Diazobutanol Complexes † of Molybdenum and Tungsten from the Reaction of Bis[1,2-bis(diphenylphosphino)ethane]bis(dinitrogen)-molybdenum or -tungsten with Tetrahydrofuran in the Presence of Alkyl Bromides

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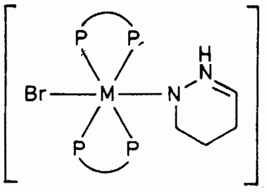
Complexes of the type $[M(N_2)_2(dppe)_2]$ [M = Mo or W; dppe = 1,2-bis(diphenylphosphino)ethane] react with tetrahydrofuran in the presence of alkyl bromides to form $[MBr(N{=}N{-}CH{-}O{-}CH_2{-}CH_2{-}CH_2)(dppe)_2]$ which are converted by H^+ into $[MBr(N{-}N{=}CHCH_2CH_2CH_2OH)(dppe)_2]^+$. The mechanism of this reaction is discussed.

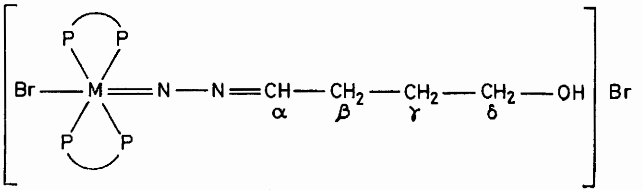
In 1975,[1] we described the formation of some unexpected products from the reaction of $[M(N_2)_2(dppe)_2]$ [M = Mo or W; dppe = 1,2-bis(diphenylphosphino)ethane] with methyl bromide in tetrahydrofuran (thf) solution. In benzene solution $[M(N_2)_2(dppe)_2]$ and MeBr give rise to yellow complexes $[MBr(N_2Me)(dppe)_2]$ which are reversibly protonated with HBr to give $[MBr(N_2HMe)(dppe)_2]$-Br.[2] The products from thf solution acidified with HBr are grey-green (M = W) or brown (M = Mo) crystalline solids which we formulated as tetrahydropyridazinido-complexes (1) ($\widehat{PP}$ = dppe) on the basis of analytical, conductivity, ^1H n.m.r., and mass spectral data.



(1)
a; M = Mo
b; M = W

We were not able to rationalise the formation of this product, neither could we discover the fate of the methyl group of the methyl bromide which is essential for formation of this product. The tetrahydropyridazinido-ligand was obviously derived in part from thf, but we were unable to determine what had happened to the oxygen of the thf.

Subsequently, X-ray structural analysis[3] of the product with M = W showed that the complexes are, in fact, diazobutanol complexes (2), and this paper describes their syntheses and properties and presents evidence bearing upon the mechanism of their formation.



(2)
a; M = Mo
b; M = W

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† The names of the complexes in this paper have been formulated in accord with draft rules of nomenclature for the hydrides of nitrogen and derived cations, anions, and ligands. Details of these rules, which have been drawn up under the auspices of the IUPAC Commission on the Nomenclature of Inorganic Chemistry, may be obtained on request from J. C.

[1] A. A. Diamantis, J. Chatt, G. A. Heath, and G. J. Leigh, *J.C.S. Chem. Comm.*, 1975, 27.

[2] A. A. Diamantis, J. Chatt, G. J. Leigh, and G. A. Heath, *J. Organometallic Chem.*, 1975, **84**, C11.

[3] P. C. Bevan, J. Chatt, R. A. Head, P. B. Hitchcock, and G. J. Leigh, *J.C.S. Chem. Comm.*, 1976, 509.

RESULTS AND DISCUSSION

The complexes $[MBr(N_2CHCH_2CH_2CH_2OH)(dppe)_2]^+$ are obtained as green-grey (M = W) or dark brown (M = Mo) substances from the reaction of $[M(N_2)_2(dppe)_2]$ with methyl bromide in thf under tungsten-filament irradiation followed by acidification with HBr. Our previously reported ^1H n.m.r. data[1] (see Table) are consistent with the *X*-ray structure. In dry solvent, we also observed a singlet at τ *ca.* 6 for (2a) which we now assign to O*H*. The irradiation of the resonance α in the spectrum of (2b) caused the collapse of resonance β, the irradiation of β altered the shape of the multiplet γ, and the irradiations of γ and β caused δ and α respectively to become singlets. In the ^{15}N analogue of (2b), α becomes a doublet of triplets due to ^{15}N coupling, $|^2J(NH)| = 10$ Hz, and we did not observe any effects of this substitution on the O*H* resonance, something which cannot be easily reconciled with our first structural proposal.[1]

The ^1H resonance for protons δ at τ = 6.58 is shifted downfield presumably due to the oxygen atom to which the methylene carbon is bound. The α resonance at low field (τ = 4.38) is in a position characteristic of diazoalkane complexes.[4] For example, the resonances corresponding to the marked protons in (3) and (4) are found at τ = 4.48 and 3.12, and τ = 4.53, respectively.[4]

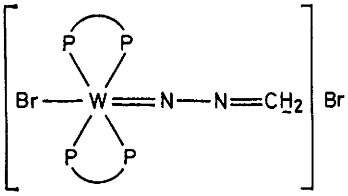
The ^{13}C n.m.r. spectrum of the tungsten diazobutanol complex shows similarities with those of its diazoalkane analogues. Thus N=*C*H has a resonance of 171.4 p.p.m. downfield from TMS (tetramethylsilane) whereas the complex (3) has a signal at 155.3 and that of (4) is at 168.7 p.p.m. (CD_2Cl_2 solution).[4]

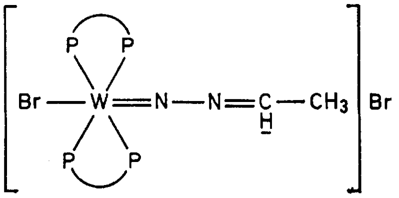
Spectral characteristics of new complexes and of some related compounds

	I.r. spectra/cm^{-1}				N.m.r.									
						^{13}C (p.p.m. downfield from $SiMe_4$)				$^1H(\tau)$				
	ν(N=N) or ν(N–N)	ν(C=N) or ν(C–N)	ν(N–H) or ν(O–H)	Phase	Solvent	α-C	β-C	γ-C	δ-C	α-H	β-H	γ-H	δ-H	Solvent
$[WBr\{N{-}N{=}CH(CH_2)_3OH\}(dppe)_2]Br$ (2b)	1 235	1 573	3 265 (2 170 in the O–D derivative)	KBr	$CDCl_3$	171.4	32.0	31.6	61.3	4.38t	8.96m	8.68m	6.58t	$CDCl_3$
$[MoBr\{N{-}N{=}CH(CH_2)_3OH\}(dppe)_2]Br$ (2a)	1 210	1 565m br	3 360br	KBr						4.34t	8.70m		6.60t	CD_2Cl_2
$[WBr\{N{-}N{=}CMe(CH_2)_3OH\}(dppe)_2][BF_4]$ (7)	1 225	1 576	3 270	KBr	CD_2Cl_2	178.1	33.4	28.4	61.7	10.80s [a]	8.45m		6.39t	CD_2Cl_2
$[WBr\{N{-}N{=}CH_2\}(dppe)_2]Br$ [b] (3)	N.a.[c]	N.a.		KBr	CD_2Cl_2	155.3				4.48d 3.12d				$CDCl_3$
$[WBr\{N{-}N{=}CHMe\}(dppe)_2]Br$ [b] (4)	N.a.	1 582		KBr	CD_2Cl_2	168.7	20.0			4.53q	9.12d			$CDCl_3$
$[WBr\{N{-}N{=}CMe_2\}(dppe)_2]Br$ [b]	N.a.	1 581		KBr	CD_2Cl_2	174.5	20.3 20.9				10.75s 8.88s			CD_2Cl_2
$[WBr\{N{-}NH(CH_2)_4OH\}(dppe)_2]Br$	N.a.	N.a.	3 365	Nujol	CD_2Cl_2	46.6	29.4	24.3	60.5	8.06dt	9.00m	9.22m	6.59t	CD_2Cl_2
$[WBr\{N{-}NH(CH_2)_4OMe\}(dppe)_2]Br$	1 210	N.a.	3 260br	Nujol	CD_2Cl_2	46.9	26.7	24.6	71.9	8.32dt	9.19m 9.43m		7.02t	CD_2Cl_2
$[WBr\{N{-}NH(CH_2)_2CHCH_2\}(dppe)_2]Br$	N.a.	N.a.	3 266br	Nujol	CD_2Cl_2	45.3	31.8	*d*	117.9	8.30dt	8.70m	5.02m	5.19m	CD_2Cl_2
$[WBr\{N{-}NH(CH_2)_3CO_2Me\}(dppe)_2]Br$	N.a.	N.a.	3 320br	Nujol						8.25m	9.15m	8.25m		CD_2Cl_2
$[WBr\{N{=}N{-}CH{-}O{-}CH_2{-}CH_2{-}CH_2\}(dppe)_2]$ (6b)	1 495	1 310		KBr	C_6D_6	88.7	29.7	25.4	66.6	5.91t	8.70m 9.03m		6.87m 6.48m	$CDCl_3$
$[MoBr\{N{=}N{-}CH{-}O{-}CH_2{-}CH_2{-}CH_2\}(dppe)_2]$ (6a)	1 510	1 300		KBr						6.20t	8.68m 9.26m		6.40m 6.64m	$CDCl_3$
$[WBr\{N{=}N(CH_2)_4OH\}(dppe)_2]$	1 500	1 315	3 350vbr	KBr						7.78t	9.20m	8.87m	6.56t	$CDCl_3$
$[WBr\{N{=}N(CH_2)_4OMe\}(dppe)_2]$	1 500	1 315		KBr						7.80t	8.90m 9.20m		6.90t	CD_2Cl_2
$[WBr\{N{=}N(CH_2)_2CHCH_2\}(dppe)_2]$	1 510	1 312		KBr						7.48t	8.40m	4.60m	5.05m 5.25m	CD_2Cl_2
$[WBr\{N{=}N(CH_2)_3CO_2Me\}(dppe)_2]$	1 537	1 313		KBr						7.74t	9.11m	8.17t		$CDCl_3$

Methyl resonance. [b] See ref. 4. [c] N.a. = not assignable. [d] Presumably obscured by phenyl carbons.

The i.r. spectrum of (2b) as the bromide salt in a Nujol mull shows ν(OH) at 3 265 cm^{-1} (2 170 cm^{-1} for the deuterio-analogue), a strong band at 1 572 cm^{-1} (1 558 cm^{-1} in the ^{15}N analogue) which is assigned to ν(C=N), and a weak band at 1 230 cm^{-1} (1 200 cm^{-1} in the ^{15}N analogue) which may arise from ν(N–N). Surprisingly, however, the i.r. spectrum of (3) does not show bands assignable to ν(C=N) or ν(N–N) although the spectrum of (4) does, and each of the compounds $[MBr(N_2R)(dppe)_2]$ (M = Mo or W; R = Me, Et, *etc.*)[2,5] has a strong band in its i.r. spectrum assignable to ν(N=N) at 1 500—1 530 cm^{-1}.


(3)


(4)

We have previously noted[3] that the N–N bond lengths in $[WCl(NNH_2)(dppe)_2]^+$, $[WBr(NNHMe)(dppe)_2]^+$, and $[WBr(NNCHCH_2CH_2CH_2OH)(dppe)_2]^+$ are similar (*ca.* 1.35 Å) and somewhat short, but indicative of formal N–N single bonds. The nitrogen–carbon bond lengths

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[4] R. Ben-Shoshan, J. Chatt, W. Hussain, and G. J. Leigh, *J. Organometallic Chem.*, 1976, **112**, C9; and unpublished data.

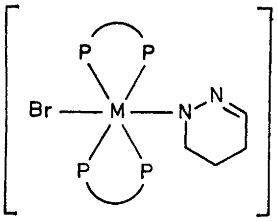
[5] J. Chatt, A. A. Diamantis, G. A. Heath, N. E. Hooper, and G. J. Leigh, *J.C.S. Dalton*, 1977, 688.

in the latter two complexes are rather different (1.48[6] and 1.29 Å,[3] respectively) as to be expected of formal N–C and N=C bonds. In $[MoI(NNHC_8H_{17})(dppe)_2]^+$ N–N is 1.259(14) Å and N–C is 1.504(17) Å,[7] whereas in $[MoI(NNC_6H_{11})(dppe)_2]$ N=N is 0.91(1) Å and N–C is 1.39(4) Å.[8] The former distance is improbably short and is believed to be an artefact of the poor quality of the crystal studied rather than a real bond length.[8] In the first molybdenum complex ν(N–N) is not recorded but ν(N=N) in the second occurs at 1 538 cm^{-1}. Thus, although N–N and N=C bond lengths in these complexes do accord with the formal structures, the i.r. data do not always permit of easy interpretation.

We reported earlier[1] that complex (2b), although then incorrectly formulated as (1), has a parent ion in the mass spectrum consistent with the formulation (1). This is evidently due to the loss of water during the vaporisation/ionisation process in the mass spectrometer, and our parent ion was the true parent minus H_2O.

The diazomethane complex (3) reacts[4] with $[H]^-$, $[CH_3]^-$, and $[Ph]^-$ to yield alkyldiazenido-complexes. Similarly, (2b) reacts with lithium tetrahydridoaluminate in diethyl ether to yield $[WBr(N{=}NCH_2CH_2CH_2CH_2OH)(dppe)_2]$, which is a functional alkyldiazenido-complex [ν(N=N) at 1 500 cm^{-1}, see Table]. Like other alkyldiazenido-complexes, it is protonated reversibly to yield $[WBr(N_2HCH_2CH_2CH_2CH_2OH)(dppe)_2]^+$ which can be obtained directly fom $[W(N_2)_2(dppe)_2]$ and $Br(CH_2)_4OH$ under tungsten-filament irradiation in benzene solution followed by the addition of hydrogen bromide. This is a synthetic confirmation of the structure for (2) deduced[3] by *X*-ray analysis. Incidentally, during investigations to clarify the mode of formation of the diazobutanol complexes, we prepared $[WBr(N_2CH_2CH_2CHCH_2)(dppe)_2]$, $[WBr(N_2CH_2CH_2CH_2CH_2OMe)(dppe)_2]$,* and $[WBr(N_2CH_2CH_2CH_2CO_2Me)(dppe)_2]$ and their protonated derivatives. (See the Experimental section and the Table.)

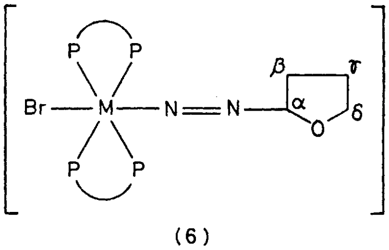
We also reported[1] that compounds (1) could be deprotonated by treatment with base to form complexes which we formulated as (5).



(5)

This formulation is obviously incorrect, and we now formulate these complexes as (6).

The complex (6b) can also be obtained from the usual preparative reaction for (2b) provided hydrogen bromide is not added. It is not easy to characterise because even with traces of acid it is converted into (2b). However, its spectral properties allow the structure to be inferred. There is no band in the i.r. spectrum (KBr disc) assignable to ν(OH). A band at 1 500 cm^{-1} is assignable to ν(N=N) and there is a further strong, sharp band at 1 310 cm^{-1} which is associated with it and may be ν(C–N).

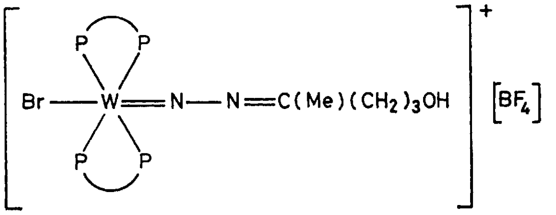


(6)

a; M = Mo

b; M = W

The assignments of the ^1H n.m.r. spectrum of (6b) were made on the basis of decoupling experiments. The shifts, and those in the ^{13}C n.m.r. spectrum (Table), are consistent with the proposed structure. We had hoped to confirm the structure of (6b) by synthesising it directly from $[W(N_2)_2(dppe)_2]$ and 2-bromotetrahydrofuran, but we were not able to achieve a satisfactory synthesis of the latter. We did characterise a product from the reaction of $[W(N_2)_2(dppe)_2]$, 2-methyltetrahydrofuran, and MeBr after acidification. The spectral properties of this complex (see Experimental section) are consistent with the structure (7).



(7)

The methyl group of the methyl bromide escapes from the reaction mixture as methane. This indicates a radical mechanism for the formation of complexes (2), 6), and (7), which proceeds by the following steps.[9]

$$[M(N_2)_2(dppe)_2] \rightleftharpoons \underset{(8)}{[M(N_2)(dppe)_2]} + N_2$$

$$(8) + RBr \longrightarrow \underset{(9)}{[M(RBr)(N_2)(dppe)_2]}$$

$$(9) \longrightarrow \underset{(10)}{[MBr(N_2)(dppe)_2]} + R\cdot$$

The thf or 2-methyltetrahydrofuran as solvent is then attacked by the radical R• as follows:

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* This complex was first prepared in our laboratories by Dr. R. Ben-Shoshan.

[6] F. C. March, R. Mason, and K. M. Thomas, *J. Organometallic Chem.*, 1975, **96**, C43.

[7] V. W. Day, T. A. George, S. D. A. Iske, and S. D. Wagner, *J. Organometallic Chem.*, 1976, **112** C55.

[8] V. W. Day, T. A. George, and S. D. A. Iske, *J. Amer. Chem. Soc.*, 1975, **97**, 4127.

[9] P. C. Bevan, J. Chatt, R. A. Head, G. J. Leigh, and C. J. Pickett, *J.C.S. Chem. Comm.*, 1977, 299.

The solvent radical now reacts with (10) to form (6) or its methyl analogue, the respective protonations of which yield (2) or (7).

Obviously the products from any given RBr depend upon the relative rates at which the putative $R^{\bullet}$ attacks the ligating N_2 or thf. With MeBr and M = W, the product is essentially all (6b). With EtBr, the major product is $[WBr(N_2Et)(dppe)_2]$ and only 10% of the dinitrogen complex is converted ultimately to the diazobutanol derivative. However, when M = Mo, both EtBr and Bu^tBr afford essentially pure (2a) in thf solution. We are at present extending this reaction type to other R and other solvents with extractable protons.

EXPERIMENTAL

Experiments were carried out under dinitrogen using purified dioxygen-free solvents and standard Schlenk-tube techniques. Carbon, hydrogen, and nitrogen analyses were by Mr. A. G. Olney, The Chemical Laboratory, The University of Sussex; halogen analyses were by Dr. A. Bernhardt, West Germany. The following spectrometers were used: i.r., Perkin-Elmer 457 and Unicam SP 2000 with KBr discs and Nujol mulls; n.m.r., JEOL PS-100 and FS-100; mass, A.E.I. MS-9. Melting points were measured in sealed tubes *in vacuo* or under dinitrogen on an Electrothermal apparatus. Conductivities were determined using a Portland Electronics bridge, and solutions generally in nitromethane. Methane was determined by gas chromatography using a Porapak P column at 50 °C in a Pye 104 chromatograph.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*(4-*diazobutan*-1-*ol*-N^2)*tungsten Bromide–Tetrahydrofuran*(1/1).—The complex $[W(N_2)_2(dppe)_2]$ (3.0 g, 2.9 mmol) was dissolved in thf (250 cm^3) and methyl bromide (1 mol equiv.) condensed in on a vacuum line. The solution was irradiated for 14 h by two 150-W tungsten-filament lamps placed *ca.* 25 cm from the reaction flask. The mixture was then filtered, the filtrate reduced to *ca.* one-third of its volume on a vacuum line and hydrogen bromide (2 mol equiv.) condensed in at −196 °C. On warming the solution to room temperature a greenish yellow precipitate formed initially, but this redissolved and on further stirring a grey *precipitate* was obtained. This was filtered off, washed with thf (4 × 10 cm^3), and dried *in vacuo* (2.3 g, 64%). The substance was recrystallised from methanol–thf as grey-green crystals, m.p. 213 °C *in vacuo* (Found: C, 55.1; H, 4.85; N, 2.3. $C_{60}H_{64}Br_2N_2O_2P_4W$ requires C, 54.9; H, 4.91; N, 2.13%).

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*(4-*diazobutan*-1-*ol*-N^2)*molybdenum Bromide–Tetrahydrofuran*(1.0/1.5).—To $[Mo(N_2)_2(dppe)_2]$ (0.5 g, 0.50 mmol) in thf (60 cm^3) was added EtBr (0.1 cm^3, 1.4 mmol) and the reaction mixture irradiated as above for 8 h. Gaseous HBr (1.5 mmol) was introduced into the vessel using a vacuum line and the reaction solution stirred at 22 °C for 1.5 h. The volume was reduced on the vacuum line to about 10 cm^3, when a greenish yellow solid separated. This was filtered off, and after storing the filtrate at 0 °C for 24 h a dark brown crystalline *solid* separated, and this was filtered off, washed with hot thf (2 × 5 cm^3), and dried *in vacuo* (0.07 g, 12%) (Found: C, 59.5; H, 5.15; N, 2.5. $C_{62}H_{68}Br_2MoN_2O_{2.5}P_4$ requires C, 59.1; H, 5.44; N, 2.22%). The same complex was isolated using Bu^tBr in place of EtBr.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*(4-*diazopentan*-1-*ol*-N^2)*tungsten Tetrafluoroborate*.—A mixture of $[W(N_2)_2(dppe)_2]$ (0.30 g, 0.29 mmol) and MeBr (0.067 g, 0.70 mmol) in 2-methyltetrahydrofuran (180 cm^3) was irradiated as above for 14 h. The resulting orange solution was filtered, the filtrate reduced *in vacuo* to 40 cm^3, and HBr (1.1 mmol) added from a vacuum line. This produced a grey microcrystalline precipitate of the bromide salt which was filtered off, washed with thf (10 cm^3), and dried *in vacuo* (0.25 g, 67%). Treatment of a methanolic solution of bromide with $Ag[BF_4]$ (1 mol equiv.) gave the *tetrafluoroborate* salt substantially quantitatively. This was recrystallised from methanol–ether–hexane as grey crystals, m.p. 229—232 °C. The compound is a 1 : 1 electrolyte in nitromethane (Found: C, 54.2; H, 4.7; N, 2.2. $C_{57}H_{58}BBrF_4N_2OP_4W$ requires C, 54.2; H, 4.63; N, 2.22%).

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*(N-*tetrahydrofuran*-2-*yldiazenido*-N′)*tungsten–Diethyl Ether*(1/1).—(*a*) A mixture of $[W(N_2)_2(dppe)_2]$ (0.57 g, 0.56 mmol) and MeBr (0.11 g, 1.1 mmol) in thf (120 cm^3) was irradiated as above for 14 h. The resultant orange solution was filtered, and the filtrate reduced *in vacuo* to give an orange oil. This was extracted with diethyl ether (2 × 50 cm^3) and the combined extracts reduced *in vacuo* to 20 cm^3. The orange *product* was precipitated with hexane (30 cm^3), filtered off, and dried *in vacuo* (0.33 g, 47%), m.p. 160 °C (decomp.).

(*b*) The appropriate diazopentanol complex (0.30 g, 0.24 mmol) was dissolved in dry ethanol (10 cm^3) under argon. Sodium ethoxide (0.16 g, 1 : 1 mol equiv.) was added and the green solution immediately became orange. The solution was evaporated to dryness *in vacuo*, the residue extracted with benzene (10 cm^3) and filtered. The benzene filtrate was reduced to 1 cm^3 in *vacuo* and the addition of diethyl ether (10 cm^3) afforded a yellow powder (0.20 g, 71%) identical by spectra and analysis with the sample obtained under (*a*) (Found: C, 56.7; H, 5.3; N, 2.25. $C_{60}H_{65}BrN_2O_2P_4W$ requires C, 58.4; H, 5.31; N, 2.27%).

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*(N-*tetrahydrofuran*-2-*yldiazenido*-N′)*molybdenum*.—To $[Mo(N_2)_2(dppe)_2]$ (0.50 g, 0.50 mmol) in thf (60 cm^3) was added EtBr (0.10 cm^3, 1.4 mmol). The mixture was stirred for 36 h and then gaseous HBr (1.5 mmol) was introduced from a vacuum line. The solution was stirred for 1 h, the volume was reduced to 20 cm^3 on a vacuum line, and a pink solid separated. This was filtered off, washed with thf, dried *in vacuo*, dissolved in CH_2Cl_2 (15 cm^3), and NEt_3 (0.2 cm^3) added. The mixture was stirred for 1 h, and then hexane (5 cm^3) added. The orange-yellow *product* was filtered, washed with water (3 × 10 cm^3) and methanol (3 × 10 cm^3), and dried *in vacuo* (0.20 g, 35%) (Found: C, 63.0; H, 5.25; N, 2.65; Br, 7.45. $C_{56}H_{55}BrMoN_2OP_4$ requires C, 62.8; H, 5.16; N, 2.61; Br, 7.45%).

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*[N-4-*hydroxybutylhydrazido*(2−)-N′]*tungsten Bromide*.—A solution of $[W(N_2)_2(dppe)_2]$ (0.53 g, 0.53 mmol) and $Br(CH_2)_4OH$ (0.20 g, 1.25 mmol) in benzene (180 cm^3) was stirred at room temperature under irradiation as above for 14 h. The orange solution was filtered, reduced to dryness *in vacuo*, and the oil washed with hexane (2 × 10 cm^3). The oil was crystallised from dichloromethane–hexane as large, dark red *crystals* (0.41 g, 64%), m.p. 218—220 °C (Found: C, 53.2; H, 4.65; N, 2.2; Br, 12.7. $C_{56}H_{58}Br_2N_2OP_4W$ requires C, 53.6; H, 4.69; N, 2.17; Br, 12.8%). The compound is a 1 : 1 electrolyte in nitromethane.

This complex was also obtained from the reaction of

[WBr{N–N=CH(CH$_2$)$_3$OH}(dppe)$_2$]Br and Li[AlH$_4$] followed by protonation of the product.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*(N-4-*hydroxybutyldiazenido*-N′)*tungsten–Diethyl Ether*(1/1).—To a solution of the above 4-hydroxybutylhydrazido(2−) complex (0.30 g, 0.24 mmol) in thf (25 cm^3) was added Li[AlH$_4$] (0.10 g, 2.6 mmol) and the solution stirred at room temperature for 2 h. The colour changed rapidly from deep red to orange. Water (2.0 cm^3) was added to the thf solution which was then evaporated to dryness *in vacuo* and the residue extracted with diethyl ether (3 × 10 cm^3). The combined extracts were dried over Na$_2$[SO$_4$], the volume reduced *in vacuo* to 15 cm^3 and cooled to −20 °C to afford small red crystals of the product (0.13 g, 46%), m.p. 182—184 °C. It was recrystallised from ether (Found: C, 58.8; H, 5.6; N, 2.25; Br, 6.6. $C_{60}H_{67}BrN_2O_2P_4W$ requires C, 58.3; H, 5.43; N, 2.27; Br, 6.48%).

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*[N-*but*-3-*enylhydrazido*(2−)-N′]*tungsten Bromide–Methanol*(1/1).—A mixture of [W(N$_2$)$_2$(dppe)$_2$] (0.72 g, 0.71 mmol) and 4-bromobut-1-ene (0.24 g, 1.78 mmol) in benzene (180 cm^3) was stirred and irradiated as above at 22 °C for 13 h. The red solution was reduced to dryness *in vacuo*, the residue washed with hexane (10 cm^3), and the washed residue crystallised from methanol–ether–hexane as light brown crystals (0.54 g, 61%), m.p. 208 °C (Found: C, 54.3; H, 5.05; N, 2.1. $C_{57}H_{60}Br_2N_2OP_4W$ requires C, 54.5, H, 4.81; N, 2.32%).

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*(N-*but*-3-*enyldiazenido*-N′)*tungsten–Dichloromethane*(1/1).—A solution of the above but-3-enylhydrazido-complex (0.12 g, 0.10 mmol) in methanol (10 cm^3) was treated with K$_2$[CO$_3$] (0.023 g, 0.17 mmol), and water (1.0 cm^3) was added to give a yellow precipitate. The mixture was evaporated to dryness *in vacuo*, washed with water (2.0 cm^3), dried *in vacuo*, and extracted with benzene (2 × 10 cm^3). The combined extracts were reduced *in vacuo* to 5 cm^3, and the product separated as orange *crystals* which were recrystallised from dichloromethane–hexane (0.089 g, 76%), m.p. 139 °C (Found: C, 55.8; H, 5.25; N, 2.25. $C_{57}H_{57}BrCl_2P_4W$ requires C, 55.7; H, 4.68; N, 2.28%).

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*[N-(4-*methoxybutyl*)*diazenido*-N′]*tungsten–Dichloromethane*(1/1).—A solution of [W(N$_2$)$_2$(dppe)$_2$] (0.97 g, 0.97 mmol) and freshly distilled Br(CH$_2$)$_4$OMe (0.18 g, 1.1 mmol) in benzene (170 cm^3) were stirred at room temperature under irradiation as above for 14 h. The red solution was then filtered and reduced to dryness *in vacuo*, and the resultant oil washed with hexane (3 × 5 cm^3). Treatment with dichloromethane–hexane afforded the product as deep-red *crystals* (0.83 g, 68%), m.p. 123—125 °C (Found: C, 54.3; H, 5.15; N, 2.25. $C_{58}H_{61}BrCl_2N_2OP_4W$ requires C, 55.1; H, 4.84; N, 2.22%).

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*[N-(4-*methoxybutyl*)*hydrazido*(2−)-N′]*tungsten Bromide–Methanol*(1/1).—Gaseous HBr (2 molar equivalents) was condensed *in vacuo* into a flask containing the diazenido-complex (0.32 g, 0.25 mmol) in thf (40 cm^3) and the mixture allowed to warm from −196 °C to room temperature. The solution, which became lighter in colour, was reduced to dryness *in vacuo*, and the resulting red oil washed with hexane (10 cm^3). Treatment with methanol–ether–hexane yielded the product as tan *crystals* (0.30 g, 93%), m.p. 200—203 °C (Found: C, 53.8; H, 5.25; N, 2.2. $C_{58}H_{64}Br_2N_2O_2P_4W$ requires C, 54.0; H, 4.97; N, 2.17%). The compound is a 1 : 1 electrolyte in nitromethane solution.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*[N-(3-*carboxymethylpropyl*)*diazenido*-N′]*tungsten*.—A mixture of [W(N$_2$)$_2$(dppe)$_2$] (0.57 g, 0.57 mmol) and Br(CH$_2$)$_3$CO$_2$Me (0.50 g, 2.76 mmol) in benzene (240 cm^3) was stirred at room temperature under irradiation as above for 13 h. The resulting red solution was filtered and reduced to dryness *in vacuo*, and the resulting residue washed with hexane (3 × 10 cm^3). Recrystallisation from dichloromethane–hexane afforded the product as large, deep red *crystals* (0.48 g, 71%), m.p. 196 °C (Found: C, 57.9; H, 4.80; N, 2.25. $C_{57}H_{57}BrN_2O_2P_4W$ requires C, 57.6; H, 4.83; N, 2.35%).

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*[N-(3-*carboxymethylpropyl*)*hydrazido*(2−)-N′]*tungsten Bromide*.—The diazenido-complex (0.21 g, 0.18 mmol) was dissolved in benzene (20 cm^3) and 2 molar equivalents of HBr added using a vacuum line. The mixture was stirred at room temperature for 0.5 h and reduced to dryness *in vacuo*, and the residue washed with hexane (10 cm^3). The residue crystallised from methanol–ether–hexane, afforded the product as tan crystals (0.19 g, 83%), m.p. 235 °C (Found: C, 53.0; H, 4.7; N, 2.2. $C_{57}H_{58}Br_2N_2O_2P_4W$ requires C, 53.9; H, 4.60; N, 2.20%).

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