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Preliminary communication

THE PROTONATION OF ALKYLDIAZENIDO DERIVATIVES OF MOLYBDENUM. THE CRYSTAL AND MOLECULAR STRUCTURE OF THE BENZENE SOLVATE OF IODO-*N*-OCTYLHYDRAZIDOBIS-[1,2-BIS(DIPHENYLPHOSPHINO)ETHANE]MOLYBDENUM IODIDE

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Summary

The monoprotonation of $MoI(N_2C_8H_{17})(dppe)_2$ (I, where dppe = 1,2-bis-(diphenylphosphino)ethane) by anhydrous HX (where X = Cl, Br, and I) to give $[MoI(NNHC_8H_{17})(dppe)_2]X$ is reported. The crystal and molecular structure of the benzene solvate of $[MoI(NNHC_8H_{17})(dppe)_2]I$ has been determined and the unique hydrogen atom located.

Recently [1] we reported the formation and structural characterization of novel alkyldiazenido derivatives of molybdenum. We now report their facile protonation by excess anhydrous hydrogen halides to form the respective *N*-alkylhydrazido, (NNHR) complexes. The reaction of excess hydrogen iodide with $MoI(N_2C_8H_{17})(dppe)_2$ (I, where dppe = 1,2-bis(diphenylphosphino)-ethane) [2] in benzene solution at room temperature rapidly produced $[MoI(NNHC_8H_{17})(dppe)_2]I$ (II). II was also obtained as a minor product in the preparation [2] of I from $Mo(N_2)_2(dppe)_2$ and 1-iodooctane. Anal. II: Found: C, 56.40; H, 5.20; I, 20.39; N, 2.13. $C_{60}H_{66}I_2MoN_2P_4$ calcd.: C, 55.92; H, 5.16; I, 19.69; N, 2.17%.

Samples of II obtained by both procedures were (separately) recrystallized from benzene/heptane solutions by slow evaporation of the solvents. The large well-shaped green single crystals resulting from both preparations were suitable for X-ray diffraction studies and proved to be isomorphous***.

Three-dimensional diffraction data for the benzene solvate of II were

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[***] The infrared and PMR spectra of both compounds are identical. Diffracted intensities for selected reflections on crystals from both preparations differed only by a constant.

collected on a computer-controlled four-circle Syntex P$\bar{1}$ Autodiffractometer using graphite-monochromated Mo-K_α radiation and full (1° wide) ω-scans. $MoI_2(N_2HC_8H_{17})(P_2C_{26}H_{24})_2 \cdot 1/2\ C_6H_6$ crystallizes in a monoclinic unit cell with: $a = 12.638(2)$, $b = 25.901(4)$, $c = 19.337(2)$ Å, $\beta = 109.75(1)°$, and $Z = 4$. The space group is $P2_1/n$ and the calculated and measured densities are 1.481 and 1.475 g/cm^3, respectively. The structure was solved using the "heavy-atom" technique and the resulting structural parameters have been refined to convergence ($R = 0.045$ for 4750 reflections having 2θ(Mo-K_α) < 43° and $I > 3\sigma(I)$) using unit-weighted full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms and isotopic thermal parameters for all hydrogen atoms (except those of the terminal methyl group of the *N*-octylhydrazido ligand). Refinement is continuing with a data set three times as large.

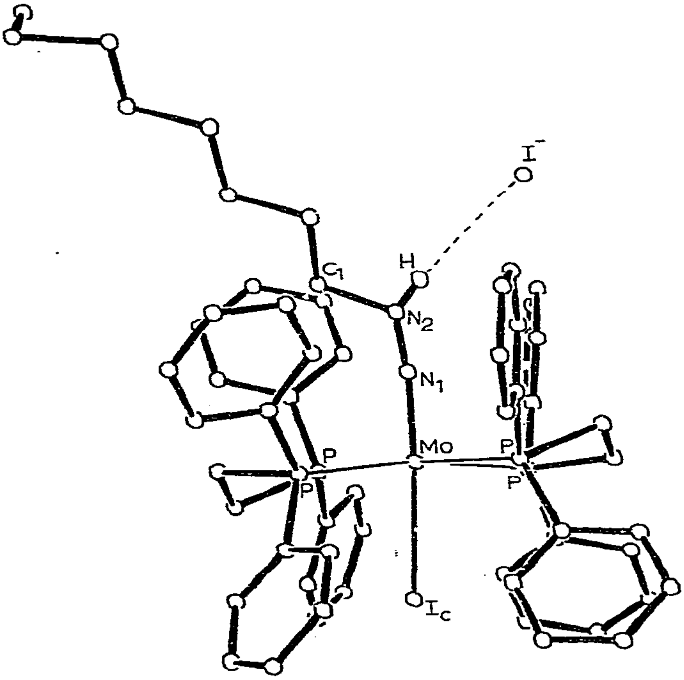

Fig.1. Perspective view (derived from an ORTEP drawing) of the molecular structure of $[MoI(N_2HC_8H_{17})(dppe)_2]I$ (II) as seen in crystals of its benzene solvate.

The *N*-octylhydrazido and iodide ligands occupy trans positions in the octahedral coordination polyhedron of II. The *N*-alkylhydrazido group is bonded in a singly bent fashion as seen in Fig. 1 with values of 174(1)°* and 120(1)° for the Mo—N(1)—N(2) and N(1)—N(2)—C(1) bond angles, respectively. Lengths of 1.801(11), 2.819(2), and 2.541(4,11,21) Å were determined for the Mo—N(1), Mo—I$_C$, and (average) Mo—P bonds of II, respec-

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*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.

tively. The six-atom (Mo, N(1), N(2), C(1), H, and I^-) grouping around the N(1)—N(2) bond is coplanar to within 0.02 Å with lengths of 1.504(17), 1.259(14), and 0.85(13) Å for the C(1)—N(2), N(1)—N(2) and N(2)—H bonds, respectively. These structural parameters are consistent with sp^2 hybridization of N(2) and *sp* hybridization of N(1); multiple bond orders (ca. 2.00) are also indicated for both the Mo—N(1) and N(1)—N(2) bonds. The Mo—I_C bond in II is significantly shorter (by 0.059 Å) than the corresponding bond in the nonprotonated and singly-bent cyclohexyldiazenido derivative, $MoI(N_2C_8H_{17})(dppe)_2$ [1]. The values of 174(12)° for the N_2—$H\cdots I^-$ angle and 3.56(1) Å for the $N_2\cdots I^-$ distance indicate the presence of hydrogen bonding. The presence of this hydrogen atom in a chemically anticipated position was clearly indicated from a difference Fourier synthesis, and its positional and (isotropic) thermal parameters were refined by full-matrix least-squares techniques.

Ibers [3] has noted that the product of monoprotonation of an alkyl- or aryl-diazenido ligand in a metal complex will depend upon its mode of bonding to that metal. Singly-bent diazenido ligands will be protonated at nitrogen atom N(2) as in $[WBr(N_2HCH_3)(dppe)_2]Br$ [4,5] $[ReCl_2(NH_3)(N_2HC_6H_5)(P(CH_3)_2C_6H_5)_2]Br$ [6], and II, while doubly-bend diazenido ligands will be protonated at nitrogen atom N(1) to give species such as $[PtCl(P(C_2H_5)_3)_2(HN_2C_6H_4F)]ClO_4$ [3] and $[RuCl(CO)_2(HN_2C_6H_5)(P(C_6H_5)_3)_2]ClO_4$ (III) [7]. The variation of N(1)—N(2) bond lengths in these five compounds (individual values of 1.32(2), 1.28(2), 1.259(14), 1.235(10), and 1.218(7) Å, respectively) is presumably the result of differences in metals and co-ligands. Differences in the bonding parameters for the alkylhydrazido ligands present in the two similar tungsten and molybdenum compounds are insignificant.

While a clearer picture of the structure-reactivity relationships for these compounds is emerging, a detailed understanding of their nature must await further studies. For example, the factors which cause the singly-bent (N(1)—N(2)—C angle of 118°) diazenido ligand in $RuCl_2(N_2C_6H_5)[P(CH_3)_2C_6H_5]_3$ [6] (and other presumably singly-bent alkyldiazenido complexes [8]) to resist protonation with either aqueous or anhydrous hydrogen chloride or bromide are not clearly understood.

The three hydrogen halide adducts of I ($[MoI(N_2HC_8H_{17})(dppe)_2]X$, where X = Cl, Br, or I) have been isolated and characterized. All are diamagnetic and 1:1 electrolytes in nitrobenzene. The strong N=N absorption of I at 1540 cm^{-1} disappears upon protonation while the N—H absorption appears at ca. 3275 cm^{-1}. The PMR signal for the hydrazido proton of II occurs as a broad singlet at τ 6.24 ppm for X = I. PMR signals for N(1)-protonated hydrazido groups such as that present in III occur significantly downfield, i.e. $< \tau$ 4.0 ppm [9] (at τ −1.75 ppm in III [7]). The closely related cationic hydrazido (N_2H_2) complexes exhibit N—H(2) PMR resonances at higher field, e.g., τ 6.98 ppm in $[WCl(N_2H_2)(dppe)_2]B(C_6H_5)_4$, (IV) [10]. A crystal structure determination [11] of IV shows both protons attached to N(2).

Investigations of the products resulting from the diprotonation of alkyldiazenido complexes of molybdenum are currently underway.

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