

Iridium Complexes of Molecular Nitrogen¹James P. Collman,² Mitsuru Kubota,³ Frederick D. Vastine,⁴ Jui Yuan Sun,⁴ and Jung W. Kang⁴*Contribution from the Departments of Chemistry, University of North Carolina, Chapel Hill, North Carolina, Harvey Mudd College, Claremont, California, and Stanford University, Stanford, California Received March 11, 1968*

Abstract: Reaction of *trans*-chlorocarbonylbis(triphenylphosphine)iridium (I) with organic azides yields a stable complex of molecular nitrogen, **3**, and organic isocyanates. Spectral and kinetic evidence supports the mechanism depicted in Figure 1. The effects of changing the character of the azide, the central metal, and the ancillary ligands on the reaction rate have been examined. These results suggest that the azide functions as an electrophile and the metal as a base in a reaction related to oxidative addition. The nitrogen complex **3** forms a higher coordinate olefin derivative **9**, but CO, triphenylphosphine, and acyl isocyanates displace nitrogen. The infrared absorption bands of coordinated nitrogen in **3**, **9**, and previously described complexes are discussed in terms of $d_{\pi}-p_{\pi}$ back-bonding.

The quest for substances which will catalyze the reduction (or oxidation) of molecular nitrogen under moderate conditions is a challenge to the modern chemist. This search is made more intriguing by the existence of nitrogen-fixing microorganisms which apparently function through the agency of transition-metal enzymes.⁵ According to rudimentary concepts of homogeneous catalysis,⁶ it is imperative that nitrogen be coordinated to a transition metal before it becomes susceptible to catalytic reduction. A variety of systems which can stoichiometrically reduce molecular nitrogen at atmospheric pressure and low temperatures has been recently reported.⁷⁻⁹ The inclusion of transition metals in these reducing systems is noteworthy. It has been presumed that intermediate nitrogen complexes are involved in these reductions, and some evidence has been advanced to support this supposition.^{9,10} Allen and coworkers reported the first stable transition-metal complex of molecular nitrogen, $[\text{Ru}(\text{NH}_3)_5\text{N}^{2+}]^{2+}$, and demonstrated that the coordinated nitrogen is susceptible to chemical reduction.¹¹ Reports of iridium,¹ cobalt,^{12,13} rhodium,¹⁴ ruthenium,^{12e} and osmium^{15a}

nitrogen complexes soon followed. Direct incorporation of gaseous molecular nitrogen into certain metal complexes has been demonstrated.^{12,16} This paper is concerned with the synthesis, reactions, and properties of an iridium nitrogen complex discovered in our laboratories.

Results and Discussion

In the course of investigating oxidative-addition reactions of d^8 complexes,^{17,18} we studied reactions between acyl azides and the coordinatively unsaturated iridium(I) carbonyl **1**, with the expectation that the pseudo-olefinic complex **1** would react with these 1,3 dipoles to form adducts such as **2** from which nitrogen might be thermally extruded affording nitrene complexes. Fortunately the reaction takes a different course.

The actual reaction between the iridium carbonyl **1** and acyl azides is outlined in Figure 1. If the solvent contains water or alcohol, the molecular nitrogen complex **3** can be isolated from the mixture. On the other hand, if dry, alcohol-free solvents are employed, the acyl isocyanate **4**, formed as an intermediate, attacks the nitrogen complex **3** displacing nitrogen to form an acyl isocyanate complex provisionally formulated as **5**. Indeed we were fortunate that the reagent-grade chloroform first used to explore this reaction between acyl azides and the iridium carbonyl **1** contained ethyl alcohol as an autoxidation inhibitor. The role of the alcohol is simple—it intercepts the acyl isocyanate **4** by forming a carbamate ester **6**. The ethyl carbamate **6b** was isolated from the reaction mixture and characterized by elemental analysis, ir and nmr spectra, mass spectral cracking pattern, and an independent synthesis. Using chloroform which contained methyl rather than

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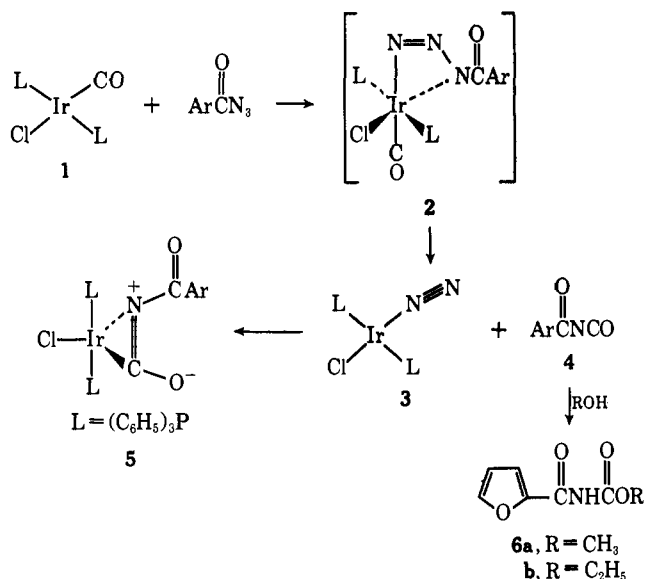


Figure 1.

ethyl alcohol, we were able to isolate and similarly characterize the methyl carbamate **6a**.

Infrared Studies. The reaction between the chlorocarbonyl **1** and α -furoyl azide in reagent chloroform (containing alcohol) was studied using ir spectroscopy at low temperatures. Rapid disappearance of the reactants was indicated by decay of bands at 1962 cm^{-1} characteristic of the carbonyl group in **1**, and at 2200 and 2145 cm^{-1} , due to the acid azide group (see Figure 2). The apparently simultaneous appearance of products was demonstrated by the growth of bands at 2105 cm^{-1} (nitrogen complex **3**) and at 1780 and 1710 cm^{-1} (ethyl carbamate **6b**). It should be noted that in this experiment the concentration of α -furoyl azide is greater than that of the iridium carbonyl **1**. Efforts to detect intermediates at low temperatures did not reveal any other bands in the 1650 – 2300-cm^{-1} region.

Low-temperature ir spectral studies of the reaction between the chlorocarbonyl **1** and α -furoyl azide in dry, alcohol-free chloroform revealed a strikingly different course compared with the results in chloroform containing alcohol. While the disappearance of the reactants was again marked by diminution of bands at 1962 , 2145 , and 2200 cm^{-1} , there were no intense peaks at 2105 (nitrogen complex **3**) or 1780 cm^{-1} (carbamate **6**) (see Figure 3). Instead, an intense band was observed at 2250 cm^{-1} , but this peak rapidly decayed. This peak, which is assigned to α -furoyl isocyanate, was not observed in some trials, and, in every case where it was observed, it decayed completely within 3 min. Weaker peaks at 2105 and 2065 cm^{-1} were also observed, as well as intense bands at 1720 , 1690 , and 1650 cm^{-1} . The latter three frequencies are characteristic of the isocyanate complexes **5** which have been isolated. Similar results were obtained from a spectral study of the reaction between benzoyl azide and the chlorocarbonyl **1**, namely short-lived peaks at 2245 and 1820 cm^{-1} , weak peaks at 2065 and 2105 cm^{-1} , and intense bands at 1720 , 1670 , and 1600 cm^{-1} .

To obtain additional support for the scheme shown in Figure 1, the course of the reaction between *p*-methylbenzoyl isocyanate and the iridium nitrogen

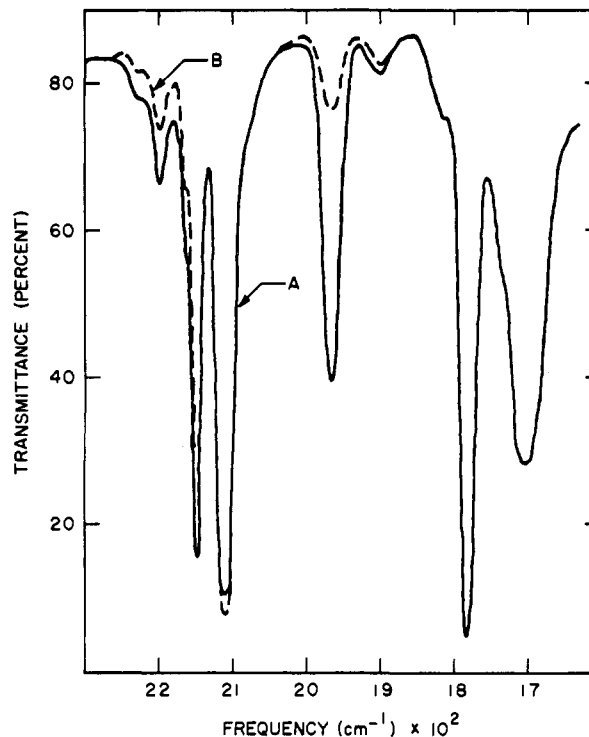


Figure 2. Infrared spectrum during the course of reaction of furoyl azide and chlorocarbonyl **1** in reagent chloroform. Time after extraction from frozen mixture: A, 2 min; B, 4 min.

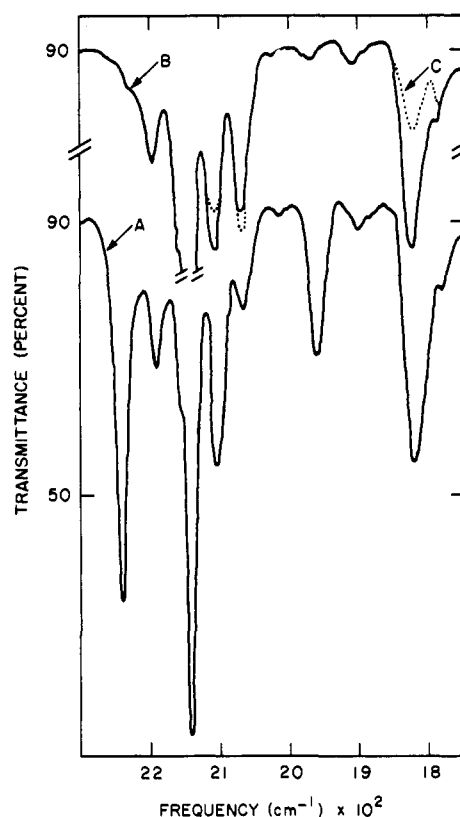


Figure 3. Infrared spectrum during the course of reaction of furoyl azide and chlorocarbonyl **1** in dry chloroform. Time after extraction from frozen mixture: A, 2 min; B, 4 min; C, 6 min.

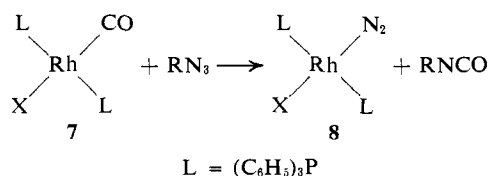
complex **3** was examined by means of low-temperature ir solution spectra. Coincident with the disappearance of the isocyanate, shown by diminishing intensity of

a peak at 2232 cm^{-1} , was the decay of the band at 2105 cm^{-1} due to the nitrogen complex **3**. Formation of the iridium isocyanate complex **5** was indicated by the development of intense bands at 1600, 1680, and 1730 cm^{-1} . A weaker band at 1780 cm^{-1} is assigned to a product from the hydrolysis of the isocyanate. The gradual growth of peaks at 2050 and 1920 cm^{-1} suggests that other competing reactions ensue, especially with the iridium nitrogen complex **3**. An acyl isocyanate iridium complex **5** was isolated from a similar reaction.

Phenyl azide also reacts with the iridium carbonyl **1** to form the nitrogen complex **3**; however, for synthetic purposes this reagent is inferior to acid azides or *p*-toluenesulfonyl azide. Infrared spectral studies of the reaction between **1** and phenyl azide provided additional evidence supporting the scheme shown in Figure 1. The reaction spectrum was characterized by diminishing intensities of peaks due to reactants (1962 cm^{-1} for **1** and 2128 and 2090 cm^{-1} for phenyl azide) and simultaneous growth of bands due to the products, the nitrogen complex **3** (2105 cm^{-1}), and phenyl isocyanate (2260 and 2280 cm^{-1}). No other bands were observed in the 2400–1600- cm^{-1} region. Apparently further reaction between phenyl isocyanate and the nitrogen complex is slow or does not occur under these conditions.

The rhodium analog of **1**, $\text{RhCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ (**7**), also reacts with organic azides to form a nitrogen complex similar to **3**. However, this rhodium nitrogen complex **8** is exceedingly labile in solution, and we did not detect it in our work. Ukhin has recently isolated chloronitrogenbis(triphenylphosphine)rhodium(I) (**8**) from the reaction between the rhodium(I) carbonyl **7** and butanoyl azide at very low temperatures and reports that this complex liberates nitrogen in chloroform.¹⁴ Our failure to detect the formation of this nitrogen complex **8** may be ascribed to the fact that the $\text{Rh}-\text{N}_2$ frequency at 2152 cm^{-1} is in the region where most of the acyl and aryl azides absorb strongly.

Spectral studies of the reactions between organic azides and the rhodium(I) chlorocarbonyl **7** are similar to those for the iridium complex **1**. The course of reaction of α -furoyl azide and the rhodium chlorocarbonyl **7** in reagent chloroform was marked by diminishing intensities at 1977 and 2145 cm^{-1} and simultaneous growth of carbamate ester peaks at 1780, 1720, 1678, and 1600–1588 cm^{-1} . The same reaction in alcohol-free chloroform was characterized by diminishing intensities of the peaks due to the reactants. A peak at 1780 cm^{-1} due to the carbamate ester was not observed. An intense band developed at 2242 cm^{-1} due to the α -furoyl isocyanate, and decayed within 20 min leaving an intense bands at 1695 cm^{-1} . Spectral studies showed that the reaction of phenyl azide and



the rhodium chlorocarbonyl **7** proceeded in the same fashion in dry or reagent chloroform. The formation of phenyl isocyanate was shown by growth of the doublet at 2280–2260 cm^{-1} . Slow subsequent hydrolysis of

phenyl isocyanate was later indicated by growth of a peak at 1705 cm^{-1} .

Kinetic Studies of the Azide Reaction. The rates of reactions of organic azides and various substituted derivatives of iridium and rhodium carbonyls in **1** and **7** were determined by measuring the intensity of the carbonyl absorption band. Linear concentration-absorbance plots showed that Beer's law is obeyed for the concentrations of iridium and rhodium carbonyls employed in this study. Plots of reciprocals of absorbance vs. time for solutions of equimolar concentrations of $\text{IrCl}(\text{CO})\text{L}_2$ and furoyl azide gave linear slopes for up to 75% completion of reaction. The rate law observed, $-\text{d}(\text{IrCl}(\text{CO})\text{L}_2)/\text{d}t = k_2(\text{IrCl}(\text{CO})\text{L}_2)(\text{RN}_3)$ is thus like that reported by Chock and Halpern for oxidative-addition reactions of iridium(I) carbonyls with H_2 , O_2 , and CH_3I .¹⁹ Comparison of the rates of the furoyl azide reaction in alcohol-free chloroform and in dry chloroform to which ethanol had been added indicated that the rate was not grossly affected by the added ethanol.

Second-order plots for the reactions of the iridium and rhodium halocarbonyls **1** and **7** with the thermally less stable aryl azides were linear in some instances up to 50% completion of reaction. Rate constants listed in Table I are based on measurements of reactions up to at least 20% completion.

Table I. Kinetic Data for Reactions of Azides with Iridium and Rhodium Carbonyl Complexes in Chloroform at 30°

Azide	Metal complex	k_2 , $M^{-1} \text{sec}^{-1}$
Furoyl azide	$\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$	1.06 ^a
		1.80 ^b
		1.67 ^c
Phenyl azide	$\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$	2.12 ^d
		0.081 ^e
		0.094
		0.121 ^f
		0.16
		0.22
		0.072
		0.23
		0.057 ^e
		0.067
4-Azidotoluene	$\text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2$	0.096 ^f
		0.089
		0.17
		0.23
		0.054
		0.107
		0.114
		0.037
		0.19
		0.034
4-Azidotoluene	$\text{RhCl}(\text{CO})(\text{Ph}(\text{C}_2\text{H}_5)_2\text{P})_2$	0.047
		0.097
		0.115
		0.115

^a Run in dry CHCl_3 at 20° ^b Run in dry CHCl_3 at 25° ^c Run at 25° in dry CHCl_3 to which a 25-fold molar excess of ethanol was added. ^d Run in dry CHCl_3 at 35° ^e Run at 25° ^f Run at 35°

The effects on the reaction rate of changing the halide, the phosphine ligands, the central metal, and the azide are presented in Table I. The kinetic patterns for the reactions of aryl azides with $[\text{IrX}(\text{CO})\text{L}_2]$ ex-

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hibit the same reactivity sequence observed¹⁹ in the addition of H₂ and O₂, namely I > Br > Cl. The same pattern prevails in the reactions of azides with the corresponding rhodium halocarbonyl complexes. The rates of reactions of the iridium complexes are generally 1.4 to 2.2 times faster than those of the corresponding rhodium complexes. Reactions of the alkylated phosphines are considerably faster than those of the corresponding triphenylphosphine complexes. The relative rates of the reactions suggest that the azide behaves as an electrophile in the rate-determining step. Thus electron-withdrawing substituents on the azide accelerate the reaction as shown by the increasing rates: *p*-azidotoluene < phenyl azide < furoyl azide. The rates of reactions of *p*-azidonitrobenzene are faster than those of phenyl azide but could not be measured in the 0.827-mm cell available in the last stage of this research.

Activation parameters were measured for three of these reactions (Table II). The low enthalpies of activa-

Table II. Activation Parameters for the Reaction of Azides with Iridium and Rhodium Complexes

Azide	Metal carbonyl	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu
Furoyl	IrCl(CO)(Ph ₃ P) ₂	7.6	-37
Phenyl	IrCl(CO)(Ph ₃ P) ₂	8.8	-34
Phenyl	RhCl(CO)(Ph ₃ P) ₂	6.7	-42

tion, values ranging from 6.7 to 8.8 kcal/mol, and large, negative entropies of activation, -34 to -42 eu, resemble those parameters reported by Chock and Halpern¹⁹ for oxidative-addition reactions of the iridium carbonyl **1**. Such values are consistent with a bimolecular reaction having a constrained configuration in the activated complex.

Six-coordinate iridium carbonyls such as [IrClI(CH₃)(CO)L₂]^{20,21} do not react with organic azides under these conditions. The coordinatively saturated iridium(I) dicarbonyl, [IrI(CO)₂L₂]²² reacts with aryl azides but only after an induction period.

Summation of the above evidence supports a mechanism in which an organic azide reacts with these coordinatively unsaturated carbonyls by forming an oxidative adduct such as **2** which rapidly collapses to products. There is no kinetic evidence to suggest that **2** is a true intermediate.

The over-all reaction of these metal carbonyls with organic azides can be thought of as an atom-transfer redox reaction. Since carbon monoxide reacts with the nitrogen complex **3** to regenerate the carbonyl **1** and a mole of nitrogen, the over-all process can be made catalytic. The role of the metal atom in facilitating this atom transfer between adjacent ligands as in **2** led us to ponder other metal-promoted atom-transfer redox reactions.²³

Characterization of the Nitrogen Complex 3. The yellow crystalline complex **3** exhibits an intense N₂ stretching band at 2105 cm⁻¹, a frequency comparable to those reported for other nitrogen complexes^{11b,15a,12} (Table III). X-Ray diffraction studies of [Ru-

Table III. Infrared CO and N₂ Frequencies

Compound	$\bar{\nu}(\text{N}_2 \text{ or CO}),$ cm ⁻¹	Δ^a
[Ru(NH ₃) ₅ N ₂]I ₂ (13) ^b	2129 ^c	201
[Os(NH ₃) ₅ N ₂]I ₂ (14) ^d	2033 ^c	297
[RhCl(N ₂)L ₂] (8) ^e	2152 ^f	178
[IrCl(N ₂)L ₂] (3)	2105 ^f	225
[IrCl(N ₂)(C ₆ H ₁₂ O ₄)L ₂] (9)	2190 ^g	140
[CoH(N ₂)L ₃] (15) ^h	2085 ^c	245
	2105	
N ₂	2330 ⁱ	...
CO	2143	...
[RhCl(CO)L ₂] (7)	1977 ^f	166
[RhH(CO)L ₃] (16) ^j	1926 ^f	217
[IrCl(CO)L ₂] (1)	1962 ^f	181
[IrCl(CO)(C ₄ H ₂ O ₃)L ₂] (17) ^k	2030 ^f	113

^a Difference in cm⁻¹ between free N₂ and coordinated N₂ or free CO and coordinated CO. ^b Reference 11. ^c Nujol mull. ^d Reference 15. ^e Reference 14. ^f CHCl₃ solution. ^g KBr disk. ^h Reference 12. ⁱ Raman frequency. ^j Reference 28a. ^k Reference 27a.

(NH₃)₅N₂]^{2+ 11b} and [CoH(N₂)L₃]¹³ show nitrogen longitudinally bound to the central metal in a manner similar to a terminal CO ligand. We presume the nitrogen in **3** is also bound in this way. In view of the pronounced tendency for the two phosphines in complexes such as **1** to remain *trans*,²¹ it seems likely that **3** also has a *trans* configuration. The far-infrared spectrum of the nitrogen complex **3** reveals a band at 325 cm⁻¹ with a shoulder at 322 cm⁻¹ which we assign to the iridium-chlorine stretching mode. Such metal-chlorine stretching modes are primarily dependent on the nature of the ligand *trans* to chloride.²⁴ Thus, it is interesting to compare these values with the Ir-Cl frequency (316 with a shoulder at 309 cm⁻¹) in the seemingly isostructural carbonyl **1**. Nitrogen would appear to exert a weaker *trans* effect than carbon monoxide. However, such effects are combinations of the π -bonding and σ -bonding characteristics of the *trans* group.

Our attempts to isolate other nitrogen complexes similar to **3**, in which other tertiary phosphines or halides stand in place of triphenylphosphine or chloride, have not been successful. The azide reaction proceeds normally, but the resulting nitrogen complexes are rapidly degraded. Apparently "softer" ligands render the nitrogen more susceptible to ligand displacement reactions. The lability of the nitrogen ligand in solutions of the rhodium complex **8**¹⁴ can be explained by the same argument.

Our preparative and ir spectral results indicate that the nitrogen complex **3** undergoes some still unresolved reaction with excess azide. Consequently, the best synthesis of **3** involves carrying out the reaction under mild conditions and removing **3** from the azide as soon as the reaction is complete. Under these circumstances, high yields of **3** are realized. Small crystals of the nitrogen complex **3** can be prepared at some expense in yield by precipitation with hot hexane. These crystals are quite stable over long periods (several months) at room temperature if they are protected from oxygen. The apparently amorphous powder obtained from the high-yield preparation seems to be less resistant to autoxidation. Solutions of the nitrogen

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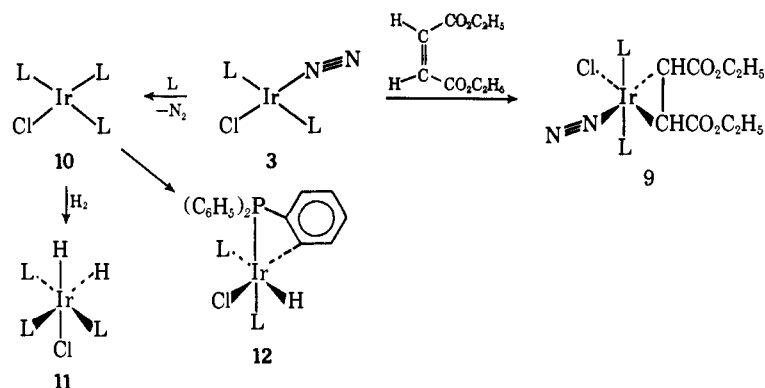


Figure 4.

complex are susceptible to autoxidation but these can be manipulated in air without extensive decomposition. Autoxidation of the nitrogen complex **3** will be described in a later paper.

Acetylenes displace nitrogen from **3**; however, certain olefins form higher coordinate nitrogen complexes.¹ Diethyl maleate forms a stable 1:1 adduct provisionally formulated as an octahedral iridium(III) complex **9**. The ir spectrum of the olefin complex **9** exhibits ester bands at 1730 and 1690 cm^{-1} . The diverse *trans* effects exerted by chloride and nitrogen could account for the difference ester frequencies.

The N_2 absorption band in the maleate complex **9** occurs at 2190 cm^{-1} , a value which reflects a reduction in the back-bonding to coordinated nitrogen as the oxidation state is raised and the olefin competes with N_2 for the available d electrons. Comparison of N_2 and CO frequencies in related complexes (Table III) reveals the role of d_π - p_π interactions in the bonding of nitrogen complexes. The differences (Δ values) between the stretching frequencies of free N_2 and coordinated N_2 or free CO and coordinated CO reflect the degree of backbonding in these structurally similar complexes. These Δ values indicate that N_2 is a more powerful π acid than CO. Third-row elements are apparently more effective in back-bonding to N_2 or CO than second-row elements, but this difference is more pronounced in the case of nitrogen. Comparisons of the N_2 and CO frequencies for the isostructural ruthenium and osmium N_2 complexes **13**¹¹ and **14**¹⁵ or the analogous rhodium and iridium CO compounds **8**⁸ and **3** also support this hypothesis. Such differences have been explained²⁵ in terms of the greater overlap of 5d compared with 4d orbitals.²⁶ The changes in N_2 frequencies as other ligands compete for back-bonding are similar to those for related CO complexes. Compare, for example, differences between N_2 frequencies in **3** and **9** with the CO frequencies exhibited by **1** and **17**.²⁷ The N_2 frequency of the cobalt complex **15**¹⁸ is reasonable when compared with the value for the isostructural rhodium carbonyl **16**.²⁸ Nitrogen is similar to NO^+ inasmuch as both are strong π acids and weak

σ donors. This analogy leads us to propose that the most stable nitrogen complexes will be found in the iron triad and that nitrogen complexes of platinum will be very labile. Nature's choice of nonheme iron as the nitrogen binding site in nitrogenases is consistent with this idea. Through synergistic interaction strong σ -donor ligands should stabilize coordinated N_2 . The N_2 stretching frequency is a good measure of stability for those nitrogen complexes which decompose by dissociative mechanisms. This is well illustrated by comparing the thermal stabilities of $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{2+}$ ($\nu_{\text{N}=\text{N}}$ 2033 cm^{-1} , dec $>300^\circ$, with $[\text{Os}(\text{NH}_3)_4(\text{N}_2)_2]^{2+15b}$ (mean $\nu_{\text{N}=\text{N}}$ 2147 cm^{-1} , dec ca. 50°).

Triphenylphosphine rapidly reacts with the iridium nitrogen complex **3** quantitatively displacing nitrogen to form the orange trisphosphine complex **10** (Figure 4). We were disappointed to find that this phosphine complex **10**, which is analogous to Wilkinson's catalyst ($\text{RhCl}(\text{PPh}_3)_3$),²⁹ is not an effective hydrogenation catalyst. The different behavior of these complexes can be accounted for in terms of coordinative unsaturation. Wilkinson has shown that a key factor in the function of this rhodium catalyst is the presence of a vacant coordination site.²⁹ The iridium analog **10** readily adds hydrogen to form **11**, but the three phosphine ligands remain tightly bound to iridium. Neither **10** nor **11** dissociates a phosphine ligand, and the potential substrate olefin is unable to enter the coordination sphere.

Bennett and coworkers have described the unusual and apparently irreversible tautomeric change to an octahedral hydride **12** when the phosphine complex **10** is heated.³⁰ This transformation can be considered an intramolecular oxidative addition and manifests the great reactivity of **10**.

The coordinatively unsaturated nitrogen complex **3** fails to add H_2 at pressures up to 4 atm. The analogous carbonyl **1** is well known for its ability to reversibly add H_2 .³¹ A survey of those d^8 complexes which add H_2 suggests that this oxidative-addition reaction is enhanced by strong σ -bonding ligands which build up the electron density of the central metal, but such additions are retarded by back-bonding ligands which act to decrease the electron density at the central metal.¹⁸ The failure of the nitrogen complex **3** to add H_2 is

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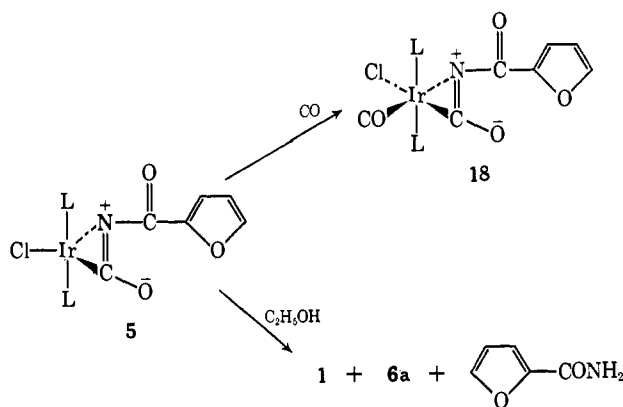
(31) L. Vaska and J. W. Diluzio, *J. Amer. Chem. Soc.*, **84**, 679 (1962).

Table IV. Aroyl Isocyanate Complexes

Isocyanate complex	Calcd, %					Found, %					Selected ir peaks, cm ⁻¹	
	C	H	N	Cl	P	C	H	N	Cl	P		
[IrCl(C ₄ H ₃ OCONCO)L ₂]	56.71	3.71	1.57	4.00	6.98	56.10	4.08	1.84	4.30	7.09	1655	1390
[IrCl(C ₄ H ₃ OCONCO)(CO)L ₂]	56.29	3.60	1.53	3.87	6.76	55.91	3.73	1.67	4.45	6.94	1630	1355 2030
[IrCl(C ₆ H ₅ CONCO)L ₂]	58.75	3.89	1.56	3.95	6.90	58.59	4.25	1.58	4.05	6.76	1655	1387
[IrCl(<i>p</i> -NO ₂ C ₆ H ₄ CONCO)L ₂]	55.95	3.60	2.97	3.76	6.57	56.17	4.08	3.08	4.29	6.36	1655	1380
[IrCl(<i>p</i> -CH ₃ C ₆ H ₄ CONCO)L ₂]	59.16	4.05	1.53	3.89	6.79	58.64	4.19	1.55	4.19	6.71	1650	1390
[IrCl(<i>p</i> -CH ₃ C ₆ H ₄ CONCO)(CO)L ₂]	58.68	3.93	1.49	3.77	6.59	58.93	3.98	1.69	4.63	6.63	1635	1350 2040
[IrCl(<i>p</i> -CH ₃ OC ₆ H ₄ CONCO)L ₂]	58.14	3.98	1.51	3.82	6.67	59.35	4.01	1.59	5.12	6.61	1655	1385
[RhCl(C ₄ H ₃ OCONCO)L ₂]	63.05	4.13	1.75	4.44	7.76	63.11	4.10	1.97	4.49	7.30	1710	1405

consonant with the previously mentioned infrared evidence indicating that N₂ is a more powerful π acid than CO, but that the latter is a better σ donor. It is unfortunate that N₂ is deactivating to H₂ addition inasmuch as this is a necessary step for catalytic hydrogenation of N₂.

A number of acyl isocyanate complexes **5** were prepared by treating the iridium carbonyl **1** with acyl azides in alcohol-free solutions.^{1a} Analytical data and selected infrared bands for **5** are gathered in Table IV. That isocyanate complexes are coordinatively unsaturated was demonstrated by the addition of 1 mole of CO to form complexes such as **18**. The carbonyl band in **18** is at 2030 cm⁻¹, supporting its formulation



as an iridium(III) complex (Table IV). Ethanolysis of **5** afforded the iridium(I) carbonyl **1**, the ethyl carbamate **6b**, and α -furoamide, a result which suggests that the acyl isocyanate fragment is still intact in complex **5**. Carbon monoxide is probably extracted from the ethanol.

Experimental Section

Infrared Spectral Study. A. A two-necked, 50-ml, pear-shaped flask, fitted with a syringe cap and a rubber stopper through which a medium porosity filter stick was attached, was flushed with nitrogen. A solution of 78 mg (0.10 mmole) of chlorocarbonyl **1**³² in 2 ml of chloroform was introduced into the flask with a syringe, and the solution was frozen with a Dry Ice-acetone bath. A solution of 15 mg (0.10 mmole) of furoyl azide in 2 ml of chloroform was then slowly introduced and frozen on the solid mass. The mixture was then allowed to partially melt while stirring vigorously with a magnetic stirrer. Inverse filtration of the partially melted solution was accomplished by immersion of the filter stick and introduction of nitrogen gas. The filtered solution was immediately introduced into a calcium fluoride cell of 1-mm sample thickness, and the infrared spectrum was recorded with a Perkin-Elmer 421 spectrophotometer. Recording of the spectrum of the sample could be initiated within a minute after it had been filtered.

(32) J. P. Collman, C. T. Sears, Jr., and M. Kubota, *Inorg. Syn.*, 11, 101 (1968).

B. The above reaction flask was flushed with nitrogen and charged with 405 mg of iridium molecular nitrogen complex **3** and 20 ml of freshly chromatographed chloroform. The solution was frozen and two drops of *p*-methylbenzoyl isocyanate³³ were added to the frozen mixture. The frozen mass was allowed to melt and samples were withdrawn by inverse filtration for spectral study. Several scans of the spectrum in the 1550–2300-cm⁻¹ region were obtained. Further additions of the isocyanate to the sample of the nitrogen complex provided opportunity for repeated observations of the reactions.

Materials for Kinetic Studies. Reagent-grade chloroform was dried by passing it through alumina. After establishing the small effect of the ethanol preservative in chloroform on the rates under investigation, all subsequent experiments were performed using reagent chloroform. Furoyl azide³⁴ which was recrystallized from acetone-water was stored in a freezer before use. The aryl azides³⁵ were distilled under reduced pressure and stored in brown bottles in a freezer. These azides were used within 3 weeks after distillation. The iridium and rhodium carbonyl complexes which were synthesized by previously described procedures^{19,21,32} were recrystallized from benzene-methanol or chloroform-ethanol and washed with ether. The absence of oxygen, halogen, or hydrogen halide adduct contaminants in the samples was established by infrared spectra. Thin-layer chromatography was used to certify purity of some of the samples. Decomposition temperatures (uncorrected), recorded on a Fisher-Johns melting point apparatus, infrared frequencies, and extinction coefficients of the CO absorption (l./mole cm) in chloroform solution are as follows: IrCl(CO)(Ph₃P)₂, 261–264°, 1962 cm⁻¹, 1066; IrBr(CO)(Ph₃P)₂, 254–256°, 1966 cm⁻¹, 1120; IrI(CO)(Ph₃P)₂, 214–218°, 1969 cm⁻¹, 1015; IrN₃(CO)(Ph₃P)₂, 1964 cm⁻¹, 1395; IrCl(CO)(Ph₂(CH₃)₂), 158–159°, 1960 cm⁻¹, 1200; RhCl(CO)(Ph₃P)₂, 187–190°, 1977 cm⁻¹, 1040; RhBr(CO)(Ph₃P)₂, 173–175°, 1979 cm⁻¹, 1081; RhI(CO)(Ph₃P)₂, 165–168°, 1981 cm⁻¹, 1011; RhCl(CO)(Ph(C₂H₅)₂)₂, 113–114°, 1964 cm⁻¹, 1062; RhBr(CO)(Ph(C₂H₅)₂)₂, 124–125°, 1966 cm⁻¹, 1100.

Kinetic Measurement. The kinetics of the reaction of furoyl azide and *trans*-IrCl(CO)(Ph₃P)₂ were studied by measuring the rate of decay of the CO stretching peak at 1962 cm⁻¹. Equal volumes of the reactants each at 1.00 × 10⁻³ M were thoroughly mixed at the reaction temperature and rapidly introduced into a 3-cm cell which had sodium chloride windows. The cell was thermostated in a Barnes variable-temperature chamber before introduction of the solution and during the course of the reaction. A Perkin-Elmer 421 spectrophotometer operated at a constant slit of 150 μ was used to record the spectra.

The kinetics of reactions of aryl azides with the iridium and rhodium carbonyl complexes were measured in a similar fashion. One drop (8.40 μ moles) of the azide was weighed in a 10-ml volumetric flask, to which was introduced an equimolar amount of iridium or rhodium complex along with 10 ml of chloroform. The solution was thoroughly mixed and then introduced into a 0.827-mm cell which had calcium fluoride windows. Precautions were taken throughout to exclude contact of the solutions with atmospheric oxygen. The cell was thermostated in an insulated chamber, the temperature of which was maintained by introducing air. A Thermistemp temperature controller, Model 71 (Yellowsprings Instrument Co.), using a thermistor taped on the cell was employed to regulate the temperature of the air. Spectra were recorded on a

(33) O. C. Billeter, *Chem. Ber.*, 36, 3218 (1903).

(34) P. A. S. Smith, *Org. Reactions*, 3, 366 (1946).

(35) R. O. Lindsay and C. F. H. Allen in "Organic Synthesis," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, pp 710–711.

Perkin-Elmer 621 spectrophotometer at constant wavelength (band maxima) and constant slit (150 μ). Spectra for determination of extinction coefficients of the metal carbonyls were obtained at a scanning rate of 20 $\text{cm}^{-1}/\text{min}$ on a chart scale of 13 cm^{-1}/in . A frequency calibration was accomplished by comparison with water vapor bands.

trans-Chloronitrogenbis(triphenylphosphine)iridium(I) (3). To a suspension of $\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$ (1.0 g, 0.256 mmole) in 12 ml of reagent chloroform (containing at least 0.75% ethanol), cooled to 0° by an ice bath, was added over a 5–10 min period a solution of α -furoyl azide (0.25 g, 0.365 mmole) in 6 ml of chloroform. The mixture was stirred for 30 min under nitrogen at 0°. The orange-yellow solution was filtered into 180 ml of cold *n*-hexane with stirring under nitrogen. The resulting yellow precipitate was collected on a filter, washed with *n*-hexane and cold ether, and sucked dry. The yield of nitrogen complex varied from 0.82 to 0.90 g (82 to 90%). A more crystalline product may be obtained by filtering the orange-yellow solution, adding to this filtrate 36 ml of boiling hexane, and gradually cooling this mixture to –20° over a 15-min period. After 10 min at 0°, the crystalline product **3** is collected on a filter, washed with hexane and ether, and dried under vacuum. Both forms give acceptable analyses. The infrared spectrum exhibits an intense band at 2105 cm^{-1} (N_2) in chloroform or as a KBr pellet. Except for a weak and variable band at 1970 cm^{-1} (CHCl_3) and an iridium-chlorine stretch at 325 cm^{-1} (Nujol), the spectrum contains no absorptions above 650 cm^{-1} other than those attributed to triphenylphosphine.

Anal. Calcd for $\text{C}_{36}\text{H}_{30}\text{ClIrN}_2\text{P}_2$: C, 55.38; H, 3.84; N, 3.58; Cl, 4.61; P, 7.94. Found: C, 55.38; H, 3.91; N, 3.61; Cl, 5.06; P, 7.60.

The crystalline form decomposes reproducibly from 150 to 152° and is relatively more stable than the amorphous form. Under an atmosphere of nitrogen or argon, the former has a shelf life of several months. Either form reacts with oxygen and turns green. Solutions of the nitrogen complex are not stable in the air, and, even in the absence of air, chloroform solutions of the complex decompose at temperatures above 25°.

The nitrogen complex **3** (34.0 mg, 0.0436 mmole) was placed in a flask attached to a gas buret. A solution of triphenylphosphine (20.2 mg, 0.0771 mmole) in 3.0 ml of toluene was introduced into the flask with a syringe through a rubber septum. Gas evolution was immediate, 1.01 ml at 22.2° (theoretical volume, 1.05 ml), and gas chromatographic analysis showed it to be nitrogen. The deviation –3.8% was reproducible and similar deviations (–3.5%) were obtained with zinc and HCl using the same apparatus.

Chloro(dimethyl maleate)nitrogenbis(triphenylphosphine)iridium (9). To a cold (0°) solution of the nitrogen complex (500 mg, 0.64 mmole) in 5 ml of chloroform was added diethyl maleate (200 mg, 1.16 mmoles) and the solution was stirred at 0–2° for 30 min. Addition of *n*-hexane resulted in the precipitation of a pale yellow solid which was collected, washed with hexane and then ether, and dried over calcium chloride *in vacuo*. Recrystallization from chloroform–hexane (1:20) at –10° afforded the pure product as a pale yellow solid. The infrared spectrum and KBr exhibits (selected) intense bands at 2190, 1730, and 1690 cm^{-1} .

Anal. Calcd for $\text{C}_{44}\text{H}_{42}\text{ClIrN}_2\text{O}_4\text{P}_2$: C, 55.46; H, 4.41, Cl, 3.78; N, 2.94; P, 6.51. Found: C, 55.32; H, 4.55; Cl, 3.99; N, 3.05; P, 6.57.

A 4-day old sample (59.75 mg, 61.8 μ moles) of this five-coordinate nitrogen complex was placed in a bulb which was evacuated and then heated at 160° for 15 min. The resulting noncondensable gas (52.5 μ moles) was identified by its mass spectral cracking pattern and by gas chromatographic analysis as nitrogen.

Reaction of Phenyl Azide with Chlorocarbonylbis(triphenylphosphine)iridium(I). To a suspension of the iridium carbonyl (1.0 g, 1.28 mmoles) in 15 ml of alcohol-free chloroform cooled to 0–5° was added phenyl azide (0.2 ml), and the mixture was stirred for 1 hr. Addition of cold hexane (100 ml) afforded a greenish-yellow precipitate which was collected on a filter, ir (KBr) 2100 (s) and 1965 (m) cm^{-1} .

Addition of a 250-mg sample of this precipitate to a solution of 84 mg of triphenylphosphine in 2 ml of chloroform resulted in the immediate evolution of nitrogen (gas chromatographic analysis) and the formation of a red color. Carbon monoxide was bubbled through a solution of the greenish-yellow precipitate in chloroform for 2 min. Evaporation of the solvent yielded $\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$, ir (KBr) 3050, 1955 (CO), 1475, 1430, and 1090 cm^{-1} .

Chloro(aryl isocyanate)bis(triphenylphosphine)iridium (5). To a suspension of $\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$ (1.0 g, 1.28 mmoles) in 15 ml of alcohol-free chloroform cooled by an ice bath was added

1.28 mmoles of aryl azide. The solution was stirred at 0° for 30 min to 1 hr (depending on the azide employed) during which gas was evolved. Dropwise addition of cold hexane (90 ml) afforded a yellow precipitate which was collected on a filter and recrystallized several times from methylene chloride–hexane. A similar procedure was used to prepare an analogous rhodium complex. Analytical data and selected infrared data are listed in Table IV. Molecular weight measurements by a Mechrolab osmometer indicated that the complexes are monomeric.

The gas evolved in the preparations using α -furoyl azide and *p*-nitrobenzoyl azide was analyzed by gas chromatography and found to be pure N_2 . Neither CO nor CO_2 were detected in the effluent gas.

Chloro(aryl isocyanate)carbonylbis(triphenylphosphine)iridium-I (18). Carbon monoxide was bubbled through a solution of $[\text{IrCl}(\text{RCONCO})[\text{P}(\text{C}_6\text{H}_5)_3]_2]$ (0.198 mmole) in 20 ml of methylene chloride for 5 min, during which the solution became lighter in color and a precipitate began to form. Evaporation of the solvent and recrystallization of the residue from methylene chloride–hexane afforded the pure carbonyl complexes. Analytical data are presented in Table IV.

Isolation of Ethyl and Methyl α -Furoylcarbamate (6). To a suspension of 2 g of $\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$ in 25 ml of chloroform (reagent grade), cooled by an ice bath, was added a solution of furoyl azide, 0.5 g (43% excess) in 10 ml of chloroform. After the mixture had been stirred for 30 min at 0°, the orange-yellow solution was filtered into 350 ml of cold *n*-hexane, and the yellow nitrogen complex was collected on a filter. The resulting filtrate was allowed to stand at room temperature for 4 hr to precipitate more of the nitrogen complex which was then removed by filtration. The solvent was evaporated from the clear filtrate at 35° *in vacuo* leaving a pale yellow solid. Thin layer chromatography (tlc) showed that this residue contained at least nine components. Preparative TLC on silica gel PF with 5% methanol in chloroform yielded the major component (acetone extraction) which was further purified by recrystallization from methylene chloride–hexane, pure ethyl α -furoylcarbamate (**6b**), mp 122–124°, identical in all respects (nmr, infrared and mass spectra, tlc, and mixture melting point) with a sample isolated from an independent synthesis.

Anal. Calcd for $\text{C}_8\text{H}_9\text{O}_4\text{N}$: C, 52.46; H, 4.92; N, 7.65; O, 34.97. Found: C, 52.84; H, 5.15; N, 7.97; O, 34.05.

Using chloroform prepared by passage through activated alumina (to remove ethanol) and then addition of 0.15 ml of methanol in an experiment otherwise identical with the one described above, pure methyl α -furoylcarbamate (**6a**), 86 mg, mp 89°, was obtained.

Anal. Calcd for $\text{C}_7\text{H}_9\text{O}_4\text{N}$: C, 49.70; H, 4.14; N, 8.29; O, 37.87. Found: C, 49.89; H, 4.25; N, 8.26; O, 38.01.

The nmr and infrared spectra of the ethyl and methyl α -furoylcarbamates are entirely consistent with their structures. The mass spectra of these compounds are very similar except that fragment *m/e* 45 which is assigned to the ethoxy ion in the former is replaced by a methoxy peak at 31 in the latter. The parent ions were not observed. Most of the major peaks, *m/e* 138, 137, 111, 95, 67, 39, 29, can be rationalized in terms of energetically favorable fragmentation processes.

Independent Synthesis of Ethyl α -Furoylcarbamate (6b). A solution of ethyl chloroformate (3.26 g, 0.03 mole) in 50 ml of alcohol-free chloroform was cooled to 0° and combined with pyridine (7.12 g, 0.09 mole) followed by α -furoamide (3.33 g, 0.03 mole).

The mixture was stirred at 0° for 4 hr and then at room temperature for 18 hr. Filtration afforded 1.11 g of unreacted furoamide (after washing with dilute HCl). The chloroform filtrate was washed with two 30-ml portions of dilute HCl and then distilled water. The resulting solution was dried over sodium sulfate. Removal of the solvent afforded a residue which was purified by preparative TLC on silica gel PF with 5% methanol in chloroform as the eluent. A small amount of the pure ethyl α -furoylcarbamate was isolated. It was identical in all respects with the sample isolated from the reaction described above.

Chlorotris(triphenylphosphine)iridium(I) (10). To a suspension of the iridium nitrogen complex **3** (0.10 g, 0.13 mmole) in 5 ml of degassed toluene in a Schlenk tube under a nitrogen atmosphere was added triphenylphosphine (3.3 mg, 0.13 mmole). The yellow suspension rapidly changed to a deep red solution and a gas (N_2) was evolved. The solution was allowed to stand at room temperature for 1 hr, and the resulting orange solid was removed by filtration under nitrogen. The ir spectrum (KBr) of the orange product showed no absorptions in the region 1600–2200 cm^{-1} and only a very weak absorption in the region 800–900 cm^{-1} . The orange product turns yellow-brown after exposure of the solid to the at-

mosphere for 2 days or the solutions for a few minutes. The compound reacts rapidly with primary alcohols affording the carbonyl 1.

Anal. Calcd for $C_{54}H_{48}ClP_3Ir$: C, 63.87; H, 4.47; P, 9.15; Cl, 3.49. Found: C, 63.77; H, 4.49; P, 9.11; Cl, 3.94.

Chlorobishydridotris(triphenylphosphine)iridium(III) (11). Hydrogen was bubbled through a solution of $IrCl_3$ in toluene. Crystals of the light yellow dihydride were collected on a filter and dried *in vacuo*, mp 165°. Infrared peaks at 2190, 2100, 850, and 815 cm^{-1} are assigned to Ir-H stretching and bending modes.

Anal. Calcd for $C_{54}H_{47}ClP_3Ir$: C, 63.78; H, 4.63. Found: C, 64.14; H, 4.87.

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Transition Metal Complexes of Alkyl Phosphites. III. Four- and Five-Coordination with Nickel(II) Cyanide^{1,2}

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Abstract: The spectral properties of the red-orange, diamagnetic, and nonelectrolytic dicyano complex $[Ni(P(OCH_3)_3)_3(CN)_2]$ indicate a *trans* trigonal-bipyramidal configuration. One molecule of phosphite is easily lost to form the yellow, diamagnetic, nonelectrolyte $[Ni(P(OCH_3)_3)_2(CN)_2]_2$. Ultraviolet-visible and infrared spectral evidence is presented which is consistent with the tentative postulate that in the solid the complex is a dicyano bridged dimer of two trigonal bipyramids such that $x = 2$. In solution, spectral data and molecular weight measurements are in agreement with partial dissociation of the dimer to a square-planar monomer which reverts to $[Ni(P(OCH_3)_3)_3(CN)_2]$ on adding excess ligand. The *trans* complexes $[NiL_3(CN)_2]$ where $L = P(O(CH_2)_3CH_3)_3$ and $C_6H_5P(OC_2H_5)_2$ are also shown to be dissociatively unstable in solution with respect to a lower complex or $Ni(CN)_2$ although no lower complexes could be isolated. The insolubility of the *trans*- $[NiL_3(CN)_2]$ where $L = P(OCH_2)_3CCH_3$ did not permit detection of dissociation in solution. An oily complex which according to spectral studies is probably *trans*- $[Ni(P(OC_6H_5)_3)_3(CN)_2]$ did not show evidence of dissociation in solution.

In a recent communication, Rick and Pruett described the preparation of the five-coordinate nickel(II) complex *trans*- $[Ni(C_6H_5P(OC_2H_5)_2)_3(CN)_2]$ which was reported to be a diamagnetic nonelectrolyte dissociatively stable in acetone.⁴ In the paper by Chastain, Rick, Pruett, and Gray preceding ours,⁵ additional examples of the type *trans*- $[NiL_3(CN)_2]$ (where $L = C_6H_5P(OC_2H_5)_2$, $(C_6H_5)_2POC_2H_5$, $C_6H_5P(OCH_3)_2$, and $P(OC_2H_5)_3$) are described and their electronic transitions assigned on the basis of self-consistent charge and configuration molecular orbital calculations. These complexes as well as the *trans* square-planar system $[Ni((C_6H_5)_2POC_2H_5)_2(CN)_2]$ were also reported to be quite stable in solution although some dissociation in acetonitrile was noticed for $[Ni(C_6H_5P(OC_2H_5)_2)_3(CN)_2]$. Prior to these disclosures, we had begun an investigation of the properties of alkyl phosphite-nickel(II) systems incorporating various coordinating anions. In view of the comparable ligand properties of organic phosphites and cyanides,^{6,7} the structural and isomeric possibilities of such mixed complexes were of interest.

(1) Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967; Abstracts, No. O16.

(2) Part II of this series: J. M. Jenkins, T. J. Huttemann, and J. G. Verkade, *Advances in Chemistry Series*, No. 62, American Chemical Society, Washington, D. C., 1967, p 604.

(3) Alfred P. Sloan Fellow.

(4) E. A. Rick and R. L. Pruett, *Chem. Commun.*, 697 (1966).

(5) B. B. Chastain, E. A. Rick, R. L. Pruett, and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 3994 (1968).

(6) E. F. Riedel and R. A. Jacobson, Abstracts, Meeting of the American Crystallographic Association, Minneapolis, Minn., 1967, p P-10.

(7) J. G. Verkade and T. S. Piper, *Inorg. Chem.*, **2**, 944 (1963).

We report here the solid diamagnetic complexes *trans*- $[Ni(P(OCH_3)_3)_3(CN)_2]$, *trans*- $[Ni(P(OCH_2)_3CCH_3)_3(CN)_2]$, and $[Ni(P(OCH_3)_3)_2(CN)_2]_2$, where x is probably 2. Spectral evidence permits postulation of the presence of *trans*- $[Ni(P(OC_6H_5)_3)_3(CN)_2]$ and *trans*- $[Ni(P(O(CH_2)_3CH_3)_3)_3(CN)_2]$ in solution. All of the $[NiL_3(CN)_2]$ complexes except where $L = P(OC_6H_5)_3$ are shown to be reversibly unstable in solution with respect to $Ni(CN)_2$ and/or what is very likely a four-coordinate *trans*- $[NiL_2(CN)_2]$ species. Solid and solution spectral measurements of $[Ni(P(OCH_3)_3)_2(CN)_2]_2$ coupled with molecular weight determinations in solution admit the strong possibility of a five-coordinate dicyano-bridged dimer $[NiL_2(CN)_2]_2$ in the solid which is in equilibrium with the planar monomeric *trans*- $[NiL_2(CN)_2]$ in solution. Furthermore, *trans*- $[Ni(P(OCH_3)_3)_3(CN)_2]$ shows evidence of dissociating partially to the planar monomer and its dimer. These observations led us to reinvestigate the $[Ni(C_6H_5P(OC_2H_5)_2)_3(CN)_2]$ complex with the result that it too was shown from spectral studies to be reversibly unstable with respect to dissociation in acetone in contrast to the report of Rick and Pruett.⁴

Experimental Section

Reagents. $Ni(CN)_2 \cdot 4H_2O$ was prepared according to a previously given method.⁸ Trimethyl phosphite, triphenyl phosphite, and tri-*n*-butyl phosphite were obtained from Eastman Kodak Co., Rochester, N. Y., and used without further purification. 4-Methyl-

(8) W. C. Fernelius and J. J. Burbage, *Inorg. Syn.*, **2**, 227 (1946).