09.1-2 MOLYBDENUM COMPLEXES OF HYDRAZIDO- AND DIAZENIDO-LIGANDS DERIVED FROM THIO- AND DITHIO-CARBAZATES.

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The reaction of $NH_2NHC(S)SMe$ and $NH_2NHC(O)SMe$ with $MoO_2(LL)_2$, $LL^- = S_2CNR_2^-$ (dtc), ONR_2^- (R = Me, Et) and $MeC(O)CHC(O)Me^-$ (acac) yields a series of mono- and dinuclear diazenido-hydrazido-complexes of molybdenum.

Some examples are:

$Mo(NNR)(NH_2NR)(dtc)_2$ R = C(S)SMe 1

$Mo(NNR)(NH_2NR)_2(ONR_2)$ R = C(S)SMe 2

$Mo(NNR)(NH_2NR)(dtc)_2$ R = C(O)SMe 3

$(dtc)(O)Mo(\mu\text{-}NNR)_2Mo(dtc)$ R = C(S)SMe 4

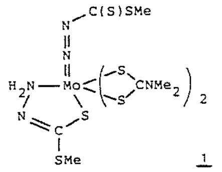
$Mo(Me_2CNNR)(NNR)(RNNR)$ R = C(S)SMe 5

1,2 and 3 contain the approximately linear diazenido-ligand NNR; 1 and 2 also the N,S-chelating hydrazido(1-)-ligand $NH_2NC(S)SMe$ and 3 the 'side on' coordinated hydrazido(1-)-ligand $NH_2NC(O)SMe$. 4 is an asymmetric dinuclear complex with a central Mo_2N_2-moiety. 5 contains a highly bent diazenido-ligand, a Schiffbase ligand and a S,N,S-chelating bis-(dithioacyl)diazene-ligand (see figures).

The Mo-N and N-N bond distances in these compounds depend strongly on the nature of the ligated dinitrogen derivatives, on their type of coordination and on the coligands.

The factors, which influence 'side on', 'end on' or 'chelating' coordination modes of hydrazido- (1-)-ligands, will be considered.

Figures:



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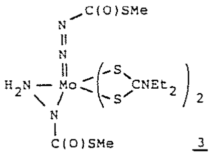

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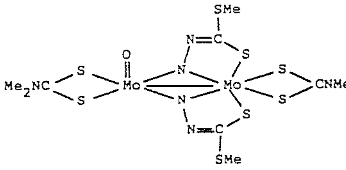

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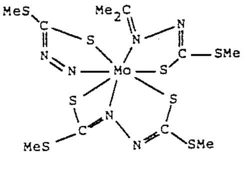

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09.1-3 PROBING THE MODE OF BONDING IN UNSATURATED SILICON COMPOUNDS; THE STRUCTURAL CRITERION.

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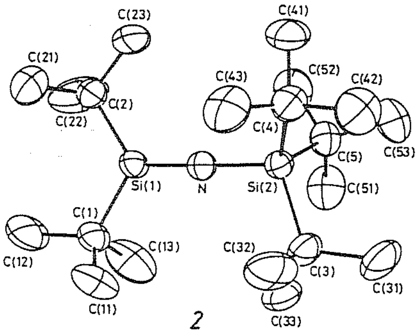
The structure of the stable, solid silene $Me_2Si{=}C(SiMe_3)(SiMetBu_2)$, (1), yields a surprisingly short Si=C double bond of 1.702(5)Å and an almost perfectly planar silene skeleton. These findings contrast with Brook's silaenol-ether $(Me_3Si)_2Si{=}C(OSiMe_3)$(1-adamantyl), (Si=C 1.764(3)Å, twist 14.6°) [1] but agree astonishingly well with previous high-level ab-initio calculations on small unstable silenes [2].

The structure of the first stable silaketimine $tBu_2Si{=}N\text{-}SitBu_3$, (2), a compound containing a silicon nitrogen double bond, supplements these findings. The Si=N-Si skeleton is essentially linear with significantly different Si-N bond lengths (Si=N 1.568(3), Si-N 1.695(3)Å), the first value being the shortest Si-N bond reported ever. The geometry of the unsaturated Si atom is planar.



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Both (1) and (2), as well as a number of other unsaturated Si compounds, form remarkably stable adducts with a variety of donors, as, e.g., THF, NMe_3, F^-, and others. In these the donor atoms bind exclusively to the unsaturated Si atom which thereby adopts a distorted tetrahedral coordination geometry with concomitant lengthening of the Si=X bond.

These structures allow important new experimental insight into the mode of bonding in unsaturated Si compounds. They amply support an essential sp^2 hybridization of unsaturated Si and substantial p overlap for the double bonds.

[1] S.C. Nyburg, et al., Acta Cryst. C41 (1985) 1632.
[2] H.F. Schaefer, Acc. Chem.Res., 15 (1982) 283.