established from the NMR data. Accordingly, the crystal structures of the vinyl complexes derived from 2-butyne, **3**, and from di-*p*-tolylacetylene, **4**, were determined. Both vinyl derivatives had trans stereochemistry (Figure 1). There are precedents for bridging vinyl ligands in clusters but all, crystallographically defined, have cis stereochemistry.[5]

One equivalent of hydrogen converted the vinyl complexes to the corresponding trans olefin and the original dimer, **1**. In a catalytic mode, the product was the trans olefin (see the degradation sequence described below). With the vinyl complexes as the catalyst, the results were the same. Our data provide a firm basis for the catalytic sequence presented in Figure 2. The rate-determining step appears to be hydrogen addition to the vinyl intermediate since the catalytic reaction rate is a sensitive function of H_2 pressure. Olefin elimination directly from this vinyl intermediate does not appear to be a kinetically significant process, at least for diarylacetylenes in either the presence or absence of H_2.

Unfortunately, alkynes also react with the bridged vinyl intermediate.[6] This process, competitive with hydrogen addition to form the trans olefin, leads to the degradation of the dinuclear complex within 5 min under catalytic conditions. The details of the chemistry that ensues vary with the nature of the acetylene; for brevity, the description here is limited to diphenylacetylene chemistry. Addition of the latter to the vinyl complex forms the mononuclear, square-planar complex[7] $Rh[\pi\text{-}(H)(R^1)C{=}C(R^2)C(R^3){=}C(R^4)][P(O\text{-}i\text{-}C_3H_7)_3]_2$ (**5**), which has been crystallographically defined (details of which will be presented in a separate article) and which has the R^1 and R^2 aryl groups trans and R^3 and R^4 cis. This latter complex was shown to be a catalyst precursor for the hydrogenation of diphenylacetylene to *cis*-stilbene. Thus, alkyne hydrogenation initiated by **1** transforms from selective trans-olefin to selective cis-olefin formation. Attempts to prevent the effective alkyne competition for the vinyl intermediate by raising the hydrogen pressure from 1 to 100 atm were only partially successful (the degradation rate was suppressed but the overall rate was so greatly enhanced that all alkyne was consumed in ~60 s, and under these conditions, substantial amounts of the first formed olefins were converted to alkanes).

Alkyne hydrogenations catalyzed by other dinuclear and also polynuclear complex precursors have been described,[8-12] but in all these reported systems, cis olefins have been the main products. However, the nuclearity of the actual catalyst intermediates was not defined in these systems although labeling studies[8] for $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\eta^2\text{-}\mu\text{-}RC_2R)$ indicated that fragmentation of the dimer was not a significant process. In any case, the presence of reactive, adjacent metal centers is not a sufficient condition[1] for trans-olefin formation in alkyne hydrogenation—the stereochemical outcome obviously depends on the intimate stereochemistry of the intermediates in the catalytic cycle. The precise electronic and steric factors that govern stereochemistry[1] in the formation of the bridging vinyl ligand are not evident from available data. Having demonstrated a principle concerning catalysis at two adjacent metal centers and having reasonably outlined the mechanistic character of the catalytic cycle, we now seek a robust trans-olefin catalytic system by dispersing and supporting dinuclear metal complexes on metal oxides.

Acknowledgment. We thank the National Science Foundation and the Division of Basic Energy Sciences of the Department of Energy for support of this Research, the National Science Foundation for a Predoctoral Fellowship for R.R.B., the Miller Institute for Research in Basic Science for a grant in the form of a Miller Professorship (E.L.M.), and Johnson-Matthey, Inc., for the loan of rhodium chloride.

Registry No. 1, 65176-62-7; **2**, 70727-45-6; **3**, 82135-63-5; **4**, 82135-62-4; **5** (R = Ph), 82135-61-3; $HRh_2(C_6H_5C{=}C(H)C_6H_5)[P(O\text{-}i\text{-}C_3H_7)_3]_4$, 82135-60-2; $(\mu\text{-}H)_2(\eta^2\text{-}\mu\text{-}C_6H_5C_2C_6H_5)Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]^4$, 82135-59-9; 2-butyne, 503-17-3; diphenylacetylene, 501-65-5; di-*p*-tolylacetylene, 2789-88-0.

Supplementary Material Available: Synthesis and characterization data for $(\mu\text{-}H)_2(\eta^2\text{-}\mu\text{-}C_6H_5C_2C_6H_5)Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$, the bridged vinyl species derived from 2-butyne, diphenylacetylene, and di-*p*-tolylacetylene, and for $[(i\text{-}C_3H_7O)_3P]_2Rh(C(C_6H_5){=}C(C_6H_5){-}C(C_6H_5){=}C(H)(C_6H_5))$ (6 pages). Ordering information is given on any current masthead page.

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Reduction of CH_3NC and CH_3CN by the Reduced Species of $[Fe_4S_4(SPh)_4]^{2-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$: Model Reactions to Nitrogenase

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Received December 18, 1981

Recently, we reported that C_2H_2 is reduced by the electrochemically reduced species of $[Fe_4S_4(SPh)_4]^{2-}$ ($[4\text{-}Fe]^{2-}$)[1] or $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ ($[Mo\text{–}Fe]^{3-}$)[2] catalytically in MeOH/THF to give C_2H_4 selectively without evolving H_2 gas and that C_2D_2 is reduced by the same catalyst in H_2O at pH 6.0 to afford *cis*-$C_2D_2H_2$ stereoselectively.[3] The close similarity of these reactions to the nitrogenase reaction has driven us to study the reduction of CH_3NC and CH_3CN by the same catalysts. Isonitrile and nitrile molecules seem to be more practical substrates than acetylene for nitrogenase model reactions, since the reductions of CH_3NC to CH_4 and CH_3NH_2[4-9] and of CH_3CN to C_2H_6 and NH_3[8-10] require six electrons as in the reduction of N_2 to NH_3. In the reduction of RNC and RCN catalyzed by some molybdenum complexes reported so far,[11-13] the amounts of CH_3NH_2 and NH_3 formed have not been determined at all. This com-

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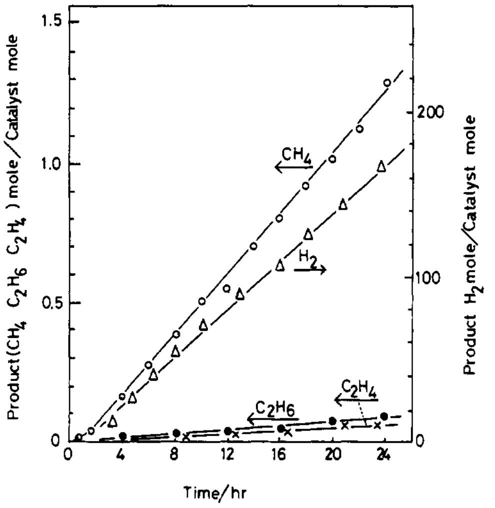


Figure 1. Plots of the amount of products vs. time in the reaction of CH_3NC with $[4\text{-Fe}]^{4-}$ in CH_3OH/THF.

Table I. Relative Amounts[a] of the Products Formed in the Reduction of CH_3NC Catalyzed by $[4\text{-Fe}]^{n-}$ ($n = 3, 4$) or $[\text{Mo-Fe}]^{5-}$ in CH_3OH/THF

product	catalyst[b] $[4\text{-Fe}]^{4-}$	$[4\text{-Fe}]^{3-}$	$[\text{Mo-Fe}]^{5-}$
CH_4	1	1	1
CH_3CH_3	0.050	2.7	0.49
CH_2CH_2	0.033	0	0
H_2	1.4×10^2	4×10^3	2×10^3

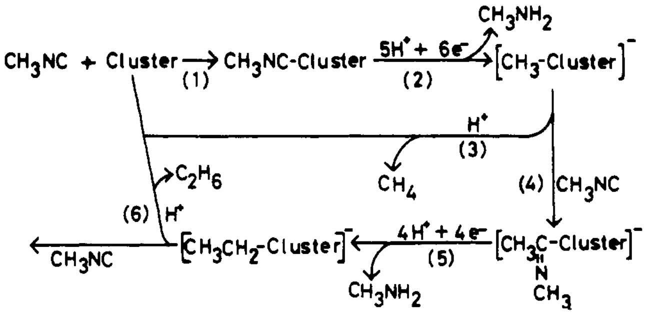
[a] The amount of CH_4 produced in each reaction was taken as unity. [b] Relative rates of the reduction by $[4\text{-Fe}]^{4-}$, $[4\text{-Fe}]^{3-}$, and $[\text{Mo-Fe}]^{5-}$ were 17:1.0:1.1 with respect to the amount of CH_4 produced.

munication describes the catalytic reduction of CH_3NC and CH_3CN by the electrochemically reduced species of $[4\text{-Fe}]^{2-}$ or $[\text{Mo-Fe}]^{3-}$ in MeOH/THF and in H_2O as novel nitrogenase model reactions.

The reduction of CH_3NC and CH_3CN was carried out under controlled potential electrolysis conditions with a Hg working electrode at the reduction potentials of $[4\text{-Fe}]^{2-}$ (2−/3−, −1.25 V, 3−/4−, −1.65 V)[14] or $[\text{Mo-Fe}]^{3-}$ (4−/5−, −1.25 V)[14] in a MeOH/THF (1:1 v/v, 40 cm^3) solution or in an aqueous suspension[15] containing the $n\text{-}Bu_4N^+$ salt of $[4\text{-Fe}]^{2-}$ (39 μmol) or $[\text{Mo-Fe}]^{3-}$ (34 μmol) and CH_3NC (17 mmol) or CH_3CN (34 mmol). Lithium chloride (24 mmol) and a $NaOH\text{-}H_3PO_4$ buffer were used as supporting electrolytes in the MeOH/THF solutions and aqueous suspensions, respectively. The reaction cells consisted of three compartments: a Hg working electrode and a platinum auxiliary electrode, which were separated by a glass frit, and a SCE reference electrode.[16]

The reduction product of CH_3NC by $[4\text{-Fe}]^{4-}$ in MeOH/THF consists of CH_4 and small amounts of C_2H_6 and C_2H_4 (Figure 1) together with a trace of C_3H_8, similar to the reduction by nitrogenase, though the concomitant H_2 evolution in the present reaction is large compared with that in the nitrogenase reaction ($H_2/CH_4 \simeq 3$).[5] There is seen an almost linear relation between the amount of the reaction products and the reaction time after the initial induction period of 1 h (Figure).[17] The number of moles of CH_4 evolved in 24 h reached ca. 130% of that of $[4\text{-Fe}]^{2-}$ present in the working electrode cell, indicating that the reduction proceeds catalytically.[18] Similar results were obtained also in the reduction of CH_3NC catalyzed by $[4\text{-Fe}]^{3-}$ and $[\text{Mo-Fe}]^{5-}$. Relative amounts of the products are summarized in Table I, which indicates that CH_4 is a major product in the reactions catalyzed by $[4\text{-Fe}]^{4-}$ and $[\text{Mo-Fe}]^{5-}$, while $[4\text{-Fe}]^{3-}$ affords C_2H_6 as a main product. The formation of C_2H_6 from CH_3NC may result from the insertion reaction of CH_3NC into the $[CH_3\text{-cluster}]^-$, as shown in the Scheme I, which has been modified from that of the RNC reduction by nitrogenase.[9] The first step in the scheme is adduct formation between CH_3NC and the cluster. The formation of such an adduct in solution has already been characterized for the $[Fe_4S_4(SR)_4]^{2-}\text{-}R'NC$ system (R = C_2H_5, $C_6H_5CH_2$; R′ = $t\text{-}C_4H_9$, $n\text{-}C_4H_9$).[19] The second step stands for the reduction of coordinated CH_3NC, which requires 5 H^+ and 6 e^-, producing CH_3NH_2 and $[CH_3\text{-cluster}]^-$, the latter of which may readily undergo an insertion reaction of either H^+ (step 3) or additional CH_3NC (step 4). The insertion of H^+ produces CH_4, while that of CH_3NC affords $[CH_3C({=}NCH_3)\text{-cluster}]^-$, which can give C_2H_6 in the subsequent reactions (steps 5 and 6). Thus, the ratio of the amount of CH_4 and C_2H_6 produced from CH_3NC may primarily depend on the relative ease of the insertion reactions of H^+ (step 3) and CH_3NC (step 4). It is therefore suggested that the rate of the insertion of CH_3NC is faster than that of H^+ in the reaction catalyzed by $[4\text{-Fe}]^{3-}$ and vice versa by $[4\text{-Fe}]^{4-}$ and $[\text{Mo-Fe}]^{5-}$.

Scheme I



When CH_3OH/THF is used as solvent, the other reduction product CH_3NH_2 reacts with HCHO, which is one of the oxidation products of MeOH at the counter Pt electrode,[20] giving a variety of amines and related compounds such as $(CH_3)_2NH$ and CH_3NHCH_2OH[21] under the present experimental conditions. So that the net amount of CH_3NH_2 produced in the catalytic reaction could be determined, the electrolysis of CH_3NC was carried out at −1.65 V (vs. SCE) for an aqueous suspension of $[4\text{-Fe}]^{2-}$ at pH 7.2.[22] The mole ratios of the reaction products in this case were $CH_4/C_2H_6/C_2H_4/H_2$ = 1.0:0.29:0.16:320, which are not very different from those obtained in MeOH/THF (Table I). The amount of CH_3NH_2 was about 10 times larger than the number of moles of the hydrocarbon formed. The total amount of hydrocarbons and CO_2 detected in the gas phase, however, is in harmony with the amount of CH_3NH_2. Aryl- or alkylisonitriles are known to react with $[Fe_4S_4L_4]^{n-}$ (L = SC_2H_5, $SCH_2C_6H_5$, etc; n = 2, 4) in the presence of excess alkyl mercaptan to give various thioformidates,[19] which are readily hydrolyzed to yield aryl- or alkylamines. In addition, alkylisonitriles undergo hydrolysis in acidic media to give alkylamines and HCOOH in equimolar amounts.[23] Carbon dioxide produced in the present

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[14] The potentials in MeOH/THF (1:1 v/v).

[15] The same potentials as in MeOH/THF were applied for an aqueous suspension.

[16] The volumes of the solution placed in the working, auxiliary, and reference electrode cells are 16, 16, and 8 cm^3, respectively.

[17] A similar induction period was observed also in the reduction of C_2H_2 (ref 3).

[18] The addition of CH_3NC to $[4\text{-Fe}]^{2-}$ in MeOH/THF (1:1 v/v) weakened the absorption band due to $[4\text{-Fe}]^{2-}$ centered at 450 nm (ε 17 000 $M^{-1}\ cm^{-1}$); see ref 19. The spectrum of $[4\text{-Fe}]^{2-}$ has, however, not changed between before and after the controlled potential electrolysis at −1.65 V for 24 h, suggesting that the Fe_4S_4 core essentially remains without decomposition during electrolysis.

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reaction may, therefore, result from the oxidation of HCOOH, which would be produced in the course of reactions, because the reaction of $[4\text{-Fe}]^{2-}$ with excess HCOOH in an aqueous suspension of pH 7.0 at room temperature has evolved a stoichiometric amount of CO_2 (based on $[4\text{-Fe}]^{2-}$) for 4 h. This result suggests that the $[4\text{-Fe}]^{2-}$ cluster is a possible model compound to formate dehydrogenases.[24]

Acetonitrile was similarly reduced in an aqueous suspension[25] of $[4\text{-Fe}]^{4-}$ or $[\text{Mo–Fe}]^{5-}$ formed electrochemically at pH 7.0 to produce C_2H_6, C_2H_4 (0.1 or 0.05 to C_2H_4), and NH_3. The amount of NH_3 produced in the reaction was 95% or 96% of the number of total moles of C_2H_6 and C_2H_4, and no $C_2H_5NH_2$ has been detected in the reaction systems. In addition, $[4\text{-Fe}]^{4-}$ and $[\text{Mo–Fe}]^{5-}$ were completely inactive to the reduction of $C_2H_5NH_2$ under the same conditions. These results indicate that the reduction of CH_3CN in the present reaction does not proceed by a stepwise mechanism, which requires two electrons in each step and should produce $C_2H_5NH_2$ as an intermediate.

Registry No. CH_3NC, 593-75-9; $[4\text{-Fe}]^{4-}$, 66213-39-6; $[4\text{-Fe}]^{3-}$, 52627-89-1; $[\text{Mo-Fe}]^{5-}$, 76125-83-2.

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Bis[bis(trifluoromethanesulfonyl)imido]xenon: A New Compound Possessing Xenon–Nitrogen Bonds

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Since the first report of the synthesis of a stable xenon–nitrogen compound,[2] no other compound of this type has been successfully prepared with a different nitrogen ligand. Until now, only $FXeN(SO_2F)_2$, $Xe[N(SO_2F)_2]_2$, and $[(FSO_2)_2NXe]_2F^+AsF_6^-$ were known.[3,4] In this communication, we report a new xenon–nitrogen compound utilizing a new ligand designed expressly for this purpose.

Reflection on the properties of the $N(SO_2F)_2$ group led us to conclude that a likely ligand for formation of a bond to xenon would be $N(SO_2CF_3)_2$ from the bis(perfluoroalkylsulfonyl)imides, $HN(SO_2R_f)_2$.[5] Several examples of these were known, but the parent member of the series, $(CF_3SO_2)_2NH$, had not been isolated. This compound was of particular interest because of the obvious comparisons one can make with $(FSO_2)_2NH$ and the fact that the CF_3SO_2 group is probably the most electron-withdrawing group in chemistry. This acid was subsequently prepared by us[6,7] and found to give a xenon-containing product upon reaction with XeF_2. This product was postulated to be $Xe[N(SO_2CF_3)_2]_2$, but there were several problems in characterizing the material. The same xenon-containing species was observed regardless of initial reaction stoichiometry. Attempts at the synthesis of a 1:1 product only resulted in poorer yields of the postulated disubstituted compound. The best xenon analyses were only 80-90% of the expected values. The product always seemed to be contaminated with the starting acid, and the best yields never exceeded 50%.

As an alternate approach to obtaining the pure compound, we investigated the use of a trimethylsilyl group to replace the acid proton. An expected advantage of this approach was the elimination of product HF, which was thought to be a major problem in promoting side reactions. Reaction of $(CF_3SO_2)_2NH$ with an excess of trimethylsilane afforded the appropriate reagent. Reaction of the silylimide with XeF_2 afforded the desired compound in high yield, as shown in the eq 1 (mmol).

$$(CF_3SO_2)_2NH\ (3.31) + Me_3SiH \xrightarrow[-H_2]{-195\text{ to }22\ ^\circ C} Me_3SiN(SO_2CF_3)_2\ (3.06) \xrightarrow[-22\text{ to }10\ ^\circ C,\ CF_2Cl_2]{XeF_2\ (1.83)} Xe[N(SO_2CF_3)_2]_2\ (1.26) + Me_3SiF + Xe\ (0.28) + \text{other volatiles} \quad (1)$$

The other products include unreacted XeF_2 and small amounts of N_2-, CF_4-, and SO_2-containing materials. The yield of the xenon compound is 75% starting from the acid, including purification of the intermediate silyl compound via pumping under dynamic vacuum for 0.5 h at 22 °C. The xenon product is purified by pumping under dynamic vacuum at 22 °C for 3 h. This illustrates the first successful use of a silyl derivative to form a bond to xenon. The reactivity can be compared to $B(OTeF_5)_3$ in the preparation of TeF_5O derivatives of xenon from xenon fluorides. The Si–N and B–O bonds have comparable reactivity and Me_3SiF and BF_3 are relatively innocuous byproducts.[8]

$Xe[N(SO_2CF_3)_2]_2$ is a fine white solid, stable at 22 °C under nitrogen or vacuum for several days without appreciable decomposition. A small sample exposed to the air decomposed after ~1 h. A quantitative xenon analysis for the formula $Xe[N(SO_2CF_3)_2]_2$ was realized after heating 0.327 g in a glass vessel to 72 °C, at which point it cleanly and abruptly decomposed. The products obtained were xenon, C_2F_6, a volatile solid and liquid, and a very small amount of a nonvolatile oil. The separation of the Xe from the C_2F_6 was difficult. Repeated transfers through a −172 °C trap gave a xenon value greater than 95 mol%. Mass spectral analysis showed little C_2F_6 in the Xe but considerable Xe in the C_2F_6, and the total Xe is nearer 99%. The volatile liquid was shown to be $(CF_3SO_2)_2NCF_3$ by its mass spectrum (CI, base *m/e* 350 amu) and its ^{19}F NMR. The volatile solid displays a singlet in the ^{19}F NMR, and its IR and mass spectrum indicate it is a form of the previously reported dimer $(CF_3SO_2NSO_2)_2$.[9] No evidence was found for $[N(SO_2CF_3)_2]_2$, a theoretical product.[3] These decomposition products are easily rationalized by eq 2 and 3. The instability of the $\cdot N(SO_2CF_3)_2$ radical compared to

$$Xe[N(SO_2CF_3)_2]_2 \xrightarrow{72\ ^\circ C} Xe + 2\cdot N(SO_2CF_3)_2 \quad (2)$$

$$\cdot N(SO_2CF_3)_2 \rightarrow C_2F_6 + (CF_3SO_2)_2NCF_3 + CF_3SO_2NSO_2 \quad (3)$$

$\cdot N(SO_2F)_2$[3] is surprising, but this has been confirmed by the photolysis of $ClN(SO_2CF_3)_2$[7] which forms CF_3Cl and $CF_3SO_2NSO_2$ quantitatively.

The mass spectrum of $Xe[N(SO_2CF_3)_2]_2$ by direct solid inlet shows no parent ion or xenon-containing fragment other than xenon. Analysis of the products evolving from a gradually heated sample by direct gas inlet gave the parent ions of Xe, $CF_3SO_2NSO_2$, and $CF_3N(SO_2CF_3)_2$ along with the expected fragments as observed in independent spectra of each product.

The Raman spectrum clearly shows the bands of a covalent $(CF_3SO_2)_2N$ group,[10] with no evidence of XeF bonds. However, a band at 826 cm^{-1} is of surprising intensity relative to other covalent $(CF_3SO_2)_2N$ derivatives.

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