

The ^{31}P chemical shift of the mutually trans phosphorus nuclei is also sensitive to the nature of L. The observed shifts appear to be correlated with the donor/acceptor properties of L in the expected manner. Thus $\delta_{\text{C}_2\text{H}_4}$ and δ_{CO} , shifts for the ethylene and carbonyl complexes, respectively, are at lower field than $\delta_{t\text{-BuNC}}$. The π -acceptor strengths of the ethylene and carbon monoxide ligands reduce the metal-centered electron densities and thereby deshield the ^{31}P nuclei relative to those of the L = isocyanide complex. The isocyanide ligand is predominantly a σ donor in complexes containing a metal of oxidation state +1 or greater.²⁷ This is consistent with the relatively high-field value of $\delta_{t\text{-BuNC}}$. A similar screening effect for isocyanide ligands has been reported in ^{13}C NMR studies.²⁸ The relative deshielding in the nitrosyl complex is also consistent with the electron-withdrawing strength of NO^+ , as described above and documented previously in terms of the π -acceptor strength of the ligand.^{23,29} The trend to higher field of the ^{31}P chemical shifts in the series L = NO^+ , N_2Ar^+ , and $\text{N}_2\text{C}_5\text{X}_4$ ¹¹ arises from the same sources responsible for the $\nu_{\text{Ir-Cl}}$ ordering. Decreased electron demand results in increased metal-centered electron density and thus in increased shielding of the ^{31}P nuclei. The dinitrogen ligand is a weaker π acceptor than CO .²² The relatively low-field value of δ_{N_2} may arise from compensation by the poor donor ability of the ligand, causing a net electron withdrawal similar to that of the nitrosyl ligand. Of interest is the high-field value of δ_{CS} . It has been suggested that while CS is only a slightly better σ donor than CO, it is a much better π acceptor.²¹ We would thus expect that δ_{CS} be greater than δ_{CO} . The unexpected screening in the thio-carbonyl complex may arise from an interaction involving occupied orbitals of the CS ligand.

The results for the complexes in which L = phosphorus ligand are disappointing. As for the stretching frequencies, there is no significant difference between any of the chemical shifts. This lack of discrimination is unexpected in light of the substantial substituent effects discussed by Tolman.³⁰ Note also the low-field shifts for the complexes in which L = phosphorus ligand. The high trans influence of these ligands indicates that they are strong σ donors.^{2a} In accord with the results described above, a substantial π -acceptor capacity would be required to produce the observed low-field shifts. However, Mason and Meek^{2a} have suggested that π interactions contribute minimally to M-P bonding. Clarification of these ambiguities must await further study. It is necessary to recognize that our ambiguous NMR results for the complexes in which L = phosphorus ligand may be a result of the substitution of benzene- d_6 for chloroform- d_1 as solvent and that in these systems steric effects may have a substantial impact not present with the nonphosphorus ligands. Finally, recent discussions of the structural cis influence in Pt(II) complexes have indicated that this parameter is largely a function of π -acceptor strength. In the majority of complexes described above, the π -acceptor strength of L appears to be correlated with the ^{31}P chemical shift of the phosphorus nuclei cis to L.

There is a striking correlation between our IR and NMR results within closely related sets of complexes. We find that stretching frequency and chemical shift data for the closely related NO^+ , N_2Ar^+ , and $\text{N}_2\text{C}_5\text{X}_4$ complexes are linearly related (Figure 1, solid line, linear correlation coefficient = 0.99). An analogous correlation (Figure 1, dashed line, linear correlation coefficient = 0.91) is present for the carbon-ligand complexes, L = CO, CS, and *t*-BuNC, but additional spec-

troscopic data for similar carbonyl-like ligand complexes are needed. Thus, information on trans influence may be obtained from ^{31}P NMR chemical shifts for at least two types of Ir(I) complexes. It is of interest to extend this technique to other types of ligands, metals, and geometries to determine general applicability in structural investigations of solution species.

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Registry No. *trans*-IrCl(PPh₃)₂(CN-*t*-Bu), 74331-50-3; *trans*-IrCl(PPh₃)₂(CS), 30106-92-4; *trans*-IrCl(PPh₃)₂(N₂C₅Cl₄), 66973-33-9; *trans*-IrCl(PPh₃)₂(N₂C₅Br₄), 73396-30-2; *trans*-IrCl(PPh₃)₂(*p*-MeOC₆H₄N₂⁺), 74331-51-4; *trans*-IrCl(PPh₃)₂(PhN₂⁺), 74331-52-5; *trans*-IrCl(PPh₃)₂(N₂), 74331-53-6; *trans*-IrCl(PPh₃)₂(NO⁺), 25246-36-0; *trans*-IrCl(PPh₃)₂(P(*p*-FC₆H₄)₃), 74331-54-7; *trans*-IrCl(PPh₃)₂(P(*O-i*-Pr)₃), 74331-55-8; *trans*-IrCl(PPh₃)₂(P(*p*-MeC₆H₄)₃), 74331-56-9; *trans*-IrCl(PPh₃)₂(P(*p*-MeOC₆H₄)₃), 74331-57-0; *trans*-IrCl(PPh₃)₂(PMe₂Ph), 74331-58-1; *trans*-IrCl(PPh₃)₃, 16070-58-9; *trans*-IrCl(PPh₃)₂(CO), 15318-31-7; *trans*-IrCl(PPh₃)₂(C₂H₄), 32761-43-6.

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Synthesis and Properties of Borohydride Derivatives

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The remarkable stability and selectivity of sodium cyanoborohydride, NaBH₃CN, induced by the strong electron-withdrawing cyanide group, establish it as one of the more important hydride reagents.^{1,2} However, due to its toxicity, sodium cyanoborohydride has found limited industrial application. Recent research activities at Ventron have been concerned with the development of new hydride reducing agents. In this note, we want to report some interesting properties of a related derivative, sodium (thiocyanato)borohydride,³ NaBH₃SCN, and a new synthetic route of NaBH₃CN.

Sodium (Thiocyanato)borohydride

Sodium (thiocyanato)borohydride was prepared according to the procedure described in the literature,³ by passing B₂H₆ into anhydrous NaSCN in ethylene glycol-dimethyl ether (monoglyme). Dioxane was then added to the filtered solution to precipitate the product, NaBH₃SCN·2(dioxane). The solid is soluble in tetrahydrofuran (THF), water, and ethanol. The infrared spectrum shows B-H stretching at 2290, 2330, and 2380 cm⁻¹. Both SCN (2180 cm⁻¹ strong) and NCS (2080 cm⁻¹ weak) groups are observed, indicating the presence of two isomers. The ¹¹B nuclear magnetic resonance spectrum was found³ to be consistent with a monosubstituted BH₄⁻.

It is interesting to note that a different result was obtained by using BH₃·THF as reactant in THF. Thus, when BH₃·THF was titrated into a suspension of NaSCN in THF, a clear solution was obtained at the point when the molar ratio of [BH₃·THF] to [NaSCN] was ~0.65. The infrared spectrum of this solution was identical with that of NaBH₃SCN·2(dioxane) in the B-H and SCN stretching regions. A white

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Table I. Reduction of Organic Substances with $\text{NaBH}_3\text{SCN}\cdot 2(\text{dioxane})$ in THF^a

subst	molar ratio (deriv/subst)	temp	reaction time, h	product ^b
$\text{C}_6\text{H}_5\text{CN}$	1.5	reflux	20	$\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2\cdot\text{HCl}$ (86)
$(\text{C}_6\text{H}_5)_2\text{CHCN}$	2.0	reflux	17	$(\text{C}_6\text{H}_5)_2\text{CHCH}_2\text{NH}_2$
$\text{C}_6\text{H}_5\text{NO}_2$	2.1	reflux	20	no reduction
$\text{C}_6\text{H}_5\text{COOCH}_3$	2.8	reflux	20	no reduction
$\text{C}_6\text{H}_5\text{CONH}_2$	1.5	reflux	21	$\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2\cdot\text{HCl}$ (75)
$\text{C}_6\text{H}_5\text{COCH}_3$	1.6	ambient	6	$\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_3$ (100)
CH_3COCH_3	1.5	ambient	6	$(\text{CH}_3)_2\text{CHOH}$ (100)
$\text{C}_6\text{H}_5\text{CHO}$	1.5	ambient	4	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ (100)
$\text{C}_6\text{H}_5\text{COCl}$	1.4	ambient	4	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ (100)

^a Reactions were not optimized. ^b Percent yields are in parentheses.

crystalline solid which analyzed approximately as $3\text{NaSCN}\cdot 2\text{BH}_3$ was obtained by reducing the volume of the solution. No attempt was made to further characterize this species. Anal. Calcd.: H, 2.23; B, 7.98; Na, 25.46. Found: H, 2.61; B, 7.95; Na, 23.80.

NaBH_3SCN is slightly more stable hydrolytically than NaBH_4 . Thus, in pH 5 buffer solution, only ~50% active hydride was lost in 10 min ($t_{1/2} = 0.035$ s for NaBH_4). NaBH_3CN is stable even in pH 3 solution.⁵ This is consistent with the stronger electron-withdrawing ability of CN in comparison to SCN. Consequently, NaBH_3SCN is expected to be a stronger reducing agent, and our results presented below demonstrated this point.

Sodium Cyanoborohydride

While NaCN reacted smoothly to give NaBH_3CN , other inorganic salts such as KI, NaOH, or NaOCN did not react with $\text{BH}_3\cdot\text{THF}$. Therefore, NaBH_3CN was made by stirring equimolar $\text{BH}_3\cdot\text{THF}$ (~1 M) with NaCN in THF in excellent yield. Alternatively, NaBH_4 and $\text{BF}_3\cdot\text{THF}^4$ were reacted in THF to generate $\text{BH}_3\cdot\text{THF}$ in situ, followed by further reaction with NaCN in the similar manner. We found that the reaction was sluggish when $\text{BF}_3\cdot\text{OEt}_2$ was used instead. NaBH_3CN , which has been prepared from NaBH_4 and HCN in THF,⁵ often discolors after several months of storage under ambient conditions. The present synthetic route does not involve the use of HCN, and the product has much better storage stability. No discoloration was observed and the decomposition was less than 5% when a sample was stored in a capped bottle for 7 months. The properties of NaBH_3CN have been well documented.^{1,2}

Reduction of Organic Functional Groups

Results of reduction using $\text{NaBH}_3\text{SCN}\cdot 2(\text{dioxane})$ are presented in Table I. THF solutions of NaBH_3SCN readily reduce benzoyl chloride and benzaldehyde to benzyl alcohol. Acetone and acetophenone are reduced to the respective secondary alcohols. While nitro and ester functional groups are not reduced, nitriles and amides are reduced to the corresponding amines in THF under refluxing conditions. Aldehydes and ketones are readily transformed into alcohols by NaBH_4 and NaBH_3CN (at pH less than 7). However, under normal conditions, nitrile or amide compounds cannot be reduced by NaBH_4 or NaBH_3CN .⁶ Although LiAlH_4 can also serve this purpose, it reduces various functional groups indiscriminately. Nitriles and amides can be reduced to the corresponding amines by NaBH_4 in the presence of a car-

boxylic acid.⁷ In view of this, NaBH_3SCN should be of considerable synthetic value due to its selectivity and operational simplicity.

Experimental Section

Materials. Sodium (thiocyanato)borohydride was prepared as described previously.³ $\text{BH}_3\cdot\text{THF}$, sodium borohydride, sodium thiocyanate, and sodium cyanide were obtained from Alfa, Ventron/Thiokol, Beverly, MA. Reagent grade nitrobenzene, benzonitrile, diphenylacetone, methyl benzoate, benzamide, benzoyl chloride, acetone, acetophenone, and benzaldehyde were obtained from Aldrich Chemical Co., Milwaukee, WI. Reagent grade THF was dried over calcium hydride before use.

Preparation of Sodium Cyanoborohydride. Two moles of $\text{BH}_3\cdot\text{THF}$ (1.0 M) was added dropwise in 1.5 h to NaCN (101.2 g, 2.06 mol) in THF (300 mL) under an N_2 atmosphere. The reaction mixture was poststirred for 4 h and then heated under flux for 7 h. When the mixture was cooled to room temperature, the small amount of unreacted NaCN was separated by filtration under an N_2 atmosphere. Evaporation of the filtrate to dryness under reduced pressure at 60 °C gave 114 g (91%) of NaBH_3CN .

Anal. Calcd for NaBH_3CN : H, 4.81; C, 19.11; CN, 41.41. Found: H, 4.30; C, 19.11; CN, 39.50.

Alternatively, $\text{BF}_3\cdot\text{THF}^4$ (2.18 mol) was added to NaBH_4 (65.7 g, 1.74 mol) suspended in THF (810 mL) cooled in an ice bath under an N_2 atmosphere. After a postaddition stirring period of 1.5 h, NaCN (112.7 g, 2.30 mol) was added slowly in small batches. When addition was complete, the reaction mixture was stirred for 4 h at room temperature and then heated under reflux for 7 h. After cooling and filtration under N_2 , the filtrate was evaporated and the residue dried in a vacuum oven to obtain 116.6 g (85%) of NaBH_3CN .

Reduction of Organic Substrates. THF solution (25 mL) of the organic substrate (~0.5 M) and $\text{NaBH}_3\text{SCN}\cdot 2(\text{dioxane})$ were stirred at room temperature or heated under reflux (Table I). The resulting solution was taken to dryness under reduced pressure, and the excess reagent decomposed with dilute HCl. The aqueous solution was extracted with CHCl_3 . The CHCl_3 solution was then washed with water and dried over anhydrous Na_2SO_4 . The product was analyzed by gas chromatography (Hewlett-Packard FM-100 Carbowax column), and the amines were isolated as hydrochlorides.⁷

Registry No. NaBH_3CN , 25895-60-7; NaBH_3SCN , 66750-84-3; $\text{BH}_3\cdot\text{THF}$, 14044-65-6; NaCN, 143-33-9; $\text{BF}_3\cdot\text{THF}$, 462-34-0; NaBH_4 , 16940-66-2; $\text{C}_6\text{H}_5\text{CN}$, 100-47-0; $(\text{C}_6\text{H}_5)_2\text{CHCN}$, 86-29-3; $\text{C}_6\text{H}_5\text{CONH}_2$, 55-21-0; $\text{C}_6\text{H}_5\text{COCH}_3$, 98-86-2; CH_3COCH_3 , 67-64-1; $\text{C}_6\text{H}_5\text{CHO}$, 100-52-7; $\text{C}_6\text{H}_5\text{COCl}$, 98-88-4; $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2\cdot\text{HCl}$, 3287-99-8; $(\text{C}_6\text{H}_5)_2\text{CHCH}_2\text{NH}_2$, 3963-62-0; $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_3$, 98-85-1; $(\text{CH}_3)_2\text{CHOH}$, 67-63-0; $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, 100-51-6; NaBH_3NCS , 74482-65-8.

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Reduction of a Coordinated Pyridine Ring in a Macrocyclic Ligand-Nickel(II) Complex

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Oxidation and reduction reactions of coordinated ligands are playing an increasingly important role in the synthesis of metal complexes. This is especially true in the case of macrocyclic ligand systems where many compounds containing new ligands have been prepared by such techniques. It might be noted that macrocyclic ligand complexes are often very inert and thus can be subjected to the sometimes harsh conditions required for these reactions.

Many examples of ligand reduction have involved the conversion of coordinated imine functions to secondary amines. A

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