tometer and NMR spectrometer used in these studies were made possible through NSF equipment grants. Fred E. Wood was a University of California Regents Fellow.

Supplementary Material Available: A list of atomic coordinates and thermal parameters for $[\mu\text{-}(Ph_2P)_2py]_3Pd_3Cl_6$ and for $[\mu\text{-}(Ph_2P)_2py]_2Rh_4(\mu\text{-}CO)(CO)_2(\mu\text{-}Cl)_2Cl_2$ (3 pages). Ordering information is given on any current masthead page.

A Bis(dinitrogen) Complex of Molybdenum: A Chemical Resemblance to Nitrogenase?[1]

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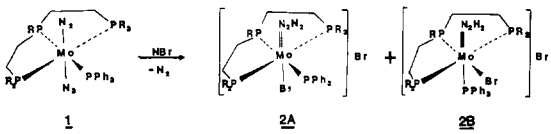
In 1978, Thorneley, Eady, and Lowe[2] reported the detection of hydrazine upon quenching the functioning enzyme nitrogenase with acid or base. On the basis of the chemistry of molybdenum and tungsten dinitrogen complexes they concluded that hydrazine was produced from an enzyme-bound dinitrogen hydride intermediate species upon quenching, and that neither hydrazine nor enzyme-bound hydrazine was an intermediate on the reduction route from dinitrogen (N_2) to ammonia.

We wish to report the first example of an analogous result in a noncatalytic ammonia-forming reaction (eq 1)[3] in which hydrazine is not a product in the reaction but is detected upon early quenching of the reaction with water. Thus, reactions of *trans*-$Mo(N_2)_2(triphos)(PPh_3)$ (**1**), where triphos = $PhP(CH_2CH_2PPh_2)_2$, with anhydrous HBr in anhydrous tetrahydrofuran (THF) carried out over a period of ≥60 h produced high yields of ammonia (eq 1) but no more than traces of hydrazine (<0.0015 mol of N_2H_4 per mol of **1**).[1] However, when volatiles were removed in vacuo from reactions that had proceeded for only short periods of time (e.g., 1 h, see Figure 1) and a H_2O/CH_2Cl_2 solvent mixture was added, hydrazine yields of up to 0.16 mol per mol of **1** were recorded.[4] No free hydrazine was present before the addition of H_2O/CH_2Cl_2 (see below).

$$2\textit{trans}\text{-}[Mo(N_2)_2(triphos)(PPh_3)] \xrightarrow[THF]{HBr} 2NH_4Br + 3N_2 + 2MoBr_3(triphos) + 2PPh_3 \quad (1)$$

Typically, reactions were carried out in one of two ways by using ca. 0.15 g (ca. 0.2 mmol) of **1** and ca. 20 mol of anhydrous HBr per mol of **1**. One method involved condensing HBr and THF onto **1** at −196 °C and allowing the mixture to reach ambient temperature. After the mixture was stirred for a fixed period of time, all volatiles were removed in vacuo and CH_2Cl_2 (10 mL) and H_2O (25 mL) added. The aqueous layer was analyzed for ammonia and hydrazine.[4] The second method involved the reaction of liquid HBr with **1** in the absence of solvent. Following the loss of 1.0 mol of N_2 per mol of **1**, a green-brown solid mixture of two isomeric hydrazido(2−) complexes resulted (eq 2).[1,5] It



1 **2A** **2B** (2)

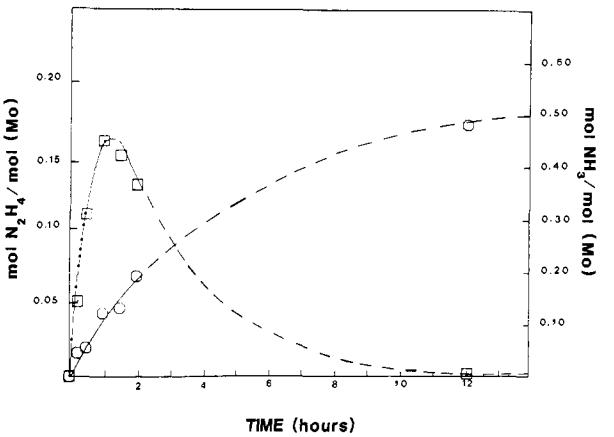


Figure 1. Variations in yields of hydrazine and ammonia vs. time. In separate experiments the reaction of **1** with HBr in THF was stopped after 0.25, 0.5, 1.0, 1.5, 2.0, and 12 h. At 60 h or longer, the yields of ammonia and hydrazine are routinely 0.72 and <0.0015 mol per mol of **1**.

is these two hydrazido(2−) complexes that react further to afford ammonia and N_2 (eq 3). To this solid was added THF, and the

$$\textbf{2A and 2B} \xrightarrow[THF]{HBr} 2NH_4Br + N_2 + 2MoBr_3(triphos) + 2PPh_3 \quad (3)$$

reaction was allowed to proceed for a fixed period of time. An identical workup procedure with that described above was used. Both methods gave similar results.

The yields of ammonia and hydrazine were plotted as a function of time (see Figure 1). Early in the reaction, following the loss of 1.0 mol of N_2, a rapid buildup of hydrazine was observed while the amount of ammonia produced was small. As the reaction proceeded a maximum yield of hydrazine was observed after 1.0 h beyond which time the yield continued to decrease. The ammonia yield (and further N_2 evolution) increased steadily with time.

The relatively rapid buildup of hydrazine corresponds very closely with the decrease in intensities of resonances due to **2B** (totally absent within 1 h) and the appearance of PPh_3 in the $^{31}P\{^1H\}$ NMR spectrum of a mixture of HBr, **2A**, and **2B** in THF.[1] No new species, other than PPh_3, were seen in the spectrum. Hydrazine could be being formed at this stage in the reaction and behaving as an intermediate on the route to ammonia. In order to investigate this possibility solid **1** was treated with liquid HBr to produce a mixture of **2A** and **2B**. Upon cooling to −196 °C, evolved N_2 was removed in vacuo, and $^{15}N_2H_4$[6] and THF were added. The reaction mixture was allowed to stir for 60 h at which time the evolved gases were collected. The aqueous extract was treated with a NaOBr solution and the gases were collected. Mass spectral determination of the ratio of N_2 isotopomers provided no evidence that $^{15}NH_4^+$ (as determined from N_2-29) had been produced in yields any greater than the background. In other words, there is no evidence for incorporation of $^{15}N_2H_4$ (present as $^{15}N_2H_5Br$) into the ammonia-forming sequence of reactions.[7]

These results suggest that early in the reaction a metal-bound dinitrogen hydride intermediate species is present in high concentration that leads to ammonia under normal reaction conditions. However, upon treatment with water this intermediate[8] produces hydrazine. That dioxygen plays no part in hydrazine formation was demonstrated by using scrupulously outgassed water and showing no decrease in the yield of hydrazine after 1 h.

(1) Reactions of Coordinated Dinitrogen. 13. Part 12: Bossard, G. E.; George, T. A.; Howell, D. B.; Koczon, L. M.; Lester, R. L. *Inorg. Chem.* **1983**, *22*, 1968-1970.

(2) Thorneley, R. N. F.; Eady, B. R.; Lowe, D. J. *Nature (London)* **1978**, *272*, 57-558. Thorneley, R. N. F.; Lowe, D. J. *Isr. J. Bot.* **1982**, *31*, 61-77.

(3) Baumann, J. A.; George, T. A. *J. Am. Chem. Soc.* **1980**, *102*,6153-6154.

(4) See ref 3 for details of ammonia and hydrazine analyses.

(5) The ratio of **2A** to **2B** is ca. 1:2.

(6) Prepared from $^{15}N_2H_6SO_4$: Browne, A. W.; Welsh, T. W. B. *J. Am. Chem. Soc.* **1911**, *33*, 1728-1734.

(7) The transitory existence of hydrazine within a solvent cage or bound to a metal cannot be eliminated by this experiment. However, the large yields of hydrazine determined early in the reaction after workup argue against these likelihoods.

(8) We believe that hydrazine is produced from the same intermediate in the reactions of **1** with HBr in benzene and toluene.[1]

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The relatively rapid buildup of a hydrazine-forming intermediate corresponds very closely with disappearance of **2B**. We are led to conclude that the loss of PPh_3 from **2B** leads to the early buildup in concentration of an intermediate in the ammonia-forming reaction that upon reaction with H_2O generates hydrazine.[9] Significantly, hydrazine was not generated by HBr (or HCl[1]) present in the reaction.[10] Later, when all **2B** has reacted, the concentration of the intermediate is low because of the slower reaction of **2A** to produce ammonia.[1]

The reaction of **2A** and **2B** to produce ammonia results in the formation of 0.5 mol of N_2 per mol of complex (eq 3). Interestingly, the formation of the hydrazine-forming intermediate does not result in any N_2 evolution. Thus, the amount of N_2 evolved, before quenching, corresponds to the amount of ammonia formed.

The behavior of **1** described in this communication is strikingly similar to that of nitrogenase.[2] No other "model" system has displayed this behavior: an analogy with the only recognized property of the substrate N_2 during turnover of the enzyme.[11] It is hoped that elucidation of the structure of the hydrazine-forming intermediate will provide a model for one of the intermediate stages in ammonia synthesis by nitrogenase. Further work in this direction is in progress.

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE80-11423.

(9) A solid begins to precipitate from the reaction solution after ca. 0.5 h. This golden-yellow solid is soluble in CH_2Cl_2 but shows no signal in the $^{31}P\{^1H\}$ NMR spectrum. This compound is not $MoBr_3$(triphos): George, T. A.; Lester, R. K., unpublished results.

(10) $(\mu_3\text{-}N_2)[(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2Ti_2][(\eta^1\text{:}\eta^5\text{-}C_5H_4)(\eta\text{-}C_5H_5)_3Ti_2]\cdot[(\eta\text{-}C_5H_5)_2(C_6H_{14}O_3)Ti]\cdot C_6H_{14}O_3$ reacts with THF/H_2O to give N_2H_4 and NH_3 but with HCl to give mainly N_2. Pez, G. P.; Apgar, P.; Crissey, R. K. *J. Am. Chem. Soc.* **1982**, *104*, 482-490.

(11) HD formation by nitrogenase occurs in the presence of D_2 and N_2. It has been proposed that dinitrogen-dependent HD formation arises from a bound reduced dinitrogen intermediate. Burgess, B. K.; Wherland, S.; Newton, W. E.; Stiefel, E. K. *Biochemistry* **1981**, *20*, 5140-5146 and references cited therein.

Preparation and Diels-Alder Reactions of 1,3-Dienes Containing both Sulfur and Nitrogen Substituents. Complete Orientational Control by the Acylamino Group

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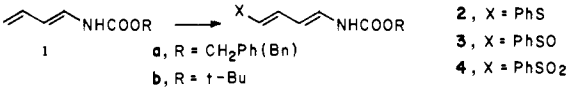
In recent years the Diels-Alder reaction of heterosubstituted 1,3-dienes has emerged as a powerful method for preparing highly functionalized ring systems.[1] As a result of the enhanced functionality imparted to their cycloadducts, dienes substituted with two differnt heteroatoms are of considerably interest, and those with oxygen and sulfur substitution have received significant attention.[2] In contrast, the Diels-Alder chemistry of 1,3-dienes containing both nitrogen and sulfur substituents is completely unexplored.[1] The successful use of heterosubstituted 1,3-dienes in synthesis typically demands knowledge of the substituent's effect on cycloaddition rate, regioselectivity, and endo stereoselectivity. Both acylamino[3] and thiophenyl[2a] substituents endow 1,3-dienes with useful Diels-Alder reactivity and positional selectivity,[1-4] although only the former substituent[3,4] exhibits good stereochemical-orienting characteristics.[5] In this communication, we describe a convenient synthesis of 1-(acylamino)-1,3-dienes that have sulfenyl, sulfinyl, and sulfonyl substitution at carbon 4. We also detail initial observations concerning Diels-Alder reactions of these new heterosubstituted 1,3-dienes, which exhibit excellent Diels-Alder reactivity, regioselectivity, and endo stereoselectivity, with regiocontrol being completely dominated by the acylamino substituent.

Dropwise addition of phenylsulfenyl chloride (1.05 equiv) at -78 °C to (*E*)-1,3-butadiene-1-carbamates **1**[6] (0.1 M in ether) and *N,N*-diisopropylethylamine (~3 equiv), followed by warming to room temperature and purification on silica gel, gave *directly*[7] 4-(phenylsulfenyl)-1,3-butadiene-1-carbamates **2** (85-95% yields) as crystalline 1:1 mixtures[8] of 1*E*,3*E* and 1*E*,3*Z* stereoisomers (eq 1). Oxidation[10] to the sulfoxides, followed by base-catalyzed



(1)

equilibration (1 M Et_3N in refluxing benzene),[9] afforded the crystalline (1*E*,3*E*)-4-(phenylsufinyl)-1,3-butadiene-1-carbamates **3** in 50-65% overall yields from **1**. Further oxidation[10] gave the corresponding (1*E*,3*E*)-4-(phenylsulfonyl)-1,3-butadiene-1-carbamates **4** (50-75% yields). These new dienes[11,12] are stable, highly crystalline solids, which are well suited for Diels-Alder transformations.

Sulfide diene carbamate **2a**[13] reacted with *N*-phenylmaleimide (110 °C, 24 h, dioxane) and phenyl vinyl ketone (56 °C, 26 h) to give endo cycloadducts[11,14] **5** and **6**[11] in 70% and 89% yields, respectively. A 4:1 mixture[13b] of cycloadducts **7** and **8** was formed from the reaction of **2a** with excess acrolein at 56 °C for 24 h (eq 2). The major endo adduct **7**[11,14] (mp 83-84 °C) could be

(1) For a recent review, see: Petrzilka, M.; Grayson, J. I. *Synthesis* **1981**, 753-786.

(2) Cf: (a) Trost, B. M.; Ippen, J.; Vladuchick, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 8116-8118. (b) Trost, B. M.; Vladuchick, W. C.; Bridges, A. J. *Ibid.* **1980**, *102*, 3548-3554. (c) Cohen, T.; Kosarych, Z. *J. Org. Chem.* **1982**, *47*, 4005-4008 and references therein.

(3) Cf: Overmap, L. E.; Freerks, R. L.; Petty, C. B.; Clizbe, L. A.; Ono, R. K.; Taylor, G. F.; Jessup, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 2816-2822 and references therein.

(4) (a) Evans, D. A.; Bryan, C. A.; Sims, C. L. *J. Am. Chem. Soc.* **1972**, *94*, 2891-2892. (b) Cohen, T.; Mura, A. J., Jr.; Shull, D. W.; Fogel, E. R.; Ruffner, R. J.; Falck, J. R. *J. Org. Chem.* **1976**, *41*, 3217-3219. Cohen, T.; Kosarych, Z. *Ibid.* **1982**, *47*, 4006-4008.

(5) Good endo stereoselectivity is seen in cycloadditions of 2-methoxy-1-(phenylthio)-1,3-butadiene.[2c,4b]

(6) Jessup, P. J.; Petty, C. B.; Roos, J.; Overman, L. E. *Org. Synth.* *1980*, *59*, 1-9.

(7) Chlorosulfenylation-dehydrochlorination has been employed to prepare 1-(phenylsulfenyl)-1,3-butadiene, see ref 4a and: Hopkins, P. B.; Fuchs, P. L. *J. Org. Chem.* **1978**, *43*, 1208-1217.

(8) Changing the base, solvent, or reaction temperature had surprisingly little effect on the ratio of stereoisomers. These mixtures could not be cleanly equilibrated to the 1*E*,3*E* isomers.[9]

(9) For related isomerizations, see: Overman, L. E.; Clizbe, L. A.; Freerks, R. L.; Marlowe, C. K. *J. Am. Chem. Soc.* **1981**, *103*, 2807-2815.

(10) *m*-Chloroperbenzoic acid (1.05 equiv) in CH_2Cl_2 at -20 °C.

(11) New compounds exhibited NMR, IR, and mass spectra and elemental compositions consistent with their assigned structures.

(12) 1*E*,3*E* isomer of **2a**: mp 94-95 °C; $J_{1,2}$ = 13 Hz, $J_{3,4}$ = 15 Hz. 1*E*,3*Z* isomer of **2a**: mp 81-82 °C; $J_{1,2}$ = 14 Hz, $J_{3,4}$ = 9 Hz. **3a**: mp 131-132 °C; $J_{1,2}$ = 12 Hz, $J_{3,4}$ = 15 Hz. **3b**: mp 146-147 °C; $J_{1,2}$ = 13 Hz, $J_{3,4}$ = 15 Hz. **4a**: mp 159-161 °C; $J_{1,2}$ = 12 Hz, $J_{3,4}$ = 14 Hz. **4b**: mp 145-146 °C; $J_{1,2}$ = 12 Hz, $J_{3,4}$ = 14 Hz.

(13) (a) A 1:1 mixture of 1*E*,3*E* and 1*E*,3*Z* dienes was employed. Careful monitoring of the reaction by HPLC showed that only the 1*E*,3*E* isomer reacted under these conditions. (b) Cycloadduct ratios were determined by HPLC and/or 250-MHz ^1H NMR analysis of crude cycloadduct mixtures.

(14) Stereochemical assignments were made from decoupled ^1H NMR spectra measured at 250 MHz. These assignments follow from arguments similar to those utilized in ref 3. Selected characterization data, diagnostic chemical shifts (δ) and coupling constants (in Hz), for representative cycloadducts. **5**: ^1H NMR $J_{3a,4}$ = 6, $J_{4,5}$ = 3, $J_{7,7a}$ = 7, $J_{6,7}$ = 4. **7**: ^1H NMR (H_1) 4.83, (H_6) 2.72, (H_4) 3.76, $J_{1,6}$ = 4, $J_{5e,6}$ = 3, $J_{5a,6}$ = 10, $J_{3,4}$ ~ 0. **10**: ^1H NMR (H_1) 4.9, (H_6) 2.65, (H_4) 3.85, $J_{1,6}$ = $J_{5e,6}$ = 3.5, $J_{5a,6}$ = 14, $J_{3,4}$ = 1.4. **11**: ^1H NMR (H_1) 4.6, $J_{1,2}$ = 3.6, (H_6) 2.95, m, half-height width = 21 Hz, (H_4) 3.85, $J_{3,4}$ = 3.1. **13**: ^1H NMR (H_1) 4.91, (H_3) 5.67, (H_6) 2.70, $J_{1,6}$ = 3.7, $J_{5a,6}$ = 13, $J_{4,5a}$ = 10. **14**: ^1H NMR (H_1) 4.92, (H_3) 6.08, (H_6) 2.65, $J_{1,6}$ = 4, $J_{5a,6}$ = 13, $J_{4,5a}$ = 10. **18**: mp 111-112 °C; ^1H NMR (H_2) 4.14, br s, half-height width = 10 Hz, (H_1 and CH*H*O*H*) 3.6-3.9, m; $J_{5a,6}$ = 11 Hz. **19**: mp 176-178 °C; IR ($CHCl_3$) 3470, 1770, 1682 cm^{-1}; ^1H NMR (H_2) 5.14, (H_1) 4.47, (H_6) 3.76, $J_{1,2}$ = 7.4, $J_{1,6}$ = 1.8; $J_{2,3}$ = 3.1; $J_{5e,6}$ = 6.6; $J_{5a,6}$ = 10.2. **20**: ^1H NMR (4 vinylic H), 5.9-6.1, m; (H_1 and OCH_2CH_2O) 3.6-4.1, m, (H_6) 3.15, br s, half-height width = 14 Hz.

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