformamide by the procedure described for **4b**. The bright yellow crystalline solid, which dissolved to give colorless solutions, was recrystallized from acetonitrile-2-propanol (yield 30%). Conductivity, $\Lambda = 109 \text{ cm}^2 \text{ mol}^{-1} \text{ ohm}^{-1}$.

Anal. Calcd: C, 22.70; H, 3.39; N, 14.17. Found: C, 22.68; H, 3.35; N, 14.60.

$[(\text{C}_5\text{H}_9\text{N}_3)\text{Pt}(\text{CNCH}_3)_2][\text{BF}_4]_2$ (**5a**). Two drops of aqueous tetrafluoroboric acid were added to a suspension of 82 mg of **5b** in 3 ml of acetonitrile. The colorless solution was filtered and crystallization was induced by the gradual addition of ether to give 66 mg (68%) of colorless crystals. Conductivity, $\Lambda = 204 \text{ cm}^2 \text{ mol}^{-1} \text{ ohm}^{-1}$.

Anal. Calcd: C, 19.17; H, 3.04; N, 12.42. Found: C, 19.41; H, 3.23; N, 12.43.

$[(\text{C}_5\text{H}_9\text{N}_3)\text{Pt}(\text{CNCH}_3)_2]\text{BF}_4 \cdot 2\text{H}_2\text{O}$ (**6b**). This complex was obtained from 2-aminopyridine by the method outlined for **4b**. The yellow-orange product, which was obtained in 40% yield, was carefully recrystallized from warm (60°) water. Conductivity, $\Lambda = 112 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$.

Anal. Calcd: C, 24.73; H, 3.40; N, 13.11. Found: C, 24.83; H, 2.80; N, 13.10.

$[(\text{C}_8\text{H}_{13}\text{N}_3)\text{Pt}(\text{CNCH}_3)_2]\text{BF}_4$ (**7b**). This complex was prepared from 2-amino-6-methylpyridine by the procedure described for **4b**. The yellow-orange product was recrystallized from acetonitrile.

Anal. Calcd: C, 28.14; H, 3.15; N, 13.67. Found: C, 27.60; H, 3.06; N, 13.44.

$[(\text{C}_5\text{H}_9\text{N}_3)\text{Pd}(\text{CNCH}_3)_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (**8**). Methyl isocyanide (0.5 ml) was added to a slurry of 0.4 g of palladium(II) chloride in 10 ml of water. After filtration, a solution of 0.2 g of 2,6-diaminopyridine in 5 ml of water was added to the filtrate. The yellow precipitate which formed was collected and washed with water. Purification was achieved through recrystallization from water acidified with two drops of hydrochloric acid.

Anal. Calcd: C, 29.65; H, 4.52; N, 18.86. Found: C, 29.36; H, 4.45; N, 18.71.

$[(\text{C}_8\text{H}_{13}\text{N}_3)\text{Pt}(\text{CNCH}_3)_2][\text{BF}_4]_2 \cdot 2\text{H}_2\text{O}$ (**9**). Methyl isocyanide (0.5 ml) and a solution of 0.20 g of 2,6-diaminopyridine in 3 ml of water were added successively to a solution of 0.4 g of potassium tetrachloroplatinate(II) in 7 ml of water. The red solid which formed was collected and washed with cold water. This solid was dissolved in a minimum volume of water and the solution was filtered.

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Aqueous tetrafluoroboric acid was added to the filtrate whereupon yellow crystals of the product formed. The complex may be recrystallized from water containing a few drops of tetrafluoroboric acid (yield 0.27 g, 48%).

Anal. Calcd: C, 20.74; H, 3.17; N, 13.19. Found: C, 20.62; H, 2.99; N, 12.97.

$[(C_9H_{13}N_6)Pt(CNCH_3)_2][BF_4]_2$ (**10**). A solution of 98 mg of iodine in 7 ml of acetonitrile was added dropwise to a solution of 198 mg of **9** in 7 ml of acetonitrile. The brown solution was filtered and 1 ml of aqueous tetrafluoroboric acid was added. Upon cooling the solution, brown microcrystals of the product formed; these were collected and washed with acetonitrile and ether and air dried (yield 70 mg). An additional 100 mg of product was obtained by allowing the mother liquor to partially evaporate to produce a total yield of 64%.

Anal. Calcd: C, 15.46; H, 1.89; N, 9.83. Found: C, 15.64; H, 2.01; N, 9.72.

$[(C_8H_{13}N_4)Pd(CNCH_3)_2]BF_4$ (**11**). This complex was prepared from biacetyldihydrazone and sodium tetrachloropalladate(II) by the procedure described for **4b**.

Anal. Calcd: C, 32.72; H, 4.35; N, 19.08. Found: C, 33.18; H, 4.47; N, 18.86.

$[(C_8H_{13}N_4)Pt(CNCH_3)_2]BF_4$ (**12**). This salt was obtained from biacetyldihydrazone by the procedure described for **4b** (yield 57%). The yellow product was recrystallized from nitromethane-1-propanol.

Anal. Calcd: C, 27.23; H, 3.62; N, 15.88. Found: C, 27.50; H, 3.61; N, 16.02.

$C_4H_{10}N_4PtI_4$ (**13**). A solution of 0.14 g (0.56 mmol) of iodine in 20 ml of acetone was added to a solution of 0.30 g (0.54 mmol) of **2** (X = I) dissolved in a minimum amount of acetone. After mixing, the solution was evaporated to one-third its volume and ether was added to precipitate the brown crystalline product, yield 0.36 g, 81%. Purification was accomplished by recrystallization from acetone-ether, m.p. 270–285° dec.

Anal. Calcd: C, 5.88; H, 1.23; N, 6.85; I, 62.14. Found: C, 5.87; H, 1.00; N, 6.79; I, 62.15.

$(C_4H_{10}N_4)PtBr_4$ (**13**). A solution of 0.22 g of bromine dissolved in a mixture of 10 ml of water and 1.5 ml of hydrobromic acid was added to a slurry of 0.47 g (0.10 mmol) of **2** (X = Br) in 15 ml of water. The yellow solution was filtered and the filtrate was concentrated by heating on a steam bath until yellow crystals formed. The product (0.50 g, 79%) was collected by filtration from the cooled mother liquor and purified by recrystallization from 10% hydrobromic acid.

Anal. Calcd: C, 7.63; H, 1.60; N, 8.91; Br, 50.82. Found: C, 7.69; H, 1.61; N, 8.81; Br, 50.56.

$(C_4H_{10}N_4)PtCl_4$ (**13**). Chlorine was passed through a slurry of 0.5 g of **2** (X = Cl) in a mixture of 40 ml of water and 2 ml of concentrated hydrochloric acid. The mixture was warmed until most of the solid dissolved and then it was filtered. The filtrate was concentrated by evaporation on a steam bath until the product began to separate as yellow crystals. After cooling the product was collected and recrystallized from 2 M hydrochloric acid, yield 0.12 g.

Anal. Calcd: C, 10.65; H, 2.23; N, 12.42. Found: C, 11.11; H, 2.09; N, 13.14.

Adducts with Electron Acceptors. The following adducts were prepared by mixing saturated acetone solutions containing the appropriate metal complex and the organic acceptor. Generally the adduct crystallized immediately from solution. The adduct was collected by filtration, washed with cold acetone, and vacuum dried.

$C_4H_{10}N_4PtI_2 \cdot C_8Cl_4O_3$. The adduct of **2** (X = I, M = Pt) with tetrachloroterphthalic anhydride was crystallized as fine yellow needles.

Anal. Calcd: C, 16.98; H, 1.19; N, 6.60. Found: C, 16.78; H, 0.95; N, 6.46.

$C_4H_{10}N_4PtI_2 \cdot C_6H_3(NO_2)_3$. The adduct of **2** (X = I, M = Pt) with 1,3,5-trinitrobenzene was obtained as yellow needles, mp 263–266° dec.

Anal. Calcd: C, 15.47; H, 1.69; N, 12.63. Found: C, 15.63; H, 1.72; N, 12.67.

$C_4H_{10}N_4PtI_2 \cdot C_8Br_4O_3$. The adduct of **2** (X = I, M = Pt) with tetrabromoterphthalic anhydride formed yellow needles, mp 270–295° dec.

Anal. Calcd: C, 14.26; H, 1.00; N, 5.54. Found: C, 14.04; H, 0.83; N, 5.45.

$C_4H_{10}N_4PdI_2 \cdot C_8Cl_4O_3$. The adduct of **2** (X = I, M = Pd) with

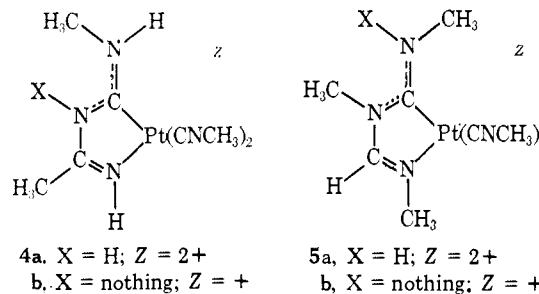
tetrachloroterphthalic anhydride separated as fine yellow needles, mp 200–240° dec.

Anal. Calcd: C, 18.96; H, 1.33; N, 7.37. Found: C, 18.99; H, 1.34; N, 7.45.

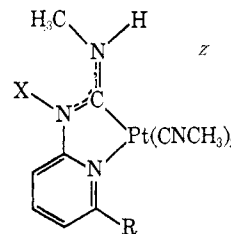
Physical Measurements. The instrumentation and techniques utilized have been described previously.^{4,5,7,8} Conductivities were measured in 10^{-3} M solutions in nitromethane.

Results

Preparation of New Chelating Ligands. The additions of aminopyridines and amidines to $M(CNCH_3)_4^{2+}$ follow a common pattern in which both addition to and displacement of isocyanide ligands occur. Acetamidine and *N,N'*-dimethylformamidine react with $Pt(CNCH_3)_4^{2+}$ to yield the chelating ligands in **4** and **5**,



respectively. Similarly 2-aminopyridine and 2-amino-6-methylpyridine react with $Pt(CNCH_3)_4^{2+}$ to produce **6** and **7**. These complexes were prepared from aqueous

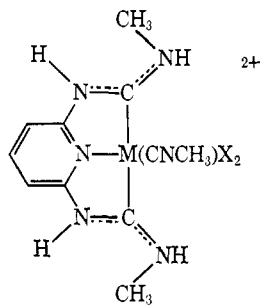


6a, X = H; R = H; Z = 2+
b, X = nothing; R = H; Z = +
7a, X = H; R = CH₃; Z = 2+
b, X = nothing; R = CH₃; Z = +

solutions of $Pt(CNCH_3)_4^{2+}$ (which was obtained by adding methyl isocyanide to $PtCl_4^{2-}$ in water⁴) and the cations were isolated as the tetrafluoroborate salts. Once isolated the complexes are quite stable. They are unaffected by water (and in some cases may be recrystallized from water), by mildly acidic conditions, or by oxygen. However, they do gradually decompose under the mildly basic conditions of their preparation. Consequently the preparative procedure was developed to allow removal of the complex from solution by continual crystallization in the presence of excess anion. These salts exhibit moderate solubility in acetonitrile, nitromethane, and dimethyl sulfoxide and somewhat less solubility in water. The chelating ligands in these complexes undergo protonation-deprotonation, and consequently each complex may exist as either a protonated dication or as the corresponding deprotonated monocation. In most cases only one form of a particular complex has been isolated. The choice of which form was isolated was dictated by the pK_a of the complex and by the relative ease of crystallization of the two forms. In the case of **5** both forms were isolated. Details of these proton transfer reactions are discussed below.

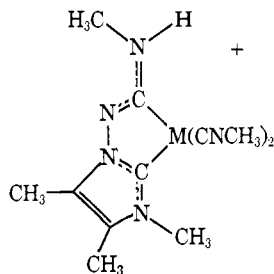
It is also possible to extend this general reaction to form a tridentate ligand. Addition of 2,6-diamino-

pyridine to $M(\text{CNCH}_3)_4^{2+}$ ($M = \text{Pd}, \text{Pt}$) produces **8** and **9**.



8, $M = \text{Pd}$; $X = \text{nothing}$
9, $M = \text{Pt}$; $X = \text{nothing}$
10, $M = \text{Pt}$; $X = \text{I}$

The reaction biacetyldihydrazone with $M(\text{CNCH}_3)_4^{2+}$ unexpectedly leads to the formation of **11** and **12**. In



11, $M = \text{Pd}$
12, $M = \text{Pt}$

this one reaction both a chelating ligand and an imidazole ring has been created. We suggest that this may occur *via* the sequence shown in eq 1 with the initial formation of the chelate ring about the metal proceeding much like the reaction of hydrazine with $M(\text{CNCH}_3)_4^{2+}$.

The structural formulations assigned to these new complexes are based on the spectroscopic data presented in Tables I and II, on the analytical and conductivity data set out in the experimental section, and also on established features of the reactions of coordinated isocyanides. Since the basis for interpretation of the

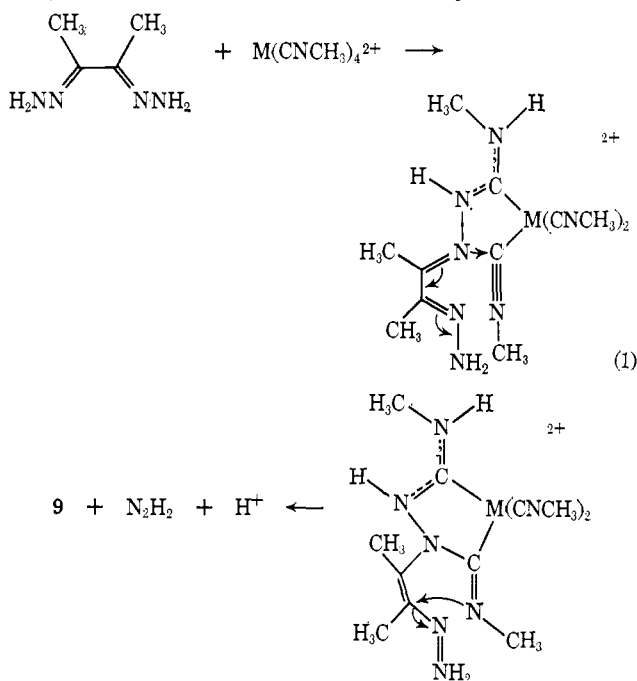


Table I. Selected Infrared Absorptions for Platinum and Palladium Complexes^a

Compound	$\nu_{\text{N-H}}$	$\nu_{\text{C=N}}$	1700–1500 cm^{-1} region
4b $[(\text{C}_4\text{H}_8\text{N}_3)\text{Pt}(\text{CNCH}_3)_2](\text{BF}_4)^d$	3397 m	2269 s	1565 m, 1534 m
	3359 m	2252 s	1516 m
4b $[(\text{C}_4\text{H}_8\text{N}_3)\text{Pt}(\text{CNCH}_3)_2](\text{BF}_4)^e$	3427 m	2266 s	1569 m, 1539 m
	3369 m	2249 s	1519 m
5a $[(\text{C}_5\text{H}_{11}\text{N}_3)\text{Pt}(\text{CNCH}_3)_2](\text{BF}_4)_2$	3308 s	2297 s	1671 s, 1620 m
		2282 s	
5b $[(\text{C}_5\text{H}_{10}\text{N}_3)\text{Pt}(\text{CNCH}_3)_2](\text{BF}_4)$		2264 s	1647 s, 1627 s
		2239 s	
6b $[(\text{C}_7\text{H}_8\text{N}_3)\text{Pt}(\text{CNCH}_3)_2](\text{BF}_4) \cdot 2\text{H}_2\text{O}$	3596 s ^b	2273 s	1635 sh, 1620 s
	3320 m	2257 s	1542 m
7b $[(\text{C}_8\text{H}_{10}\text{N}_3)\text{Pt}(\text{CNCH}_3)_2](\text{BF}_4)$	3435 m	2273 s	1618 m, 1567 m
		2251 s	1544 m
8 $[(\text{C}_9\text{H}_{13}\text{N}_3)\text{Pd}(\text{CNCH}_3)]\text{-Cl}_2 \cdot 2\text{H}_2\text{O}$	3310 s ^b	2264 m	1642 s, 1612 s
	3160 sh		1587 s, 1523 s
9 $[(\text{C}_9\text{H}_{13}\text{N}_3)\text{Pt}(\text{CNCH}_3)]\text{-}(\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$	3600 s ^b	2264 m	1647 s, 1617 s
	3540 sh		1587 s, 1520 s
10 $[(\text{C}_9\text{H}_{13}\text{N}_3)\text{Pt}(\text{CNCH}_3)_2]\text{-}(\text{BF}_4)_2$	3340	2315 w	1655 s, 1640 m
	s, br		1598 m, 1532 m
11 $[(\text{C}_8\text{H}_{13}\text{N}_4)\text{Pd}(\text{CNCH}_3)_2](\text{BF}_4)$	3450 m	2245 s	1625 w, 1560 m
	3445 m	2255 s	1505 s
12 $[(\text{C}_8\text{H}_{13}\text{N}_4)\text{Pt}(\text{CNCH}_3)_2](\text{BF}_4)$	3461 m	2265 s ^c	1630 w, 1521 s
	3447 m	2250 s	

^a Obtained from Fluorocarbon mulls. ^b Also $\nu_{\text{O-H}}$. ^c In acetonitrile solution this band occurs as a single absorption at 2255 cm^{-1} . ^d Yellow form. ^e Red form.

spectroscopic data has been developed at length previously,^{2-5,7} only comments pertinent to the structure of the novel compounds **11** and **12** will be presented here. As is the case with other similar complexes with two cis isocyanide ligands, the infrared spectra of **11** and **12** show two isocyanide stretching frequencies with a splitting of 15 cm^{-1} . The presence of a single NHCH_3 group is indicated by the observation of one N-H stretching frequency in the infrared spectrum of **12** in solution and by the observation of pmr resonances characteristic of this unit. This methyl group produces a doublet at τ 7.3 ($J_{\text{HNCH}} = 5.5$ Hz) which is coupled to the broad N-H resonance at τ 3.8. Additional splitting of the methyl resonance is present in the platinum complex due to coupling to ^{195}Pt . The resonances of the isocyanide methyl groups and the methyl group attached to the nitrogen of the imidazole ring give rise to two resonances in the case of the palladium complex and to a complex multiplet in the case of the platinum analog. Coupling to ^{195}Pt is clearly present for all of these resonances for **12** as is expected for methyl hydrogens which are separated from the metal by four bonds. The other methyl groups of the imidazole ring give rise to two distinct resonances at *ca.* τ 7.8. Consistent with their distance from the metal, no coupling to ^{195}Pt is seen for these resonances in **12**. Additionally, the electronic spectrum of such complexes are sensitive to the chelate ring structure and proton distribution (*vide infra*) and consequently the similarity of the electronic spectra of **12** and **1b** ($M = \text{Pt}$) indicates that a common chelate unit is present. However, unlike **1b** and related species, **11** and **12** are irreversibly destroyed in the presence of acid.

Ligand Protonation and Deprotonation. It has been previously demonstrated³ that the ligands in complexes such as **1a** ($M = \text{Pt}, \text{Pd}$) are acidic and that a proton may be removed from one of the interior chelate ring

Table II. Pmr Spectra of Palladium and Platinum Complexes

Complex	Chemical shift τ (intensity; coupling constant, Hz)			
	HNCH ₃	CNCH ₃	N-H	Other
2 (C ₄ H ₁₀ N ₄)PtI ₂ ^a	7.12 (6; $J_{\text{HNCH}} = 4.9$, $J_{\text{PtH}} = 2.6$)		2.04 (2; $J_{\text{HNCH}} = 4.9$) -1.38 (2)	
4b [(C ₄ H ₈ N ₃)Pt(CNCH ₃) ₂](BF ₄) ^a	7.14 (3; $J_{\text{HNCH}} = 4.5$, $J_{\text{PtH}} = 3$)	6.47 (3; $J_{\text{Pt-H}} = 10$) 6.54 (3; $J_{\text{Pt-H}} = 18$)	1.98 (1; $J_{\text{HNCH}} = 4.5$) 1.30 (1)	7.84 (3)
5a [(C ₅ H ₁₁ N ₃)Pt(CNCH ₃) ₂](BF ₄) ₂ ^b	6.49 (3; $J_{\text{HNCH}} = 5.0$, $J_{\text{PtH}} = 2$)	6.30 (9) ^d	1.65 (1; $J_{\text{HNCH}} = 5.0$)	6.70 (3; $J_{\text{PtH}} = 2$) 1.97 (1)
5b [(C ₅ H ₁₀ N ₃)Pt(CNCH ₃) ₂](BF ₄) ^b		6.46 (9) ^d		6.78 (3; $J_{\text{PtH}} = 10.5$) 7.00 (3; $J_{\text{PtH}} = 2$) 2.47 (1)
6b [(C ₇ H ₈ N ₃)Pt(CNCH ₃) ₂](BF ₄) ^b	6.95 (3; $J_{\text{HNCH}} = 5.5$, $J_{\text{PtH}} = 6.3$)	6.34 (3; $J_{\text{PtH}} = 18.4$) 6.34 (3; $J_{\text{PtH}} = 6.8$)	3.50 (1; $J_{\text{HNCH}} = 5.5$)	2.80 (1) ^e 2.15 (1) ^e 3.22 (1) ^e 1.66 (1) ^e
7b [(C ₈ H ₁₀ N ₃)Pt(CNCH ₃) ₂](BF ₄) ^b	7.01 (3; $J_{\text{HNCH}} = 5$)	6.47 (3; $J_{\text{PtH}} = 10$) 6.39 (3; $J_{\text{PtH}} = 20$)	3.58 (1; $J_{\text{HNCH}} = 5$)	7.43 (3) 3.30 (1) ^e 3.04 (1) ^e 2.40 (1) ^e
9 [(C ₉ H ₁₃ N ₃)Pt(CNCH ₃)](BF ₄) ₂ ^a	7.07 (6; $J_{\text{HNCH}} = 4.0$)	6.52 (3; $J_{\text{PtH}} = 20$)	0.42 (2; $J_{\text{HNCH}} = 4$) -0.98 (2)	3.41 (2; $J_{\text{HCCH}} = 8.5$, $J_{\text{PtH}} = 10$) 2.32 (1; $J_{\text{HCCH}} = 8.5$)
11 [(C ₈ H ₁₃ N ₄)Pd(CHCN ₃) ₂](BF ₄) ^c	7.36 (3; $J_{\text{HNCH}} = 5.5$)	6.40 (6)	3.92 (1; $J_{\text{HNCH}} = 5.5$)	7.90 (3) 7.86 (3) 6.46 (3)
12 [(C ₈ H ₁₃ N ₄)Pt(CNCH ₃) ₂](BF ₄) ^c	7.22 (3; $J_{\text{HNCH}} = 5.5$, $J_{\text{PtH}} = 3$)	6.36 (3) 6.33 (3)	3.87 (1; $J_{\text{HNCH}} = 5.6$)	7.87 (3) 7.82 (3) 6.46 (3)
13 (C ₄ H ₁₀ N ₄)PtI ₄ ^c	6.63 (6; $J_{\text{HNCH}} = 5.4$, $J_{\text{PtH}} = 3$)		1.64 (2; $J_{\text{HNCH}} = 5.4$) -1.38 (2)	

^a In (CD₃)₂SO. ^b In CD₃NO₂. ^c In (CD₃)₂CO. ^d Broad multiplet with PtH coupling due to methyl groups on terminal chelate nitrogen and isocyanide ligands. ^e Pyridine ring protons, complex coupling pattern observed and analyzed but not reported.

nitrogens to give **1b**. Both forms may be isolated, and, in the deprotonated form, the proton remaining on the interior chelate nitrogens is rapidly exchanged between the two chelate ring nitrogen atoms in solution at room temperature.⁵ Similar acid-base behavior has been observed for other monodentate diaminocarbene ligands,¹⁵ and this behavior is also displayed by the new chelating ligands described above.

The proton transfer reactions may be effectively demonstrated by direct titration in aqueous solution. Thus titrations of **6b** with hydrochloric acid or **8** with sodium hydroxide give well-defined breaks in the titration curves after the addition of one equivalent of titrant. The pK_a values and equivalent weights for these and some related complexes are set out in Table III. As can be seen from these data there is an appre-

Table III. Acidities of Complexes in Aqueous Solution

Compound	pK_a^a	Equiv wt (calcd)
[Pd(C ₄ H ₈ N ₄)(CNCH ₃) ₂]Cl, 1b	4.9	340 (337)
[Pt(C ₄ H ₈ N ₄)(CNCH ₃) ₂]Cl, 1b	5.0	431 (426)
[Fe(C ₄ H ₁₀ N ₄)(CNCH ₃) ₄][PF ₆] ₂	8.3	629 (624)
[Ru(C ₄ H ₁₀ N ₄)(CNCH ₃) ₄][PF ₆] ₂	8.3	672 (669)
[Pt(C ₇ H ₈ N ₃)(CNCH ₃) ₂][BF ₄], 6b	5.9	490 (490)
[Pd(C ₅ H ₁₃ N ₃)(CNCH ₃)Cl] ₂ , 8	7.3	416 (411)

^a Reported for the acid form of the various species.

ciable difference in the acidity of the bis(carbene) ligand derived from hydrazine depending on whether it is bound to a six-coordinate d⁶ metal or a four-coordinate d⁸ metal center. However, the acidity does not

vary appreciably when the metal is changed from a first- to a second-row or second- to a third-row metal.

When possible, proton loss occurs preferentially from one of the interior chelate ring nitrogens. This has been established for **1** earlier⁵ and is established in the case of **4**, **6**, and **7** by direct observation by pmr of an NHCH₃ group in the deprotonated species **4b**, **6b**, and **7b**. Presumably one of the two ring nitrogens of **8** and **9** is also deprotonated when these cations are treated with base. However, the situation in the case of the ligand **5** is different because of the pattern of ring substitution. In this case the acid-base behavior of the ligand has been established by isolation of both forms (**5a** and **5b**) of the complex. The presence of an NHCH₃ group in the protonated form is clearly demonstrated by both infrared observation of a sharp N-H stretching vibration and by the pmr spectrum. However, the deprotonated species (**5b**) lacks an N-H stretch in the infrared and the terminal methyl group produces a singlet resonance in the pmr spectrum thereby further indicating a lack of a proton at that terminus of the ligand. Other evidence for the acidic nature of terminal NHCH₃ groups in such bidentate ligands has come from static⁶ and dynamic⁷ proton exchange studies but **5b** is the first complex isolated without a proton in this position.

Electronic Spectra. The complexes with bidentate chelating ligands exhibit spectral features which indicate that the MC₂N₂ unit behaves as a distinct chromophore. The two lowest energy transitions for these complexes occur in the region 24,000–40,000 cm⁻¹ and generally exhibit extinction coefficients in the range 1.5–6 × 10³; these data are set out in Table IV. The complexes **1b**, **4b**, **5b**, and **10**, which have undergone loss of a proton from a nitrogen that is a part of the MC₂N₂ chelate unit,

(18) B. Crociani and T. Boschi, *J. Organometal. Chem.*, **24**, C1 (1970).

Table IV. Lowest Energy Electronic Transitions

Compound	ν_{\max} , cm^{-1} (ϵ) ^a	
1a Pt(C ₄ H ₁₀ N ₄)(CNCH ₃) ₂ ²⁺	30,000	32,300
1b Pt(C ₄ H ₆ N ₄)(CNCH ₃) ₂ ⁺	24,400 (1900)	31,000 (2,000)
1a Pd(C ₄ H ₁₀ N ₄)(CNCH ₃) ₂ ²⁺	33,400	39,700
1b Pd(C ₄ H ₆ N ₄)(CNCH ₃) ₂ ⁺	29,000 (2320)	36,400 (3,980)
4a Pt(C ₄ H ₉ N ₃)(CNCH ₃) ₂ ²⁺	31,600 (3100)	34,400 (8,300)
4b Pt(C ₄ H ₅ N ₃)(CNCH ₃) ₂ ⁺	28,000 (3600)	32,300 (2,700)
6a Pt(C ₇ H ₉ N ₃)(CNCH ₃) ₂ ²⁺	31,000 (6300)	33,600 (6,300)
6b Pt(C ₇ H ₅ N ₃)(CNCH ₃) ₂ ⁺	25,300 (4900)	32,100 (2,400)
5a Pt(C ₃ H ₁₁ N ₃)(CNCH ₃) ₂ ²⁺	30,500 (2400)	32,200 (5,100)
5b Pt(C ₃ H ₁₀ N ₃)(CNCH ₃) ₂ ⁺	30,100 (4080)	32,900 (3,620)
12 Pt(C ₈ H ₁₃ N ₄)(CNCH ₃) ₂ ⁺	25,700 (1400)	31,000 (11,800)

^a Obtained from acetonitrile solutions.

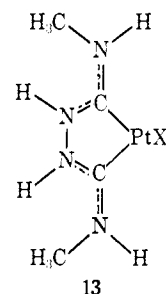
are yellow or orange in solution and exhibit an absorption band in the region 24,000–29,000 cm^{-1} . Upon protonation these complexes are converted into the corresponding dications, and the low energy transition is shifted by 3600–5700 cm^{-1} to higher energy. This pattern is not followed by complexes **5a** and **5b**. The lowest energy transition observed for **5b** occurs at much higher energy than the corresponding transition in **1b**, **4b**, **5b**, and **10**, and there is only a slight shift in this band upon protonation to form **5a**. Thus the spectra of both **5a** and **5b** resemble that of **4a**, and all of these have a similar pattern of substituents on the PtC₂N₂ ring.

In the solid state the complexes **1b** and **4b** show additional low energy transitions which are not present in their solution spectra. The tetrafluoroborate salt of **4b** crystallizes in two forms (one yellow, the other red). The yellow form exhibits absorption at 27,000 and 33,000 cm^{-1} which correlates with the absorption spectrum observed for solution of either the red or yellow form. The red form produces an absorption at 20,000 cm^{-1} which is not present in the solution spectrum. In addition to giving the same electronic spectrum in solution, both forms also produce, as solids, virtually identical infrared spectra. Salts of the cation **1b** ($M = \text{Pt}$) exhibit features in their electronic spectra recorded from the solid which depend on the anion involved. The spectrum obtained for the tetraphenylborate salt of **1b** displays absorptions at 25,000 and 31,000 cm^{-1} which correlate with those obtained from solution. However, with other anions an intense absorption at lower energy, which has no component in the solution spectrum, occurs as follows: **1b**-Cl·4H₂O ($M = \text{Pt}$), 21,000 cm^{-1} ; **1b**-Br·4H₂O, 19,000 cm^{-1} ; **1b**-I·4H₂O, 17,000 cm^{-1} ; **1b**-N₃·2H₂O, 17,000 cm^{-1} ; **1b**-ClO₄·2H₂O, 18,500 cm^{-1} . Upon drying these salts, the low energy transition moves to lower energy and the reddish brown hydrated salts are converted into crystalline green solids. For the anhydrous chloride salt of **1b** ($M = \text{Pt}$) this absorption occurs at 9000 cm^{-1} . The change in the spectrum which occurs upon dehydration is reversible.

It is unlikely that the above observation involve coordination of the anions to platinum. In the case of the two forms of **4b**-BF₄, a poorly coordinating anion is involved. Again with **1b**, another poorly coordinating anion, perchlorate, is present in one of the salts containing an anomalous electronic transition. Furthermore, in the case of **1b** the spectrum of the complex in solution is unaffected by the nature of the anion and also unaffected by changes in solvent. The spectra of **1b** in ethanol, water, acetonitrile, nitromethane, pyridine, and dimethyl sulfoxide are essentially identical. A

more likely explanation for the additional absorptions observed in the solids involves formation of stacks of cations in the solid state so that linear chains of platinum atoms are formed. It is known^{19,20} that such stacking phenomena cause additional electronic absorptions in the solid state. Moreover, in some cases the energy of these transitions appears to be related to the distance between platinum atoms. This distance in salts of Pt(CN)₄²⁻ is a function of the counterion and the extent of hydration present in crystals. It is easily conceivable that the nature of the anion and the degree of hydration in crystals containing stacks of cations could control the separation between the platinum centers. It is also likely that the presence of a very bulky anion like tetraphenylborate will preclude the formation of such stacks of cations, and it is known that the cations do not stack in the tetraphenylborate salt of a methyl derivative of **1b** ($M = \text{Pt}$).⁵

Oxidative Reactions. Although oxidation might have been expected to affect several portions of these new chelates, particularly the metal-carbon and nitrogen-nitrogen bonds, these complexes are remarkably stable to oxidative conditions and the only well-defined oxidative process that has been observed is halogen addition to platinum. Thus, as has been briefly reported earlier,²¹ halogens add to **2** to yield the corresponding Pt(IV) complexes, **13**. The great similarity of



the infrared spectra of related pairs of complexes **2** and **13** indicates that the bidentate ligands survive this reaction unchanged. The pmr spectra of the iodo complexes, which are the only complexes with sufficient solubility for measurement, also indicate that the same bidentate ligand is present in **2** and **13** ($X = \text{I}$).

During attempts to oxidize complexes of the type **2** with quinones, transient intense color changes occurred which were suspected to be due to the formation of charge-transfer adducts. However, it was not possible to isolate any crystalline products from this reaction. With weaker acceptor molecules (1,3,5-trinitrobenzene, tetrachloroterphthalic anhydride, and tetrabromoterphthalic anhydride) it has been possible to obtain yellow crystalline adducts of **2** ($M = \text{Pt}$ or Pd , $X = \text{I}$). The infrared spectra of these adducts are superpositions of the infrared spectra of their two respective components and consequently the adducts are formulated as charge-transfer adducts with molecular ground states. Since halide ions alone form charge-transfer complexes, it was unfortunately not possible to investigate the role of coordinated halide in the formation of these adducts because of the limited solubility of **2** when X is bromide or chloride.

(19) K. Krogman, *Angew. Chem., Int. Ed. Engl.*, **8**, 35 (1969).

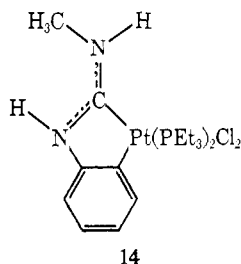
(20) T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.*, **1**, 99 (1972).

(21) A. L. Balch, *J. Organometal. Chem.*, **37**, C19 (1972).

Few Pt(IV) complexes containing isocyanide ligands have been reported. Attempts to oxidize Pt(II) isocyanide complexes have been thwarted by the apparent ability of coordinated isocyanide to reduce Pt(IV).⁴ However, we have found that **9** undergoes oxidation with iodine to yield **10**; the infrared spectrum of **10** indicates that the tridentate ligand has remained intact in this reaction. Consistent with an oxidative addition reaction, the stretching frequency of the coordinated isocyanide has increased by 51 cm⁻¹ upon oxidation.

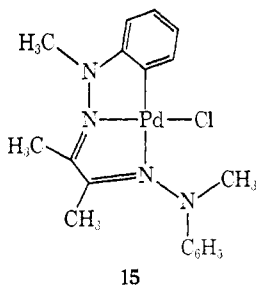
Discussion

All of the new ligands described above are expected to be planar as a consequence of the extended π system present in each. The geometry about the C-N bonds has been assigned in accord with previous observations⁵ which indicate that, when possible, substituents arrange themselves in an amphi configuration about each MCN₂ unit. No evidence for the existence of more than a single isomer of each compound has been found. The geometry of the chelate in **6** and **7** is expected to be similar to that determined²² for the closely related bidentate ligand found in **14**. Other attempts



to prepare chelating carbene ligands through the reaction of bidentate nucleophiles, including 2-aminopyridine, with Pd(CNC₆H₅)₂Cl₂ lead only to the formation of monodentate carbene ligands; the failure to form chelates has been ascribed to steric factors.²³

The formation of the tridentate ligand in complexes **8** and **9** indicates that a considerable degree of in-plane angular distortion is allowed in the formation of these chelate rings. Inspection of models, as well as consideration of the known structure of **15**,²⁴ which like **8** and **9** contains two fused five-membered rings, suggests that



the trans C-Pt-C bond angle in **8** and **9** is reduced from the ideal value of 180° by about 20°. The preparation of **7** indicates that an unreacted amino group could have been accommodated in the 6-position of the pyr-

(22) K. W. Muir, R. Walker, J. Chatt, R. L. Richards, and G. H. D. Royston, *J. Organometal. Chem.*, **56**, C30 (1973).

(23) R. Zanella, T. Boschi, M. Nicolini, and V. Belluco, *J. Organometal. Chem.*, **49**, C91 (1973).

(24) G. Bombicri, L. Caglioti, L. Cattalini, E. Forsellini, G. Gasparin, R. Graziani, and P. A. Vigato, *Chem. Commun.*, 1415 (1971).

Table V. Infrared Spectra of Platinum(II), Platinum(IV), and Charge-Transfer Complexes in the Region 4000–700 cm⁻¹ ^a

C ₄ H ₁₀ N ₄ PtI ₂	3350 m, 3345 m, 3255 s, 3150 m, 3090, 1582 s, 1527 s, 1504 s, 1432 w, 1424 w, 1368 m, 1202 m, 1150 m, 1012 m
C ₄ H ₁₀ N ₄ PtI ₄	3250 m, 3190 m, 3145 m, 3085 m, 3040 w, 1640 sh, 1604 vs, 1535 m, 1497 m, 1430 m, 1190 m, 1149 m, 1086 w, 1008 m
C ₄ H ₁₀ N ₄ PtBr ₄	3320 s, 3300 s, 3230 m, 3180 m, 3100 m, 3060 w, 3030 w, 1657 w, 1620 vs, 1543 m, 1500 s, 1440 w, 1428 m, 1302 w, 1237 w, 1195 m, 1158 m, 1090 w, 1008 m
C ₄ H ₁₀ N ₄ PtCl ₄	3380 m, 3320 s, 3180 sh, 3140 sh, 3105 m, 3070 w, 3020 m, 1665 m, 1630 vs, 1596 m, 1550 m, 1535 m, 1507 m, 1235 w, 1192 m, 1152 m, 1114 w, 1085 w, 1020 w, 1008 m
C ₄ H ₁₀ N ₄ PtI ₂ ·C ₆ Cl ₃ O ₃ ^b	3340 sh, 3315 s, 1915 w, 1848 s, 1790 s, 1776 s, 1577 s, 1535 m, 1494 s, 1301 s, 1234 s, 1221 s, 1200 m, 1172 s, 1146 m, 1091 w, 1012 w, 914 w, 910 s, 758 m, 738 sh, 734 s
C ₄ H ₁₀ N ₄ PtI ₂ ·C ₆ Br ₃ O ₃ ^b	3360 m, 3310 s, 1860 s, 1820 s, 1780 s, 1580 s, 1530 m, 1497 s, 1275 m, 1215 m, 1201 s, 1185 sh, 1142 m, 1091 w, 1015 w, 920 s, 730 s
C ₄ H ₁₀ N ₄ PtI ₂ ·C ₆ H ₃ (NO ₂) ₃ ^b	3340 m, 3320 w, 3225 s, 3080 m, 1625 s, 1582 s, 1548 s, 1530 sh, 1492 m, 1200 m, 1245 m, 1080 m, 1010 m, 921 m, 914 s, 730 s, 712 s
C ₄ H ₁₀ N ₄ PdI ₂ ·C ₆ Cl ₃ O ₃ ^b	3315 sh, 3270 s, 1910 w, 1865 sh, 1843 m, 1789 m, 1776 s, 1578 s, 1538 m, 1490 m, 1310 m, 1235 m, 910 m, 739 s, 731 s

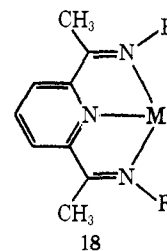
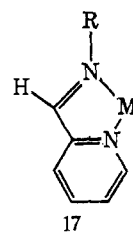
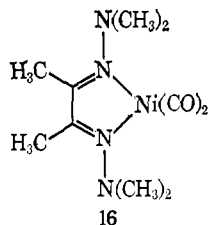
^a Recorded from Nujol mulls, data for the regions (3000–2800 and 1470–1350 cm⁻¹) obscured by Nujol not reported. ^b Italicized vibrations occur within ±5 cm⁻¹ of vibrations of the free organic acceptor.

idine ring in a bidentate chelate. Nevertheless the formation of the additional chelate ring occurs without the usual entropic advantages of expelling a previously bound ligand. Despite the unfavorable geometry, the complexes **8** and **9**, which contain these tridentate ligands, appear to be as robust as the monochelate complexes **6** and **7**.

The complexes **4**, **5**, **6**, and **7** contain a new type of chelating ligand which contains both a trigonal carbon donor and an imine nitrogen donor. These ligands, the bis(carbene) ligands found in **1** and **2**, and the well-known α -dimine ligands form a series of complexes involving unsaturated MC₂N₂ ring systems. This series is particularly unusual for metal chelates because the position of the atoms within the ring differs among the various members. In accord with valence bond theory the electron density of the π system varies appreciably within these different chelate rings. A comparison can be made between the bis(carbene) ligands of **1** and **2** and the π -isoelectronic dihydrazone ligands found in **15** and **16**.²⁵ Structural studies^{3,5} indicate that the bis(carbene) ligands including the exo NR₂ units are planar. From the structural data available on dihydrazone ligands (compounds **15** and **16**), it is apparent that the α -diimine chelate is less electron withdrawing than the bis(carbene) ligands since the exo NR₂ groups of **15** and **16** adopt pyramidal configurations about nitrogen.

The construction of chelating ligands by the addition

(25) H. D. Hansen and K. Krogman, *Z. Anorg. Allg. Chem.*, **389**, 247 (1972).



of amines and isocyanides parallels the formation of polydentate ligands from the condensation of aldehydes and amines. In the first case the isocyanide provides the carbon donor center while in the Schiff base formation the amine provides the nitrogen donor. Consequently the amine plays the same role in the formation of carbene chelates as the aldehyde does in the formation of polydentate Schiff base ligands. Thus, hydrazine, 2-aminopyridine, and 2,6-diaminopyridine are used to form the chelating ligands in **1**, **6**, and **8**, respectively, while carbonyl compounds—biacetyl, pyridine-2-aldehyde, and 2,6-diacetylpyridine—are used to form the analogous ligands of compounds **16**, **17**,¹⁷ and **18**.²⁶ Clearly a number of other chelating ligands may be obtained from the amine–isocyanide reaction, but it remains to be seen if such ligands may be constructed

(26) J. D. Curry, M. A. Robinson, and D. H. Busch, *Inorg. Chem.*, **6**, 1570 (1967).

about metals other than palladium and platinum. Ligands such as carbon monoxide and NO^+ which are isoelectronic with isocyanides are known to undergo the addition of nucleophiles such as amines. Consequently, these may also be expected to form related chelating ligands, and at least one parallel exists. The reaction of $\text{Mn}(\text{CO})_5\text{Br}$ with lithiated amidines produces a chelating ligand analogous to that found in **5b**.²⁷ However, the addition of hydrazine to metal carbonyls generally produces coordinated isocyanate rather than a chelating ligand²⁸ and so completely parallel behavior is not to be expected.

Acknowledgment. This research was supported by Grant GM 18357 from the National Institutes of Health.

(27) T. Ingltis, M. Kilner, and T. Reynoldson, *J. Chem. Soc., Chem. Commun.*, 774 (1972).

(28) R. J. Angelici, *Accounts Chem. Res.*, **5**, 335 (1972).

On the Kinetic Trans Effect in Square Planar Transition Metal Complexes

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Abstract: It is shown that the trans effect series for square planar d^8 complexes can be related to two spectrochemical parameters. The first one is the octahedral field splitting Dq ; the second parameter, τ , accounts for the relative importance of σ and π bonding ($\tau = \pi'/\sigma'$). In the kinetic analysis of the substitution reactions under consideration, the role of the ligand field activation energy (LFAE) has been investigated. The LFAE was considered to be the difference between the ligand field stabilization energy of a trigonal bipyramidal transition state and that of the square planar metal complex. Both energies can be expressed in terms of the relevant spectrochemical parameters. It is found that the experimental trans effect series can be reproduced qualitatively from the predicted variation of the LFAE as a function of Dq and τ . In the same way, predictions can be made on the kinetic cis effect. In this case, however, the limited range of experimental data makes the results less conclusive.

The trans effect has been studied most thoroughly for square planar d^8 systems, especially for Pt(II) complexes. The following series of ligands, A, is shown in order of decreasing rate of substitution of the ligand, T, trans to A: $\text{C}_2\text{H}_4 \sim \text{CO} \sim \text{CN}^- > \text{R}_3\text{P} \sim \text{H}^- > \text{CH}_3^- > \text{C}_6\text{H}_5^- > \text{NO}_2^- > \text{I}^- > \text{SCN}^- > \text{Br}^- > \text{Cl}^- > \text{py} > \text{NH}_3 > \text{H}_2\text{O}, \text{OH}^-$. The observed rate constants span a range of about five or six orders of magnitude.

In order to rationalize these experimental data, it has been supposed that the Pt–T bond is weakened by the Pt–A interaction.¹ The Pt–T weakening—a purely thermodynamic effect—is usually called the trans influence.²

(1) A. A. Grinberg, *Acta Physicochim. URSS*, **3**, 573 (1935).

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

It has been studied rather extensively by measuring Pt–T bond distances, infrared stretching frequencies, and nmr coupling constants.³ Attempts to understand the trans influence usually invoke the role of the Pt 6s and 6p orbitals in the A–Pt–T bonding.^{3–5} Although the bond weakening data could explain part of the rate variations, a more complete understanding of the trans effect requires consideration of the transition state.

Different authors have shown how the energy of the transition state can be affected by the nature of the A

(3) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).

(4) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965.

(5) S. S. Zumdahl and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 6669 (1968).