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 $\delta_{C_2H_4}$ 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$_2$Ar$^+$, and N$_2$C$_5$X$_4$[11] arises from the same sources responsible for the $\nu_{Ir\text{-Cl}}$ 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 thiocarbonyl 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$_2$Ar$^+$, and N$_2$C$_5$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 spectroscopic 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.

Contribution from the Ventron Division, Thiokol Corporation, Beverly, Massachusetts 01915

Synthesis and Properties of Borohydride Derivatives

Benjamin C. Hui

The remarkable stability and selectivity of sodium cyanoborohydride, NaBH$_3$CN, 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] NaBH$_3$SCN, and a new synthetic route of NaBH$_3$CN.

Sodium (Thiocyanato)borohydride

Sodium (thiocyanato)borohydride was prepared according to the procedure described in the literature,[3] by passing B$_2$H$_6$ into anhydrous NaSCN in ethylene glycol–dimethyl ether (monoglyme). Dioxane was then added to the filtered solution to precipitate the product, NaBH$_3$SCN·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 ^{11}B nuclear magnetic resonance spectrum was found[3] to be consistent with a monosubstituted BH$_4^-$.

It is interesting to note that a different result was obtained by using BH$_3$·THF as reactant in THF. Thus, when BH$_3$·THF was titrated into a suspension of NaSCN in THF, a clear solution was obtained at the point when the molar ratio of [BH$_3$·THF] to [NaSCN] was ~0.65. The infrared spectrum of this solution was identical with that of NaBH$_3$SCN·2(dioxane) in the B–H and SCN stretching regions. A white

(27) Malatesta, L.; Bonati, F. "Isocyanide Complexes of Metals"; Wiley: London, 1969; pp 25–28.
(28) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1.
(29) Horrocks, W. D.; Taylor, R. C. *Inorg. Chem.* **1963**, *2*, 723.
(30) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(1) C. F. Lane, *Synthesis*, 135 (1975).
(2) R. O. Hutchins and N. R. Natale, *Org. Prep. Proced. Int.*, **11** (5), 201 (1979).
(3) V. D. Aftandilian, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **83**, 2471 (1961).

Table I. Reduction of Organic Substances with
NaBH₃SCN·2(dioxane) in THF[a]

subst	molar ratio (deriv/ subst)	temp	reaction time, h	product[b]
C₆H₅CN	1.5	reflux	20	C₆H₅CH₂NH₂·HCl (86)
(C₆H₅)₂CHCN	2.0	reflux	17	(C₆H₅)₂CHCH₂NH₂
C₆H₅NO₂	2.1	reflux	20	no reduction
C₆H₅COOCH₃	2.8	reflux	20	no reduction
C₆H₅CONH₂	1.5	reflux	21	C₆H₅CH₂NH₂·HCl (75)
C₆H₅COCH₃	1.6	ambient	6	C₆H₅CH(OH)CH₃ (100)
CH₃COCH₃	1.5	ambient	6	(CH₃)₂CHOH (100)
C₆H₅CHO	1.5	ambient	4	C₆H₅CH₂OH (100)
C₆H₅COCl	1.4	ambient	4	C₆H₅CH₂OH (100)

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

crystalline solid which analyzed approximately as
3NaSCN·2BH₃ 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.

NaBH₃SCN is slightly more stable hydrolytically than
NaBH₄. Thus, in pH 5 buffer solution, only ~50% active
hydride was lost in 10 min ($t_{1/2}$ = 0.035 s for NaBH₄).
NaBH₃CN is stable even in pH 3 solution.[5] This is consistent
with the stronger electron-withdrawing ability of CN in com-
parison to SCN. Consequently, NaBH₃SCN is expected to
be a stronger reducing agent, and our results presented below
demonstrated this point.

Sodium Cyanoborohydride

While NaCN reacted smoothly to give NaBH₃CN, other
inorganic salts such as KI, NaOH, or NaOCN did not react
with BH₃·THF. Therefore, NaBH₃CN was made by stirring
equimolar BH₃·THF (~1 M) with NaCN in THF in excellent
yield. Alternatively, NaBH₄ and BF₃·THF[4] were reacted in
THF to generate BH₃·THF in situ, followed by further re-
action with NaCN in the similar manner. We found that the
reaction was sluggish when BF₃·OEt₂ was used instead.
NaBH₃CN, which has been prepared from NaBH₄ 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 de-
composition was less than 5% when a sample was stored in
a capped bottle for 7 months. The properties of NaBH₃CN
have been well documented.[1,2]

Reduction of Organic Functional Groups

Results of reduction using NaBH₃SCN·2(dioxane) are
presented in Table I. THF solutions of NaBH₃SCN readily
reduce benzoyl chloride and benzaldehyde to benzyl alcohol.
Acetone and acetophenone are reduced to the respective sec-
ondary alcohols. While nitro and ester functional groups are
not reduced, nitriles and amides are reduced to the corre-
sponding amines in THF under refluxing conditions. Aldeh-
ydes and ketones are readily transformed into alcohols by
NaBH₄ and NaBH₃CN (at pH less than 7). However, under
normal conditions, nitrile or amide compounds cannot be re-
duced by NaBH₄ or NaBH₃CN.[6] Although LiAlH₄ can also
serve this purpose, it reduces various functional groups in-
discriminately. Nitriles and amides can be reduced to the
corresponding amines by NaBH₄ in the presence of a car-

boxylic acid.[7] In view of this, NaBH₃SCN should be of
considerable synthetic value due to its selectivity and opera-
tional simplicity.

(4) H. C. Brown, "Organic Syntheses via Boranes", Wiley, New York, 1975.
(5) R. C. Wade, E. A. Sullivan, J. B. Berschied, Jr., and K. F. Purcell, *Inorg. Chem.* 9, 2146 (1970).
(6) Sodium Borohydride Brochure, Ventron Division, Thiokol Corp., Jan 1979.
(7) N. Umino, T. Iwakuma, and N. Itoh, *Tetrahedron Lett.,* 2875 (1976).

Contribution from the School of Chemistry,
Georgia Institute of Technology, Atlanta, Georgia 30332

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

E. Kent Barefield

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 mac-
rocyclic 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 con-
version of coordinated imine functions to seconary amines. A