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Preliminary communication

A DIAZOMETHANE COMPLEX OF TUNGSTEN

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Summary

Methylene bromide reacts with $[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ in benzene solution, under tungsten filament light irradiation, to yield $[WBr(N_2CH_2)(Ph_2PCH_2CH_2PPh_2)_2]Br$ which contains diazomethane as a ligand.

In continuation of our general survey of the reactions of alkane mono- and di-halides with molybdenum and tungsten bis(dinitrogen) complexes [1], we have investigated the reaction of 1,2-dibromoethane and of dibromomethane with $[W(N_2)_2(dppe)_2]$ (dppe = 1,2-bis(diphenylphosphinoethane)) under tungsten filament light irradiation in benzene solution. The former gives no identifiable organonitrogen product, but the latter yields a complex, isolated in about 30% yield, containing N_2CH_2 as a ligand (reaction 1). It is a diamagnetic crystalline solid and a 1:1-electrolyte in nitromethane.

$$[W(N_2)_2(dppe)_2] + CH_2Br_2 \rightarrow [WBr(N_2CH_2)(dppe)_2]Br + N_2 \qquad (1)$$

The ^1H NMR spectrum in CD_2Cl_2 shows, in addition to the resonances arising from the dppe protons, a pair of doublets, total intensity 2, each showing a splitting of 14 Hz and with centres separated by 1.44 ppm. Irradiating either doublet causes the other to collapse to a singlet. In the ^{13}C NMR spectrum in CD_2Cl_2 solution there is a broad peak at 155.27 ppm downfield from tetramethylsilane, in addition to the dppe carbon resonances. We assign these proton and carbon resonances to the hydrogen and carbon atoms of the unique methylene.

The complex does not react with hydrogen bromide in benzene to generate a complex of $-N{=}N\text{-}CH_3$ but such reaction occurs with lithium aluminium hydride in ether to give the known $[WBr(N_2CH_3)(dppe)_2]$ which is a methyldiazenido-complex [2]. Methyllithium reacts analogously to

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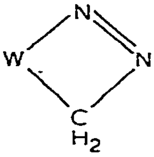
produce the known ethyldiazenido-complex [$WBr(N_2CH_2CH_3)(dppe)_2$] (reaction 2) [2].

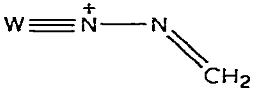
$$[WBr(N_2CH_2)(dppe)_2]Br + R^- \rightarrow [WBr(N_2CH_2R)(dppe)_2] + Br^- \qquad (2)$$

($R = H$ or CH_3)

In formal terms, the complex [$WBr(N_2CH_2)(dppe)_2$]Br is a derivative of diazomethane and constitutes the first example of a diazomethane complex Two formal structures A and B may be envisaged for the N_2CH_2 moiety. In A the N_2CH_2 moiety is formally a dianionic ligand and will carry some negative charge. In B it carries formally only one negative charge and in view of the formal positive charge on the ligating nitrogen atom may even be slightly positively charged overall. The structure B is thus most consistent with the observed electrophilicity of the ligand. Both structures can be used to rationalise the non-equivalence of the methylene hydrogens. The IR spectrum is equivocal. There is no band between 1510 and 1530 cm^{-1}, which is the region of $\nu(N{=}N)$ in the alkyldiazenido-complexes [3], and no band between 1200 and 1400 cm^{-1}, which we can with certainty assign to $\nu(C{=}N)$; these observations are consistent with a highly conjugated system. Neither the ^1H nor the ^{13}C NMR spectrum shows signs of coupling to tungsten, which would be expected if there were a direct tungsten—carbon bond [4]. We therefore believe that the complex probably contains the grouping B.



(A)



(B)

A previous claim [5] to a "protonated diazomethane complex" merely uses a fanciful name for a methyldiazenido complex. In fact, diazomethane complexes may only rarely be obtainable directly from diazomethane, e.g. because diazomethane tends to produce methylene insertion into metal—halogen and metal—hydrogen bonds.

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