ω-Diazobutanol Complexes from the Reaction of Tetrahydrofuran with Bis(dinitrogen) Complexes of Molybdenum and Tungsten: *X*-Ray Crystal Structure of $[MBr\{N{-}N{=}CH(CH_2)_3OH\}(Ph_2PCH_2CH_2PPh_2)]^+[PF_6]^-$

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Summary A complex derived from the reaction of tetrahydrofuran with bis-[1,2-bis(diphenylphosphino)ethane]bis(dinitrogen)tungsten, and previously formulated as a tetrahydropyridazine derivative, has been shown by *X*-ray structural analysis to be bis-[1,2-bis(diphenylphosphino)ethane]bromo-(ω-diazobutanol-N^2)tungsten hexafluorophosphate.

$$[M(N_2)_2(dppe)_2] + C_4H_8O \xrightarrow[h\nu]{MeBr} [X] \xrightarrow{HBr} \underset{(\mathbf{1})}{[MBr\{N{-}N{=}CH(CH_2)_3OH\}(dppe)_2]Br} \qquad (1)$$

(X = unknown intermediate or intermediates)

We have recently described[1] the reaction of $[M(N_2)_2(dppe)_2]$ [M = Mo or W, dppe = 1,2-bis(diphenylphosphino)ethane] with thf (tetrahydrofuran) in the presence of methyl bromide under tungsten filament irradiation. This produces, after addition of hydrogen bromide, substances (**1**) which we formulated as bis[bis(diphenylphosphino)-ethane]bromo(tetrahydropyridazido)-tungsten or -molybdenum bromides on the basis of spectroscopic evidence.[1,2] We have now determined the structure of the hexafluorophosphate salt of (**1**; M = W) and infer that the substances (**1**) are ω-diazobutanol complexes obtained by the novel overall reaction (1). The *X*-ray study has been long delayed by lack of suitable crystals. The structure (see Figure) was obtained by standard diffraction analysis methods based on 4167 independent reflections (Mo-K_α radiation). At present $R = 6{\cdot}8\%$, based on the refinement of atomic positions and selected heavy atom anisotropic temperature parameters only. The crystals of the hexafluorophosphate salt of (**1**; M = W) are monoclinic, space group $P2_1/n$, $a = 17{\cdot}43(1)$, $b = 17{\cdot}28(1)$, $c = 19{\cdot}00(1)$ Å, $\beta = 100{\cdot}85(2)°$, $Z = 4$. The W–N and N–N bond lengths correspond to those in hydrazido(2−) complexes[3] (see Table). They indicate that the W–N bond order is about 3 and the N–N bond order is about 1, which accords with the linear W–N–N chain. Evidently, in the tungsten ω-diazobutanol complex, the diazo-ligand is behaving essentially as a dianionic 4-electron ligand, as in (a), and the metal is formally in the oxidation state (iv). It is not formally in the oxidation state (ii) as it would be were the diazobutanol behaving as a neutral ligand, which would give a structure best represented as $\mathrm{W} \leftarrow \mathrm{N} \mathrel{\overset{\cdot\cdot}{=}} \mathrm{N} \mathrel{\overset{\cdot\cdot}{=}} \mathrm{CH[CH_2]_3OH}$, with a linear N–N–C system. We expect the complex (**1**; M = Mo) to have a structure exactly analogous to that of (**1**; M = W).

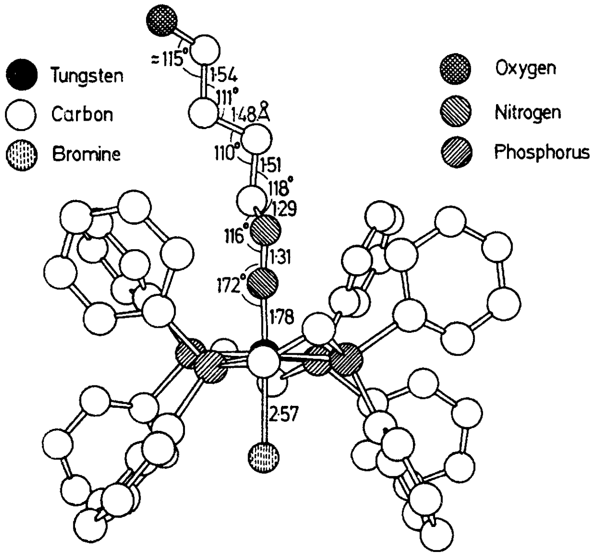
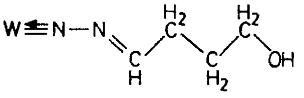


FIGURE. The structure of $[\mathrm{WBr\{N_2CH(CH_2)_3OH\}(dppe)_2}]^+$, together with selected bond lengths (Å) and angles. E.s.d. W-N, 0·01; N-N, 0·02; C-C, *ca.* 0·04.



$\mathrm{W{\leftarrow}N{-}N{=}CH{-}CH_2{-}CH_2{-}CH_2{-}OH}$

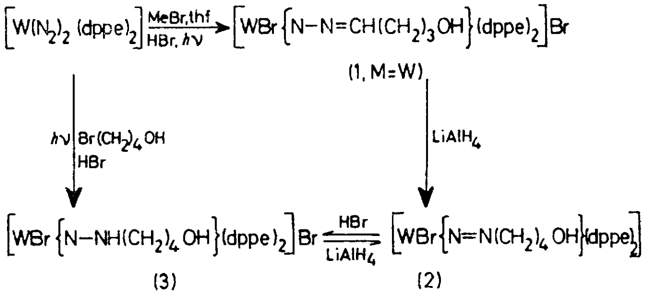
(a)

In the ^{13}C n.m.r. spectra of (**1**; M = W), the chemical shift of the C bonded to N (171·4 p.p.m. w.r.t. $\mathrm{Me_4Si}$) is similar to that of the unique C atom in the diazomethane complex $[\mathrm{WBr(N_2CH_2)(dppe)_2}]^+$ (155·3 p.p.m.),[5] and our previously reported physical data are all consonant with the new structure.

TABLE

	W-N/Å	N-N/Å	M-N-N°
$[\mathrm{WCl(N{-}NH_2)(dppe)_2}]^+$	1·73(1)	1·37(2)	171(1)[4]
$[\mathrm{WBr\{N{-}NH(Me)\}(dppe)_2}]^+$	1·768(14)	1·32(2)	174(1)[3]
$[\mathrm{WBr\{N{-}N{=}CH(CH_2)_3OH\}{-}(dppe)_2}]^+$	1·778(14)	1·306(22)	172(1)

The ω-diazobutanol ligand in the above complexes is electrophilic. In the complex (**1**; M = W) it is reduced by hydride ion to the corresponding 2-(4-hydroxybutyl)diazenido(1—)-N^1 complex (**2**) (see Scheme) and that product is protonated by hydrogen bromide to give the corresponding 2-(4-hydroxybutyl)hydrazido(2—)-N^1 complex (**3**). The complex (**3**) reverts to (**2**) by reaction with $\mathrm{LiAlH_4}$ (acting as a base) and can also be prepared directly from the reaction of 4-bromobutanol with $[\mathrm{W(N_2)_2(dppe)_2}]$ under irradiation with tungsten filament light followed by the addition of hydrogen bromide (see Scheme).



SCHEME

We have not yet demonstrated the role of methyl bromide in the formation of (**1**). At least two complexes are intermediate between $[\mathrm{W(N_2)_2(dppe)_2}]$ and (**1**; M = W) and the first of these already contains a cleaved thf residue. The complexes (**1**) are the first substituted diazomethane complexes to be identified, and the first diazomethane complexes of any type derived from molybdenum. A diazomethane complex of tungsten is already known.[5]

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