Chemical Evolution of a Nitrogenase Model. 15. Reduction of Coordinated Isonitriles in Mononuclear Complexes of Oxomolybdate(IV) and Their Use as Catalysts for the Reduction of Acetylene and Nitrogen[1]

E. L. Moorehead, B. J. Weathers, E. A. Ufkes, P. R. Robinson, and G. N. Schrauzer*

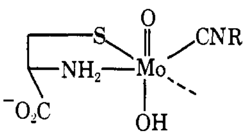
Contribution from the Department of Chemistry,
University of California at San Diego, Revelle College,
La Jolla, California 92092. Received March 22, 1977

Abstract: The reduction of coordinated isonitrile in cationic complexes of oxomolybdate(IV) of composition $[Mo(O)(X)(CN\text{-}R)_4]^+Y^-$ (X, e.g., Cl^-; R = CH_3; Y = PF_6^-) produces methylamine, CH_4, C_2H_6, C_2H_4, and traces of C_3H_6 and C_3H_8. The same products have previously been observed on reduction of isonitriles with functional nitrogenase and with molybdothiol model systems of nitrogenase. The reduction of coordinated $CH_3\text{-}NC$ is clearly stimulated by ATP and $P_3O_{10}{}^{5-}$, essentially *unaffected* by ADP and AMP, and inhibited by $P_2O_7{}^{4-}$ and $PO_4{}^{3-}$. In the presence of ATP, molecular nitrogen partially inhibits the production of hydrocarbons from coordinated $CH_3\text{-}NC$ and is itself reduced to ammonia via diimide and hydrazine as the intermediates. Acetylene is catalytically reduced mainly to C_2H_4. Evidence for an insertion reaction involving coordinated $CH_3\text{-}NC$ and C_2H_2 was obtained, giving rise to the formation of C_3H_6, a product which is not observed in other catalytic systems.

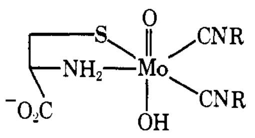
The enzymatic reduction of isonitriles by nitrogenase (N_2-ase) is remarkable inasmuch as it leads to the formation of products with new C–C bonds according to the overall reaction eq 1:[2-5]

$$1\text{–}3R\text{–}NC + 6\text{–}14e^- + 6\text{–}14H^+ \xrightarrow{\text{enzyme, ATP, }Mg^{2+}} 1\text{–}3RNH_2, + CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8 \quad (1)$$

Reaction eq 1 was successfully duplicated in molybdothiol model systems of N_2-ase.[6] From the results obtained it was concluded that isonitriles are reduced at the molybdenum active site via end-on-bonded primary intermediates. The intermediates were postulated to be derivatives of oxomolybdate(IV) with one or two molecules of isonitrile attached to molybdenum as shown in structures I and II:

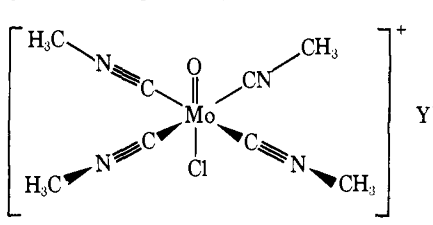


I



II

Recently, cationic complexes of isonitriles of oxomolybdate(IV) have been prepared[7] and structurally characterized[8] by Lippard and his school. These complexes possess the general composition $[Mo(O)(X)(CN\text{-}R)_4]^+Y^-$ (X, e.g., Cl^-; R, e.g., CH_3; Y^-, e.g., PF_6^-). The structure of the complex with R = CH_3, designated[9] complex III, resembles those of the anions $[Mo(O)(OH)(CN)_4]^{3-}$ and $[Mo(O)(H_2O)(CN)_4]^{2-}$ which have also been determined.[10] We have shown in recent papers of this series[1,11-13] that these anions can be regarded as models of reactive intermediates in the molybdothiol-catalyzed reduction of CN^-. Moreover, we also demonstrated that these salts of oxomolybdate(IV) become catalysts of the reduction of N_2-ase substrates under appropriate experimental conditions.[11] Complex III contains end-on-bonded isonitrile ligands and thus may be similarly considered as a model of intermediates such as I or II. The relation of III to the parent binuclear oxo-bridged L(+)-cysteine complex of oxomolybdate(V) (complex I[9]) can be readily demonstrated (see Experimental Section) by reacting it with isonitriles in mildly acidic aqueous acetonitrile (eq 2):



III, Y^-, e.g., PF_6^- or I_3^-

$$[Mo_2O_4Cys_2]^{2-} + 4RNC + Cl^- + H_2O \rightarrow [Mo(O)(Cl)(CN\text{-}R)_4]^+ + MoO_4{}^{2-} + 2[CysH]^- \quad (2)$$

Accordingly, complex III was expected to yield CH_3NH_2, CH_4, C_2H_4, C_2H_6, etc., on reaction with reducing agents in analogy to eq 1. We shall show in the following that this is indeed the case and moreover these reactions are stimulated by ATP. Finally, reactions of fragments of complex III generated under reducing conditions with acetylene and molecular nitrogen will also be reported.

Results

Reduction of Coordinated Methyl Isocyanide in the Absence of ATP. Complex III reacts with BH_4^- in pH 9.6 borate buffer at ambient temperature to yield CH_3NH_2 and a mixture of CH_4, C_2H_4, and C_2H_6 in the molar ratios of 1:0.10:0.15. In addition, traces of C_3 hydrocarbons (C_3H_6 and C_3H_8) are also formed. The yields of the latter are invariably low and for this reason will not be shown except where necessary. The hydrocarbon product ratios are essentially independent of reaction time. However, the hydrocarbon yields are influenced by a number of variables such as reaction temperature, pH, concentration of reactants, etc. The reactions were followed until 5–10% of the total isonitrile was reduced. At sufficietly high concentrations of BH_4^- and long reaction times, conversions (based on hydrocarbon yields in the gas phase) of up to 30% were achieved, but in most other experiments no special attempts were made to maximize the yields. The formation of CH_3NH_2 was confirmed by direct colorimetric assays. A number of complexes analogous to III with different isonitrile ligands were prepared as well and were qualitatively shown to behave similarly under reducing conditions. However, complexes with isonitrile ligands such as $C_6H_{11}NC$, $t\text{-}C_4H_9NC$, or $C_6H_5CH_2NC$ were found to be insufficiently soluble and thus less suitable for detailed investigations.

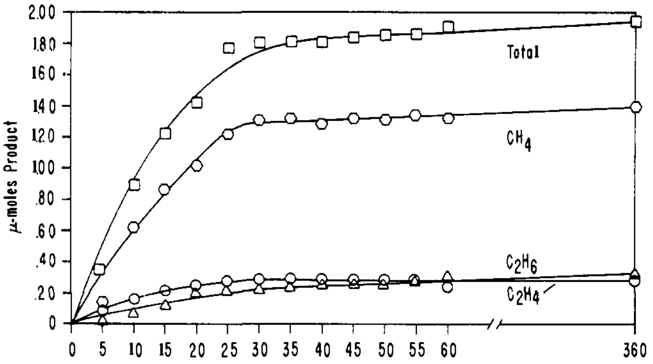


Figure 1. Time plot of the reduction of coordinated CH_3NC in complex III by BH_4^- in the *absence* of ATP. Reaction solutions contained, in a volume of 4.0 mL: complex III, 54.8 μmol; BH_4^-, 0.66 mmol (initial concentrations), in 0.2 M pH 9.6 borate buffer. Total hydrocarbons (□) are the molar sums of yields of CH_4 (○), C_2H_6 (△), and C_2H_4 (○), at various time points.

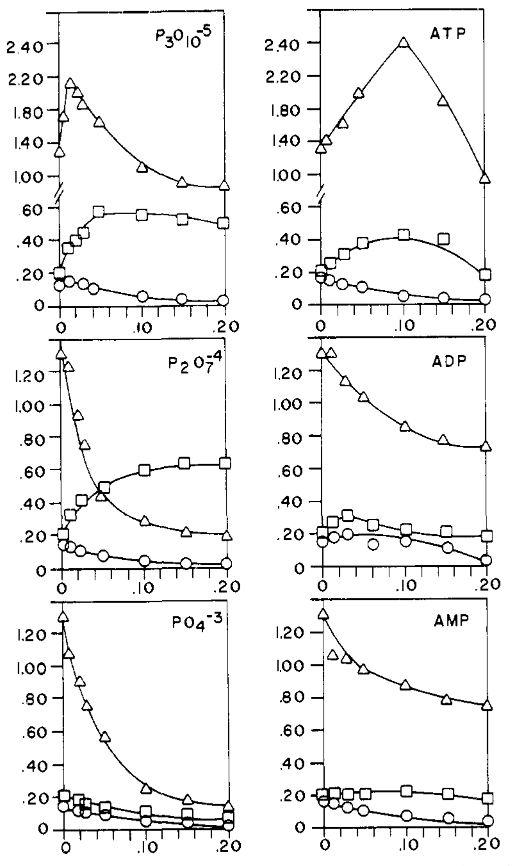


Figure 2. Concentration-yield profiles for CH_4 (△), C_2H_4 (□), and C_2H_6 (○) generated from complex III on reduction with $NaBH_4$ in the presence of six different phosphates. Yields were measured after 1 h of reaction at 23 °C. Reaction conditions as in the legend to Figure 1, except for the presence of the (sodium) salts of the respective phosphates. All phosphate solutions were pH adjusted to afford terminal pH values of the reaction solutions of between 9.7 and 10.0. Abscissas denote yields in micromoles. Ordinates show the concentrations of the added phosphates in millimoles/liter.

In Table I, hydrocarbon yields and product ratios from the reduction of complex III under a variety of conditions are summarized. A time dependence of the hydrocarbon production is shown in Figure 1.

The reduction of coordinated CH_3NC in III is not appreciably affected by anions such as Cl^-, ClO_4^-, and SO_4^{2-} (supplied as the sodium salts). However, PO_4^{3-} and $P_2O_7^{4-}$ inhibit, while $P_3O_{10}^{5-}$ stimulates the hydrocarbon production. The three anions have different effects on the production of CH_4, C_2H_6, and C_2H_4, as follows from Figure 2. For example, PO_4^{3-} inhibits the formation of CH_4, C_2H_6, and C_2H_4, while $P_2O_7^{4-}$ inhibits the production of CH_4 and C_2H_6, and *stimulates* the formation of C_2H_4.

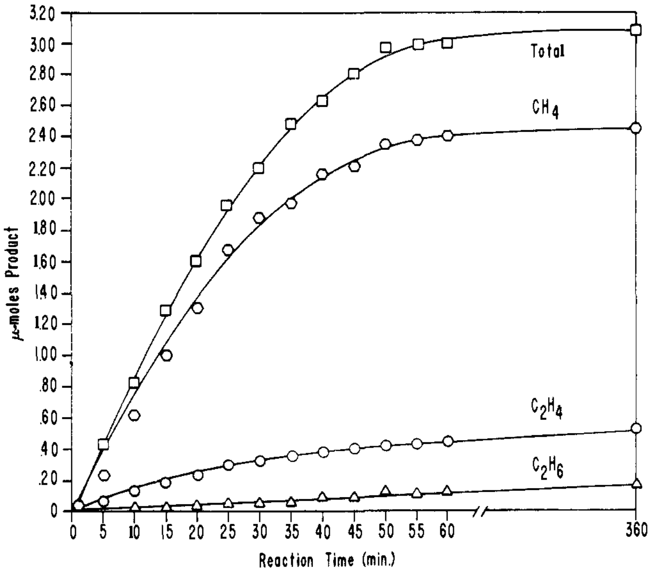


Figure 3. Time plot of the reduction of coordinated CH_3NC in complex III by BH_4^- in the *presence* of ATP. Reaction conditions as in legend to Figure 1, except that the solution contained 0.40 mmol of ATP at t = 0.

Reduction in the Presence of ATP. The addition of ATP to the reaction systems causes only a slight increase in the initial rates of hydrocarbon production but over longer reaction times a nearly twofold increase of the hydrocarbon yields is observed (see Figure 3). ATP causes a significant increase of the CH_4 production and a slight decline of the yields of C_2H_6. The CH_4/C_2H_4 ratios remain essentially unaffected (see Table I and Figure 2). ADP and AMP do not show clear stimulatory effects nor are they strong inhibitors. Their hydrocarbon yield-concentration profiles are distinctly different from those of $P_2O_7^{4-}$ and PO_4^{3-} (Figure 2). It should be stressed that these studies were performed in a carefully controlled pH range and at several time points at each concentration. It was concluded from these experiments that the individual effects of the anions or nucleoside phosphates were real and not simply due to variable pH or nonspecific salt effects.

Reduction of Acetylene. Since the reduction of coordinated isonitrile can be reasonably expected to proceed in a stepwise manner, fragments of complex III generated during its reduction could act as *catalysts* for the reduction of other substrates. Acetylene was chosen for these experiments because of its importance as an alternate substrate of N_2-ase and the ease with which it is reduced. The reduction of III in the presence of C_2H_2 caused the production of significant amounts of C_2H_4, indicating that a catalytic reduction of C_2H_2 did occur. ATP stimulated the C_2H_4 production two- to threefold, as is shown in Table II. In addition to C_2H_4 small amounts of C_2H_6, CH_4, and of C_3H_6 (propylene) are observed. The yields of C_2H_6 increase with increasing partial pressure of C_2H_2; they are also somewhat enhanced by ATP. The yields of CH_4 *decrease* with increasing partial pressure of C_2H_2; those of C_3H_6 are essentially independent of C_2H_2 pressures between 0.15 and 1 atm (see Table II). The yields of the C_4 hydrocarbons are particularly low in the presence of ATP, and even at 1 atm of C_2H_2 less than 1% of all products formed are either butene-1 or butadiene-1,3. The reactive fragments of complex III thus are relatively selective catalysts for the reduction of C_2H_2 to C_2H_4.

Table I. Reduction of Coordinated CH_3NC in Complex III under Various Conditions[a]

No.	Concn of variable, M; exptl conditions	Concn of III, mM	24-h yields,[d] μmol in gas phase	Hydrocarbon product ratios CH_4:C_2H_6:C_2H_4
1	No ATP; pH 9.6–9.9	1.1	0.50	100:4:24
2		2.7	0.97	100:9:27
3		7.0	1.77	100:13:25
4		14.0	2.44	100:20:18
5		26.6	2.67	100:20:14
6		46.7	3.04	100:21:14
7	+ATP = 0.0; pH 9.6–9.9	14.1	2.38	100:20:18
8	0.005	14.1	2.42	100:10:30
9	0.01	14.1	2.53	100:12:28
10	0.025	14.1	2.86	100:9:25
11	0.05	14.1	3.10	100:8:23
12	0.10	14.1	3.20	100:6:20
13	0.20	14.1	2.32	100:5:24
14	0.27	14.1	1.82	100:2:23
15	+ATP = 0.10, pH[b] 9.95	14.0	3.25	100:4:20
16	$+P_3O_{10}^{5-}$ = 0.10; pH 10.0	14.0	1.75	100:2:43
17	Cl^- = 0.10; pH 9.70	14.0	2.40	100:10:20
18	SO_4^{2-} = 0.10; pH 9.89	14.0	2.38	100:8:15
19	None[c]; pH 9.89	14.0	2.28	100:18:15
20	AMP = 0.10; pH 9.98	14.0	1.17	100:9:20
21	ClO_4^- = 0.10; pH 9.70	14.0	2.17	100:11:17
22	ADP = 0.10; pH 10.0	14.0	1.82	100:6:18
23	$P_2O_7^{4-}$ = 0.10; pH 9.95	14.0	1.05	100:8:151 (!)
24	PO_4^{3-} = 0.10; pH 9.90	14.0	1.09	100:6:36
25	PO_4^{3-} = 0.20; pH[b] 9.90	14.0	0.94	100:5:43

[a] Reaction solutions contained, in a total volume of 4.0 mL: complex III and ATP as indicated (initial concentrations), in 0.2 M pH 9.6 borate buffer. The initial concentration of $NaBH_4$ was 0.165 M in all cases. Reaction vessels were initially flushed with argon; reaction temperature, 23 °C. [b] Terminal pH values. [c] Control. [d] Sum of micromoles of hydrocarbons.

Table II. Reduction of C_2H_2 with Catalytic Amounts of Complex III in the Presence and Absence of ATP[a]

Reaction time, h	pC_2H_2, initial, atm	Yields, μmol of hydrocarbons with/without ATP					
		CH_4	C_2H_6	C_2H_4	C_3H_6[b]	C_4H_8	C_4H_6
1	0	2.3/1.3	0.05/0.30	0.42/0.26	0.1/0.1	0/0	0/0
	0.15	2.3/1.2	7.3/8.4	58.9/46.6	0.6/1.0	0.1/0.8	0.6/1.1
	0.50	1.5/0.75	15.8/16.5	133/95.1	0.98/0.63	2/2.7	2.3/5.3
	1.0	1.2/0.60	20.7/26.5	245/120	0.80/0.89	4/5.8	4.1/9.3
20	0	2.6/1.5	0.17/0.30	0.51/0.28	0.1/0.1	0/0	0/0
	0.15	2.5/1.4	22.7/10.1	73.2/51.6	0.99/1.6	0.8/0.9	0.6/1.3
	0.50	1.6/0.86	29.9/19.4	229/96	1.0/1.2	2.3/3.1	2.6/5.6
	1.0	1.2/0.70	45.2/27.1	455/125	0.72/1.2	4.2.6.0	5.8/12

[a] Reaction solutions contained, in a volume of 4.0 mL: complex III, 54.7 μmol; $NaBH_4$, 0.165 M; ATP, where indicated, 0.10 M (initial concentrations), in 0.2 M pH 9.6 borate buffer. [b] Due to the similarity of the GLPC retention times of C_4H_{10} and C_3H_6 the formation of C_3H_6 was confirmed by mass spectrographic analysis. Moreover, the C_2H_2 was tested for C_3 contaminants such as methylacetylene and allene, both of which could give rise to propylene under the conditions of the experiments; neither CH_3C_2H nor $CH_2{=}C{=}CH_2$ was detectable by GLPC.

Reactions in the Presence of Nitrogen. The yields of hydrocarbons from coordinated CH_3NC are lower if the reduction of complex III is performed under N_2 and in the presence of ATP (see Table III). In Figure 4, a difference function of the isonitrile reduction under argon and nitrogen is shown which indicates that N_2 exerts the strongest inhibitory effect after about 15 min of reaction. Using $^{30}N_2$-enriched N_2 as the substrate we observed the highest concentration of a compound in which the original N–N bond of N_2 is still intact *also* after about 15 min of reaction (see Figure 4). This compound could be either diimide (N_2H_2) or hydrazine. From the overall yields of N_2 reduced we conclude that the main product which is formed during the first 15 min of reaction is N_2H_2 which in turn decomposes and disproportionates, giving rise to the gradual accumulation of NH_3 in the reaction solution. The yields of reduced nitrogen products also increase with increasing partial pressure of N_2, as does the degree of inhibition of hydrocarbon production during the reaction. If the reaction solutions are quenched with fumaric acid, a diimide trapping agent that also was used in previous experiments,[12-14] the yields of reduced nitrogen products in the reaction solutions are lower than if succinic acid is employed instead, consistent with the presence of diimide. Moreover, less N_2 is reduced if the reduction of complex III is performed in solutions containing fumarate, while succinate has no effect on the yields. The present N_2-reducing system thus behaves as the other molybdenum-based model systems of N_2-ase. In the absence of ATP, some N_2 reduction occurs as well, as is shown in Table III, even though the yields of hydrocarbons are not markedly different as compared to identical runs under argon.

Discussion

The oxomolybdate(IV) moiety prefers π-bonding ligands in the equatorial and σ-bonding ligands in the axial positions.

Table III. Reduction of Molecular Nitrogen with $NaBH_4$-Complex III, with and without ATP[a]

Conditions	Reaction time, min	pN_2, initial, atm	Yields, μequiv		Yields, μmol, of			Total CH_3NC reduced, μmol
			NH_3	N_2H_2[b]	CH_4	C_2H_6	C_2H_4	
With ATP	15	0 (Ar)	0	0	0.82	0.06	0.22	1.1
	15	0.15	0.64	0.78	0.80	0.06	0.22	1.1
	15	0.50	1.3	2.82	0.57	0.06	0.21	0.84
	15	0.75	2.55	4.95	0.54	0.06	0.19	0.79
	15	1.00	3.2	7.0	0.51	0.06	0.17	0.74
No ATP	15	0 (Ar)	0	0	0.71	0.14	0.18	1.0
	15	1.00	2.6	2.0	0.50	0.04	0.23	0.77
With ATP, + succinate	15	1.00	3.25	4.22	0.54	0.03	0.15	0.72
With ATP, + fumarate	15	1.00	1.29	0.95	0.51	0.04	0.16	0.71
No ATP	20 (h)	1.00	3.1	1.9	1.4	0.36	0.38	2.14
With ATP	1	1.00	0.13	0.65	0.03	Trace	0.01	0.04 (0.04)[c]
	5	1.00	0.57	1.2	0.28	Trace	0.04	0.32 (0.33)
	10	1.00	1.24	2.0	0.55	0.02	0.11	0.68 (0.77)
	15	1.00	2.44	7.6	0.93	0.03	0.16	1.12 (1.26)
	20	1.00	1.87	3.2	1.23	0.04	0.21	1.48 (1.59)
	30	1.00	1.65	2.8	1.83	0.06	0.31	2.20 (2.28)
	40	1.00	1.33	2.8	2.09	0.09	0.35	2.53 (2.60)
	60	1.00	1.32	1.6	2.40	0.11	0.43	2.94 (3.00)
	80	1.00	1.32	1.0	2.54	0.11	0.49	3.14 (3.21)

[a] Effect of nitrogen at different partial pressures from coordinated isonitrile. Reaction solutions contained, in a total volume of 4.0 mL: complex III, 54.7 μmol; $NaBH_4$, 0.165 M; ATP, where indicated, 0.10 M (initial concentrations), in 0.2 M pH 9.6 borate buffer. [b] All nitrogen experiments were performed with $^{30}N_2$-enriched N_2; N_2H_2 denotes yields of reduced products that could either be N_2H_2 or N_2H_4 (as calculated from observed mass peaks of $^{30}N_2$ after hypobromite oxidation). [c] Values in parentheses denote yields under argon from parallel experiments.

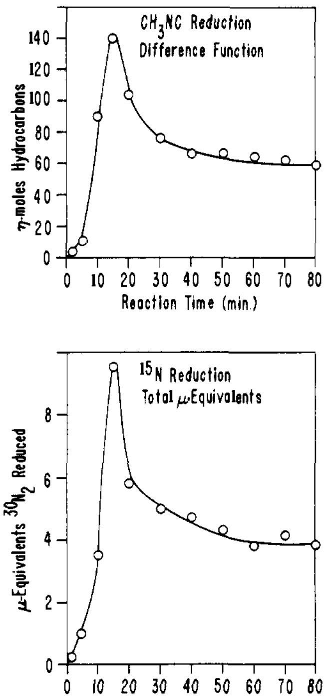
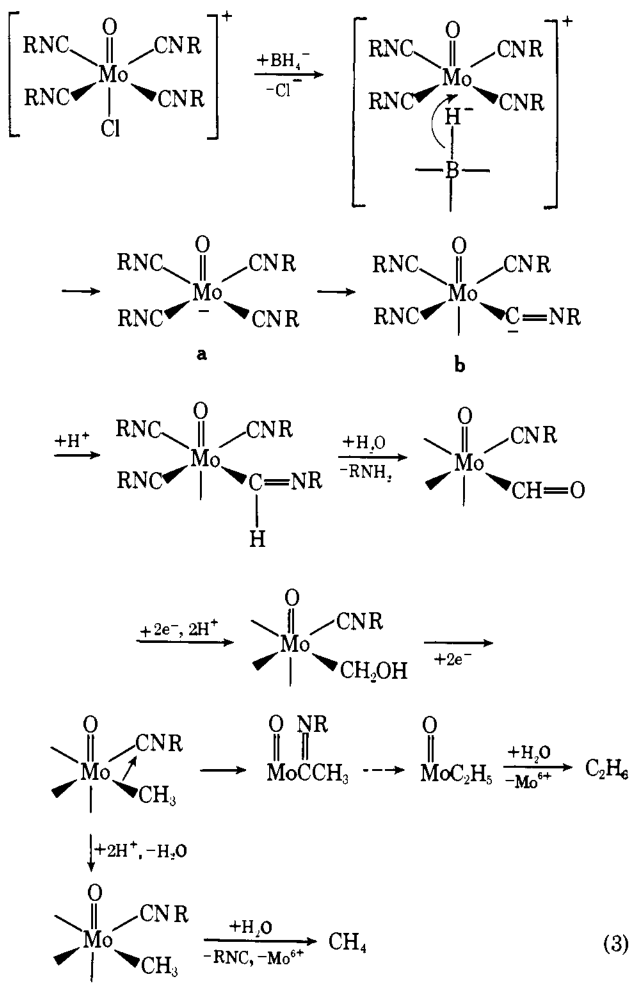


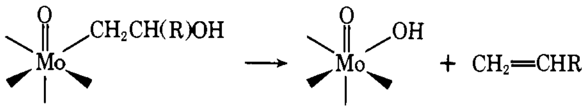
Figure 4. Reduction of coordinated CH_3NC in the presence of 1 atm of N_2. Upper curve: Difference plot of total yields of hydrocarbons produced under argon and under nitrogen. Lower curves: Yields of reduced nitrogen products (of N_2H_2 and NH_3) in the reaction solutions after different reaction times; total reaction volume, 4.0 mL; initial amounts of complex III, 54.8 μmol; of BH_4^-, 0.66 mmol; and of ATP, 0.40 mmol.

The first step in the reduction of the isonitrile ligands in III by borohydride may therefore consist in the transfer of two electrons from the reductant to molybdenum through axial attack as shown in eq 3. The resulting species (**a**), formally a derivative of oxomolybdate(II), is as such unstable and is rapidly converted into **b**, which undergoes further reactions as outlined. Equation 3 depicts a mechanism of isonitrile reduction which



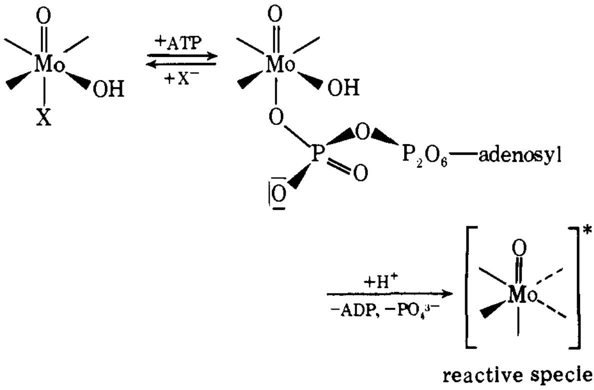
(3)

is virtually identical with that postulated in ref 6 and hence need not be discussed in full detail. Our work demonstrates that mononuclear complexes of isonitriles with oxomolybdate(IV) yield amines and hydrocarbons on reaction with reducing agents in apparent analogy to reaction eq 1; the analogy is further strengthened by the observed stimulatory effect of ATP. Since up to 14 electrons and protons must be transferred to the bound substrate(s) for reduction to C_1-C_3 hydrocarbons, the Mo-C bond in the intermediates is evidently sufficiently resistant or kinetically stable against hydrolysis to prevent premature loss of partially reduced bound residues. The alkanes are ultimately released through the hydrolysis of terminal alkylmolybdenum species as indicated in eq 3. Accordingly, alkane formation occurs preferentially under conditions of high electron transfer efficiency, i.e., when the concentration of reductant is high. Olefin production is favored at low concentrations of reducing agent. Under these conditions the formation of terminal alkylmolybdenum species is retarded, giving rise to intermediates which tend to decompose with elimination of olefins, as has been amply discussed in ref 6. We emphasize again that olefins can form from isonitriles by several mechanisms; we favor the elimination according to eq 4 although this might not be the only reaction pathway:



(4)

The inhibitory effect of anions such as PO_4^{3-} or $P_2O_7^{4-}$ on hydrocarbon production from complex III is plausibly attributed to their competition with the reductant (BH_4^- or products derived therefrom) for the free coordination site(s) on molybdenum. The resulting complexes may have different stabilities, thus explaining the different effects of PO_4^{3-} and $P_2O_7^{4-}$. It is of interest to note that ClO_4^- had a pronounced inhibitory (or oxidizing) effect in reactions with the cyano complexes of oxomolybdate(IV),[11] indicating that relatively minor modification of the effective charge on molybdenum produces significant reactivity differences. The stimulation of hydrocarbon production by ATP and the lack of stimulation by ADP and AMP are also important as this shows that the present system behaves as the other model systems of N_2-ase studied (see ref 11 and literature cited therein). We assume that ATP forms intermediate complexes with the oxomolybdate species acting as catalysts of ATP hydrolysis to ADP and inorganic phosphate. During the cleavage of the terminal P-O-P bond inert hydroxyl group(s) on molybdenum could be removed, giving rise to oxomolybdate species which are more rapidly reduced. These complex phenomena are difficult to express by means of one equation; eq 5 merely summarizes main features of mechanistically complicated events:

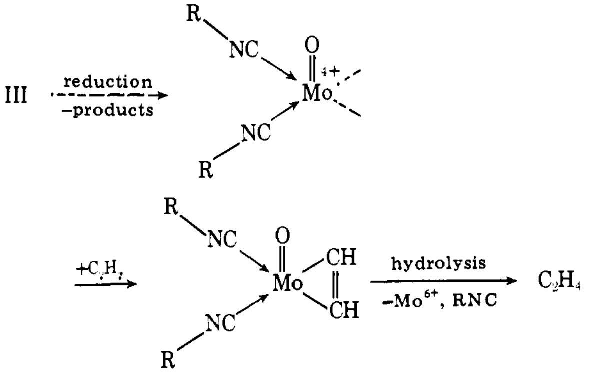


(5)

The failure of ADP or AMP to stimulate hydrocarbon production is due to their diminished tendency to undergo molybdate-catalyzed hydrolysis. The effect of $P_3O_{10}^{5-}$ may be related to that of ATP; similar stimulatory effects of $P_3O_{10}^{5-}$ have not yet been observed in other N_2-ase model systems.

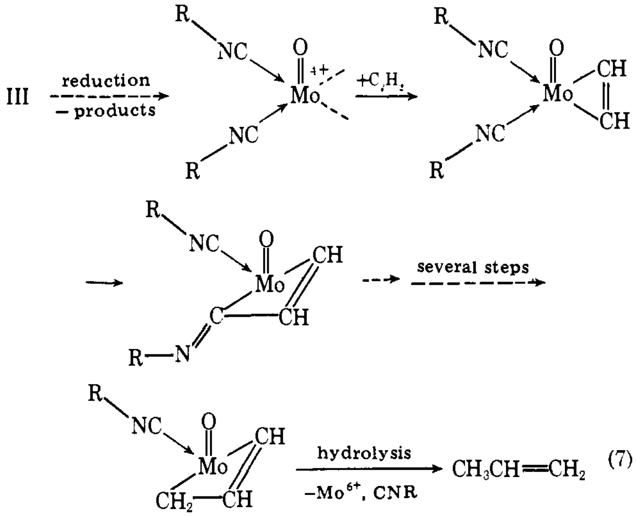
Reactions with Acetylene. The catalytic reductions of C_2H_2 are typical of those observed in other modifications of the N_2-ase model systems except for the enhancement of the yields of *propylene*, a product of which only traces are formed in the absence of C_2H_2. Schematic representations of reactions leading to C_2H_4 and C_3H_6 are given in eq 6 and 7.

Ethylene Formation



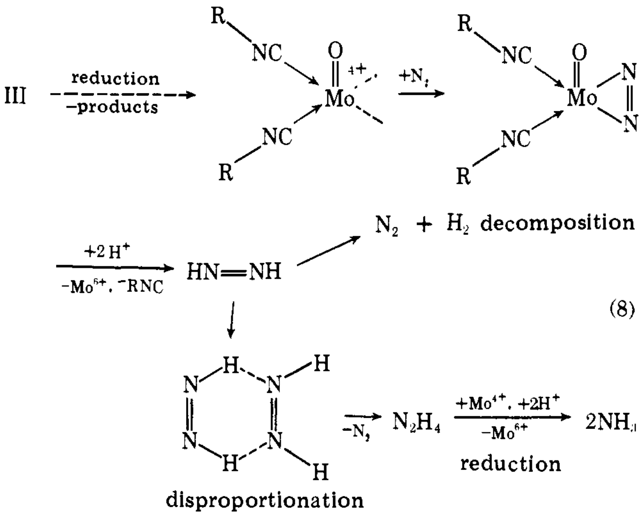
(6)

Propylene Formation



(7)

Reactions with Molecular Nitrogen. Reactive fragments of complex III reduce molecular nitrogen in a manner consistent with the diimide mechanism proposed in 1974,[12] which since has been shown to operate in other N_2-reducing systems as well.[13-15] Essential mechanistic steps are summarized in eq 8. Our results suggest that fragments of III, once generated,



(8)

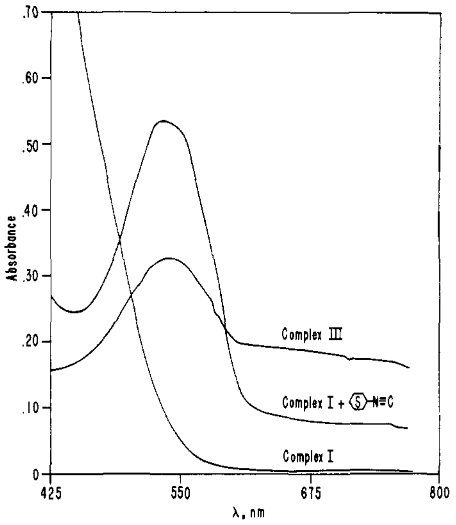


Figure 5. Demonstration of the conversion of complex I into complex III according to eq 2: $[Mo_2O_4Cys_2]^{2-} + 4RNC + Cl^- + H_2O \rightarrow [Mo(O)(Cl)(CNR)_4]^+ + MoO_4^{2-} + 2CysH^-$. Reaction solutions in 9:1 CH_3CN/H_2O contained at $t = 0$: complex I, 4 mM; c-$C_6H_{11}NC$, 40 mM in a total volume of 3 mL. To this solution 50 μL of 12 N HCl was injected. A purple color develops within 60 s; from the intensity of the d-d transition at 545 nm ($\epsilon = 133\ M^{-1}\ cm^{-1}$) the yield of complex III was quantitative in terms of eq 2.

react with N_2 in a catalytic cycle which is maintained during the initial 15–30 min of reaction in the presence of ATP. In the absence of ATP, the stationary concentrations of the reactive fragments of III are lower, as are the yields of reduced N_2 products. Nitrogen does not seem to interfere with the actual reduction of coordinated isonitrile in III since the hydrocarbon product ratios are not significantly different from those observed under argon (see Table III).

Concluding Remarks

It is now well established that mononuclear oxomolybdate complexes possess the necessary properties to duplicate reactions which occur at the substrate reducing site of N_2-ase. Our earlier suggestions concerning the oxidation state of molybdenum in the active reduced forms of the molybdothiol catalysts are now well supported by the recent work with cyano complexes of oxomolybdate(IV)[11-14] and the present studies. The conversion of coordinated isonitriles to hydrocarbons requires multiple electron- and proton-transfer steps, the elimination of primary amine and of water, until the terminal isonitrile carbon atom is converted to an alkyl group. The fact that such complex sequential reactions occur in protic media suggests that at least some of the postulated organomolybdenum intermediates may be sufficiently stable for detection or isolation under appropriate noncatalytic conditions.

Experimental Section

Reagents and Chemicals. All standard chemicals were of analytical or reagent grade purity and were used without further purification. Methyl isocyanide was synthesized according to the procedure given in ref 16. The salt $[Mo(O)(Cl)(CNCH_3)_4]^+PF_6^-$ (complex III) and related isonitrile complexes were prepared by the method of Novotny and Lippard[7] and characterized by elemental analysis, infrared, NMR, and UV-vis spectroscopy. The compounds slowly decompose on exposure to air and were for this reason stored in a vacuum desiccator over Dri-Rite.

Typical Experimental Procedures. (a) Reduction of Coordinated Isonitrile. Stock solutions of complex III cannot be prepared due to the insufficient stability of the complex cation in aqueous solutions. Therefore, weighed samples of the complex were transferred into 38-mL reaction bottles and flushed with 99.995% argon for 20 min. The weight of complex was usually 25.0 mg (54.8 μmol), unless specified otherwise. The reaction bottles and silicone rubber seals are marketed by Pierce Chemical Co., Rockford, Ill. Prior to each experiment, the argon gas phase was analyzed for contaminants (e.g., H_2, O_2, N_2, hydrocarbons) by GLPC using a Hewlett-Packard Model 700 laboratory gas chromatograph equipped with a 6-ft molecular sieve 5A column and a thermal conductivity detector for H_2, O_2, or N_2. For hydrocarbon determinations, a Varian Model 1440 Aerograph gas chromatograph was employed, fitted with a 6-ft phenyl isocyanate–Porasil C, 80–100 mesh column, using FID detection. As a general rule, the total molybdenum content of the reaction solutions was determined after conclusion of the experiments, to assure correctness of the initial weights of complex III employed. The Mo assay used for this purpose was colorimetric, consisting of the addition of 5.0 mL of 30% H_2O_2, followed by (after 5–10 min) the addition of 10.0 mL of a 2 N aqueous $HClO_4$ solution. The resulting yellow solution was diluted to 100 mL with water and the absorbance measured at 330 nm, using either a Beckman DB-G grating spectrophotometer or a Beckman DK-2A ratio recording spectrophotometer. Solutions of ATP (0.4 M) were prepared by adding the appropriate amount of 1 N NaOH and 0.2 M pH 9.6 borate buffer such that the resulting pH of this solution was 9.6. The solution was kept on ice at all times and never stored longer than 5 min prior to use. To initiate reactions, 2.0 mL of 0.2 M pH 9.6 borate buffer was added to the argon-filled reaction bottles, followed by 1.0 mL of the ATP solution. Immediately thereafter, at $t = 0$, 1.0 mL of 0.66 M $NaBH_4$ in water was injected. The total solution volume thus was 4.0 mL. Experiments conducted in the absence of ATP required the addition of 3.0 mL of 0.2 M pH 9.6 borate buffer to produce the same total solution volume after the addition of 1 mL of the $NaBH_4$ solution at $t = 0$. As has been outlined in previous papers of this series (see, e.g., ref 11) the gas pressure in the reaction bottles was kept constant by means of 50-mL "pressure-releasing" syringes. Hydrocarbon products in the gas phase were determined by withdrawing 0.5-mL samples at convenient time points as outlined above. The reproducibility of yields determined in this fashion was on the order of ±1.5%. Further details of experimental design are included in the legends of figures and tables. For control purposes, the terminal pHs of the reaction solutions were determined as well and were found to be within ±0.1 pH unit of the average value of 9.95.

(b) Inhibition and Substrate Reduction Experiments. Experiments in the presence of gaseous inhibitors or substrates (i.e., N_2 or C_2H_2) were performed as described in section a above except that the bottles were initially filled with the respective gases other than argon. The sodium salts of anionic inhibitors (e.g., Na_2HPO_4) were added to the reaction solutions by dissolving them in pH 9.6, 0.2 M borate buffer. Where changes of pH occurred, the resulting solutions were pH adjusted to 9.6 through addition of either NaOH or the protic acids of the inhibitor salts. These solutions were subsequently injected into the reaction bottles such that the total solution volume was always 4.0 mL.

(c) Nitrogen Reduction Experiments. All experiments were performed with normal N_2 enriched with at least 20% of $^{30}N_2$. The reaction conditions are specified in the legends to Figure 4 and Table III. Prior to hypobromite oxidation, residual substrate nitrogen was removed by bubbling a stream of argon through the reaction solutions. Sample workup was subsequently performed following a recently described method[17] which offers advantages over the earlier techniques in that it does not require the use of a high vacuum apparatus. Known volumes of the gas phase were analyzed mass spectrographically for isotopes of nitrogen, using a LKB 9000 mass spectrometer. The yields of $^{29}N_2$ were corrected for natural abundance as usual, assuming this percentage to be 0.74.

(d) Detection of Methylamine. The formation of methylamine as a product of the reduction of CH_3NC was demonstrated by analyzing samples of the gas phase after completion of the reactions and application of the ninhydrin test.

(e) Conversion of Complex I into Complex III. To demonstrate that the binuclear L(+)-cysteine complex of oxomolybdate(V) (complex I) is converted into complex III, solutions of complex I in 9:1 CH_3CN/H_2O were treated with excess c-$C_6H_{11}NC$ and subsequently acidified with a few drops of 2 N HCl. A purple color characteristic of the cation of complex III develops on standing; the optical absorption spectra (Figure 5) of such solutions confirm the presence of III in the yields expected according to eq 2.

Acknowledgments. This work was supported by Grant No. CHE76-10890 and by Institutional Grant No. GT 18245, both from the National Science Foundation. We thank Dr. S. J. L. Lippard (Columbia University) for sending us a preprint of his paper (ref 8) prior to publication, and Ms. Kim Freeman for skillful experimental assistance.

References and Notes

(1) Paper 14 of this series: P. R. Robinson, E. L. Moorehead, B. J. Weathers, E. A. Ufkes, T. M. Vickrey, and G. N. Schrauzer, *J. Am. Chem. Soc.*, **99**, 3657 (1977).

(2) R. W. F. Hardy and E. K. Jackson, *Fed. Proc., Fed. Am. Soc. Exp. Biol.*, **26**, 725 (1967).

(3) M. Kelly, *Biochem. J.*, **107**, 1 (1968).

(4) M. Kelly, J. R. Postgate, and R. L. Richards, *Biochem. J.*, **102**, 1c (1967).

(5) M. Kelly, *Biochim. Biophys. Acta*, **171**, 9 (1968); **191**, 527 (1969).

(6) G. N. Schrauzer, P. A. Doemeny, G. W. Kiefer, and R. H. Frazier, *J. Am. Chem. Soc.*, **94**, 3604 (1972). Also see: G. N. Schrauzer, *Angew. Chem., Int. Ed. Engl.*, **14**, 514 (1975).

(7) M. Novotny and S. J. Lippard, *Inorg. Chem.*, **13**, 828 (1974).

(8) C. T. Lam, D. L. Lewis, and S. J. Lippard, *Inorg. Chem.*, **15**, 989 (1976).

(9) Previously, the binuclear L(+)-cysteine complex of oxomolybdate(V) was frequently referred to as complex I. The salt $K_2Mo(O)(H_2O)(CN)_4$ was later[13] called complex II; hence, the adopted nomenclature for the related isonitrile complex of oxomolybdate(IV) is historically justified.

(10) P. R. Robinson, E. O. Schlemper, and R. K. Murmann, *Inorg. Chem.*, **14**, 2035 (1975).

(11) G. N. Schrauzer, P. R. Robinson, E. L. Moorehead, and T. M. Vickrey, *J. Am. Chem. Soc.*, **97**, 7069 (1975).

(12) G. N. Schrauzer, G. W. Kiefer, K. Tano, and P. A. Doemeny, *J. Am. Chem. Soc.*, **96**, 641 (1974).

(13) G. N. Schrauzer, P. R. Robinson, E. L. Moorehead, and T. M. Vickrey, *J. Am. Chem. Soc.*, **98**, 2815 (1976).

(14) E. L. Moorehead, P. R. Robinson, T. M. Vickrey, and G. N. Schrauzer, *J. Am. Chem. Soc.*, **98**, 6555 (1976).

(15) S. I. Zones, T. M. Vickrey, J. G. Palmer, and G. N. Schrauzer, *J. Am. Chem. Soc.*, **98**, 7289 (1976).

(16) R. E. Schuster, J. E. Scott, and J. Casanova, Jr., "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 772.

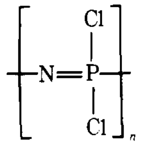
(17) P. R. Robinson and E. L. Moorehead, *Anal. Lett.*, **10**, 147 (1977).

Communications to the Editor

Synthesis of Alkyl and Aryl Phosphazene High Polymers

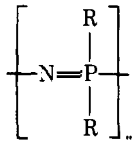
Sir:

Earlier, we reported the first syntheses of stable, high molecular weight poly(organophosphazenes) of formula $[NP(OR)_2]_n$, $[NP(NHR_2)]_n$, and $[NP(NR_2)_2]_n$[1-3] by the interaction of poly(dichlorophosphazene) (I) with alkoxides, aryl oxides, or amines. Since that time more than 70 different macromolecules based on these structures have been prepared in different laboratories.[4] These species now comprise a new class of high polymers with unusual fundamental and technological properties. However, all these polymers possess organic side groups bonded to phosphorus through oxygen or nitrogen and, for this reason, reaction pathways exist that permit depolymerization or decomposition at temperatures above 200 °C. It was anticipated that a new range of phosphazene polymers, perhaps with higher thermal stabilities and unique physical properties, might be accessible if alkyl or aryl groups could be bonded directly to phosphorus through carbon-phosphorus bonds (II).



$$\left[-N=PCl_2-\right]_n$$

I

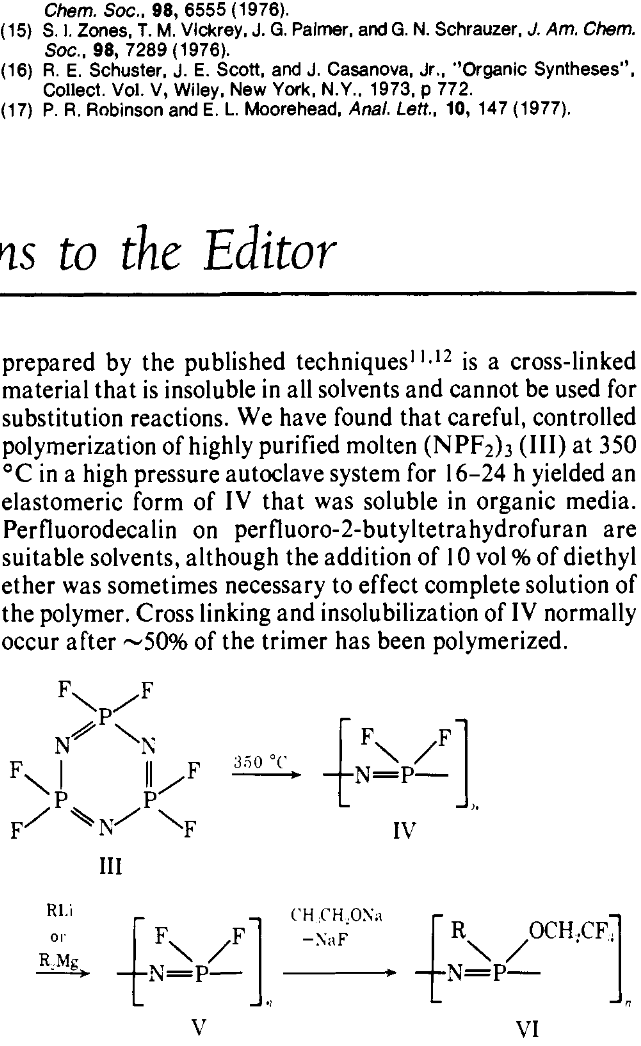


$$\left[-N=PR_2-\right]_n$$

II

A few earlier attempts had been made to achieve this end. Polymer I had been allowed to react with Grignard or organolithium reagents,[5,6] but the elemental compositions and properties of these products were incompatible with the expected structures. In fact, earlier work in our laboratory showed that such reagents degrade the phosphazene skeleton of I in preference to replacement of halogen. Similar ring cleavage reactions have been reported when the cyclic $(NPCl_2)_{3\text{ or }4}$ interact with Grignard or organolithium reagents.[7,8] However, small-molecule *fluoro*cyclophosphazenes, such as $(NPF_2)_{3\text{ or }4}$[9,10] are less susceptible to skeletal cleavage under these conditions, and it was of interest to examine the reactions of high polymeric $(NPF_2)_n$ with organometallic reagents.

We report here that high-molecular-weight poly(difluorophosphazene) (IV) is a suitable substrate for reaction with some organometallic reagents. The poly(difluorophosphazene) prepared by the published techniques[11,12] is a cross-linked material that is insoluble in all solvents and cannot be used for substitution reactions. We have found that careful, controlled polymerization of highly purified molten $(NPF_2)_3$ (III) at 350 °C in a high pressure autoclave system for 16–24 h yielded an elastomeric form of IV that was soluble in organic media. Perfluorodecalin on perfluoro-2-butyltetrahydrofuran are suitable solvents, although the addition of 10 vol % of diethyl ether was sometimes necessary to effect complete solution of the polymer. Cross linking and insolubilization of IV normally occur after ~50% of the trimer has been polymerized.



The soluble poly(difluorophosphazene) reacted cleanly with aryllithium reagents or with dialkylmagnesium compounds to yield partly substituted, soluble, high-molecular-weight poly(aryl- or alkylphosphazenes) (V). The remaining fluorine in V was removed by reaction with nucleophiles, such as CF_3CH_2ONa, to yield hydrolytically stable, mixed substituent polymers such as VI. Attempts to achieve total replacement of fluorine in IV led to a marked shortening of the chains, although up to 80–90% of the fluorine could be replaced by alkyl or aryl without the polymer incurring a serious decline in molecular weight. The products of these reactions are flexible or elastomeric materials with unusual combinations of physical properties. The following are examples of typical reactions.

Phenyllithium prepared from bromobenzene (26.2 g, 0.17 mol) and excess lithium in diethyl ether (200 mL) was added to a solution of IV (4.6 g, 0.055 mol) in perfluorobutyltetrahydrofuran (175 mL) and diethyl ether (12 mL) as a heterophase suspension in tetrahydrofuran (THF) (1000 mL). After a 6-min reaction at 21 °C, the mixture was treated with a solution prepared from trifluoroethanol (18 ml, 0.25 mol)