Organometallics 1984, *3,* 205–208

Mechanistic Studies of Nickel-Catalyzed Addition of DCN and $H^{13}CN$ to Pentenenitriles†

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Received July 11, 1983

The addition of DCN and $H^{13}CN$ to pentenenitriles using a Ni[P(O-*p*-tolyl)$_3$]$_4$ catalyst and $AlCl_3$, $ZnCl_2$, and BPh_3 Lewis acids permits the assignment of major dinitrile product reaction pathways. Patterns of deuterium incorporation in recovered pentenenitriles are consistent with nickel hydride catalysis of both cis–trans and double-bond olefin isomerization reactions. ^{1}H NMR analyses show Ni–^{13}CN bonding in a $HNiL_3{}^{13}CN{\cdot}A$ complex, but not in the analogous $HNiL_4{}^{+13}CN{\cdot}A^-$ complex. H/D exchange occurs via orthometalation with Ni[P(O-*p*-$MeOC_6H_4$)$_3$]$_4$ but not with Ni[P(O-*p*-tolyl)$_3$]$_4$.

The nickel-catalyzed addition of HCN to butadiene forms the basis of an industrial process for the manufacture of adiponitrile.[1] We recently reported various mechanistic aspects of this chemistry, including the effects of Lewis acids and olefin structure and the spectroscopic characterization of various nickel intermediates involved.[2] It is the purpose of this paper to describe the results of DCN and $H^{13}CN$ labeling experiments that provide additional mechanistic information.

Earlier papers reported that addition of strong acids, such as H_2SO_4, to NiL_4 complexes (L = phosphorus ligands) causes protonation at nickel to give cationic five-coordinate $HNiL_4{}^+X^-$ complexes.[3a,b] A subsequent paper described the formation of five-coordinate $HNiL_3CN$ complexes from the addition of HCN to NiL_3 and NiL_4 complexes.[4] Trigonal-bipyramidal structures were established by ^{1}H and ^{31}P NMR. We now report that addition of Lewis acids to solutions of $HNiL_3CN{\cdot}A$ complexes causes the formation of both $HNiL_4{}^+CN{\cdot}A^-$ and $HNiL_3CN{\cdot}A$ complexes. Figure 1a shows the ^{1}H NMR spectrum of a THF solution containing 0.8 M Ni[P(OEt)$_3$]$_4$, 0.8 M $ZnCl_2$, and 1.4 M HCN. The quartet at δ −16.6 is assigned to HNi[P(OEt)$_3$]$_3$CN·$ZnCl_2$ complex and the quintet at δ −14.4 is assigned to a HNi[P(OEt)$_3$]$_4{}^+$-CN·$ZnCl_2{}^-$ complex. That only the $HNiL_3CN{\cdot}A$ complex contained Ni–CN bonding was shown by a duplicate experiment using $H^{12}CN/H^{13}CN$ (45/55) (Figure 1b). Only the quartet shows additional ^{13}C–H splitting. Good agreement was obtained between the observed spectrum and a spectrum calculated for the trigonal-bipyramidal complex with $J_{^{31}P-H}$ and $J_{^{13}C-H}$ coupling constants of 36 and 38 Hz, respectively.[5a,b]

Infrared measurements further support the $HNiL_4{}^+$-$CN{\cdot}A^-$ and $HNiL_3CN{\cdot}A$ structural assignments. Table I lists CN stretching frequencies obtained for THF solutions of NiL_4, HCN, and the Lewis acids $ZnCl_2$, $AlCl_3$, and BPh_3, where L = P(OEt)$_3$ or P(O-*p*-$MeOC_6H_4$)$_3$. For both phosphorus ligands, all three Lewis acids cause an increase in ν_{CN} in the $HNiL_3CN{\cdot}A$ complexes, with BPh_3 giving the greatest increases. Also, higher ν_{CN} frequencies were obtained for the HNi[P(O-*p*-$MeOC_6H_4$)$_3$]$_3$CN·A complexes than for the corresponding HNi[P(OEt)$_3$]$_3$CN·A complexes. A similar dependence of ν_{CN} on choice of phosphorus ligands has been noted for $HNiL_3CN$ complexes in the absence of Lewis acids.[4] The dependence of ν_{CN} on choice of both phosphorus ligand and Lewis acid supports the $HNiL_3CN{\cdot}A$ assignment. Each solution containing a Lewis acid also gave rise to a second CN stretching band at higher frequency, assignable to $HNiL_4{}^+CN{\cdot}A^-$, based on reference solution of $Et_3NH^+CN^-$ in THF and the corresponding Lewis acids.

Table I. IR CN Stretching Frequencies of $HNiL_4{}^+CN{\cdot}A^-$ and $HNiL_3CN{\cdot}A$ Complexes[a]

	stretching freq ν_{CN}, cm^{-1}			
	L = P(OEt)$_3$		L = P(O-*p*-$MeOC_6H_4$)$_3$	
Lewis acid	$HNiL_3$-CN·A	$HNiL_4{}^+$-CN·A$^-$	$HNiL_3$-CN·A	$HNiL_4{}^+$-CN·A$^-$
none	2120[b]		2128[c]	
$ZnCl_2$	2131	2165	2148	2165
$AlCl_3$	2126	2181	2142	2181
BPh_3	2170	2237	2176 (2184)[c]	2237

[a] Ranges in concentrations of reagents were 0.5–0.8 M NiL_4, 0.7–1.0 M Lewis acid, and 1.4–2.3 M HCN in THF. [b] Measured in CH_2Cl_2 solution.[4] [c] Measured in CH_2Cl_2 solution using HNi[P(O-*p*-tolyl)$_3$]$_3$CN.[4]

We recently described various effects of the Lewis acids BPh_3, $ZnCl_2$, and $AlCl_3$ on nickel-catalyzed pentenenitrile hydrocyanation.[2] Under the conditions used (68 °C, neat pentenenitrile (PN) solvent, mole ratios of Ni[P(O-*p*-tolyl)$_3$]$_4$:P(O-*o*-tolyl)$_3$:Lewis acid:PN[6] of 1:10:2:40, and 40 mol of HCN/mol of Ni/h) equilibration of 3-pentenenitrile (3PN) and 4-pentenenitrile (4PN) occurs competitively with hydrocyanation. Comparable experiments using DCN and $H^{13}CN$ now provide additional insight as to which dinitrile formation pathways predominate. In all experiments the recovered unreacted pentenenitriles and dinittrile products were isolated by preparative GC and were analyzed by ^{1}H and ^{13}C NMR. In some cases mass spectral analyses were also done to determine extents of deuterium enrichment. Table II gives a comparison of average monodeuteration found in dinitrile products, as well as in 3-pentenenitrile. Agreement between the mass spectral and NMR results was generally good, with some excep-

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† Contrubition No. 3314.

(1) (a) Chem. *Eng. News* **1981**, 30. (b) Drinkard, W. C.; Kassal, R. J. U.S. Patent 3 496 217, 1970. Drinkard, W. C. U.S. Patent 3 496 218, 1970.

(2) Tolman, C. A.; Seidel, W. C.; Druliner, J. D.; Domaille, P. J. *Organometallics*, in press.

(3) (a) Drinkard, W. C.; Eaton, D. F.; Jesson, J. P.; Lindsey, R. V., Jr. *Inorg. Chem.* **1970**, *9*, 392. (b) Tolman, C. A. *Ibid.* **1972**, *11*, 3128.

(4) Druliner, J. D.; English, A. D.; Jesson, J. P.; Meakin, P.; Tolman, C. A. *J. Am. Chem. Soc.* **1976**, *98*, 2156.

(5) (a) $J_{^{13}C-H}$ coupling constants in the range of 42–56 Hz have been reported for trans H–M–CN coupling in Ir, Rh, and Pt complexes, compared with 5.7 Hz for corresponding cis $J_{^{13}C-H}$ coupling constants.[5b] (b) Whitesides, G. M.; Maglio, G. *J. Am. Chem. Soc.* **1969**, *91*, 4980.

(6) The mole ratio of PN isomers used in $H^{13}CN$ and DCN experiments was approximately 3:96:1:0 for 4PN:3PN:2PN:2Me3BN.

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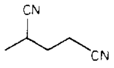
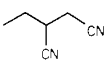
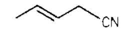
Table II. Comparison of Average Percent Monodeuteration in Dinitrile Products and in Recovered 3-Pentenenitrile Determined by ^{1}H NMR and Mass Spectroscopy

		av % monodeuteratn[a]							
		ADN		MGN		ESN		3PN	
		(NCCH$_2$CH$_2$)$_2$ α β							
Lewis acid	temp, °C	MS	NMR	MS	NMR	MS	NMR	MS	NMR
ZnCl$_2$	60	34	36	39	*b*	*b*	*b*	<5	0
AlCl$_3$	68	48	≥17[c]	63	93	9	36	15	22

[a] Reactions were carried out in neat pentenenitrile solvent[6] with Ni[P(O-*p*-tolyl)$_3$]$_4$, P(O-*p*-tolyl)$_3$, Lewis acid, and PN in a mole ratio of 1:10:2:240. DCN was fed continuously at a rate of 40 mol of DCN/mol of Ni/h. [b] Not determined. [c] Only a lower limit could be determined for ADN using ^{1}H NMR, based on a ratio of α/β proton integrals.

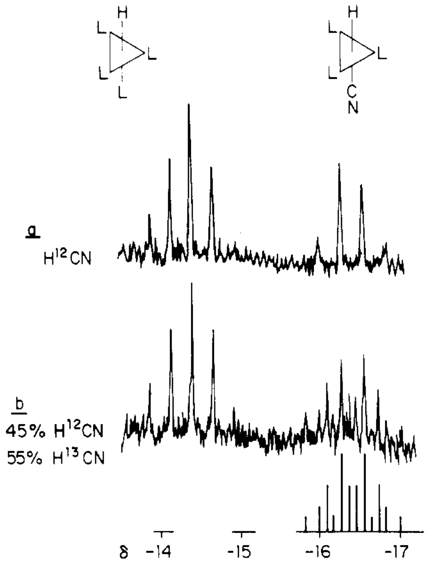


Figure 1. ^{1}H NMR spectra of solutions of 0.8 M Ni[P(OEt)$_3$]$_4$ and 0.8 M ZnCl$_2$ in THF with (a) 1.4 M H^{12}CN or with (b) 1.4 M H^{12}CN/H^{13}CN (45/55). The four phosphorus ligands of HNiL$_4^+$ were equivalent on the NMR time scale.[13]

tions. ^{1}H NMR percentages of monodeuteration in ADN can be low when deuterium incorporation occurs in 3PN in competition with deuterocyanation, as is evident for the AlCl$_3$ case. The mass spectral measurements involved calculations using nonparent peaks because of fragmentation of the dinitrile products in the electron-impact mode used. Thus, depending on the deuterium enrichment in different fragments, low values could sometimes result, as in the case of ESN and the Lewis acid AlCl$_3$. Incorporation of deuterium in different positions of dinitrile products was determined by ^{1}H NMR. The resulting conclusions about which hydrocyanation pathways predominant are supported by the ^{1}H NMR measurements and are not limited by a lack of absolute agreement between the mass spectral and ^{1}H NMR techniques. The possible pathways leading to the observed dinitrile products—adiponitrile (ADN), 2-methylglutaronitrile (MGN), and 2-ethylsuccinonitrile (ESN)—are shown in Figure 2.

Under the reaction conditions used for addition of H^{13}CN (68 °C), essentially no MGN is formed via hydrocyanation of 2Me3BN, using either ZnCl$_2$ or AlCl$_3$ (Figure 2a).[7] To distinguish between 3PN and 4PN as precursors of MGN, experiments were done by using DCN (Table III).

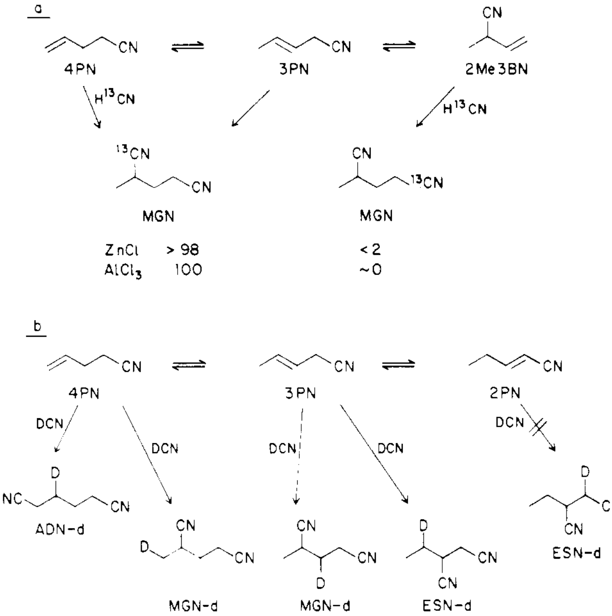
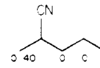
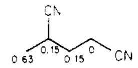
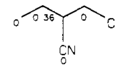


Figure 2. Reaction pathways for dinitrile formation from pentenenitriles.

Table III. Deuterium Incorporation in ADN-*d*, MGN-*d*, and ESN-*d* from Addition of DCN to Pentenenitriles[a]

DN-*d*	D incorporatn[8]	Lewis acid	temp, °C
ADN-*d*	(NCCH$_2$CH$_2$) α β 0 0.45	ZnCl$_2$	80
MGN-*d*		ZnCl$_2$	80
ADN-*d*	(NCCH$_2$CH$_2$)$_2$ α β 0 1.0	ZnCl$_2$	68
MGN-*d*		AlCl$_3$	68
ESN-*d*		AlCl$_3$	68

[a] Reactions were carried out in neat pentenenitrile solvent[6] with Ni[P(O-*p*-tolyl)$_3$]$_4$, P(O-*p*-tolyl)$_3$, Lewis acid, and PN in a mole ratio of 1:10:2:240. DCN was fed continuously at a rate of 40 mol of DCN/mol of Ni/h. Deuterium incorporation was determined by ^{1}H NMR.

Experiments with ZnCl$_2$ gave nearly completely regiospecific deuteration in both ADN-*d* and MGN-*d*, both products being derived only from 4PN and not from 3PN. Recovered 3PN contained no significant deuterium. The fact that the deuterium in the ADN-*d* and MGN-*d* was added regiospecifically to 4PN indicates that isomerization

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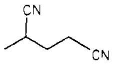
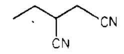
(7) Although hydrocyantion of 2Me3BN occurs readily, isomerization of 3PN to form 2Me3BN occurs only very slowly at 68 °C.

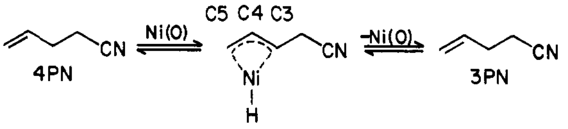
(8) The deuterium isotopic purity of DCN, prepared from D$_2$O (99.8%) *d*), P$_2$O$_5$, and NaCN, varied from 40 to 100%, depending on the amounts of H$_2$O contamination in sources of P$_2$O$_5$ used.

Table IV

	ADN		MGN				ESN			
	$(NCCH_2CH_2)_2$									
	α	β								
chem shift, ppm (δ)	2.50	1.85	1.30	2.80	2.00	2.50	1.15	1.85	2.80	2.80
^{1}H integral	2	2	3	1	2	2	3	2	1	2
deuterated product integral	2.00	1.93	2.37	0.85	1.85	2.00	3.00	1.64	1.00	2.00
deuterium incorporation	0	0.17	0.63	0.15	0.15	0	0	0.36	0	0

of 3PN to 4PN takes place independently of the deuterocyanation step. Tolman has shown, for the Ni[P(OEt)$_3$]$_4$/D$_2$SO$_4$ system, that 1-butene can be isomerized to the thermodynamic mixture of 1- and 2-butenes at 25 °C with a ratio of rates of isomerization to deuteration of 170.[9] The MGN-*d* prepared with AlCl$_3$ contained deuteration at C-3 and C-4, as well as at C-5, based on 3PN and 4PN. The predominant precursor of the MGN-*d* was, however, again 4PN. Relative rates of hydrocyanation of 4PN vs. 3PN in the range of 510–620, for BPh$_3$, ZnCl$_2$, and AlCl$_3$, have been reported based on rate measurements.[2] In the AlCl$_3$ experiment, deuteration in the ESN-*d* was found only in the –CH$_2$– group of the ethyl group, indicative of ESN-*d* formation from 3PN but not from 2PN. The fact that conjugated olefins containing electron-withdrawing groups do not undergo hydrocyanation has been discussed.[2] Analogous deuterocyanation experiments using BPh$_3$ were uninformative because the recovered 3PN and 4PN showed complete scrambling of deuterium in the C-3, C-4, and C-5 positions.

The observed deuteration using BPh$_3$ and AlCl$_3$ (Table II) at C-4, as well as at C-3 and C-5, in recovered 3PN is consistent with olefin double-bond isomerization catalyzed by addition and elimination of nickel hydride species. A mechanism involving oxidative addition of Ni(0) to allylic C–H bonds to give π-allyl intermeiate 1 would lead to deuteration only at C-3 and C-5. Cis–trans double-bond isomerization of 3PN and 2PN most likely also proceeds via addition and elimination of nickel hydride species. For example, *cis*- and *trans*-2PN were equilibrated at 25 °C using 0.2 M Ni[P(OEt)$_3$]$_4$ and 1.0 M CF$_3$CO$_2$D in *cis*-2PN/CH$_3$CO$_2$H (50/50) solvent for 24 h. The recovered *trans*-2PN contained 27% deuteration, only at C-3. Isomerization of *cis*- and *trans*-2PN via intermediate 2 is consistent with the known stabilizing influence of α-cyano substituents on alkylmetal complexes.[2]



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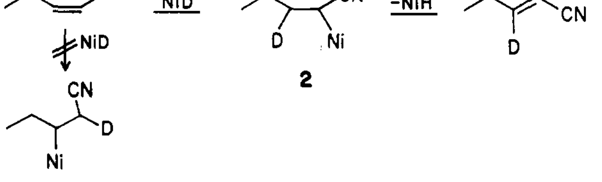

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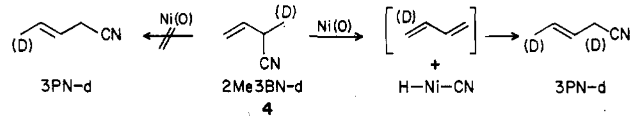
A related isomerization reaction involves an apparent 1,3-allylic CN group migration of 2Me3BN (2-methyl-3-butenenitrile) to 3PN. Experiments using Ni[P(O-*p*-tolyl)$_3$]$_4$ and ZnCl$_2$ at 110 °C in 2Me3BN-*d* solvent, 4 (0.7 deuterium at the CH$_3$ position), gave rise to 3PN-*d* with statistical deuteration at C-2 and C-5. The results are consistent with dehydrocyanation to butadiene rather than a 1,3-allylic CN group shift for isomerization of 2Me3BN to 3PN.



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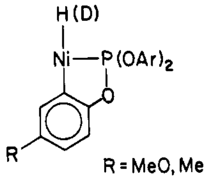
Attempted deuterocyanation experiments using Ni[P(O-*p*-MeOC$_6$H$_4$)$_3$]$_4$ at 64 °C in place of Ni[P(O-*p*-tolyl)$_3$]$_4$ led to unexpected decreases in isotopic purity of the DCN. The decreased deuterium enrichment resulted from orthodeuteration of the P(O-*p*-MeOC$_6$H$_4$)$_3$ ligand, which did not occur with P(O-*p*-tolyl)$_3$. The more favorable electron-withdrawing Hammett substituent constant, σ meta,[10] for MeO (+0.12) than for Me (−0.07), is consistent with formation of ortho-metalated intermediate 5 for R = MeO.[11]



5

Experimental Section

Compounds and Solvents. Solutions were prepared in inert atmospheres of nitrogen in a Vacuum Atmospheres, Inc., drybox. Solvents were purified by distillation under nitrogen. Pentenenitrile solvents were prepared by nickel(0)-catalyzed hydrocyanation of butadiene.[14] Nickel(0) complexes Ni[P(OEt)$_3$]$_4$, Ni[P(O-*p*-tolyl)$_3$]$_4$, and Ni[P(O-*p*-MeOC$_6$H$_4$)$_3$]$_4$ were obtained from Dr. R. G. Downing and can be prepared from nickelocene and the appropriate ligand as described by Olechowski et al.[15] The phosphite compounds P(OEt)$_3$, P(O-*p*-tolyl)$_3$, P(O-*p*-MeOC$_6$H$_4$)$_3$ were prepared by reaction of the corresponding alcohol with PCl$_3$, using the general method given by Kosolapoff.[16] AlCl$_3$ and ZnCl$_2$ were used as obtained from Aldrich Chemical Co. BPh$_3$ was obtained from Orgmet Chemical Co. and can be purified by recrystallization from acetonitrile. HCN was obtained from Fumico, Inc., Amarillo, TX, and was stored at 0 °C, after dis-

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[10] Gould, E. S. "Mechanism and Structure in Organic Chemistry": Holt, Rinehart and Winston, Inc.: New York, 1962; p 221.

[11] The subject of orthometalation in metal complexes has been recently reviewed.[12]

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[13] Jesson, J. P. "Transition Metal Hydrides"; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; Vol. 1, Chapter 4, p 75.

[14] Drinkard, W. C.; Lindsey, R. V. U.S. Patent 3 496 215, 1970.

[15] Olechowski, J. R.; McAlister, C. G.; Clark, R. F. *Inorg. Chem.* **1965**, *4*, 246.

[16] Kosolapoff, G. M. "Organophosphorus Compounds"; Wiley: New York, 1950; p 184.

tillation to remove SO_2 stabilizer. *Caution: HCN is extremely toxic and should be used only in a well-ventilated hood. Heavy rubber gloves should be used, and any contact with skin or clothing should be avoided.* DCN was prepared by slow addition of $NaCN/D_2O$ to a stirred solution of D_3PO_4/D_2O. The liberated DCN was dried by vaporizing it through a tube containing P_2O_5.

Instrumentation. All proton NMR spectra were recorded by using a Varian HA-100 spectrometer. Mass spectra were obtained under electron-impact conditions by using a CEC 21-104 spectrometer. IR spectra were recorded by using a Perkin-Elmer 221 spectrometer. Mono- and dinitrile products were isolated by preparatory GC at 185 °C using a 20 ft × $^1/_4$ in. stainless steel column packed with ECNSS-coated Carbowax 20 M.

Typical Hydrocyanation Procedure. Addition of DCN to 3PN Using $ZnCl_2$ and Ni[P(O-*p*-tolyl)$_3$]$_4$. A 50-mL, three-neck, round-bottom flask was equipped with Teflon-coated stirring bar, heating mantle, thermometer, N_2-inlet tube, and N_2-outlet tube. The flask was charged with 26 mL (266 mmol) of 3PN, 8.5 mL (26.6 mmol) of P(O-*p*-tolyl)$_3$, 0.27 g (2.0 mmol) of $ZnCl_2$, and 1.8 g (1.2 mmol) of Ni[P(O-*p*-tolyl)$_3$]$_4$. The temperature of the stirred solution was adjusted to 60 °C. A glass 10-mL bubbler was immersed in a wet ice bath and was charged with 5 mL of ice-cold DCN. A flow of N_2 through the DCN was adjusted to vaporize 1.0 mL/h (0.6 mmol/h) of DCN into the inlet tube of the reactor. Following vaporization of the DCN, the reaction mixture was filtered and distilled to give a mixture of dinitrile products. Separate samples of ADN-*d* and MGN-*d* were obtained by preparatory GC for ^1H NMR analysis.

^1H NMR Analysis of Dinitrile Products for Deuterium Incorporation. ^1H NMR spectra of 10–50-μL fractions of dinitrile products, dissolved in $CDCl_3$ with Me_4Si internal standard, were obtained and peak integrals were recorded. Reference ^1H NMR spectra of undeuterated dinitriles were used for calculation of amounts of deuteration, by differences in integrals of reference and deuterated compounds. Table IV gives an analysis of dinitrile products obtained by Ni[P(O-*p*-tolyl)$_3$]$_4$-catalyzed addition of DCN to 3PN at 68 °C, using $AlCl_3$.

Registry No. 4PN, 592-51-8; 3PN, 4635-87-4; 2PN, 13284-42-9; 2Me3BN, 16529-56-9; $ZnCl_2$, 7646-85-7; $AlCl_3$, 7446-70-0; BPh_3, 960-71-4; HNi[P(OEt)$_3$]$_3$CNZnCl$_2$, 87655-30-9; HNi[P(OEt)$_3$]$_4^+$·CNZnCl$_2^-$, 25358-26-3; HNi[P(O-*p*-MeOC$_6$H$_4$)$_3$]$_3$CNZnCl$_2$, 87655-31-0; HNi[P(O-*p*-MeOC$_6$H$_4$)$_3$]$_4^+$·CNZnCl$_2^-$, 87727-23-9; HNi[P(OEt)$_3$]$_3$CN, 59284-99-0; HNi[P(O-*p*-MeOC$_6$H$_4$)$_3$]$_3$CN, 25358-27-4; HNi[P(OEt)$_3$]$_3$CNAlCl$_3$, 87655-32-1; HNi[P(OEt)$_3$]$_4^+$·CNAlCl$_3^-$, 87758-25-6; HNi[P(O-*p*-MeOC$_6$H$_4$)$_3$]$_3$CNAlCl$_3$, 87655-33-2; HNi[P(O-*p*-MeOC$_6$H$_4$)$_3$]$_4^+$·CNAlCl$_3^-$, 87727-24-0; HNi[P(OEt)$_3$]$_3$CNBPh$_3$, 87655-34-3; HNi[P(OEt)$_3$]$_4^+$·CNBPh$_3^-$, 87727-25-1; HNi[P(O-*p*-MeOC$_6$H$_4$)-CNBPh$_3$, 87655-35-4; Ni[P(OEt$_3$)]$_4$, 14839-39-5; Ni[P(O-*p*-tolyl)$_3$]$_4$, 36700-08-0; Ni[P(O-*p*-MeOC$_6$H$_4$)$_3$]$_4$, 14285-90-6; hydrogen, 1333-74-0.

Transfer of Hydrogen from Carbon–Hydrogen Bonds. Synthesis, Structure, and Reactions of Tris[(triphenylstannyl)methyl]methane[1]

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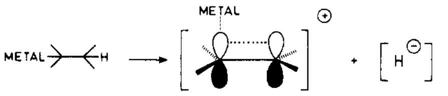
Received July 22, 1983

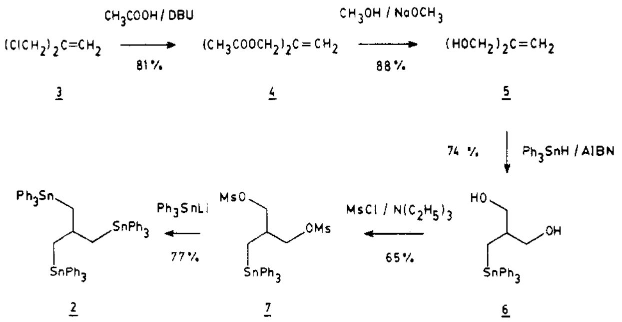
Compounds in which a carbon–hydrogen bond is adjacent to several carbon–metal bonds promise to be particularly good donors of hydrogen. The synthesis, structure, and redox reactions of one member of this group of compounds, tris[(triphenylstannyl)methyl]methane (2), are reported. Triphenylcarbenium is reduced to triphenylmethane less rapidly by stannane 2 than by bis[(triphenylstannyl)methyl]methane (11). The unexpectedly low reactivity of stannane 2 is due to the adoption of a C_3 conformation in which the central carbon–hydrogen bond is sterically shielded and gauche to the adjacent carbon–tin bonds.

The transfer of hydrogen from a carbon–hydrogen bond is an important and deceptively simple process.[2] To see how favorable this reaction can be when circumstances are ideal, we have begun to study covalent compounds designed to be particularly good donors of hydride or hydrogen.[3] Compounds in which a carbon–hydrogen bond is adjacent to a carbon–metal bond are promising candidates, since loss of hydride or hydrogen may lead to a carbocation or radical stabilized by hyperconjugation (eq 1).[4,5] If an intermediate is actually formed,[6] it can be further stabilized by increasing the number of adjacent carbon–metal bonds. We have therefore begun to study the ability of tris(metallomethyl)methanes (1) to serve as formal donors of hydride. This ability should increase as



(1)

Scheme I



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[1] Presented in part at the 65th Conference of the Canadian Institute of Chemists, Toronto, June 2, 1982.

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