Figure 3. Plot of log k_f for reaction 1 against log k_f^I for reaction 8.

in the nature of the substituent R on the ligands $(RO)_2PS_2^-$ and $ROCS_2^-$ is relfected to the same extent in the variation of the rate constants for reaction 1 and reaction 8. This is an interesting point in that the ligand phosphorodithioate bears two substituents R while the ligand xanthate bears only one. Therefore, the effect of the substituent R is better exerted in the nickel xanthate complexes. In other words, inductive and, to a lower extent, mesomeric effects are better transmitted through the xanthate skeleton than they are through that of phosphorodithioate.

Registry No. Ni(methyl xanthate)$_2$ (complex form), 52152-08-6; Ni(ethyl xanthate)$_2$ (complex form), 21375-69-9; Ni(n-propyl xanthate)$_2$ (complex form), 52139-57-8; Ni(isopropyl xanthate)$_2$ (complex form), 52057-73-5; Ni(n-butyl xanthate)$_2$ (complex form), 52139-58-9; Ni(sec-butyl xanthate)$_2$ (complex form), 71582-36-0; Ni(benzyl xanthate)$_2$ (complex form), 53566-80-6; Ni(allyl xanthate)$_2$ (complex form), 71582-37-1; Ni(methoxyethyl xanthate)$_2$ (complex form), 71582-38-2; Ni(2,6-dimethylphenyl xanthate)$_2$ (complex form), 66539-49-9; Ni(cyclohexyl xanthate)$_2$ (complex form), 53566-81-7; Ni(methyl xanthate)$_2$(bpy), 71582-39-3; Ni(ethyl xanthate)$_2$(bpy), 29827-24-5; Ni(n-propyl xanthate)$_2$(bpy), 71597-04-1; Ni(isopropyl xanthate)$_2$(bpy), 71582-40-6; Ni(n-butyl xanthate)$_2$(bpy), 71582-41-7; Ni(sec-butyl xanthate)$_2$(bpy), 71582-42-8; Ni(benzyl xanthate)$_2$(bpy), 71582-43-9; Ni(cyclohexyl xanthate)$_2$(bpy), 71582-44-0; Ni(allyl xanthate)$_2$(bpy), 71582-45-1; Ni(methoxyethyl xanthate)$_2$(bpy), 71582-46-2; Ni(2,6-dimethylphenyl xanthate)$_2$(bpy), 71606-76-3; bpy, 366-18-7; Ni(n-butyl xanthate)$_2$(py)$_2$, 71629-33-9; Ni(sec-butyl xanthate)$_2$(py)$_2$, 71597-49-4; Ni(allyl xanthate)$_2$(py)$_2$, 71597-50-7; Ni(methoxyethyl xanthate)$_2$(py)$_2$, 57739-18-1; Ni(methyl xanthate)$_2$ (salt form), 3427-49-4; Ni(ethyl xanthate)$_2$ (salt form), 3269-24-7; Ni(n-propyl xanthate)$_2$ (salt form), 5573-88-6; Ni(isopropyl xanthate)$_2$ (salt form), 3882-73-3; Ni(n-butyl xanthate)$_2$ (salt form), 16839-24-0; Ni(sec-butyl xanthate)$_2$ (salt form), 71565-82-7; Ni(benzyl xanthate)$_2$ (salt form), 68992-49-4; Ni(allyl xanthate)$_2$ (salt form), 71565-79-2; Ni(methoxyethyl xanthate)$_2$ (salt form), 71565-80-5; Ni(2,6-dimethylphenyl xanthate)$_2$ (salt form), 66367-47-3; Ni(cyclohexyl xanthate)$_2$ (salt form), 71565-81-6.

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Dinitrogen Complexes of Iridium. Influence of Ancillary Ligands

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The comparison of synthetic, reactivity, and bonding properties of dinitrogen and carbon monoxide as isoelectronic ligands in transition metal complexes has been of interest for many years.[1] The effect of ancillary ligands on the properties of metal carbonyls has been extensively studied, but similar effects on metal–dinitrogen complexes have not been widely investigated because of their limited stabilities. The range of dinitrogen complexes of Ir(I), *trans*-[Ir(PR$_3$)$_2$(N$_2$)X], isolated thus far is limited to PR$_3$ = PPh$_3$ and X = Cl,[2] Br,[3,4] or N$_3$.[3] Spectral evidence for the formation of complexes with X = Cl and PR$_3$ = PEtPh$_2$, PBuPh$_2$, PMe$_2$Ph, or PEt$_2$Ph and X = I and PR$_3$ = PPh$_3$ has been previously reported.[3] We have examined iridium–dinitrogen complexes prepared by reaction 1[2] for a variety of substituted phosphines, triphenylarsine, and

$$\textit{trans-}[Ir(PR_3)_2(CO)X] + R'N_3 \rightarrow$$
$$\textit{trans-}[Ir(PR_3)_2(N_2)X] + R'NCO \quad (1)$$
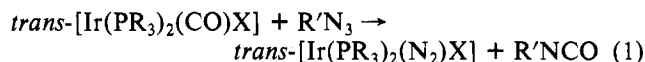
anions X. Dinitrogen as a ligand for Ir(I) appears to be particularly sensitive to the electronic and steric properties of other ligands in the complex. The reasons for the lower stabilities of dinitrogen–iridium(I) complexes with other ligands have not yet been explained. To elucidate features which contribute to the stability and difficulty in isolability of dinitrogen–iridium(I) complexes, we have conducted an extensive study of reaction 1 using a variety of ancillary ligands. In the course of these studies we have isolated four new iridium–dinitrogen complexes including the first dinitrogen–iridium complex containing triphenylarsine and obtained IR data which indicate that ancillary ligands affect the CO and N$_2$ stretching frequencies in a similar fashion.

Experimental Section

The synthesis and characterization of the carbonyliridium(I) complexes *trans*-[IrL$_2$(CO)X] have been described previously.[5] The purity of the complexes were ascertained by noting the absence of extraneous IR absorption bands in the 2000–2200-cm^{-1} region where

Ir(III)–CO compounds are known to absorb. Reagent grade chloroform was deoxygenated by thoroughly purging with dry argon or nitrogen. A Perkin-Elmer Model 621 grating infrared spectrophotometer was used to record spectra. To obtain accurate (± 1 cm^{-1}) readings of maxima of peaks, we recorded spectra on expanded scale (10 cm^{-1}/19 mm chart) at slow (14 cm^{-1}/min) scan rates in the region of interest.

The reactions of furoyl azide and the iridium(I) carbonyl complexes in chloroform solutions were followed by observing the spectra in the 2300–1750-cm^{-1} region immediately after mixing the reagents in a 1-mm CaF$_2$ cell.

trans-Fluoro(dinitrogen)bis(triphenylphosphine)iridium(I) and Other Dinitrogen–Iridium Complexes. A 0.44-g (0.6 mmol) sample of [Ir(PPh$_3$)$_2$(CO)F] was partially dissolved in 15 mL of degassed dichloromethane at 0 °C. A few drops of ethanol were added to the solution to ensure the formation of the carbamate ester upon addition of the furoyl azide. A 0.52-g (3.8 mmol) sample of furoyl azide was added directly to the cold solution. The reaction mixture was stirred for 20 min. Ten milliliters of cold (0 °C) degassed heptane was added to the solution; the solvent was then removed in vacuo until a yellow precipitate formed. The solid was filtered off, washed with three 5-mL portions of anhydrous ether, and dried in vacuo at 56 °C; yield 0.22 g, 50%. IR ν(N$_2$) 2062 cm^{-1} (Nujol). Melting point: turns dark green at 145–150 °C and turns black at 155–160 °C. Anal. Calcd for C$_{36}$H$_{30}$P$_2$N$_2$FIr: C, 56.61; H, 3.96; N, 3.67. Found: C, 56.41; H, 3.89; N, 3.53.

Similar procedures were used to prepare the following dinitrogen complexes.

(Cyanato)(dinitrogen)bis(triphenylarsine)iridium(I), [Ir(AsPh$_3$)$_2$-(N$_2$)NCO]. Anal. Calcd for C$_{37}$H$_{30}$ON$_3$IrAs$_2$: C, 50.79; H, 3.45; N, 4.80. Found: C, 49.30; H, 3.53; N, 4.86. Melting point 150–180 °C. IR ν(N$_2$) 2106 cm^{-1} (Nujol).

(Cyanato)(dinitrogen)bis(triphenylphosphine)iridium(I), [Ir(PPh$_3$)$_2$(N$_2$)NCO]. Anal. Calcd for C$_{37}$H$_{30}$ON$_3$IrP$_2$: C, 56.48; H, 3.84; N, 5.34. Found: C, 56.33; H, 3.80; N, 5.06. Melting point 202 °C.

Chloro(dinitrogen)bis(*p*-tolylphosphine)iridium(I), [Ir(P(*p*-CH$_3$C$_6$H$_4$)$_3$)$_2$(N$_2$)Cl]. Anal. Calcd for C$_{42}$H$_{42}$N$_2$ClIrP$_2$: C, 58.36; H, 4.89; N, 3.24. Found: C, 57.88; H, 4.84; N, 3.35. Melting point 117–120 °C. IR ν(N$_2$) 2090 cm^{-1} (Nujol).

Results and Discussion

Evidence for Ir–CO to Ir–N$_2$ Conversion. A wide assortment of iridium(I) carbonyls shown in Table I was synthesized and characterized by microanalysis[5] and their CO stretching frequencies in the 1960-cm^{-1} region. The absence of absorption in the 2000–2100-cm^{-1} region indicated that these metal carbonyls were not contaminated by their O$_2$, HCl, or Cl$_2$ adducts. The reactions of these iridium(I) carbonyls with furoyl azide in CHCl$_3$ were followed by IR spectral observation of the disappearance of ν(CO), the appearance of ν(N$_2$) near 2100 cm^{-1}, and, where R′ is an acyl group such as furoyl, the appearance of a band at 1780 cm^{-1} due to the carbamate ester resulting from the solvolysis of R′NCO. When it was not possible to observe ν(N$_2$) for the iridium–dinitrogen complex because of rapid thermal dissociation or rapid substitution of dinitrogen by other ligands or the presence of other absorption bands in the 2100 cm^{-1} region, the observation of the decay of ν(CO) at 1960 cm^{-1} and the growth of the 1780-cm^{-1} band were crucial in establishing whether or not the dinitrogen compound was initially formed.

The reported nonreactivity of benzoyl azide with [Ir(PPh$_3$)$_2$(CO)NCS] has been attributed to the low nucleophilicity of the iridium complex.[3] An earlier report also indicated that the thiocyanato complex does not react with oxygen. We found that a solution of [Ir(PPh$_3$)$_2$(CO)NCS] in benzene under 20 psi oxygen for 0.5 h readily gave the dioxygen adduct characterized by ν(CO) at 2000 cm^{-1} and ν(IrO$_2$) at 858 cm^{-1}. We have also previously reported the kinetics of the reaction of methyl iodide with the thiocyanato complex.[5] A casual IR examination of a CHCl$_3$ solution of furoyl azide and [Ir(PPh$_3$)$_2$(CO)NCS] in the 2100-cm^{-1} region indicated only absorption due to the NCS ligand (as if there

was no reaction), but the rapid disappearance of the ν(CO) at 1971 cm^{-1} and the concomitant appearance of the carbamate ester band at 1780 cm^{-1} indicated that an Ir–N$_2$ complex was formed in the reaction and that the ν(N$_2$) for this complex was obscured by the strong CN band of the SCN ligand at 2100 cm^{-1}. The assignment of ν(N$_2$) for the thiocyanato complex is discussed after the following consideration.

The slow disappearance of ν(CO) with concomitant slow appearance of the carbamate ester 1780-cm^{-1} absorption band was observed in the reaction of furoyl azide with the weakly nucleophilic complexes such as [Ir(P(OPh)$_3$)$_2$(CO)Cl], [(Ir(CO)$_2$(PPh$_3$)$_2$H], or [Ir(PPh$_3$)$_3$(CO)H], but for each of these complexes no ν(N$_2$) for the expected dinitrogen complex was observed. No 1780-cm^{-1} carbamate ester band was observed in the reaction of furoyl azide with [Ir(PPh$_3$)$_2$(CS)Cl] and [Ir(SbPh$_3$)$_2$(CO)Cl] after 15 min of reaction.

Assignment of ν(N$_2$). Since the IR frequencies due to ν-(Ir–H), ν(N$_2$) in azido complexes, ν(CN) in thiocyanato complexes, and ν(CO) in Ir(III)–CO complexes are in the 2050–2150-cm^{-1} region, it was necessary to verify assignment of ν(N$_2$) in the spectra of the dinitrogen complexes. The assignment was based on the rapid loss of N$_2$ (hence of ν(N$_2$)) upon reaction of *trans*-[Ir(PR$_3$)$_2$(N$_2$)X] with CO,[2] PPh$_3$,[2] olefins,[6] or reagents which undergo oxidative addition to iridium(I) complexes. As mentioned earlier, furoyl azide (0.73 mmol) reacts with *trans*-[Ir(P(OPh)$_3$)$_2$(CO)Cl] (0.12 mmol) slowly in 5 mL of CHCl$_3$ as shown by loss of ν(CO) (requires over 24 h) and formation of carbamate ester (1780 cm^{-1}). Additionally, a species with IR absorption at 2074 cm^{-1} was formed. That this absorption is not due to ν(N$_2$) was readily demonstrated by its persistence when the species was treated with CO or PPh$_3$. That this band is not due to ν(N$_2$) was further confirmed by microanalytical analysis which showed the absence of nitrogen in the compound. The band at 2074 cm^{-1} is probably due to ν(Ir–H) for a species formed by insertion of Ir into a C–H bond of the triphenyl phosphite ligand such as shown in the decomposition of [Ir(PPh$_3$)$_2$(N$_2$)Cl].[7]

The assignment of ν(N$_2$) for the complex Ir(N$_2$)NCS(P-(C$_6$H$_5$)$_3$)$_2$ is complicated by strong absorption at 2090 cm^{-1} due to ν(CN) of the NCS ligand. The compound has an absorption band at 2111 cm^{-1} which because of its decay upon treatment with Ph$_3$P is assigned to ν(N$_2$). Carbon monoxide added to the solution leads to formation of Ir(CO)$_2$NCS(P-(C$_6$H$_5$)$_3$)$_2$ with absorption due to NCS at 2090 cm^{-1}.

The lifetime of the absorption bands assigned to ν(N$_2$) in Table I were generally shorter when the dinitrogen compounds were examined in the presence of excess furoyl azide. For example, [Ir(AsPh$_3$)$_2$(N$_2$)Cl] decomposes slowly in CHCl$_3$ solution, but in the presence of excess furoyl azide, the decomposition as shown by the disappearance of ν(N$_2$) at 2094 cm^{-1} was rapid. The dinitrogen complex apparently reacts with the acyl azide with evolution of N$_2$. The reaction with the acyl isocyanates was previously reported.[2c] These reactions of the dinitrogen complexes with the acyl azide and isocyanate are more rapid with iridium complexes with more basic ligands.

Furoyl azide reacted rapidly with [Ir(PPh$_2$Me)$_2$(CO)Cl] to form the carbamate ester and a product with IR absorption at 2098 cm^{-1} presumably due to [Ir(PPh$_2$Me)$_2$(N$_2$)Cl]. The 2098-cm^{-1} absorption band was rapidly lost in the presence of excess furoyl azide but not as rapidly in the presence of excess [Ir(PPh$_2$Me)$_2$(CO)Cl]. The IR spectral features of the decay of the 2098-cm^{-1} band with concomitant formation of a new species with absorption at 2050 cm^{-1} are shown in Figure 1. As this new species with the 2050-cm^{-1} band does not react with CO or PMePh$_2$, it is likely that the species with absorption at 2050 cm^{-1} is not [Ir(PMePh$_2$)$_2$(N$_2$)Cl]. A solid which was isolated with an IR band at 2047 cm^{-1} (Nujol) has microanalytical data which conform approximately to the formulation

Table I. Infrared Data (cm^{-1}) for *trans*-[IrL$_2$(CO)X] and *trans*-[IrL$_2$(N$_2$)X] in Chloroform

no.	L	X	ν(CO)	ν(CO)/2143	ν(N$_2$)	ν(N$_2$)/2330
1	PPh$_3$	F	1951	0.9104	2088	0.8961
2	PPh$_3$	Cl	1957	0.9132	2103	0.9026
3	PPh$_3$	Br	1961	0.9151	2109^a	0.9052
4	PPh$_3$	I	1963	0.9160	2113^{a,b}	0.9069
5	PPh$_3$	N$_3$	1959	0.9141	2104^c	0.9030
6	PPh$_3$	NCO	1962	0.9155	2109^d	0.9052
7	PPh$_3$	NCS	1973	0.9207	2111^e	0.9060
8	PPh$_3$	CF$_3$CO$_2$	1967	0.9179	2109	0.9052
9	P(p-CH$_3$C$_6$H$_4$)$_3$	Cl	1958	0.9137	2100^f	0.9013
10	PPh$_2$Me	Cl	1957	0.9132	2099^g	0.9009
11	PPh$_2$Me	Br	1961	0.9151	2110 (?)	0.9056
12	PPhMe$_2$	Cl	1953	0.9113	2091^h	0.8974
13	PEt$_3$	Cl	1938	0.9043	2075^i	0.8906
14	AsPh$_3$	Cl	1955	0.9123	2094^j	0.8987
15	AsPh$_3$	Br	1958	0.9137	2093	0.8983
16	AsPh$_3$	N$_3$	1954	0.9118	2102^k	0.9021
17	AsPh$_3$	NCO	1960	0.9146	2101	0.9017
	P(OPh)$_3$	Cl	2000			
	[Ir(CO)$_2$(PPh$_3$)$_2$H]		1983, 1922		2105 (?)^l	
	[Ir(CO)(PPh$_3$)$_3$H]		1915		m	
	[Ir(PPh$_3$)$_2$(CO)(CH$_3$CN)] BF$_4$		2005		n	

^{a} Fitzgerald and Wu-Lin^4 reported 2095 cm^{-1} (Nujol) for these compounds. ^{b} Degrades to form species with absorption band at 2069 cm^{-1}. This species does not react with CO or PPh$_3$. ^{c} ν(N$_3$) at 2072 cm^{-1}. ^{d} ν(NCO) at 2264 cm^{-1}. ^{e} Overlapped with ν(SCN) at 2094 cm^{-1}. ^{f} ν(N$_2$) at 2090 cm^{-1} (Nujol). ^{g} Degrades to product with band at 2050 cm^{-1}. ^{h} Degrades to species with band at 2051 cm^{-1}. ^{i} Degrades to species with absorption at 2056 and 2035 cm^{-1}. ^{j} ν(Ir–Cl) at 325 cm^{-1}. ^{k} ν(N$_3$) at 2060 cm^{-1} (12); ν(N$_2$) at 2097 cm^{-1} (Nujol). ^{l} Rapid reaction forming 1780-cm^{-1} carbamate ester species. Species with absorption at 2105 cm^{-1} formed but decays to form a species with absorption at 2090 cm^{-1}. A third species with absorption at 2040 cm^{-1} formed and then decays. Both 2040- and 2090-cm^{-1} species are not changed upon addition of PPh$_3$. ^{m} ν(Ir–H) is at 2120 cm^{-1}. Slow reaction leading to carbamate ester (1780 cm^{-1}); species with band at 2040 cm^{-1} found. ^{n} Carbamate ester formed, but no evidence for ν(N$_2$).
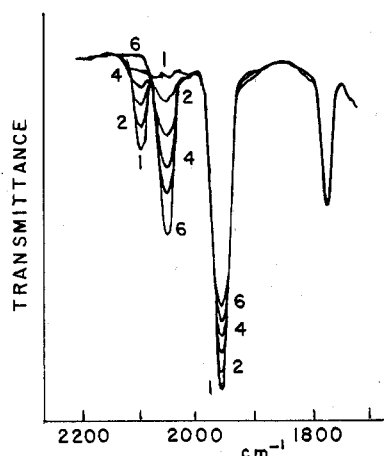

Figure 1. Infrared spectra of solution of [Ir(PMePh$_2$)$_2$(CO)Cl] and furoyl azide in chloroform at (1) 1 min, (2) 5 min, (3) 9 min, (4) 14 min, and (5) 30 min.

(PMePh$_2$)$_2$Cl(CO)IrN$_2$IrCl(PMePh$_2$)$_2$. Anal. Calcd for C$_{53}$H$_{52}$OCl$_2$Ir$_2$N$_2$P$_4$: C, 48.5; H, 3.99; Cl, 5.40; N, 2.13. Found: C, 48.0; H, 3.87; Cl, 5.93; N, 1.19. This species may have a bridged N$_2$ which would not have an IR-active ν(N$_2$). We have not been able to obtain analytically pure crystals of this material so its structure must remain speculative at this stage.

As shown in Table I the complexes with more basic ligands such as [Ir(PPh$_3$)$_2$(CO)I], [Ir(PMe$_2$Ph)$_2$(CO)Cl], and [Ir(PEt$_3$)$_2$(CO)Cl] also form dinitrogen complexes with ν(N$_2$) in the 2075–2100-cm^{-1} region which decay with concomitant formation of peaks in the 2050–2069-cm^{-1} region which are not due to the [Ir(PR$_3$)$_2$(N$_2$)X] complexes. Rather, the peaks are due to ν(CO) as mentioned for the PMePh$_2$ complex or to ν(Ir–H) in ortho-metalated species mentioned earlier.^{7}

The similarity of bonding of Ir–N$_2$ and Ir–CO was noted previously by Chatt, Melville, and Richards.^{3} The range of ν(CO) and ν(N$_2$) values for *trans*-[Ir(PPh$_3$)$_2$(CO)X] and *trans*-[Ir(PPh$_3$)$_2$(N$_2$)X] shown in Table I varies over a small
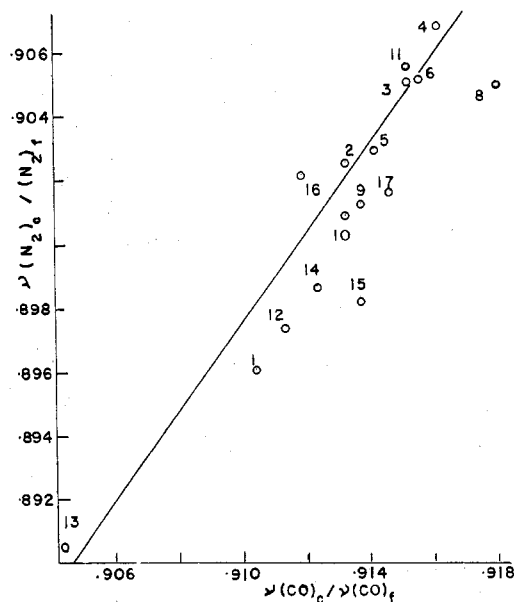

Figure 2. Fractional change of IR stretching frequencies of coordinated and free carbon monoxide and dinitrogen in *trans*-[IrL$_2$(CO)X] and *trans*-[IrL$_2$(N$_2$)X]. Key to compounds is given in Table I.

range, 22 and 25 cm^{-1}, respectively. The electronic effects of the anion X trans to N$_2$ and CO are thus rather small. Similarly the variation of ν(CO) for *trans*-[Ir(AR$_3$)$_2$(CO)Cl] for a variety of phosphines and arsines is 35 cm^{-1} and the corresponding variation of ν(N$_2$) for *trans*-[Ir(AR$_3$)$_2$(N$_2$)Cl] is 38 cm^{-1}. A previously reported variation of 14 cm^{-1} for ν(CO) for carbonyls and 53 cm^{-1} for ν(N$_2$) for the corresponding dinitrogen complexes is now shown to be in error. The anomalous large difference for ν(N$_2$) was previously attributed to greater electron drift to antibonding orbitals of N$_2$ or to some fortuitous effect such as "coupling of degenerate molecular vibrations".^{3}

When the data are plotted as in Figure 2 to show the ratio ν(N$_2$)$_c$/ν(N$_2$)$_f$ and ν(CO)$_c$/ν(CO)$_f$ (c = coordinated and f =

free ligand), there is good indication that the ancillary substituted phosphine and arsines and anion X ligands appear to influence the $\nu(N_2)$ and $\nu(CO)$ to the same extent. Mössbauer[8] and IR intensity measurements[9] suggest that N_2 is a weaker σ donor and π acceptor than CO, but the π-acceptor capacity is more important than the σ-donor propensity for N_2. It is interesting to note that cis and trans ancillary ligands appear to have the same effect on N_2 and CO bonded to Ir.

Isolation of Iridium–Dinitrogen Complexes. The IR spectral studies of solutions of $[Ir(PR_3)_2(CO)Cl]$ and furoyl azide in $CHCl_3$ gave indication of the relative stabilities of dinitrogen complexes. This information was used to direct our efforts to isolate $trans$-$[Ir(PPh_3)_2(N_2)F]$, $trans$-$[Ir[(p$-CH_3-$C_6H_4)_3P]_2(N_2)Cl]$, $trans$-$[Ir(PPh_3)_2(N_2)(NCO)]$, and $trans$-$Ir[(AsPh_3)_2(N_2)(NCO)]$. While only dinitrogen complexes of Ir with organophosphine ligands had been previously reported, we found that organoarsine–carbonyl–iridium(I) complexes react with acyl azides to form dinitrogen complexes. Solid $trans$-$[Ir(AsPh_3)_2(N_2)Cl]$ and $Ir(AsPh_3)_2(N_2)(NCO)]$ were isolated, but satisfactory microanalytical data were obtained only for the latter complex. The lower stability of arsine compared to phosphine derivatized dinitrogen complexes has been previously noted for Re(I) and Mo(0) complexes.[10] It is of interest to note that the cyanate anion appeared to give the most stable dinitrogen complexes.

The lower stabilities of dinitrogen–iridium complexes which have lower values of $\nu(N_2)$ indicative of stronger Ir–N_2 bonds were previously ascribed to the need for satisfaction of the electron donor rather than π-acceptor function of the dinitrogen ligand.[3] We conclude from the present study that whether a dinitrogen complex can be formed from reaction 1 and isolated does not depend solely on the effect of ancillary ligands on the stability of the Ir–N_2 bond. The additional significant factors are, first, the favorable kinetics[2c] of reaction 1 leading to formation of the dinitrogen complex and, second, the kinetics of substitution and oxidative addition reactions of the dinitrogen complex. The short lifetimes of the $[Ir(PR_3)_2(N_2)X]$ complexes with low $\nu(N_2)$ (hence stronger Ir–N_2 bonds) observed for complexes with more basic and sterically less hindered PR_3 can be attributed to their greater reactivity with the reactant acyl azide or byproduct acyl isocyanate or intramolecular insertion of Ir into C–H bonds of coordinated phosphine.[7]

Registry No. $trans$-$[Ir(PPh_3)_2(N_2)F]$, 71700-02-2; $trans$-$[Ir(PPh_3)_2(N_2)Cl]$, 21414-18-6; $trans$-$[Ir(PPh_3)_2(N_2)Br]$, 25036-66-2; $trans$-$[Ir(PPh_3)_2(N_2)I]$, 38255-33-3; $trans$-$[Ir(PPh_3)_2(N_2)N_3]$, 25036-67-3; $trans$-$[Ir(PPh_3)_2(N_2)NCO]$, 71700-03-3; $trans$-$[Ir(PPh_3)_2(N_2)NCS]$, 71700-04-4; $trans$-$[Ir(PPh_3)_2(N_2)CF_3CO_2]$, 71700-05-5; $trans$-$[Ir(P(p$-$CH_3C_6H_4)_3)_2(N_2)Cl]$, 71700-06-6; $trans$-$[Ir(PPh_2Me)_2(N_2)Cl]$, 71700-07-7; $trans$-$[Ir(PPh_2Me)_2(N_2)Br]$, 71700-08-8; $trans$-$[Ir(PPhMe_2)_2(N_2)Cl]$, 28667-94-9; $trans$-$[Ir(PEt_3)_2(N_2)Cl]$, 71700-09-9; $trans$-$[Ir(AsPh_3)_2(N_2)Cl]$, 71700-10-2; $trans$-$[Ir(AsPh_3)_2(N_2)Br]$, 71700-11-3; $trans$-$[Ir(AsPh_3)_2(N_2)N_3]$, 71700-12-4; $trans$-$[Ir(AsPh_3)_2(N_2)NCO]$, 71700-13-5; $trans$-$[Ir(P(OPh)_3)_2(N_2)Cl]$, 71700-14-6; $Ir(CO)_2(PPh_3)_2H$, 17250-59-8; $Ir(CO)(PPh_3)_3H$, 17250-25-8; $[Ir(PPh_3)_2(CO)(CH_3CN)]BF_4$, 49745-75-7; $trans$-$[Ir(PPh_3)_2(CO)F]$, 32356-62-0; $trans$-$[Ir(PPh_3)_2(CO)Cl]$, 15318-31-7; $trans$-$[Ir(PPh_3)_2(CO)Br]$, 15842-08-7; $trans$-$[Ir(PPh_3)_2(CO)I]$, 19472-16-3; $trans$-$[Ir(PPh_3)_2(CO)N_3]$, 21414-23-3; $trans$-$[Ir(PPh_3)_2(CO)NCO]$, 28195-62-2; $trans$-$[Ir(PPh_3)_2(CO)NCS]$, 28195-61-1; $trans$-$[Ir(PPh_3)_2(CO)CF_3CO_2]$, 50442-04-1; $trans$-$[Ir(P(p$-$CH_3C_6H_4)_3)_2(CO)Cl]$, 28195-56-4; $trans$-$[Ir(PPh_2Me)_2(CO)Cl]$, 15318-32-8; $trans$-$[Ir(PPh_2Me)_2(CO)Br]$, 19354-07-5; $trans$-$[Ir(PPhMe_2)_2(CO)Cl]$, 21209-82-5; $trans$-$[Ir(PEt_3)_2(CO)Cl]$, 21209-85-8; $trans$-$[Ir(AsPh_3)_2(CO)Cl]$, 23954-42-9; $trans$-$[Ir(AsPh_3)_2$-$(CO)Br]$, 14040-53-0; $trans$-$[Ir(AsPh_3)_2(CO)N_3]$, 42482-39-3; $trans$-$[Ir(AsPh_3)_2(CO)NCO]$, 42556-35-4; $trans$-$[Ir(P(OPh)_3)_2$-$(CO)Cl]$, 42482-37-1.

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**Meridional
Tris(pyridine)tris(thiocyanato-N)chromium(III) and Its
Conversion to the Cyanato-N Analogue by a Novel Method**

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Chromium(III) normally shows a strong affinity for oxygen donors,[1] while the ambidentate cyanate ion is known to be predominantly nitrogen bonded.[2] We, therefore, expected a potential for linkage isomerism in the chromium(III)–cyanate system. The absence of stable linkage isomers of chromium(III) with simple ligands in the solid state and the existence of only a single cyanato linkage isomer[3] provided additional incentive for this work. We report here a new method for the synthesis of a (cyanato-N)chromium(III) complex in the solid crystalline state.

The only chromium(III)–cyanato complex reported before, tetraphenylarsonium hexakis(cyanato-N)chromate(III),[4] was obtained as a green oil, which solidified under vacuum. The material gave unsatisfactory analyses for chromium and carbon. All of our attempts for direct synthesis of any chromium(III)–cyanato complex in the pure state starting from other chromium(II) or chromium(III) compounds were unsuccessful. It was found that tris(pyridine)tris(thiocyanato-N)chromium(III) in pyridine reacts with potassium bromate to form the corresponding cyanato-N compound. The basic reaction appears to be

$$[Cr(py)_3(NCS)_3] + 4BrO_3^- \rightarrow$$
$$[Cr(py)_3(NCO)_3] + 4Br^- + 3SO_3$$
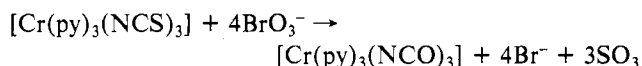
There have been several studies[5] on the oxidation of free and captive thiocyanates since 1900. The products of these reactions depend on both the nature and concentrations of the thiocyanate-containing moiety and the oxidizing agent, as well as the pH of the reactions. Sulfur is generally oxidized to sulfate, and various nitrogen-containing species including cyanide, cyanate, and ammonia are formed.

Werner[6] used the formation of coordinated ammonia by the oxidation of thiocyanate on a variety of bis(ethylenediamine)(thiocyanato)cobalt(III) complexes as evidence of co-