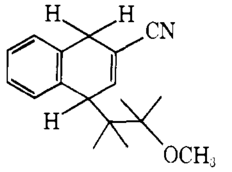
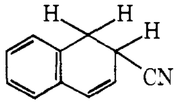
(k_d'), including chemical reaction (k_p), may be more rapid in the latter case, relative to k_f'. Interestingly, the exciplex from 2-NN and TME differs from 1-NN and TME[7,11a] in being nonfluorescent.

The remaining evidence derives from solvent effects. In benzene, the fluorescence of the 1-NN-TME exciplex[7] has $\Phi_{\lim} = 0.04$, and adduct **1** is formed. In acetonitrile, both exciplex fluorescence[7] and cycloaddition still occur, but with much lower efficiencies than in benzene. Similarly, with 2-NN and TME, formation of **2** is *totally quenched* in methanol; instead, products of photoreduction of 2-NN (e.g., **3** and **4**) are observed.[15e] Also, the fluorescence of 2-NN is quenched at the diffusion controlled rate (K_{sv} = 148 M^{-1}) in methanol. Thus, both quenching and reaction of 2-NN with TME apparently proceed by different mechanisms in methanol and benzene.



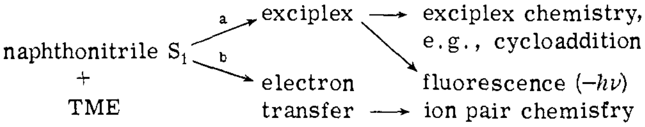
3



4

Each of the above pieces of data is an indication rather than a requirement of exciplex intermediacy in the cycloadditions. However, taken together the results make a strong case for Scheme II.[1,10,12,13,28-30] Path (a) is favored in benzene but (b) predominates in acetonitrile and methanol. In some solvents, both (a) and (b) pathways may be important.

Scheme II



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(26) (a) These calculations of ΔH in nonpolar media, using electrochemical data from polar media, can give erroneous estimates of the heats of formation of the exciplex. This is because the electrostatic attraction (stabilization) in the charge-transfer complex will be significant in the less polar media (−0.13 eV, ref 24b), and will be variable because the encounter distance will in general be different for different exciplexes. However, our point is simply that the K_{sv}'s in Table I are qualitatively in agreement with the above estimates of ΔH. (b) We thank Dr. G. N. Taylor for these suggestions.
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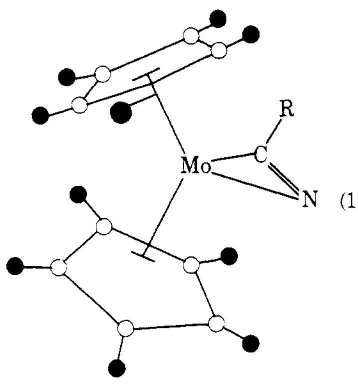
Reduction of New π-Bound Molybdenocene-Nitrile Complexes via Isolatable Iminium Intermediates

Sir:

In our continuing efforts to elucidate the possible role of electron deficient molybdenum species in nitrogenase, unique new molybdenocene complexes of organic nitriles have been prepared. Treatment of various nitriles with in situ generated molybdenocene[1,2] has resulted in the first synthesis of π-bound molybdenum-nitrile complexes (eq 1). Primary support for the suggested mode of coordination is the dramatic reduction in the infrared stretching frequency of the nitrile group. Acetonitrile, trifluoroacetonitrile, and benzonitrile complexes exhibit intense C≡N stretches at 494, 526, and 489 cm^{-1}, respectively, below that of the parent nitrile. These are the greatest reductions in C≡N stretching frequency ever observed upon coordination of these molecules. All of the molybdenum complexes are red, air-sensitive, sublimable solids. Mass spectra, ^1H and ^{19}F NMR data, and elemental analyses are consistent with the proposed structures.

Sterically induced η^2 coordination has been suggested

$(C_5H_5)_2MoCl_2 + 2Na/Hg + RCN \longrightarrow$

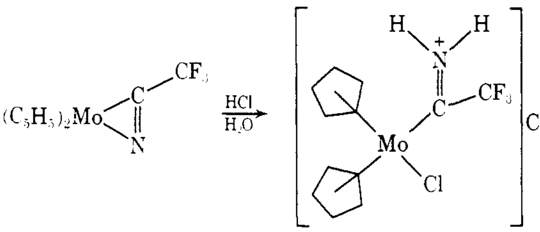


(1)

R = CH_3, CF_3, and C_6H_5

for a few dinitrile complexes,[3,4a] but the small reduction of ν_{CN} suggests that the C≡N bonds have a significant amount of triple bond character and recent studies have reformulated[4b] these complexes as σ bound. In contrast, the complexes reported here represent an unambiguous, preferential η^2 coordination of nitriles to a molybdenum metal center and exhibit a reduction of the carbon-nitrogen bond to one of essentially double bond character. One similar complex has been reported,[5] but only the fluoronitrile, CF_3CN, formed a complex and this ligand was labile. In the present case, edge-on coordination of RCN occurs nearly regardless of the nature of R, and the complexes are extremely stable. Since recent evidence suggests the nitrogenase enzyme contains only one Mo atom[6,7] and it has been proposed that nitriles are bound edge-on in this system,[8] these new complexes offer potentially valuable structural and chemical information persuant to these investigations.

Treatment of toluene solutions of $(C_5H_5)_2Mo(CF_3CN)$ with gaseous HCl gave quantitatively a unique blue-purple, water soluble precipitate with an unusual iminium structure (eq 2). Infrared spectra of the above salt shows a N-H stretch at 3170 cm^{-1}, which shifts to 2340 cm^{-1} upon deuteration. A strong C═N absorption at 1618 cm^{-1} and a Mo-Cl stretch at 265 cm^{-1}, coupled with absence of a Mo-H stretch, further supports the above structure.[9] Proton NMR in D_2O shows a singlet due to cyclopentadienyl protons at τ 4.57. No resonance due to N-H protons appears, presumably because of rapid exchange with the solvent. If the cation is precipitated from aqueous solution with $NaBPh_4$, an acetone soluble salt, $[(C_5H_5)_2MoCl(CF_3CNH_2)]^+$, BPh_4^- is obtained. Proton NMR of this complex in deuterioacetone shows a sharp singlet at τ 3.97 due to cyclopentadienyl protons and a broad absorption at τ 5.89 due to N-H protons. The latter absorption rapidly disappears with concomitant increase in the hydridoacetone signal. The N-H absorption may be regenerated by redissolving the complex in $(CH_3)_2C$═O. Infrared spectra of the tetraphenylboron salt show two very sharp, equal intensity N-H absorptions at 3275 and 3118 cm^{-1}, a strong C═N absorption at 1608 cm^{-1}, a strong Mo-Cl absorption at 230 cm^{-1}, and no Mo-H absorptions. Elemental analyses of both salts are consistent with the proposed formulations.



(2)

Further similarities of the molybdenocene system to nitrogenase are suggested by the facile reduction of this new iminium complex to ammonia.

$$[(C_5H_5)_2MoClCF_3CNH_2]^+, Cl^- + NaBH_4 \xrightarrow{OH^-} NH_3 + (C_5H_5)_2MoH_2 + \text{hydrocarbon}^{10} \quad (3)$$

The overall reduction of CF_3CN may be represented as:

$$CF_3CN \xrightarrow{(C_5H_5)_2Mo} \xrightarrow{H^+} \xrightarrow[OH^-]{NaBH_4} NH_3 + \text{hydrocarbon} + (C_5H_5)_2MoH_2 \quad (4)$$

Nitrogenase[11,12] and Schrauzer's Mo-thiol model system[8] yield analagous products using similar reagents and reaction conditions.

Different authors have alternately suggested dihapto[13] or monohapto[14] coordination of dinitrogen to molybdenum in nitrogenase, and model compounds have been isolated that are consistent with either proposal.[15,16] Electronically similar nitriles assume a dihapto configuration upon coodination, which is converted to a monohapto system upon protonation. Coupled with the recent work of Bercaw et al.[17] demonstrating an equilibrium between monohapto and dihapto titanocene-dinitrogen complexes, the possibility of monohapto-dihapto interconversion or equilibrium should be considered in the nitrogenase reduction of dinitrogen and alkyl cyanides.

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