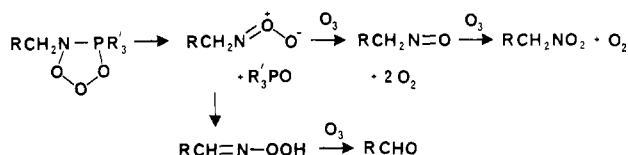
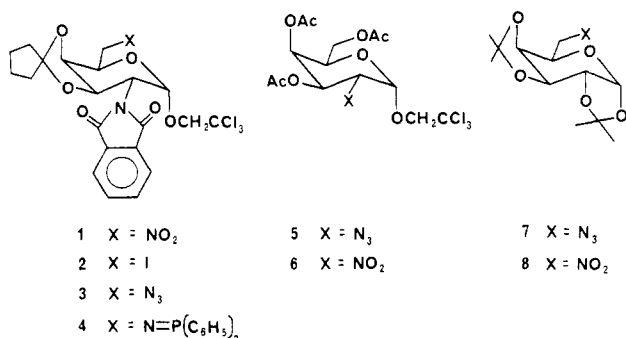


of interest to discover other oxidants that can replace ozone and modifications of the reaction that may produce higher yields.

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 experimental observations. 2-Nitroso-2,4,4-trimethylpentane⁸ 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



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A Sulfur-Ligated Molybdenum Complex That Reduces Dinitrogen to Ammonia. The Crystal and Molecular Structure of *trans*-Mo(N₂)₂(PMePh₂)₂(PPh₂CH₂CH₂SMe)

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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 osmium⁴ and one of rhenium.⁵ The complexes

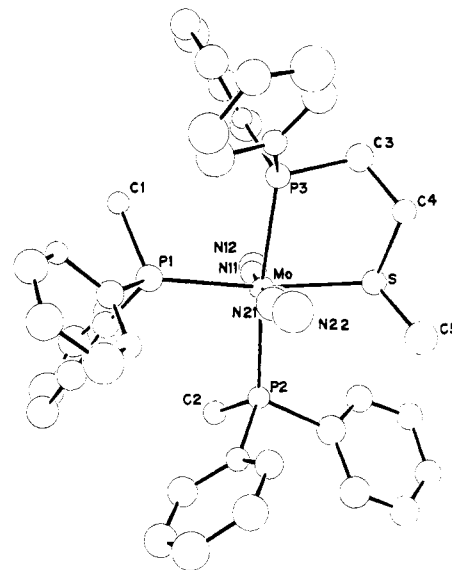


Figure 1. Molecular structure of 1.

[M(N₂)(SCN)(PPh₂CH₂CH₂PPh₂)₂]⁺, M = Mo, W, may contain an S-bonded SCN⁻ ligand.⁶ An unstable complex, Mo(N₂)₂-(PMe₂Ph)₂(PhSCH₂CH₂SPh), was identified by elemental analysis as being the product of a substitution reaction of the sulfur chelate for phosphine ligands in *cis*-Mo(N₂)₂(PMe₂Ph)₄ at -78°C .⁷ We have discovered that the complex *trans*-Mo(N₂)₂-(PMePh₂)₄⁸ undergoes a similar reaction with the ligand PPh₂CH₂CH₂SMe⁹ to give the first stable molybdenum complex of this type, *trans*-Mo(N₂)₂(PMePh₂)₂(PPh₂CH₂CH₂SMe) (1). This complex reacts with sulfuric acid at 23°C in methanol to give ammonia.

Complex 1 was prepared by stirring a suspension of Mo-(N₂)₂(PMePh₂)₄ with 1.2 equiv of PPh₂CH₂CH₂SMe 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 characterized¹⁰ and a preliminary single-crystal X-ray structure determination has verified its molecular structure (Figure 1).¹¹ The coordination geometry

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(10) Anal. Calcd for C₄₁H₄₃N₄P₃SMo: 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; ³¹P NMR (THF, 85% H₃PO₄, atom numbers refer to Figure 1) 64.1 (dd, P(3)), 32.4 (dd, P(1)), 23.4 ppm (dd, P(2)). ²J₁₂ = 12.4, ²J₁₃ = 13.3, ²J₂₃ = 117.5 Hz; ¹H NMR (C₆D₆, Me₄Si, refer to Figures 1 and 2, supplementary material) δ 1.44 (d, ⁴J_{PH} = 1.0 Hz, H₃CS), 1.63 (d, ²J_{PH} = 5.0 Hz, H₃C(1)), 1.77 (d, ²J_{PH} = 5.0 Hz, H₃C(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, H₂C(3)), 2.02 (dd, ²J_{PH} = 4.0, ²J_{HH} = 2.0, ³J_{HH} $<$ 2 Hz, HC(4)).

(11) Crystal data for 1: 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 Å³, and *D*_{calc} = 1.33 g cm⁻³ for *Z* = 8; $\lambda(\text{Mo K}\alpha)$ = 0.71069 Å, $\mu(\text{Mo K}\alpha)$ = 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 σ (*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).

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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 N₂ 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, $\nu(\text{N}_2)$, are observed for toluene solutions of I (2014 w, 1942 s cm⁻¹) whereas only one is observed for Mo(N₂)₂(PMePh₂)₄ (1928 s cm⁻¹). The small N₂ 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(PPh₂CH₂CH₂SMe)(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(PPh₂CH₂CH₂SMe)(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 ³¹P NMR resonances of complex I¹⁰ can be unequivocally assigned by comparison with spectra for the complexes Mo(N₂)₂(PMePh₂)₂(py)^{8d} and Mo(N₂)₂(PMePh₂)₂(PPh₂CH₂CH₂PPh₂).^{8a,b,15}

The chemistry of complex I resembles that of some molybdenum dinitrogen complexes coordinating by four phosphorus donors¹⁶⁻¹⁸ in that it yields ammonia at 23 °C when it is treated with strong acid. When complex I is treated with 15 mol of H₂SO₄ in methanol at 23 °C then 1.1 mol of N₂ and 0.05 of mol H₂ 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 N₂ and 0.7 of mol H₂ are evolved, and 0.3 mol of NH₃ and 0.0 mol of N₂H₄ are detected. The yield of ammonia is less than that observed for Mo(N₂)₂(PMePh₂)₄ (0.66 mol) and Mo(N₂)₂(PMePh₂)₂(PPh₂CH₂CH₂PPh₂) (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-) intermediate¹⁹ and explain the reduced yield of ammonia. Other sulfur ligands are being examined but attempts to displace two phosphine ligands from Mo(N₂)₂(PMePh₂)₄ by use of MeSCH₂CH₂SMe or EtSCH₂CH₂SEt result in immediate displacement of all dinitrogen.

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a grant for the diffractometer from the Natural Sciences and Engineering Research Council of Canada.

Registry No. I, 89958-79-2; *trans*-Mo(N₂)₂(PMePh₂)₄, 33248-03-2; *trans*-Mo(N₂)₂(PMePh₂)₂(PPh₂CH₂CH₂PPh₂), 65498-66-0; NH₃, 7664-41-7; N₂, 7727-37-9; H₂, 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.

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

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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.

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(15) *trans*-Mo(N₂)₂(PMePh₂)₂(PPh₂CH₂CH₂PPh₂). ³¹P NMR (THF, reference 85% H₃PO₄, 81 MHz) 63.3 (AA', 2P, PPh₂CH₂), 22.0 ppm (XX', 2P, PMePh₂), ²J_{AX'} (trans) = 105.8, ²J_{AX'} (cis) = -16.0, ²J_{AA'} = 2.2, ²J_{XX'} = 12.6 Hz.

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