# Communications to the Editor

## Photochemical Reactions of Alkyl Halides with Coordinated Dinitrogen. Formation and Structural Characterization of Novel Alkyldiazenido Derivatives of Molybdenum[1]

*Sir:*

The activation of small molecules is of current interest. As a continuation of our studies concerning the reactions of coordinated dinitrogen,[2] this report describes the photochemical reactions[3] of chloro-, bromo-, and iodomethane and α-bromo-*p*-xylene and iodocyclohexane with $Mo(N_2)_2(dppe)_2$ (**1**) (where dppe = 1,2-bis(diphenylphosphinoethane)) to form $MoCl(N_2)(dppe)_2$, a mixture of $MoBr(N_2)(dppe)_2$ and $MoBr(N_2CH_3)(dppe)_2$, $MoI(N_2CH_3)(dppe)_2$, $MoBr(N_2)(dppe)_2$, and $MoI(N_2C_6H_{11})(dppe)_2$, respectively. The molecular stereochemistry (as determined by single-crystal X-ray diffraction) of the first transition metal complex which contains an alkyldiazenido ligand is also reported.

Irradiation[4] of a benzene solution of an equimolar mixture of iodomethane and **1** for 17 hr at 40° produced 1 equiv of dinitrogen and a yellow solid, $MoI(N_2CH_3)(dppe)_2$,[5] (**2**) that was crystallized from dichloromethane–diethyl ether solution in low yield. Similarly, yellow-orange $MoI(N_2C_6H_{11})(dppe)_2$ (**3**) was prepared from iodocyclohexane and **1** (84 hr at 18°). **3** was crystallized from benzene–heptane solution (80% yield). **2** and **3** are air-stable in the solid state; in nondeoxygenated solutions, **3** decomposes much more rapidly than **2**. The infrared spectra (CsI pellet) of **2** and **3** both exhibit strong absorptions at 1543 and 1550 cm$^{-1}$, respectively, that may be attributed to the nitrogen–nitrogen stretching vibration of the alkyldiazenido ligand. The position of the $\nu_{NN}$ stretching vibrations suggests[6] a singly bent configuration for the alkyldiazenido ligands.

Single crystals of **2** and the benzene solvate of **3**, suitable for X-ray diffraction studies were grown by slow evaporation of the solvents given above. Three-dimensional diffraction data on both compounds were collected on a computer-controlled four-circle Syntex $P\bar{1}$ Autodiffractometer using Nb-filtered (**2**) or graphite monochromated (**3**) Mo K$\bar{\alpha}$ radiation and ω scans. Single crystals of **2** were larger and diffracted considerably better than those of **3**. Both structures were solved using the "heavy-atom" technique and the resulting structural parameters have been refined to convergence in cycles of empirically weighted full-matrix least-squares refinement which employed anisotropic thermal parameters for all non-hydrogen atoms.

Crystal data and refinement results are as follows. $MoI(N_2CH_3)(P_2C_{26}H_{24})_2$ (**2**): triclinic; $P\bar{1}$; $a = 10.371$ (1), $b = 10.628$ (1), $c = 12.699$ (2) Å; $\alpha = 103.81$ (1), $\beta = 95.34$ (1), $\gamma = 118.12$ (1)°; $Z = 1$; $d_{calcd} = 1.52$, and $d_{measd} = 1.54$ g cm$^{-3}$; $R = 0.098$ for 4211 independent reflections having $2\theta_{MoK\bar{\alpha}} < 55°$ and $I > 2\sigma(I)$. $MoI(N_2C_6H_{11})(P_2C_{26}H_{24})_2 \cdot 0.5\ C_6H_6$ (**3**): monoclinic; $P2_1/c$; $a = 12.643$ (6), $b = 21.351$ (7), $c = 20.422$ (5) Å; $\beta = 98.91$ (3)°; $Z = 4$; $d_{calcd} = 1.38$, $d_{measd} = 1.40$ g cm$^{-3}$; $R = 0.082$ for 5400 independent reflections having $2\theta_{MoK\bar{\alpha}} < 45.8°$ and $I > \sigma(I)$.

The alkyldiazenido and iodide ligands occupy trans positions in the octahedral coordination polyhedral of both molecules. The relatively small and quite similar size of the methyldiazenido and iodide groups when bonded to the Mo atom in **2** allowed the packing of these molecules into the lattice to be dictated primarily by the bulky dppe ligands. This was reflected in a statistical disordering of the complexed methyldiazenido and iodide ligands about the crystallographic inversion center coincident with the molybdenum atom in single crystals of **2**. This prevented an accurate characterization of the molecular structure.

Although single crystals of the benzene solvate of **3** were not of the highest quality, it was possible by optimizing the data collection procedures (slow scan rates and long background counts) with monochromated radiation to obtain data of sufficient quality to allow a qualitative and semiquantitative description of the structure. The cyclohexyldiazenido group of **3** is bonded in a singly bent fashion as seen in Figure 1 with a Mo–N–N bond angle of 176 (1)° and an N–N–C bond angle of 142 (2)°. Lengths of 1.95 (1),[7] 2.878 (1),[7] and 2.522 (3, 4, 7) Å[7] were determined for the Mo–N, Mo–I, and average Mo–P bonds of **3**, respectively. The N–N and N–C bonds of the cyclohexyldiazenido ligand have lengths of 0.91 (1) and 1.39 (4) Å, respectively, with the unusually short N–N distance almost certainly being an artifact of the diffraction data resulting from the poor quality of the crystals. The bonding parameters for the Mo–N–N unit could not be improved through least-squares refinement of a model in which the N–N distance was initially set at (a more reasonable value of) 1.17 Å. The somewhat unexpected axial attachment of the diazo group to the bulky cyclohexane ring of the diazenido ligand is presumably the result of steric interactions between it and the nearby phenyl rings of the dppe ligands. Crystal structure determinations for a number of transition metal complexes containing coordinated aryldiazenido ligands[6,8,9] have revealed only the singly[9] or doubly bent[6,8] modes of bonding for this ligand.

The geometry of the cyclohexyldiazenido ligand and the absence of paramagnetic behavior[10] of compound **3** at room temperature are consistent with the formulation of **3**, and by inference **2**, as either molybdenum(0) complexes with the alkyldiazenido ligands acting as two-electron donors or molybdenum(II) complexes with the alkyldiazenido ligands acting as four-electron donors.[11]

Irradiation[4] of a benzene solution of an equimolar mixture of bromomethane and **1** for 62 hr at 40° produced a mixture of solid products together with dinitrogen, methane, ethane, and a trace of dihydrogen.[12] Only two of the solid products have been characterized, namely $MoBr(N_2)(dppe)_2$ (**4**) and $MoBr(N_2CH_3)(dppe)_2$[13] (**5**). **4** is a yellow, air-stable solid when crystallized from benzene–methanol. The infrared spectrum of **4** (CsI pellet) exhibits, in addition to those bands characteristic of the dppe ligands, a strong band at 1966 cm$^{-1}$ due to the nitrogen–nitrogen stretching vibration. **5** is an air-stable orange-yellow solid when crystallized from dichloromethane–diethyl ether. Based upon elemental analysis and the similarity of its infrared spectrum ($\nu_{N=N}$ 1538 cm$^{-1}$ (vs)) to that of **2**, **5** is believed to contain the methyldiazenido ligand. However, irradiation[4] of a benzene solution containing equimolar amounts of α-bromo-*p*-xylene and **1** for 62.5 hr at 19° produced **4** as the only molybdenum-containing product in 48% yield. **4** gave a spin-only value[10] for $\mu_{eff}$ (corrected for di-

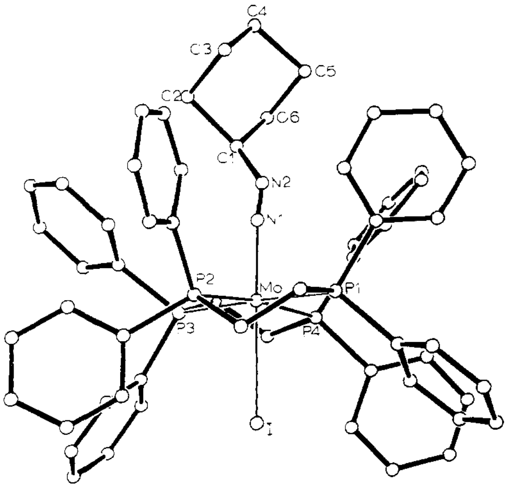

**Figure 1.** Perspective view (derived from an ORTEP drawing) of the molecular structure of $MoI(N_2C_6H_{11})(dppe)_2$ (**3**) as seen in crystals of its benzene solvate.

amagnetism) at 21° of 1.83 $B_\mu$. This value is comparable to $\mu_{\text{eff}}$ for other molybdenum(I)-dppe containing compounds.[14]

Under similar conditions chloromethane and **1** reacted to produce methane, dinitrogen, dihydrogen, and $MoCl(N_2)(dppe)_2$ (**6**). **6** was crystallized from benzene-methanol solution with one methanol of solvation. **6** was first reported by Smith and coworkers.[15] In the infrared spectrum (CsI pellet) noteworthy absorptions were observed at 1966 and 311 $cm^{-1}$ due to $\nu_{\text{N}\equiv\text{N}}$ and $\nu_{\text{Mo—Cl}}$, respectively.[16]

Two points critical to discussions of mechanisms for these reactions can be noted at this time. Firstly, **1** has an absorption maximum at 376 nm ($\epsilon$ 14,500) that may be tentatively assigned[17] to a charge transfer transition between metal orbitals and dinitrogen antibonding orbitals. Secondly, in all the reactions reported herein one dinitrogen is retained by the metal, either as an unreacted dinitrogen ligand or incorporated in an alkyldiazenido ligand.

Investigation of the chemical and physical properties of these interesting compounds and the mechanisms of their formation are in progress, as are attempts to grow high-quality single crystals of **3** and the other compounds reported herein for X-ray diffraction studies.

## References and Notes

(1) Presented in part at the International Symposium on Nitrogen Fixation, Pullman, Wash., June 3–7, 1974.

(2) T. A. George and C. D. Seibold, *Inorg. Chem.*, **12,** 2548 (1973).

(3) Iodomethane reacts with **1** in benzene, at room temperature, and in the dark to produce $MoI(N_2CH_3)(dppe)_2$ (>60 hr). However, no reaction between **1** and chloro- and bromomethane occurs in the dark.

(4) Irradiation at 366 nm with a 100-W B-100A Blak-Ray Lamp, Ultra-Violet Products, Inc., San Gabriel, Calif.

(5) Calculated for **2**·$CH_2Cl_2$; $C_{54}H_{53}Cl_2I_2MoN_2P_4$: C, 56.51; H, 4.66; N, 2.44; halogen, 17.24. Found: C, 54.70; H, 4.51; N, 2.33; halogen, 16.67. An ion cyclotron resonance spectrum of gases evolved when a sample of **2**·$CH_2Cl_2$ was decomposed at 220° showed dichloromethane to be present.

(6) A. P. Gaughan, Jr., B. L. Haymore, J. A. Ibers, W. H. Myers, T. E. Nappier, and D. W. Meek, *J. Am. Chem. Soc.*, **95,** 6859 (1973).

(7) The first number in parentheses is the root mean square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the average value, respectively.

(8) A. P. Gaughan, Jr., and J. A. Ibers, *Inorg. Chem.*, **14,** 352 (1975).

(9) J. V. McArdle, A. J. Schultz, B. J. Corden, and R. Elsenberg, *Inorg. Chem.*, **12,** 1676 (1973); R. Mason, K. M. Thomas, J. A. Zubieta, P. G. Douglas, A. R. Galbraith, and B. L. Shaw, *J. Am. Chem. Soc.*, **96,** 260 (1974); G. Avitabile, P. Ganis, and M. Nemiroff, *Acta Crystallogr., Sect. B*, **27,** 725 (1971).

(10) We thank Dr. E. R. Domb of our physics department for determining the magnetic moments of compounds **2, 3** and **4.**

(11) We thank one of the referees for suggesting this alternative bonding scheme.

(12) We thank Dr. M. L. Gross for ion cyclotron resonance spectra of gases evolved in these reactions.

(13) Similar products from the photochemical reactions of bromoalkanes have been observed: A. A. Diamantis, J. Chatt, G. J. Leigh, and G. A. Heath, *J. Organomet. Chem.*, **84,** C11 (1975).

(14) For examples see ref 1.

(15) J. K. Alkinson, A. H. Mawby, and D. C. Smith, *Chem. Commun.*, 157 (1971).

(16) In $Mo(N_2)_2(dppe)_2$ and $MoCl_2(dppe)_2$, $\nu_{\text{N}\equiv\text{N}}$ and $\nu_{\text{Mo—Cl}}$ occur at 1979 and 305 $cm^{-1}$, respectively.

(17) I. M. Trietel, M. T. Flood, R. E. Marsh, and H. B. Gray, *J. Am. Chem. Soc.*, **91,** 6512 (1969).

(18) One of us (S.D.A.I.) thanks Conoco for a Summer Fellowship, 1974.

**Victor W. Day,* T. Adrian George,* S. D. Allen Iske[18]**
*Department of Chemistry, University of Nebraska–Lincoln*
*Lincoln, Nebraska 68508*
*Received February 18, 1975*

## 7-*cis*,9-*cis*- and 7-*cis*,9-*cis*,13-*cis*-Retinal. A Stereoselective Synthesis of 7-*cis*,9-*cis*-β-Ionylideneacetaldehyde[1]

*Sir:*

Earlier we reported the preparation of four 7-cis isomers of retinal by a six-step nonselective reaction sequence.[2] By this scheme the separation of isomers, particularly pairs around the 9,10-double bond, presented difficulty. Since then, we have been able to effect HPLC separation of 7-*cis*- and 7-*cis*,9-*cis*-retinal but are still unable to resolve the remaining isomeric pair (7-cis,13-cis and 7-cis,9-cis,13-cis) by this technique.[3] Similar difficulties exist in separating retinal precursors, such as the $C_{15}$-trienals and $C_{18}$-tetraenones. We therefore sought to undertake the completely stereoselective synthesis of the trienals[1] in order to prepare specific retinal isomers wherein the configuration of the trisubstituted 9,10-double bond would be totally unambiguous.

In designing schemes to a single isomer of β-ionylideneacetaldehyde (**1**) we found little guidance from available literature. There were no reports of stereoselective syntheses of the two 7-trans trienals despite the fact that these compounds are important precursors to vitamin A.[4] Pure *tt*-**1** and *tc*-**1** were only obtained by fractional crystallization of an aldehyde derivative followed by regeneration of the free aldehyde. This procedure was clearly inapplicable to the preparation of 7-cis isomers because of the sensitivity of the 7-cis geometry to regeneration reactions involving carbonium ion intermediates and failure on our part to obtain satisfactory crystalline derivatives.

Of the several approaches we have attempted, Scheme I was found to be highly stereoselective and led to isomerically pure 7-*cis*,9-*cis*-β-ionylideneacetaldehyde.

Acetoxylation of β-ionone with $Pb(OAc)_4$ in refluxing benzene (3 hr) gave *trans*-10-acetoxy-β-ionone (**2**) bp 120–124° (0.5 Torr), in 35–45% yield.[5,6] The Horner reaction of **2** with the sodium salt of triethylphosphonoacetate in benzene (room temperature, 3 hr) was highly stereoselective (*tt*-**3**/*tc*-**3** = 19),[7] giving *tt*-**3** in 78% yield as a nearly colorless crystalline solid, mp 75.5–76.0° (from aqueous ethanol). Irradiation of *tt*-**3** (0.0425 *M* in benzene) for 8 hr at 10° (uranium glass filter, 200-W medium pressure Hg lamp) in the presence of benzanthrone (0.0045 *M*, $E_T$ = 47 kcal/mol) as sensitizer gave 7-*cis*- and 7-*cis*,9-*cis*-**3** in a ratio of 1:10.5.[8] After crystallization from aqueous methanol 7-*cis*,9-*cis*-**3** was obtained as a low melting solid, mp 50–52°. Upon acid-catalyzed methanolysis, 7-*cis*,9-*cis*-**3** gave the corresponding 7-*cis*,9-*cis*-9-hydroxymethyltriene ester, **4.** In this reaction the corresponding hydroxy ester derivative of 7-*cis*-**3** was converted to butenolide, **4a.**[8] This minor product was also prepared by acid-catalyzed methanolysis of *tt*-**3** followed by photosensitized isomerization of