equally broadened and diminished argues for either σ-fluxional or π-bonding. The observation that C(2) and C(3) display chemical shifts in opposite directions argues against π-bound Mulliken-type outer complexes similar to the central-bound (arene)$Cr(CO)_3$.[6] For these reasons, we favor fluxional σ-bonding. Furthermore, the small upfield shift by C(3) would suggest that mercury is bonding somewhat preferentially at this site.

Further indication of fluxional behavior is demonstrated by the ^1H NMR spectra of $CpPPh_3HgX_2$ (X = Cl, Br, I). The cyclopentadienyl hydrogens remain in the δ 6.0-6.6 region and the "aromatic" appearance of the AA'BB' pattern of the cyclopentadienyl moiety is evident though the resolution on our 60-MHz instrument was inadequate to determine coupling constants. There is a small halogen-dependent chemical shift (downfield) in the order of Cl > Br > I, with the shift of the cyclopentadienyl protons being greater than that of the phenyl protons.

Additional studies have shown that several other metal halides and carbonyl complexes of $CpPPh_3$ and related ylides are readily formed.

Acknowledgment. We wish to thank the WKU Faculty Research Program for financial support and Drs. Stan Smith and John Layton (University of Kentucky) for the ^{13}C NMR spectra.

References and Notes

(1) G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, **2**, 32 (1956); T. S. Piper and G. Wilkinson, *ibid.*, **3**, 104 (1956); H. P. Fritz, *Adv. Organomet. Chem.*, **1**, 239 (1964); A. N. Nesmeyanov, G. G. Dvoryantseva, N. S. Kochetkova, R. B. Materikova, and Yu. N. Schienker, *Dokl. Akad. Nauk SSSR*, **159**, 847 (1964); G. G. Dvoryantseva, K. F. Turchin, R. B. Materikova, Yu. N. Schienker, and A. N. Nesmeyanov, *ibid.*, **166**, 808 (1966); A. N. Nesmeyanov, L. A. Fedorov, R. B. Materikova, E. I. Fedin, and N. S. Kochetkova, *Tetrahedron Lett.*, 3755 (1968).

(2) P. West, M. C. Woodville, and M. D. Rausch, *J. Am. Chem. Soc.*, **91**, 5649 (1969); F. A. Cotton and T. J. Marks, *ibid.*, **91**, 7281 (1969); E. Maslowsky, Jr., and K. Nakomoto, *Inorg. Chem.*, **8**, 1108 (1969); W. Kitching and B. F. Hegarty, *J. Organomet Chem.*, **16**, P39 (1969); F. A. Cotton, D. L. Hunter, and J. D. Jamerson, *Inorg. Chim. Acta*, **15**, 245 (1975); A. J. Campbell, C. E. Cottrell, C. A. Fyfe, and K. R. Jeffrey, *Inorg. Chem.*, **15**, 1326 (1976).

(3) H. L. Ammon, G. L. Wheeler, and P. H. Watts, Jr., *J. Am. Chem. Soc.*, **95**, 6198 (1973).

(4) Z. Yoshida, S. Yoneda, and Y. Murata, *J. Org. Chem.*, **38**, 3537 (1973).

(5) Other complexes displaying fluxional behavior are known to be sensitive to steric effects: B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962); J. S. McKekechnie and I. C. Paul, *J. Am. Chem. Soc.*, **88**, 5927 (1966); T. H. Whitesides and R. A. Rudnik, *Inorg. Chem.*, **15**, 874 (1976).

(6) P. A. W. Dean, D. G. Ibbott, and J. B. Stothers, *Can. J. Chem.*, **54**, 166 (1976); G. A. Olah, S. H. Yu, and D. G. Parker, *J. Org. Chem.*, **41**, 1983 (1976).

Norman L. Holy*

Department of Chemistry, Western Kentucky University
Bowling Green, Kentucky 42101

Norman C. Baenziger, Richard M. Flynn, Dale C. Swenson

Department of Chemistry, University of Iowa
Iowa City, Iowa 52242

Received July 21, 1976

Preparation and Properties of Dinitrogen–Molybdenum Complexes. 5.[1] Conversion of the Coordinated Dinitrogen into a Hydrazone Type N_2CRR' Ligand

Sir:

Recent studies on the dinitrogen complexes of molybdenum, tungsten, titanium, and zirconium have disclosed that the coordinated dinitrogen of these complexes reacts with several reagents such as sulfuric acid,[2] hydrogen halides,[3] alkyl halides,[4,5] benzoyl chloride,[6] or tetrahydrofuran.[7] In a previous paper[8] we reported that *trans*-$[Mo(N_2)_2(dpe)_2]$[9] (dpe = $Ph_2PCH_2CH_2PPh_2$) (**1**) reacts with fluoroboric acid to yield a hydrazide (2−) complex *trans*-$[MoF(NNH_2)(dpe)_2]BF_4$ (**2**) in a good yield.

$$trans\text{-}[Mo(N_2)_2(dpe)_2] + HBF_4 \rightarrow trans\text{-}[MoF(NNH_2)(dpe)_2]BF_4 \quad (1)$$

We wish here to describe the reaction of **2** with aldehydes and ketones which affords a new potential method of the conversion of the coordinated dinitrogen to a series of hydrazone type ligands

$$trans\text{-}[MoF(NNH_2)(dpe)_2]BF_4 + RR'C{=}O \rightarrow [MoF(N_2CRR')(dpe)_2]BF_4 + H_2O \quad (2)$$

(R = CH_3CH_2, R' = H; R = Ph, R' = H; R = R' = CH_3)

although Chatt and his co-workers recently prepared the analogous complexes $[WBr(N_2CH_2)(dpe)_2]Br$ from **1** and dibromomethane[5] and $[MBr\{NN{=}CH(CH_2)_3OH\}(dpe)_2]Br$ (M = Mo or W) from **1** and tetrahydrofuran in the presence of methyl bromide[7] under irradiation.

When an excess of propionaldehyde (about 8 mol equiv) was reacted with **1** in dichloromethane at ambient temperature for 30 min, the original orange color of the solution turned brownish green and the addition of hexane afforded *trans*-$[MoF(N_2CHCH_2CH_3)(dpe)_2]BF_4$ as brownish green crystals in 82% yield. Anal. Calcd for $C_{55}H_{54}N_2F_5P_4BMo$: C, 61.81; H, 5.10; N, 2.62. Found: C, 61.52; H, 5.07; N, 2.50. Gas chromatographic analysis of the reaction mixture showed the quantitative formation of water according to eq 2. The infrared spectrum of the complex exhibits an intense band at 1565 cm^{-1} assigned to ν(C=N), which shifts to 1550 cm^{-1} upon ^{15}N substitution. The ^1H NMR spectrum shows a triplet band at 5.4 ppm assigned to methine proton, a multiplet band at 1.4 ppm assigned to methylene protons, and a triplet band at 0.6 ppm assigned to methyl protons in a ratio of 1:2:3, indicating that the complex consists of one isomer, although syn and anti isomers about C=N double bond are possible. The ^{19}F NMR spectrum shows a band at 83.0 ppm above benzotrifluoride assigned to fluoroborate anion and a quintet band at 50.3 ppm (J_{F-P} = 30 Hz) in a ratio of about 4:1. This indicates that the $CH_3CH_2CHN_2$ ligand and fluoride anion are trans to each other.

The reaction of benzaldehyde with **1** also gave an analogous green solid $[MoF(N_2CHPh)(dpe)_2]BF_4$ in 25% yield, although a longer reaction time (about 20 h) was required at ambient temperature compared with propionaldehyde. Anal. Calcd for $C_{59}H_{54}N_2F_5P_4BMo$: C, 63.45; H, 4.88; N, 2.51; F, 8.51; P, 11.09. Found: C, 63.29; H, 4.87; N, 2.56; F, 8.46; P, 11.13. In this case were given red crystals as by-product, which did not contain nitrogen.

In addition to aldehydes, **1** reacted with acetone at a refluxing temperature for 27 h to yield $[MoF(N_2C(CH_3)_2)(dpe)_2]BF_4$-$CH_3COCH_3$ as greenish brown crystals in 38% yield. Anal. Calcd for $C_{58}H_{60}N_2OF_5P_4BMo$: C, 61.82; H, 5.38; N, 2.49. Found: C, 62.29; H, 5.42; N, 2.34. Solvating acetone was easily lost on recrystallization from dichloromethane-hexane. This reaction was remarkably accelerated in the presence of an acid, as is usually found in the condensation reaction of aldehydes with hydrazines and amines. Thus, only 1 h of stirring of a mixture of **1** and acetone was enough

Table I. Infrared Data of $[MoF(N_2CRR')(dpe)_2]BF_4$[a]

R	R'	ν(C=N), cm^{-1}	ν(C=^{15}N), cm^{-1}
CH_3CH_2	H	1565	1550
C_6H_5	H	1525	
CH_3	CH_3	1585	

[a] KBr disks.

at a refluxing temperature if a small amount of aqueous fluoroboric acid was added.

The infrared data of the hydrazone type complexes obtained are given in Table I. The ν(C=N) band of the complex derived from benzaldehyde is considerably lower than those of the complexes derived from acetone and propionaldehyde. This is explained by the resonance effect of the phenyl group. We are presently investigating the reactivities of these hydrazone type complexes, especially their reduction to hydrazine derivatives.

References and Notes

(1) Part 4: T. Tatsumi, H. Tominaga, M. Hidai, and Y. Uchida, *J. Organomet. Chem.*, **114**, C27-C29 (1976).
(2) J. Chatt, A. J. Pearman, and R. L. Richards, *Nature (London)*, **253**, 39-40 (1975).
(3) Y. G. Borodko, L. N. Ivleva, L. M. Kachapina, S. I. Salienko, A. K. Shilova, and A. E. Shilov, *J. Chem. Soc., Chem. Commun.*, 1178 (1972); J. Chatt, G. A. Heath, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 2074-2082 (1974); J. M. Manriquez, R. D. Sanner, R. E. Marsh, and J. E. Bercaw, *J. Am. Chem. Soc.*, **98**, 3042-3044 (1976).
(4) A. A. Diamantis, J. Chatt, G. J. Leigh, and G. A. Heath, *J. Organomet. Chem.*, **84**, C11-C12 (1975); V. W. Day, T. A. George, and S. D. A. Iske, *J. Am. Chem. Soc.*, **97**, 4127-4128 (1975); V. W. Day, T. A. George, S. D. A. Iske, and S. D. Wagner, *J. Organomet. Chem.*, **112**, C55-C58 (1976).
(5) R. Ben-Shoshan, J. Chatt, W. Hussain, and G. J. Leigh, *J. Organomet. Chem.*, **112**, C9-C10 (1976).
(6) E. E. van Tamelen, and H. Rudler, *J. Am. Chem. Soc.*, **92**, 5253-5254 (1970); J. Chatt, G. A. Heath, and G. J. leigh, *J. Chem. Soc., Chem. Commun.*, 444-445 (1972); T. Tatsumi, M. Hidai, and Y. Uchida, *Inorg. Chem.*, **14**, 2530-2534 (1975).
(7) P. C. Bevan, J. Chatt, R. A. Head, P. B. Hitchcock, and G. J. Leigh, *J. Chem. Soc., Chem. Commun.*, 509 (1976).
(8) M. Hidai, T. Kodama, M. Sato, M. Harakawa, and Y. Uchida, *Inorg. Chem.*, in press.
(9) M. Hidai, K. Tominari, Y. Uchida, and A. Misono, *Chem. Commun.*, 1392 (1969).

Masanobu Hidai,* Yasushi Mizobe, Yasuzo Uchida

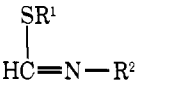
Department of Industrial Chemistry, University of Tokyo Hongo, Bunkyo-ku, Tokyo 113, Japan

Received July 27, 1976

Azetidin-2-oxo-4-thiones. Novel Thermolytic Products of β-Lactam Sulfoxides

Sir:

The thermal rearrangement of penicillin sulfoxides to deacetoxycephalosporin,[1] as well as that of similar β-lactam sulfoxides, provides a useful tool for the chemical interconversion of β-lactam antibiotics.[2] This rearrangement involves the intermediacy of sulfenic acids. As part of our studies on β-lactams related to penicillins and cephalosporins[3] we have investigated the thermolysis of the β-lactam sulfoxides **7** and **8.** We report herein an unusual rearrangement of these sulfoxides to the corresponding azetidin-2-oxo-4-thiones **11** and **12** which are thiomalonic acid imides, a hitherto unreported class of compounds.

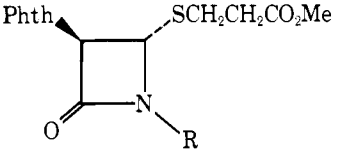


1, R^1 = Me; R^2 = $C(CO_2Me)=CMe_2$
2, R^1 = $CH_2CH_2CO_2Me$; R^2 = $C(CO_2Me)=CMe_2$
3, R^1 = Me; R^2 = $CH(CO_2\text{-}t\text{-}Bu)CH_2O\text{-}t\text{-}Bu$
4, R^1 = $CH_2CH_2CO_2Me$; R^2 = $CH(CO_2\text{-}t\text{-}Bu)CH_2O\text{-}t\text{-}Bu$

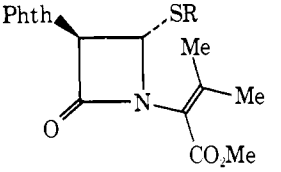
Treatment of the thioformimidate **2,** obtained by warming the thioformimidate **1**[4] and methyl 3-mercaptopropionate, with phthaloylglycyl chloride gave the trans β-lactam **5** (mp 92-93 °C, 56%).[5] Similarly, **3,** prepared by S-methylation (MeI, NaH in toluene) of *O-tert*-butyl-*N*-thioformyl-*d,l*-serine *tert*-butyl ester, was converted through **4** into the β-lactam **6** which consisted of a 1:1 mixture of two trans diastereoisomers.[5]

Oxidation of the 4-carbomethoxyethylthio-β-lactam **5** with *m*-chloroperbenzoic acid in $CHCl_3$ at −35 °C gave the corresponding sulfoxide **7** (mp 156-157 °C, 98%): NMR δ ($CDCl_3$) 2.10 (s, Me), 2.31 (s, Me), 2.7-3.0 (m, SCH_2CH_2CO), 3.65 (s, OMe), 3.87 (s, OMe), 5.4 (d, J = 2.5 Hz, azetidinone 4-H), 6.05 (d, J = 2.5 Hz, azetidinone 3-H), and 7.7-8.0 (m, aromatic H); ν_{max} (film), 1790, 1775, 1735, and 1725 cm^{-1}. A similar oxidation of **6** (CH_2Cl_2, −40 °C) afforded the sulfoxide **8** (79%) as a mixture of the two trans isomers separated by chromatography. NMR of one isomer: δ ($CDCl_3$) 1.21 (s, O-*t*-Bu), 1.54 (s, O-*t*-Bu), 2.86 (m, $SCH_2CH_2CO_2$), 3.62 (s, OMe), 3.6-3.9 (m, $CHCH_2O\text{-}t\text{-}Bu$), 4.76 (t, $NCHCO_2$), 5.49 (d, J = 2.5 Hz, azetidinone 4-H), 6.02 (d, J = 2.5 Hz, azetidinone 3-H), and 7.8 br (m, aromatic); NMR of the other isomer, δ ($CDCl_3$) 1.21 (s, O-*t*-Bu), 1.53 (s, O-*t*-Bu), 2.87 (m, $SCH_2CH_2CO_2$), 3.60 (s, OMe), 4.10 (d, $CHCH_2O\text{-}t\text{-}Bu$), 4.79 (t, $NCHCO_2$), 5.30 (d, J = 2 Hz, azetidinone 4-H), 6.15 (d, J = 2 Hz, azetidinone 3-H), and 7.9 br (m, aromatic).

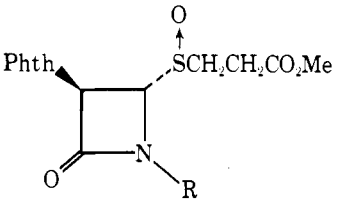
Sulfoxides bearing a hydrogen substituent at a β-carbon atom are thermolyzed to olefins and sulfenic acids.[6] This process which involves a C to O hydrogen shift is facilitated when the migrating hydrogen atom is made more acidic.[7,8] It was therefore anticipated that thermolysis of the unsymmetrical sulfoxide **7** should give the corresponding β-lactam 4-sulfenic acids **9** and methyl acrylate. This prediction was corroborated by trapping the sulfenic acid with dihydropyran according to Barton's procedure.[9] Thus, heating (80-85 °C, sealed tube) **7** in dihydropyran with $AlBr_3$ as catalyst for 20 h gave the dihydropyranyl derivative **10** (71%); NMR δ ($CDCl_3$) 1.5-2.0 (m, dihydropyran $=CCH_2CH_2-$), 2.08 (s, Me), 2.30 (s, Me), 3.8-4.1 (m, dihydropyran OCH_2), 3.83 (s, OMe), 5.40 (d, J = 3 Hz, azetidinone H), 5.51 (d, J = 3 Hz, azetidinone H), 6.75 br (s, dihydropyran vinylic H), and 7.8-8.0 (m, aromatic); ν_{max} ($CHCl_3$) 1785, 1765, 1730, and 1720 cm^{-1}.



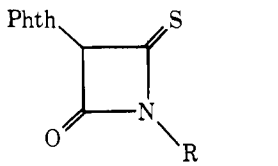
5, R = $C(CO_2Me)=CMe_2$
6, R = $CH(CO_2\text{-}t\text{-}Bu)CH_2O\text{-}t\text{-}Bu$



9, R = OH
10, R =



7, R = $C(CO_2Me)=CMe_2$
8, R = $CH(CO_2\text{-}t\text{-}Bu)CH_2O\text{-}t\text{-}Bu$



11, R = $C(CO_2Me)=CMe_2$
12, R = $CH(CO_2\text{-}t\text{-}Bu)CH_2O\text{-}t\text{-}Bu$

Phth = phthalimido

However, in the absence of a trapping agent, the sulfenic acid **9,** formed by the thermolysis of the sulfoxide **7** (sealed tube; 80-100 °C in C_6H_6, CCl_4, or $CHCl_3$), gave the azetidin-2-oxo-4-thione **11** (mp 164-167 °C >80%): NMR δ ($CDCl_3$) 2.20 (s, Me), 2.44 (s, Me), 3.80 (s, OMe), 5.97 (s, azetidine H), and 7.8-8.0 (m, aromatic); ν_{max} ($CHCl_3$) 1830, 1780, 1740, and 1730 cm^{-1}; mass spectrum *m/e* (M^+ 358, 330, 299, 203, and 187). A similar thermolysis (105 °C for 24 h) of **8** afforded the azetidin-2-oxo-4-thione, **12,** NMR δ ($CDCl_3$) 1.18 (s, O-*t*-Bu), 1.51 (s, O-*t*-Bu), 4.0 br (m, $CH_2O\text{-}t\text{-}Bu$), 4.85, br (m, $NCHCO_2$), 5.90 (s, azetidine H), 7.88 (m, aro-