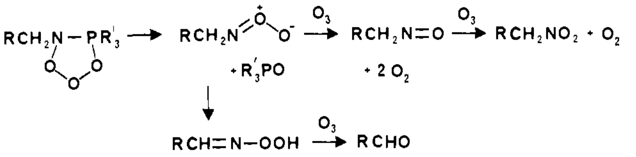
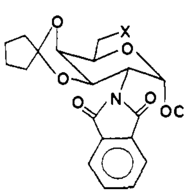
of interest to discover other oxidants that can replace ozone and modifications of the reaction that may produce higher yields.

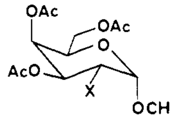
The mechanism by which a 1:1 adduct of ozone and a phosphine imine decomposes to form a nitro compound can only be surmised with the information now available. One attractive possibility is the following:



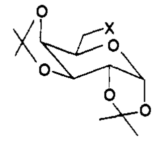
This mechanism requires that 3 equiv of ozone should be consumed relative to phosphine imine and also that the nitroso intermediate be converted by ozone to the corresponding nitro compound. Both of these are in accord with our expermental observations. 2-Nitroso-2,4,4-trimethylpentane[8] was oxidized instantaneously by ozone in CH_2Cl_2 at -78 °C to form the corresponding nitro compound.[9] Finally, this scheme is consistent with the observation that carbonyl compounds are formed as byproducts and are favored by an α-phenyl substituent in the azide precursor.[10]



1 X = NO_2
2 X = I
3 X = N_3
4 X = $N{=}P(C_6H_5)_3$



5 X = N_3
6 X = NO_2



7 X = N_3
8 X = NO_2

---

(8) Corey, E. J.; Gross, A. W. *Tetrahedron Lett.* **1984**, *25*, 491.

(9) The oxidation of α-chloro nitroso compounds to the corresponding nitro compounds by ozone at -60 °C has been reported: Barnes, M. W.; Patterson, J. M. *J. Org. Chem.* **1976**, *41*, 733.

(10) This research was assisted financially by grants from the National Institutes of Health and the Sweden-America Foundation.

A Sulfur-Ligated Molybdenum Complex That Reduces Dinitrogen to Ammonia. The Crystal and Molecular Structure of *trans*-$Mo(N_2)_2(PMePh_2)_2(PPh_2CH_2CH_2SMe)$

Robert H. Morris,* Joel M. Ressner, Jeffery F. Sawyer, and Mahmoud Shiralian

Department of Chemistry and the Scarborough Campus
University of Toronto, Toronto
Ontario, Canada M5S 1A1

Received January 9, 1984

A primary objective of research into chemical systems that mimic the action of nitrogenase is the synthesis of dinitrogen complexes of molybdenum which contain sulfur-donor ligands.[1,2] Several iron-molybdenum-sulfur clusters have been prepared that have spectroscopic properties similar to the nitrogenase cofactor but they do not react with dinitrogen.[3] Dinitrogen complexes of transition metals containing sulfur ligands have proven difficult to make and to date only two complexes have been well characterized, one of osmium[4] and one of rhenium.[5] The complexes $[M(N_2)(SCN)(PPh_2CH_2CH_2PPh_2)_2]^-$, M = Mo, W, may contain an S-bonded SCN^- ligand.[6] An unstable complex, $Mo(N_2)_2(PMe_2Ph)_2(PhSCH_2CH_2SPh)$, was identified by elemental analysis as being the product of a substitution reaction of the sulfur chelate for phosphine ligands in *cis*-$Mo(N_2)_2(PMe_2Ph)_4$ at -78 °C.[7] We have discovered that the complex *trans*-$Mo(N_2)_2(PMePh_2)_4$[8] undergoes a similar reaction with the ligand $PPh_2CH_2CH_2SMe$[9] to give the first stable molybdenum complex of this type, *trans*-$Mo(N_2)_2(PMePh_2)_2(PPh_2CH_2CH_2SMe)$ (I). This complex reacts with sulfuric acid at 23 °C in methanol to give ammonia.

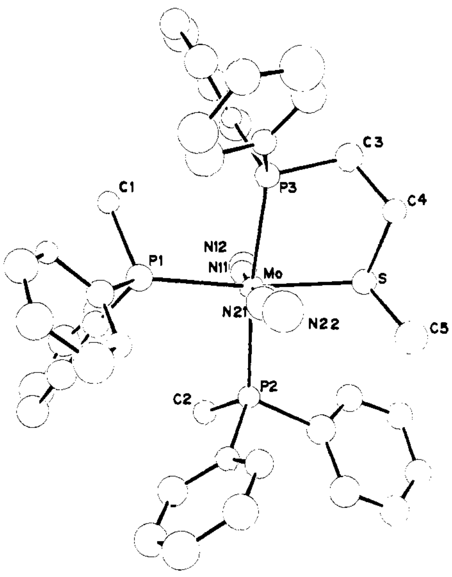


Figure 1. Molecular structure of I.

Complex I was prepared by stirring a suspension of $Mo(N_2)_2(PMePh_2)_4$ with 1.2 equiv of $PPh_2CH_2CH_2SMe$ in ether/benzene (5/1, v/v) for 2 h under dinitrogen. The product was isolated as slightly oxygen-sensitive, red-purple crystals by adding ether to the concentrated reaction solution and cooling to 5 °C (yield 40%). The complex was fully characterized[10] and a preliminary single-crystal X-ray structure determination has verified its molecular structure (Figure 1).[11] The coordination geometry

---

(1) (a) Chatt, J.; Richards, R. L. *J. Organomet. Chem.* **1982**, *239*, 65. (b) Dilworth, J. R.; Neaves, B. D.; Pickett, C. J.; Chatt, J.; Zubieta, J. A. *Inorg. Chem.* **1983**, *22*, 3524.

(2) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.

(3) See references in: Averill, B. A. *Struct. Bonding (Berlin)* **1983**, *53*, 59.

(4) Cruz-Garritz, D.; Torrens, H.; Leal, J.; Richards, R. L. *Trans. Met. Chem.* **1983**, *8*, 127.

(5) Chatt, J.; Crabtree, R. H.; Dilworth, J. R.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, 2358.

(6) Chatt, J.; Leigh, G. J.; Neukomm, H.; Pickett, C. J.; Stanley, D. R. *J. Chem. Soc., Dalton Trans.* **1980**, 121.

(7) Aresta, M.; Sacco, A. *Chim. Ital.* **1972**, *102*, 755.

(8) (a) George, T. A.; Kovar, R. A. *Inorg. Chem.* **1981**, *20*, 285. (b) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2139. (c) Azizian, H.; Luck, R.; Morris, R. H.; Wong, H. *J. Organomet. Chem.* **1982**, *238*, C24. (d) Morris, R. H.; Ressner, J. M. *J. Chem. Soc., Chem. Commun.* **1983**, 909.

(9) (a) Ross, E. P.; Dobson, G. R. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2363. (b) Adams, R. D.; Blankenship, C.; Segmuller, B. E.; Shiralian, M. *J. Am. Chem. Soc.* **1983**, *105*, 4319. (c) Bressan, M.; Morandini, F.; Rigo, P. *Inorg. Chim. Acta* **1983**, *77*, L139.

(10) Anal. Calcd for $C_{41}H_{43}N_4P_3SMo$: C, 60.59; H, 5.33; N, 6.89. Found: C, 60.90; H, 5.43; N, 6.33. IR (toluene) 2014 w, 1942 s cm^{-1}; ^{31}P NMR (THF, 85% H_3PO_4, atom numbers refer to Figure 1) 64.1 (dd, P(3)), 32.4 (dd, P(1)), 23.4 ppm (dd, P(2)), $^2J_{12} = 12.4$, $^2J_{13} = 13.3$, $^2J_{23} = 117.5$ Hz; ^1H NMR (C_6D_6, Me_4Si, refer to Figures 1 and 2, supplementary material) δ 1.44 (d, $^4J_{PH} = 1.0$ Hz, H_3CS), 1.63 (d, $^2J_{PH} = 5.0$ Hz, $H_3C(1)$), 1.77 (d, $^2J_{PH} = 5.0$ Hz, $H_3C(2)$), 1.86 (dd, $^3J_{PH} = 6.0$, $^2J_{HH} = 2.0$, $^3J_{HH} \leq 1$ Hz, HC(4)), 1.89 (s, br, $^2J_{PH}$, $^2J_{HH}$, $^3J_{HH} \leq 2$ Hz, $H_2C(3)$), 2.02 (dd, $^3J_{PH} = 4.0$, $^2J_{HH} = 2.0$, $^3J_{HH} < 2$ Hz, HC (4)).

(11) Crystal data for I: small red plates were obtained from benzene/ether solutions after several attempts. The small crystals scattered X-rays poorly so that only a partial data set was collected and this has limited the precision of the data. Space group: *Pbca*; $a = 18.48$ (2) Å, $b = 20.49$ (2) Å, $c = 20.67$ (2) Å, $U = 7825$ Å^3, and $D_{calcd} = 1.33$ g cm^{-3} for $Z = 8$; λ(Mo K$\bar{\alpha}$) = 0.71069 Å, μ(Mo K$\bar{\alpha}$) = 5.3 cm^{-1}. The structure was solved by the use of the Patterson Function and refined by least squares to $R = 0.095$, $R_W = 0.107$ for 1209 observed reflections ($I > 2.5\sigma(I)$). Selected bond distances (Å): Mo-S, 2.483 (8); Mo-P1, 2.443 (9); Mo-P2, 2.500 (8); Mo-P3, 2.457 (9); Mo-N11, 1.98 (2); Mo-N21, 2.00 (3).

0002-7863/84/1506-3683$01.50/0

about the molybdenum is octahedral and the Mo–P and Mo–N bonds lengths are typical of molybdenum dinitrogen complexes.[12] The small sulfur-donor group introduces an asymmetry in the molecule, which is expressed in a bending of the linear N_2 groups toward the sulfur (angles MoNN are 168 (3)°, 174 (3)°). The N–N distances (1.04 (3), 1.10 (3) Å) are not significantly different although two IR modes, $\nu(N_2)$, are observed for toluene solutions of I (2014 w, 1942 s cm^{-1}) whereas only one is observed for $Mo(N_2)_2(PMePh_2)_4$ (1928 s cm^{-1}). The small N_2 ligands fit snugly in pockets defined by the phenyl and methyl groups on the other ligands. Bonds to the chelate ligand (Mo–S, 2.483 (8), Mo–P3, 2.457 (9) Å) are shorter than corresponding bonds in $Mo(PPh_2CH_2CH_2SMe)(CO)_4$ (2.560 (1), 2.542 (1) Å).[9b] The phosphorus–sulfur ligand has a bite angle of 80.3 (3)° in complex I.

The ^1H NMR spectrum shows that the sulfur methyl protons are coupled to phosphorus P1 trans to sulfur ($^4J_{PH}$ = 1.0 Hz at 80 or 200 MHz).[10] This coupling is not present for the free ligand or the complex $Mo(PPh_2CH_2CH_2SMe)(CO)_4$ and its existence proves that the thioether, despite its poor donor properties,[13] is not dissociating on the NMR time scale.[14] The ^{31}P NMR resonances of complex I[10] can be unequivocally assigned by comparison with spectra for the complexes $Mo(N_2)_2(PMePh_2)_3(py)$[8d] and $Mo(N_2)_2(PMePh_2)_2(PPh_2CH_2CH_2PPh_2)$.[8a,b,15]

The chemistry of complex I resembles that of some molybdenum dinitrogen complexes coordinating by four phosphorus donors[16-18] in that it yields ammonia at 23 °C when it is treated with strong acid. When complex I is treated with 15 mol of H_2SO_4 in methanol at 23 °C then 1.1 mol of N_2, and 0.05 of mol H_2 are evolved over 18 h. After this time the solution is evaporated, treated with excess KOH (40%), and tested for ammonia and hydrazine according to literature procedures.[16] At this stage ca. 0.3 mol of N_2 and 0.7 of mol H_2 are evolved, and 0.3 mol of NH_3 and 0.0 mol of N_2H_4 are detected. The yield of ammonia is less than that observed for $Mo(N_2)_2(PMePh_2)_4$ (0.66 mol) and $Mo(N_2)_2(PMePh_2)_2(PPh_2CH_2CH_2PPh_2)$ (0.56 mol) under identical conditions.[16] Hydrogen (0.2 mol) was only detected for reactions with the latter complex.[16] This suggests that reducing equivalents are diverted from ammonia to hydrogen production in the reaction involving complex I. The contribution of the sulfur ligand to this apparent difference in reactivity is not clear but merits further study.

Attempts are now being made to isolate a hydrazido(2−) intermediate[19] and explain the reduced yield of ammonia. Other sulfur ligands are being examined but attempts to displace two phosphine ligands from $Mo(N_2)_2(PMePh_2)_4$ by use of $MeSCH_2CH_2SMe$ or $EtSCH_2CH_2SEt$ result in immediate displacement of all dinitrogen.

Acknowledgment. This work was supported by a grant from the Atkinson Charitable Foundation and by grants to R.H.M. and a grant for the diffractometer from the Natural Sciences and Engineering Research Council of Canada.

Registry No. I, 89958-79-2; *trans*-$Mo(N_2)_2(PMePh_2)_4$, 33248-03-2; *trans*-$Mo(N_2)_2(PMePh_2)_2(PPh_2CH_2CH_2PPh_2)$, 65498-66-0; NH_3, 7664-41-7; N_2, 7727-37-9; H_2, 1333-74-0.

Supplementary Material Available: Listings of positional parameters (Table I), bond angles (Table II), bond distances (Table III), and the observed and calculated structure factors (Table IV) along with the ^1H NMR spectrum of I (Figure 2) and its preparation (13 pages). Ordering information is given on any current masthead page.

---

[12] (a) Carmona, E.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 3014; (b) *J. Organomet. Chem.* **1982**, *238*, C63. (c) Forder, R. A.; Prout, K. *Acta Crystallogr., Sect. B* **1974**, *30*, 3778. (d) Uchida, Y.; Uchida, T.; Hidai, M.; Kodama, T. *Ibid.* **1975**, *31*, 1197.

[13] (a) Sanger, A. R.; Day, R. W. *Inorg. Chim. Acta* **1982**, *62*, 99. (b) Kuehn, C. G.; Isied, S. S. *Prog. Inorg. Chem.* **1980**, *27*, 153. (c) Rigo, P.; Bressan, M.; Basato, M. *Inorg. Chem.* **1979**, *18*, 860.

[14] (a) Abel, E. W.; Bhatti, M. M.; Orell, K. G.; Sik, V. *J. Organomet. Chem.* **1981**, *208*, 195. (b) Abel, E. W.; Booth, M.; Orrell, K. G.; Pring, G. M.; Cameron, T. S. *J. Chem. Soc., Chem. Commun.* **1981**, 29.

[15] *trans*-$Mo(N_2)_2(PMePh_2)_2(PPh_2CH_2CH_2PPh_2)$. ^{31}P NMR (THF, reference 85% H_3PO_4, 81 MHz) 63.3 (AA′, 2P, PPh_2CH_2), 22.0 ppm (XX′, 2P, $PMePh_2$), $^2J_{AX'}$ (trans) = 105.8, $^2J_{AX}$(cis) = −16.0, $^2J_{AA'}$ = 2.2, $^2J_{XX'}$ = 12.6 Hz.

[16] Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 1852.

[17] (a) George, T. A.; Koczon, L. M. *J. Am. Chem. Soc.* **1983**, *105*, 6334. (b) Baumann, J. A.; George, T. A. *Ibid.* **1980**, *102*, 6153.

[18] Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1980**, *102*, 7461 and references therein.

[19] (a) Bossard, G. E.; George, T. A.; Howell, D. B.; Koczon, L. M.; Lester, R. K. *Inorg. Chem.* **1983**, *22*, 1968. (b) Anderson, S. N.; Chatt, J.; Fakley, M. E.; Richards, R. L. *J. Chem. Soc., Dalton Trans* **1981**, 1973 and references therein.

Photoenolization of α-(2,4,6-Triisopropylphenyl)acetophenone

Peter J. Wagner* and Michael A. Meador

Chemistry Department, Michigan State University
East Lansing, Michigan 48824

Received March 12, 1984

Hart and Giguere just reported indirect evidence for the transient photochemical production of ketones from several stable enols.[1] We wish to report the photointerconversion of keto and enol forms of a similarly congested ketone via a biradical intermediate.

We have already reported that several α-(*o*-tolyl)acetophenones photocyclize quantitatively and in high quantum efficiency to 2-phenyl-2-indanols.[2] We have also studied the title compound (TipAP).[3] When a 0.025 M benzene solution of this ketone is irradiated at 313 nm with a 450-W mercury arc, it cyclizes to the corresponding 2-phenyl-2-indanol derivative, which was isolated and identified by its spectra.[5] Packed column and capillary GC analysis at elevated temperatures both indicated a quantitative yield of this product in a quantum yield of only 0.04. Since the other α-tolylacetophenones studied all cyclize in high quantum yields,[2] we felt that the unusually low efficiency for TipAP might indicate competitive formation of enol, as already observed for acyclic 1,5-biradicals.[6]

^1H NMR spectra of cyclopentane solutions of TipAP irradiated with 300-nm Rayonet lamps showed a weak vinyl proton resonance at δ 6.1 during the early stages of reaction. However, by the time all ketone had reacted, no vinyl signal remained and the NMR spectrum was the same as that of isolated indanol. A deaerated dioxane-d_8 solution 0.2 M in TipAP was irradiated with Rayonet 350-nm lamps until no methylene signal at δ 4.6 was visible in the NMR spectrum. The spectrum was entirely different from that of indanol product. There were two vinyl proton singlets at δ 6.10 and 5.93 in a 4:1 ratio. We assign these to the *Z* and *E* enols; the rest of the NMR spectrum is consistent with these structures.[7] From the relative intensities of the vinyl resonances and that due to the indanol methyl at δ 0.78, we estimate a 15:1 ratio of enols/indanol.

---

[1] Hart, H.; Giguere, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 7775.

[2] Meador, M. A.; Wagner, P. J. *J. Am. Chem. Soc.* **1983**, *103*, 4484.

[3] The acronym recognizes Fuson's use of "tip" as an abbreviation for 2,4,6-triisopropylphenyl in his pioneering studies of stable enols and of TipAP itself.[4]

[4] Fuson, R. C.; Armstrong, L. J.; Chadwick, D. H.; Kneisley, J. W.; Rowland, S. P.; Shenk, W. J., Jr.; Soper, Q. F. *J. Am. Chem. Soc.* **1945**, *67*, 386.

[5] Of particular interest here are the proton NMR resonances for the OH at δ 2.14 and for the ring methyls at δ 1.36 and 0.78.

[6] Wagner, P. J.; Chiu, C. *J. Am. Chem. Soc.* **1979**, *101*, 7134.

[7] Hart and Giguere found similar chemical shifts for similar enol ethers.[1] The only other major NMR resonances were at δ 2.7 (s, 1 H, a readily exchangeable OH), 1.37 and 1.44 (2 overlapping d, 18 H, J = 10 Hz), 3.30 (septet, 3 H, J = 10 Hz), and 6.9–8.0 (complex, 7 H).