Reactions of *trans*-Bis[1,2-bis(diphenylphosphino)ethane]bis(dinitrogen)-tungsten and -molybdenum with α,ω-Dibromides, $Br(CH_2)_nBr$ (n = 2–12)

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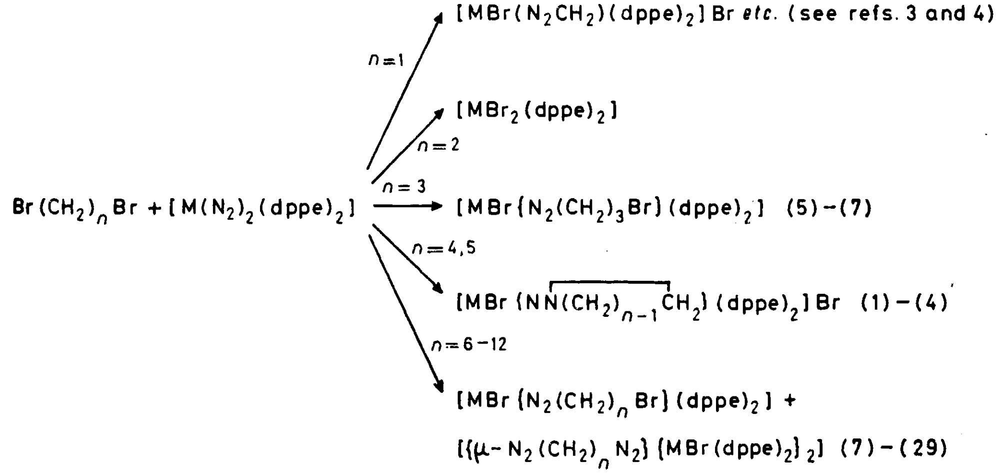
The reactions of *trans*-$[M(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ (M = Mo or W) with $Br(CH_2)_nBr$ under irradiation in benzene solution yield products which are a function of n. For n = 3, complexes containing the group $N_2(CH_2)_3Br$ are formed. For n = 4 or 5, complexes with rings $N(CH_2)_n$ are formed and for n = 6—12 two series of complexes, containing either $N_2(CH_2)_nN_2$ or $N_2(CH_2)_nBr$ are isolated. Members of the two series may be isolated as diazenido-complexes $[MBr\{N_2(CH_2)_nBr\}(Ph_2PCH_2CH_2PPh_2)_2]$ or $[\{\mu\text{-}N_2(CH_2)_nN_2\}\{MBr(Ph_2PCH_2CH_2PPh_2)_2\}_2]$ respectively, both of which can be protonated reversibly to hydrazido(2−)-forms.

WE have recently described in detail the reactions between alkyl halides, RX, and the molybdenum and tungsten dinitrogen complexes *trans*-$[M(N_2)_2(dppe)_2]$ [dppe = 1,2-bis(diphenylphosphino)ethane].[1] The products are generally diazenido-complexes *trans*-$[MX(N_2R)(dppe)_2]$, and the mechanism of formation is clearly understood.[2] We have also investigated the reactions of *trans*-$[M(N_2)_2(dppe)_2]$ with *gem*-bromides, $R^1R^2CBr_2$, which form diazoalkane complexes *trans*-$[MBr(N_2CR^1R^2)(dppe)_2]Br$, among other products.[3,4] In this paper we present our results on reactions of α,ω-dibromides, $Br(CH_2)_nBr$ (n = 2—12) with *trans*-$[M(N_2)_2(dppe)_2]$. We undertook this work with two aims in mind. First, we wished to discover whether these dibromides would dialkylate giving complexes containing the groupings $=N{-}\overline{NCH_2(CH_2)_{n-2}CH_2}$ or perhaps $\leftarrow N{=}\overline{NCH_2(CH_2)_{n-2}CH_2}$. The only example of a dialkylation known to us was of $[W(N_2)_2(dppe)_2]$ and MeBr which yield $[WBr(NNMe_2)(dppe)_2]Br$.[1] Secondly, we wished to discover whether the dibromides would bridge between dinitrogen molecules to produce dinuclear complexes containing the grouping $M{-}N{=}N{-}(CH_2)_n{-}N{=}N{-}M$. Part of this work has been published in preliminary form,[5] and the results are summarised in the Scheme.



SCHEME Reactions of $[M(N_2)_2(dppe)_2]$ with α,ω-dibromides

RESULTS AND DISCUSSION

(*i*) *Reactions of* $Br(CH_2)_nBr$, n = 2.—The reaction of $Br(CH_2)_2Br$ with $[M(N_2)_2(dppe)_2]$ leads to $[MBr_2(dppe)_2]$ and C_2H_4. This has been ascribed to the instability of the radical $BrCH_2CH_2{\cdot}$.[2]

(*ii*) *Reactions of* $Br(CH_2)_nBr$, n = 4 or 5.—As in all these reactions, those involving tungsten complexes were invariably cleaner with yields reaching 80%, but in the reactions in sections (*iii*) and (*iv*) described below the yields were much lower, and the desired product was often only one of many, and not necessarily the major product. Consequently, there were considerable problems of purification.

The formulation of compounds (1)—(4) (Table 1) as ring compounds containing the grouping $\overline{N{-}CH_2(CH_2)_{n-2}CH_2}$ is based on the following data (see Tables 1 and 2). The compounds are 1 : 1 electrolytes in nitromethane. They are not diazenido-complexes. This follows from the absence of bands assignable to ν(N=N) in the i.r. spectra, although there are strong bands at 1 315 for (1) and 1 345 for (2) in the ν(N−N) region, and from the shape of the phenyl resonances in the ^1H n.m.r. spectra [see part (*e*) of the Figure, and below]. In the ^1H n.m.r. spectra of (1) and (2) the methylene protons

TABLE 1

Products of reactions of $[M(N_2)_2(dppe)_2]$ and $Br(CH_2)_nBr$ (n = 4 or 5)

Complex	Colour	M.p. (θ_c/°C)	Conductivity Λ/ ohm^{-1} cm^2 mol^{-1}	Analyses * (%) C	H	N	Br
(1) $[WBr\{NN(CH_2)_4\}(dppe)_2]Br\cdot 1.5CH_2Cl_2$	Gold	222—224	66	50.9 (51.1)	4.45 (4.40)	2.20 (2.05)	11.6 (11.8)
(2) $[MoBr\{NN(CH_2)_4\}(dppe)_2]Br\cdot 1.5CH_2Cl_2$	Green-yellow	207—209 (decomp.)		56.7 (55.4)	4.65 (4.75)	2.50 (2.75)	
(3) $[WBr\{NN(CH_2)_5\}(dppe)_2]Br\cdot 2CH_2Cl_2$	Red	220—222	76	50.4 (50.3)	4.40 (4.45)	1.95 (2.00)	12.2 (11.3)
(4) $[MoBr\{NN(CH_2)_5\}(dppe)_2]Br$	Pale yellow	212—214		59.1 (59.4)	5.25 (5.05)	2.40 (2.15)	

* Calculated values are given in parentheses.

TABLE 2

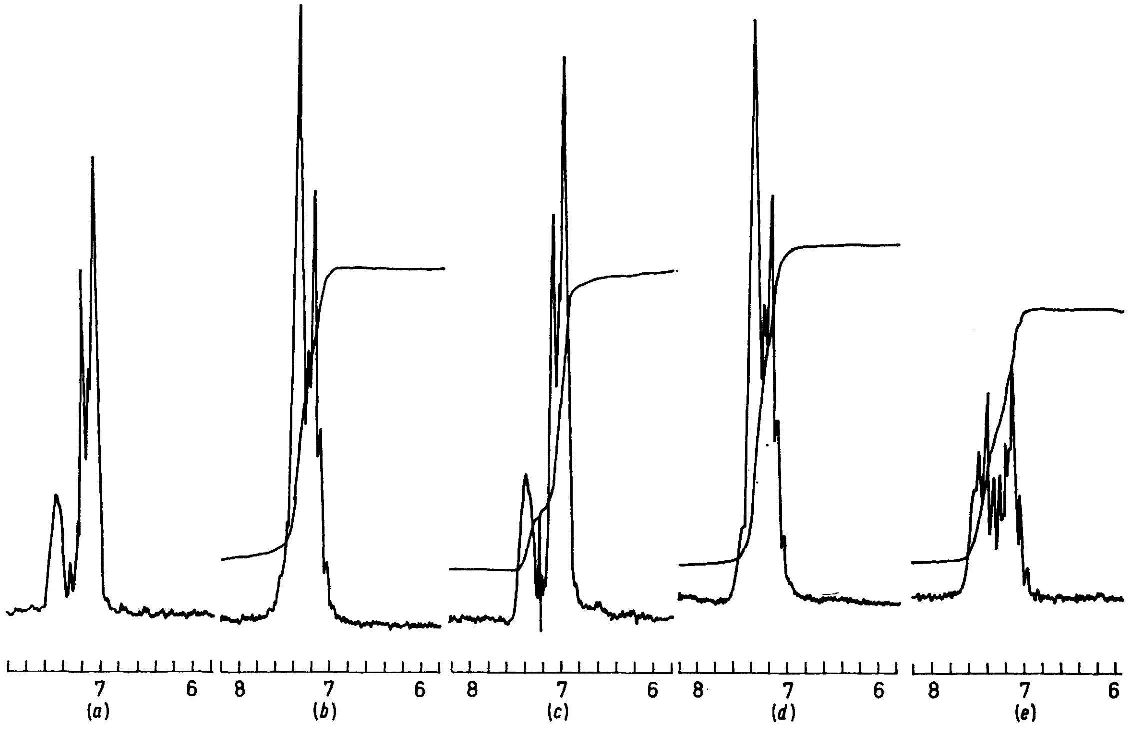
Hydrogen-1 and ^{13}C n.m.r. parameters of $[MBr\{=N-\overline{NCH_2(CH_2)_{n-2}C}H_2\}(dppe)_2]Br$

Complex	Solvent	$-\overline{NCH_2(CH_2)_{n-2}C}H_2$ ^1H n.m.r. (τ) [a]	Solvent	$-\overline{NCH_2(CH_2)_{n-2}C}H_2$ ^{13}C n.m.r. (p.p.m.) [b]
(1)	$CDCl_3$	7.80—8.04 (m, 4) 8.90—9.20 (m, 4)	CD_2Cl_2	48.47, 23.78
(2)	CD_2Cl_2	8.41(t?, br, 4) 9.24 (t?, br, 4)	CD_2Cl_2	50.11, 25.18, 22.20
(3)	$CDCl_3$	7.96—8.28 (m, 4) 9.00—9.24 (m, 6)		
(4)	CD_2Cl_2	8.38 (s?, br, 4) 9.25 (s?, br, 6)		

[a] Numbers in parentheses are relative intensities, s = singlet, t = triplet, m = multiplet, br = broad. [b] Downfield from $SiMe_4$.

derived from the dibromide produce a pair of multiplets (rought triplets) of equal intensity, whereas (3) and (4) produce two multiplets of intensity ratio 2 : 3. Dichloromethane of solvation is also observed. In the ^{13}C n.m.r. spectra the methylene chains of (1) and (2) give rise to two types of carbon resonance, and (3) and (4) to three.

The n.m.r. (but not the analytical) data could be accommodated on the basis of a linear structure $=N-(CH_2)_n-N=$, but in that case the nitrogen atoms designated should be basic and give rise to hydrazido(2—)-complexes with acids, which they do not, although (2) and (4) slowly decompose in the presence of aqueous HBr to deposit



Phenyl regions of the ^1H n.m.r. spectra of (*a*) $[WBr\{N_2(CH_2)_9Br\}(dppe)_2]$ in CD_2Cl_2; (*b*) $[WBr\{N_2H(CH_2)_9Br\}(dppe)_2][BF_4]$ in $CDCl_3$; (*c*) $[\{\mu\text{-}N_2(CH_2)_9N_2\}\{WBr(dppe)_2\}_2]$ in CD_2Cl_2; (*d*) $[\{\mu\text{-}N_2H(CH_2)_9HN_2\}\{WBr(dppe)_2\}_2][BF_4]_2$ in $CDCl_3$; and (*e*) $[WBr\{=N-\overline{NCH_2(CH_2)_3C}H_2\}(dppe)_2]Br$ in CD_2Cl_2. Scale in δ with respect to $SiMe_4$

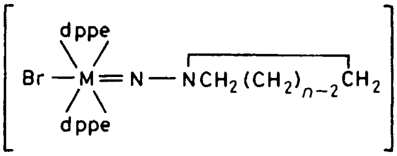
TABLE 3

Hydrazido(2−)-complexes of molybdenum and tungsten

Complex	Colour	M.p. (θ_c/°C)	Λ [a]/ ohm^{-1} cm^2 mol^{-1}	Analyses (%) [b] C	H	N	Br
(8) $[WBr\{N_2H(CH_2)_6Br\}(dppe)_2]Br\cdot MeOH$	Golden brown	137—150 (decomp.)	101	51.8 (51.9)	4.85 (4.80)	2.20 (2.05)	17.1 (17.6)
(9) $[\{\mu\text{-}N_2H(CH_2)_6HN_2\}\{WBr(dppe)_2\}_2]Br_2$	Dark brown	205—208	146	55.0 (54.5)	4.95 (4.55)	2.25 (2.30)	13.0 (13.2)
(10) $[MoBr\{N_2H(CH_2)_6Br\}(dppe)_2]Br$	Red	145—148		55.7 (55.9)	5.20 (4.90)	2.20 (2.25)	
(11) $[WBr\{N_2H(CH_2)_7Br\}(dppe)_2]Br$	Dark brown	140—144	72	53.1 (52.6)	5.20 (4.7)	2.3 (2.10)	17.3 (17.8)
(12) $[\{\mu\text{-}N_2H(CH_2)_7HN_2\}\{WBr(dppe)_2\}_2]Br_2$	Salmon	205—207	143	54.6 (54.7)	4.85 (4.60)	2.15 (2.30)	13.4 (13.2)
(13) $[WBr\{N_2H(CH_2)_8Br\}(dppe)_2][BF_4]\cdot 0.25OEt_2$	Light brown	206—208	80	53.0 (52.8)	4.50 (4.9)	2.05 (2.0)	11.3 (11.5)
(14) $[\{\mu\text{-}N_2H(CH_2)_8HN_2\}\{WBr(dppe)_2\}_2][BF_4]_2$	Brick-red	218—222	116	53.8 (54.6)	5.02 (4.65)	2.05 (2.25)	7.0 (6.5)
(15) $[MoBr_2\{NH(CH_2)_8Br\}(dppe)_2]Br$	Brown	147—149		57.3 (56.6)	5.10 (5.15)	2.35 (2.20)	
(16) $[WBr\{N_2H(CH_2)_9Br\}(dppe)_2][BF_4]$	Pale brown	202—205	85	53.6 (53.0)	5.05 (4.90)	2.1 (2.0)	10.4 (11.5)
(17) $[\{\mu\text{-}N_2H(CH_2)_9HN_2\}\{WBr(dppe)_2\}_2][BF_4]_2$	Brown	151—153	182	54.5 (54.7)	4.85 (4.70)	2.05 (2.25)	7.2 (6.4)
(18) $[\{\mu\text{-}N_2H(CH_2)_9HN_2\}\{MoBr(dppe)_2\}_2][BF_4]_2$	Brown	193—195		59.0 (58.9)	5.1 (5.05)	2.55 (2.45)	
(19) $[WBr\{N_2H(CH_2)_{10}Br\}(dppe)_2][BF_4]$	Light brown	201—203	81	54.0 (53.5)	5.0 (4.10)	2.15 (1.95)	11.1 (11.3)
(20) $[\{\mu\text{-}N_2H(CH_2)_{10}HN_2\}\{WBr(dppe)_2\}_2][BF_4]_2\cdot 0.25CH_2Cl_2$	Pink			54.3 (54.5)	4.90 (4.75)	2.15 (2.30)	6.5 (6.0)
(21) $[\{\mu\text{-}N_2H(CH_2)_{10}HN_2\}\{MoBr(dppe)_2\}_2]Br_2$	Light brown	151—154		59.0 (59.4)	5.75 (5.15)	2.40 (2.45)	
(22) $[WBr\{N_2H(CH_2)_{11}Br\}(dppe)_2][BF_4]$	Brown	192—193	81	53.3 (53.6)	4.8 (5.05)	2.0 (2.0)	11.0 (11.3)
(23) $[\{\mu\text{-}N_2H(CH_2)_{11}HN_2\}\{WBr(dppe)_2\}_2][BF_4]_2$	Pink	210—211	165	55.1 (55.1)	5.0 (4.80)	2.25 (2.25)	7.1 (6.4)
(24) $[MoBr\{N_2H(CH_2)_{11}Br\}(dppe)_2][BF_4]$	Brown	180—183		57.6 (57.2)	5.45 (5.40)	2.10 (2.10)	
(25) $[\{\mu\text{-}N_2H(CH_2)_{11}HN_2\}\{MoBr(dppe)_2\}_2][BF_4]_2$	Light brown	209		59.2 (59.2)	5.60 (5.20)	2.35 (2.4)	
(26) $[\{\mu\text{-}N_2H(CH_2)_{12}HN_2\}\{WBr(dppe)_2\}_2][BF_4]_2$	Light brown	200—201	160	55.2 (55.3)	4.95 (4.85)	2.25 (2.20)	6.9 (6.3)
(27) $[\{\mu\text{-}N_2H(CH_2)_{12}HN_2\}\{MoBr(dppe)_2\}_2][BF_4]_2$	Light brown	192—195	150	59.5 (59.4)	5.10 (5.25)	2.50 (2.40)	

[a] In nitromethane. [b] Calculated values are given in parentheses.

nitrogen-free pink crystals, which were not identified. The only reasonable formulation of (1)—(4) is as shown. The confirmation that these are indeed ring compounds is the fact that treatment of (1) and (4) with $Li[AlH_4]$ followed by base distillation gives pyrrolidine and piperidine, respectively.[6] It is unlikely that these amines could form preferentially during the destructive reduction of open-chain complexes.



(*iii*) *Reactions of* $Br(CH_2)_nBr$, $n = 3$.—The reaction of $[M(N_2)_2(dppe)_2]$ with $Br(CH_2)_3Br$ produces the bromopropyldiazenido-complexes. As in all these reactions we found it impossible to ensure complete absence of protic

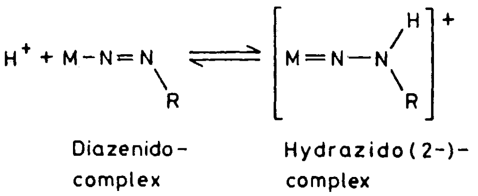
TABLE 4

Diazenido-complexes of molybdenum and tungsten

Complex	Colour	M.p. (θ_c/°C)	Analysis (%) * C	H	N	Br
(7) $[WBr\{N_2(CH_2)_3Br\}(dppe)_2]$	Orange-yellow	170—173	55.1 (54.6)	4.50 (4.50)	2.40 (2.30)	13.2 (13.2)
(28) $[WBr\{N_2(CH_2)_7Br\}(dppe)_2]$	Orange	128—130	56.9 (57.0)	5.35 (5.0)	2.45 (2.15)	12.3 (12.2)
(29) $[\{\mu\text{-}N_2(CH_2)_7N_2\}\{WBr(dppe)_2\}_2]$	Orange-red	195—196	58.8 (58.6)	5.05 (4.85)	2.45 (2.45)	7.3 (7.0)
(30) $[MoBr\{N_2(CH_2)_7Br\}(dppe)_2]\cdot Pr^iOH$	Orange-yellow	175	60.8 (60.1)	5.60 (5.70)	2.30 (2.25)	
(31) $[WBr\{N_2(CH_2)_8Br\}(dppe)_2]\cdot C_6H_6$	Orange	182—184	58.0 (58.3)	5.05 (5.20)	2.25 (2.05)	11.9 (11.7)
(32) $[\{\mu\text{-}N_2(CH_2)_8N_2\}\{WBr(dppe)_2\}_2]\cdot 2OEt_2$	Orange	138—141	59.2 (59.7)	5.45 (5.35)	2.30 (2.25)	6.5 (6.6)
(33) $[MoBr\{N_2(CH_2)_8Br\}(dppe)_2]$	Orange	130	60.8 (60.4)	5.30 (5.4)	2.40 (2.35)	
(34) $[WBr\{N_2(CH_2)_9Br\}(dppe)_2]\cdot 0.5C_6H_6$	Orange-red	176—178	57.9 (57.6)	5.60 (5.2)	2.2 (2.10)	12.0 (12.0)
(35) $[\{\mu\text{-}N_2(CH_2)_9N_2\}\{WBr(dppe)_2\}_2]\cdot 0.5C_6H_6$	Orange	179—180	59.7 (59.6)	5.20 (5.15)	2.45 (2.35)	6.9 (6.7)
(36) $[\{\mu\text{-}N_2(CH_2)_{10}N_2\}\{MoBr(dppe)_2\}_2]$	Orange	117—120	63.1 (63.9)	5.90 (5.45)	2.45 (2.60)	
(37) $[MoBr\{N_2(CH_2)_{11}Br\}(dppe)_2]$	Orange	80	62.6 (61.3)	5.90 (5.70)	2.25 (2.25)	
(38) $[\{\mu\text{-}N_2(CH_2)_{11}N_2\}\{MoBr(dppe)_2\}_2]$	Orange	115—117	63.5 (64.1)	5.95 (5.50)	2.35 (2.60)	
(39) $[\{\mu\text{-}N_2(CH_2)_{12}N_2\}\{MoBr(dppe)_2\}_2]$	Orange	128—130	62.8 (64.2)	6.0 (5.55)	2.45 (2.60)	

* Calculated values are given in parentheses.

acid. Hence the product was generally a mixture of diazenido- and hydrazido-(2—)-complexes which precipitated from the benzene solvent [see preparation of (6), in the Experimental section]. To simplify work-up, we often added acid to convert all the product to the salt [see preparation of (5)] and reconverted this to the diazenido-complex by subsequent base treatment [see preparation of (7)]. Further details are in Tables 3 and 4.



The formulations of (5) and (6) are based on the i.r. spectra (see Table 5) which show bands assignable to ν(NH), what may be ν(N–N), and no bands assignable to ν(N=N). On the other hand ν(N=N) is clearly detectable in the spectrum of (7) (Table 7). Further, the ^{1}H n.m.r. data are diagnostic (Tables 6 and 8). The Figure [(*a*)—(*d*)] shows typical spectra in the phenyl region of hydrazido(2—)- and of diazenido-complexes. The patterns are entirely characteristic. The reasons are not at all clear, but all the compounds discussed in this paper conform to these patterns, with the exception of the ring compounds which have a further characteristic pattern shown in part (*e*) of the Figure. This does not seem to be a consequence of the geometry of the phenyl groups as far as one can judge from the few solid-state structures which are known.

We have so far been unable to find compounds in the reaction mixtures containing the grouping $N{-}N{-}(CH_2)_3{-}N{-}N$. This is surprising because we have previously characterised[4] $[(dppe)_2BrMo(N_2CH_2N_2)MoBr(dppe)_2]$ and such dinuclear species form with all the other dibromides $Br(CH_2)_nBr$ (n = 6—12). We believe that the failure to

TABLE 5

Selected i.r. data [a] (cm^{-1}) for hydrazido(2—)-complexes

Complex	ν(N–H)	Region of ν(N–N)
(*a*) Complexes of type $[MBr\{N_2H(CH_2)_nBr\}(dppe)_2]^+$		
(5) W, n = 3	3 250—3 210m,br [b]	1 330m (sh)
(6) Mo, n = 3	n.a.	1 330m (sh)
(8) W, n = 6	3 400—3 320m,br [b]	1 335w (sh)
(10) Mo, n = 6	n.a.	1 335w (sh); 1 315w (sh)
(11) W, n = 7		1 330w,br
(13) W, n = 8	3 260w (sh) [b]	1 358m (sh)
(15) Mo, n = 8	n.a.	1 315w (sh); 1 340w
(16) W, n = 9	3 268w (sh) [b]	1 358m (sh); 1 320w (sh) [b]
(19) W, n = 10	3 250m (sh) [b]	1 408m (sh); 1 358m (sh) [b]
(22) W, n = 11	3 300—3 230w,br	1 405w (sh); 1 355w (sh); 1 330w (sh)
(24) Mo, n = 11	3 300—3 250w,br	1 335w (sh); 1 310w (sh)
(*b*) Complexes of the type $[MBr(dppe)_2\{N_2H(CH_2)_nN_2H\}MBr(dppe)_2]^{2+}$		
(9) W, n = 6		1 330w (sh)
(12) W, n = 7		1 335w (sh)
(14) W, n = 8	3 300—3 230m,br [b]	1 330m (sh)
(17) W, n = 9	3 300—3 220m,br	1 330w (sh)
(18) Mo, n = 9	3 300—3 200m,br	1 330w (sh); 1 305w (sh)
(20) W, n = 10	3 290—3 260m,br [b]	1 330w,br [b]
(21) Mo, n = 10	n.a.	1 335w (sh); 1 310w (sh)
(23) W, n = 11	3 310—3 240m,br	1 320w (sh)
(25) Mo, n = 11	3 300—3 240m,br	1 330w (sh); 1 310w (sh)
(26) W, n = 12	3 300—3 240m,br [b]	1 320w (sh)
(27) Mo, n = 12	3 300—3 250m,br	1 325w (sh); 1 305w (sh)

[a] Generally in KBr discs, m = medium, w = weak, br = broad, sh = sharp, n.a. = not assigned. [b] In hexachlorobutadiene.

TABLE 6

Selected ^{1}H n.m.r. data for hydrazido(2—)-complexes [a]

Complex	Solvent	C*H*$_2$Br (τ)	$N_2(CH_2)_{n-1}$ or $N_2(CH_2)_nN_2$ (τ)
(*a*) Complexes of the form $[MBr\{N_2H(CH_2)_nBr\}(dppe)_2]^+$			
(5) W, n = 3	CD_2Cl_2	7.20t (2)	9.06—9.32m (2), 8.74—9.24m (2)
(6) Mo, n = 3	CD_2Cl_2	7.28t (2)	8.04—8.38m (2), 8.68—9.02m (*ca.* 2)
(8) W, n = 6 [b]	$CDCl_3$	6.64t (2)	8.16—8.52m, 8.68—9.16m, 9.28—9.64m (*ca.* 10)
(10) Mo, n = 6	CD_2Cl_2	6.62t (2)	8.02—8.47m, 8.67—9.12m, 9.17—9.57m (*ca.* 10)
(11) W, n = 7 [c]	CD_2Cl_2	6.53t (2)	8.05—8.37m, 8.57—8.89m, 8.93—9.21m, 9.25—9.65m (*ca.* 12)
(13) W, n = 8	CD_2Cl_2	6.55t (2)	8.00—8.42m, 8.48—9.15m, 9.20—9.78m (14)
(15) Mo, n = 8	CD_2Cl_2	6.56t (2)	7.98—8.40m, 8.43—8.88m, 8.08—9.68m (*ca.* 14)
(16) W, n = 9	$CDCl_3$	6.52t (2)	7.96—8.44m, 8.48—9.20m, 9.28—9.72m (16)
(19) W, n = 10	$CDCl_3$	6.56t (2)	8.00—8.44m, 8.50—9.20m, 9.28—9.76m (18)
(22) W, n = 11	CD_2Cl_2	6.60t (2)	8.02—8.42m, 8.48—9.10m, 9.18—9.64m (20)
(24) Mo, n = 11 [d]	CD_2Cl_2	6.55t (2)	7.90—8.30m, 8.40—9.10m, 9.20—9.70m (20)
(*b*) Complexes of the form $[(dppe)_2MBr\{N_2H(CH_2)_nN_2H\}MBr(dppe)_2]^{2+}$			
(9) W, n = 6 [e]	$CDCl_3$		8.04—8.68m (4), 9.36—9.96m (8)
(12) W, n = 7 [f]	$CDCl_3$		8.16—8.48m (4), 9.08—9.32m, 9.36—9.88m (10)
(14) W, n = 8	CD_2Cl_2		8.05—8.45m (4), 9.00—9.30m, 9.33—9.67m (12)
(17) W, n = 9	$CDCl_3$		8.00—8.44m (4), 8.88—9.20m, 9.28—9.68m (14)
(18) Mo, n = 9	CD_2Cl_2		8.00—8.40m (4), 8.86—9.20m, 9.26—9.64m (14)
(20) W, n = 10	$CDCl_3$		8.05—8.45m (4), 8.81—9.18m, 9.21—9.77m (16)
(21) Mo, n = 10	CD_2Cl_2		8.10—8.50m (4), 8.64—8.95s, 8.95—9.40m, 9.40—9.60m (16)
(23) W, n = 11	CD_2Cl_2		8.10—8.40m (4), 8.60—9.10m, 9.25—9.68m (18)
(25) Mo, n = 11 [g]	CD_2Cl_2		7.97—8.27m (4), 8.57—9.07m, 9.17—9.60m (18)
(26) W, n = 12	CD_2Cl_2		8.08—8.04m (4), 8.60—9.22m, 9.28—9.70m (20)
(27) Mo, n = 12 [h]	CD_2Cl_2		8.04—8.40m (4), 8.60—9.20m, 9.28—9.80m (*ca.* 20)

[a] In all compounds PC*H*$_2$C*H*$_2$P are found as a multiplet, of correct intensity τ 6.5—7.8; relative intensities in parentheses, s = singlet, t = triplet, m = multiplet, br = broad. [b] N*H*, τ 49.96—5.16s,br (1). [c] N*H* under C*H*$_2$Br (1). [d] N*H*, τ 5.95—6.18s,br (1). [e] N*H*, τ 5.20—5.68s,br (1). [f] N*H*, τ 5.92—6.28s,br (1). [g] N*H*, τ 5.77—6.00s,br (1). [h] N*H*, τ 5.80—6.06s,br (1).

isolate such a species in this case is a practical problem associated with relative solubility and ease of crystallisation.

(*iv*) *Reactions of* $Br(CH_2)_nBr$, $n = 6$—12.—The data relating to these reactions are collected in Tables 3—8. The general pattern seems to be that all the dihalides form two series of complexes, one containing the grouping $N{-}(CH_2)_nBr$ and the other the grouping $N{-}(CH_2)_n{-}N$. Both series of complexes occur in protonated [hydrazido-(2—)-] and non-protonated (diazenido-) forms. However, we were not always able to isolate both forms for each metal, neither did the material we isolated represent 100% of the product. Difficulties in crystallisation, particularly with the long-chain compounds, large quantities of unwanted material such as $[MBr_2(dppe)_2]$, especially in molybdenum systems, and decomposition during work-up, again especially in molybdenum systems, ensured that only a portion of the identified materials was actually isolated. The formulation of the complexes follows from the spectra, and will not be discussed further. We have no evidence for ring structures from any of these dibromides, either of the form already isolated for $n = 4$ and 5, or of the form $\overline{M{-}N{=}NCH_2(CH_2)_nCH_2N{=}N}$. Although when we began this work we hoped that it might be possible to find complexes containing the latter structure, our better understanding [2] of the mechanism of alkylation makes it very unlikely that they ever form.

TABLE 7

Selected i.r. data [a] (cm^{-1}) for diazenido-complexes

Complex	$\nu(N{=}N)$ [b]	Region of $\nu(C{-}N)$, $\nu(N{-}N)$ *etc.*
(*a*) Complexes of the type $[MBr\{N_2(CH_2)_nBr\}(dppe)_2]$		
(7) W, $n = 3$	1 510—1 480s,br	1 312s,br; 1 262m,br
(28) W, $n = 7$	1 530—1 480s,br	1 310s,br; 1 270s,br
(30) Mo, $n = 7$	1 510—1 500s,br	1 315s,br
(31) W, $n = 8$	1 530—1 500s,br	1 308s,br
(33) Mo, $n = 8$	1 560—1 500s,br	1 315s,br
(34) W, $n = 9$	1 530—1 490s,br	1 310s,br
(37) Mo, $n = 11$	1 560—1 500s,br	1 315s,br
(*b*) Complexes of the type $[(dppe)_2MBr\{(N_2CH_2)_nN_2\}MBr(dppe)_2]$		
(29) W, $n = 7$	1 530—1 490s,br	1 310s,br
(32) W, $n = 8$	1 530—1 490s,br	1 310s,br
(35) W, $n = 9$	1 535—1 480s,br	1 310s,br; 1 270w,br
(36) Mo, $n = 10$	1 560—1 500s,br	1 315s,br
(38) Mo, $n = 11$	1 550—1 500s,br	1 315s,br
(39) Mo, $n = 12$	1 560—1 500s,br	1 315s,br

[a] In KBr discs unless otherwise indicated; s = strong, m = medium, w = weak, br = broad. [b] This is a symmetrical strong broad peak, and very characteristic.

TABLE 8

Selected ^1H n.m.r. data for diazenido-complexes [a]

Complex	Solvent	CH_2Br (τ)	NCH_2 (τ)	Other organonitrogen protons
(*a*) Complexes of the type $[MBr\{N_2(CH_2)_nBr\}(dppe)_2]$				
(7) W, $n = 3$	C_6D_6	6.92t (2)	7.64t (2)	8.68—8.96m (2)
(28) W, $n = 7$	$CDCl_3$	6.56t (2)	7.76t (2)	8.01—8.42m, 8.56—8.84m, 8.92—9.61m (10)
(30) Mo, $n = 7$ [b]	CD_2Cl_2	6.57t (2)		7.92—8.30m, 8.35—9.65m (17)
(31) W, $n = 8$	CD_2Cl_2	6.56t (2)	7.72t (2)	8.01—8.28m, 8.56—8.82m, 8.96—9.44m (12)
(33) Mo, $n = 8$	CD_2Cl_2	6.60t (2)	8.17t (2)	8.20—9.63, several m (12)
(34) W, $n = 9$	CD_2Cl_2	6.60t (2)	7.76t (2)	8.00—8.32m, 8.60—8.96m, 9.02—9.56m (14)
(37) Mo, $n = 11$	CD_2Cl_2	6.55t (2)	8.09t (2)	8.30—9.70, several m (18)
(*b*) Complexes of the type $[(dppe)_2MBr\{N_2(CH_2)_nN_2\}MBr(dppe)_2]$				
(24) W, $n = 7$	CD_2Cl_2		7.34t (4)	8.97—9.65m (10)
(32) W, $n = 8$	CD_2Cl_2		7.69t (4)	8.93—9.57m (12)
(35) W, $n = 9$	CD_2Cl_2		7.65t (4)	8.93—9.09m, 9.13—9.57m (14)
(36) Mo, $n = 10$	CD_2Cl_2		8.05t (4)	8.52—9.52m (16)
(38) Mo, $n = 11$	CD_2Cl_2		8.08t (4)	8.43—9.73m (18)
(39) Mo, $n = 12$	CD_2Cl_2		8.06t (4)	8.42—9.60m (20)

[a] In all compounds, PCH_2CH_2P are found as a multiplet of correct intensity, $\tau = 6.8$—7.9; relative intensities in parentheses, t = triplet, m = multiplet. [b] NCH_2 obscured by dppe methylenes; ' other protons ' includes Pr^iOH alkyl protons.

The relationship between the ultimate structure formed and n in $Br(CH_2)_nBr$ is quite clear. For $n = 1$, the complexes formed are primarily diazoalkane complexes.[3,4] There are no products with organonitrogen moieties for $n = 2$, for well understood reasons.[2] For $n = 3$, the open-chain products are obtained, presumably because a ring, $-\overline{N(CH_2)_2CH_2}$, would be too strained. For $n = 4$ and 5, rings form, presumably exclusively, the driving force apparently being the same as for chelate-ring formation in complex chemistry. For $n = 6$—12, rings are apparently again not favoured and open-chain compounds form. Steric resistance to the formation of dinuclear complexes seems not to be significant, even though we did not isolate dinuclear complexes for $n = 3$. A dinuclear complex has been isolated in the case of $n = 1$.[4]

EXPERIMENTAL

Experiments were generally carried out under dry dinitrogen and in dioxygen-free solvents. Standard Schlenk-tube and vacuum techniques were employed for all manipulations. Carbon, hydrogen, nitrogen, and halogen analyses were by Mr. and Mrs. A. Olney in the School of Molecular Sciences, the University of Sussex. For spectroscopic studies the following instruments were used: Perkin-Elmer 577 (i.r.); JEOL PS100 (^1H n.m.r.); and JEOL PFT100 (^{13}C n.m.r.). Melting points were determined in air using a Reichert hot-stage microscope. Conductivities were measured with a Portland Electronics bridge in nitromethane solutions. Irradiations were carried out with two 150-W tungsten-filament lamps *ca.* 30 cm from the flask. The compounds $[M(N_2)_2(dppe)_2]$ were prepared by literature methods,[7] and the dibromides were obtained commercially.

Bis{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*(N-*pyrrolidinylimido*)*tungsten Bromide–Dichloromethane* (1/1.5) (1).—A solution of $[W(N_2)_2(dppe)_2]$ (1.0 g, 1.0 mmol) and $Br(CH_2)_4Br$ (0.12 cm^3, 1.0 mmol) in benzene (60 cm^3) was stirred under irradiation for 5 h. A brown-yellow *solid* separated, which was crystallised from a dichloromethane–hexane mixture to give golden leaflets, yield 0.87 g, 65%.

Bis{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*(N-*pyrrolidinylimido*)*molybdenum Bromide–Dichloromethane* (1/1.5) (2).—A solution of $[Mo(N_2)_2(dppe)_2]$ (1.0 g, 1.2 mmol) and $Br(CH_2)_4Br$ (0.14 cm^3) in benzene (50 cm^3) was stirred under irradiation for 4 h, and then in the dark for a further 9 h. The green-yellow *solid* which separated was filtered off and recrystallised from dichloromethane–hexane, yield 0.68 g, 60%.

Bis{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*(N-*piperidinoimido*)*tungsten Bromide–Dichloromethane* (1/2) (3).—The complex $[W(N_2)_2(dppe)_2]$ (1.0 g, 1.0 mmol) was dissolved in benzene (60 cm^3), $Br(CH_2)_5Br$ (0.14 cm^3, 1.0 mmol) was added, and the solution was stirred under irradiation for 6 h. A brown-yellow solid separated. The *solid* was filtered off, washed with benzene (3 × 5 cm^3), and crystallised from a dichloromethane–hexane mixture to give red needles, yield 0.98 g, 70%.

Bis{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*(N-*piperidinoimido*)*molybdenum Bromide* (4).—A solution of $[Mo(N_2)_2(dppe)_2]$ (1.0 g, 1.2 mmol) and benzene (50 cm^3) was mixed with $Br(CH_2)_5Br$ (0.17 cm^3, 1.2 mmol) and the solution irradiated for 2.5 h. After allowing to stand overnight, the mixture was filtered, and the *residue* washed with benzene, and dried *in vacuo*, yield 1.03 g, 75%.

Bis{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*{3-*bromopropylhydrazido*(2—)-N′}*tungsten Tetrafluoroborate–Diethyl Ether* (1/0.5) (5).—To a solution of $[W(N_2)_2(dppe)_2]$ (1.0 g, 1.0 mmol) in benzene (60 cm^3) was added $Br(CH_2)_3Br$ (0.1 cm^3, 1 mmol) and the solution was stirred under irradiation for 8 h. The solution was reduced to dryness *in vacuo*, the residue dissolved in benzene (30 cm^3) and treated with an excess of $HBF_4{\cdot}OEt_2$. Subsequent removal of the solvent and stirring in diethyl ether (25 cm^3) gave a brown-yellow solid which was extracted with methanol (40 cm^3). The insoluble yellow solid was filtered off. The methanolic solution was reduced *in vacuo* to *ca.* 20 cm^3, diethyl ether and hexane were added, and the mixture was stored at 0 °C overnight. An orange-yellow *solid* separated. Recrystallisation from a methanol–ether–hexane mixture gave maroon coloured plates, yield 0.77 g, 60%, m.p. 156—158 °C, Λ 76 ohm^{-1} cm^2 mol^{-1} (Found: C, 51.3; H, 4.45; Br, 12.1; N, 1.80. $C_{57}H_{60}BBr_2FN_2O_{4.5}P_4W$ requires C, 51.4; H, 4.20; Br, 12.0; N, 2.10%).

Bis{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*{3-*bromopropylhydrazido*(2—)-N′}*molybdenum Bromide* (6).—This was prepared by the same method as for (5), but with irradiation for 5 h. After reaction, the solution was filtered, and the *solid* recrystallised from methanol–diethyl ether–hexane as yellow crystals, yield 50%, m.p. 195—197 °C (Found: C, 54.2; H, 4.5; N, 2.40. $C_{55}H_{65}Br_3N_2P_4W$ requires C, 54.9; H, 4.6; N, 2.30%).

Treatment with $K_2[CO_3]$ in benzene and subsequent recrystallisation of the benzene-soluble portion from diethyl ether–hexane–benzene yielded an orange solid, which on the basis of analysis and i.r. spectrum appeared to be the 3-bromodiazenido-complex corresponding to (6). Alternatively, the benzene filtrate from the preparation of (6) was taken down dry and recrystallised from diethyl ether–hexane–benzene. This was an impure sample of the same diazenido-complex judged by analysis, and i.r. and ^1H n.m.r. spectra.

Bis{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*(3-*bromopropyldiazenido*)*tungsten* (7).—To a methanolic solution of (5) (0.10 g, 0.07 mmol) was added $K_2[CO_3]$ (0.096 g, 0.7 mmol) and the solution was stirred for 1 h. An orange-yellow *solid* separated, which was filtered off, washed with water (6 × 1 cm^3), methanol (6 × 2 cm^3), and pentane (3 × 1 cm^3), and dried *in vacuo* for 1 h, yield 0.059 g, 70%.

The molybdenum analogue was obtained in very low yield by a similar method, and was characterised by its ^1H n.m.r. spectrum.

Bis{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*{6-*bromohexylhydrazido*(2—)-N′}*tungsten Bromide–Methanol* (1/1) (8) *and* μ-[1,6-*Bis*{*hydrazido*(2—)-N′}*hexane*]-*bis*[*bis*{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromotungsten*] *Dibromide* (9).—A solution of $[W(N_2)_2(dppe)_2]$ (1.0 g, 1.0 mmol) and $Br(CH_2)_6Br$ (0.14 cm^3, 1.0 mmol) in benzene (60 cm^3) was stirred under irradiation for 8 h. The volume was reduced to *ca.* 30 cm^3 and gaseous HBr (2 mmol) was condensed into the solution at −196 °C on a vacuum line. The mixture was warmed to room temperature and left stirring for 1.5 h. The cloudy solution was evaporated to dryness *in vacuo* and the residue extracted with methanol (50 cm^3). A pink-brown *solid* was left behind, which was filtered off and crystallised from a dichloromethane–diethyl ether–hexane mixture as dark brown crystals of (9), yield 0.1 g, 8%.

The methanolic solution remaining after the isolation of (9) was reduced *in vacuo* to *ca.* 20 cm^3, diethyl ether (8 cm^3) and hexane (3 cm^3) added, and the mixture filtered. On keeping at 0 °C overnight, an orange-brown solid separated in low yield. It was filtered off and the filtrate reduced to dryness *in vacuo* to give a brown-yellow *product*. Crystallisation from a methanol–diethyl ether–hexane mixture gave golden brown crystals of (8), yield 0.7 g, 55%.

Bis{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*{6-*bromohexylhydrazido*(2—)-N′}*molybdenum Bromide* (10).—This was obtained similarly to (8), but with a shorter radiation time (5 h). There was no indication of a dinuclear species, and the *product* was recrystallised from methanol–diethyl ether–hexane as red crystals, yield 30%. The major product of the reaction was $[MoBr_2(dppe)_2]$.

Bis{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*{7-*bromoheptylhydazido*(2—)-N′}*tungsten Bromide* (11) *and* μ-[1,7-*Bis*{*hydrazido*(2—)-N′}*heptane*]*bis*[{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromotungsten*] *Dibromide* (12).—The reaction solution containing $[W(N_2)_2(dppe)_2]$ (0.8 g, 0.8 mmol) and $Br(CH_2)_7Br$ (0.14 cm^3, 0.08 mmol) in benzene (50 cm^3) was stirred under irradiation for 8 h. The solution was reduced *in vacuo* to *ca.* 30 cm^3, HBr gas (2 mmol) was introduced from a vacuum line and the mixture was left stirring for 0.5 h. The solution was evaporated to dryness *in vacuo* and the residue was dissolved in methanol (30 cm^3) and filtered off. To the methanolic solution, diethyl ether (10 cm^3) and hexane (6 cm^3) were added, when the solution turned slightly turbid. The solution was filtered and stored at 0 °C for 12 h. The *product* separated as a salmon coloured solid. Recrystallisation from a methanol–diethyl ether–hexane mixture gave salmon coloured crystals of (12), yield 0.46 g, 50%.

The remaining methanolic solution after the isolation of (12) was concentrated to dryness *in vacuo*; repeated crystallisation (three times) of the residual *solid* from a methanol–diethyl ether–hexane mixture yielded (11) as dark brown crystals, yield 0.18 g, 16%. Attempts to obtain the molybdenum analogues yielded only impure materials, and considerable amounts of [$MoBr_2(dppe)_2$].

Bis{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*{8-*bromooctylhydrazido*(2—)-N′}*tungsten Tetrafluoroborate–Diethyl Ether* (1/0.25) (13) *and* μ-[1,8-*Bis*{*hydrazido*(2—)-N′}*octane*}-*bis*[*bis*{1,2-*bis*(*diphenylpyosphino*)*ethane*}*bromotungsten*] *Bis*(*tetrafluoroborate*) (14).—A benzene solution of [$W(N_2)_2$(dppe)$_2$] (1.0 g, 1.0 mmol) and $Br(CH_2)_8Br$ (0.2 cm^3, 1 mmol) was stirred for 8 h under irradiation. Addition of an excess of $HBF_4{\cdot}OEt_2$ followed by removal of the solvent *in vacuo* and stirring in diethyl ether gave a brown-yellow solid. It was stirred in methanol (40 cm^3) for 0.5 h, the yellow solid which remained was filtered off. The filtrate was reduced *in vacuo* to *ca.* 25 cm^3, diethyl ether (10 cm^3) and hexane (5 cm^3) were added, and the solution was stored at 0 °C for 12 h. A *solid* (a) separated, which was isolated by filtration; the filtrate was preserved for further separation. Repeated crystallisation of (a) from a methanol–diethyl ether–hexane mixture afforded (14) as brick-red crystals, yield 0.7 g, 55%.

The filtrate was kept at 0 °C for 12 h. Some impurity separated, which was filtered off. The filtrate was reduced to dryness *in vacuo* and the *residue* crystallised twice from a methanol–ethane–hexane mixture to yield light brown crystals of (13), yield 0.16 g, 12%.

The molybdenum analogue of (13), compound (15), was obtained in similar fashion after 5 h irradiation. We also obtained an impure sample of the dinuclear analogue of (14). Yields were very low (10%).

Bis{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*{9-*bromononylhydrazido*(2—)-N′}*tungsten Tetrafluoroborate* (16) *and* μ-[1,9-*Bis*{*hydrazido*(2—)-N′}*nonane*]-*bis*[*bis*{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromotungsten*] *Bis*(*tetrafluoroborate*) (17).—The complex [$W(N_2)_2$(dppe)$_2$] (1.0 g, 1 mmol) and $Br(CH_2)_9Br$ (0.19 cm^3, 1 mmol) in benzene (60 cm^3) were stirred under irradiation for 8 h. An excess of $HBF_4{\cdot}OEt_2$ was added and the solution was stirred for 0.5 h. The volume was reduced to dryness *in vacuo* and the resultant buff coloured *solid* was stirred in diethyl ether (30 cm^3) and filtered off. Crystallisation from a methanol–ethane–hexane mixture gave brown crystals of (17), yield 0.4 g, 32%.

The remaining solution after the isolation of (17) was evaporated to dryness *in vacuo* and successive crystallisation (four times) of the residual *solid* from a methanol–diethyl ether–hexane mixture afforded pale brown crystals of (16), yield 0.25 g, 18%.

The synthesis of the molybdenum analogues of (16) and (17) was attempted, but the mononuclear complex could not be obtained pure. The dinuclear complex (18) was eventually obtained in 5% yield after many recrystallisations.

Bis{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*{10-*bromodecylhydrazido*(2—)-N′}*tungsten Tetrafluoroborate* (19) *and* μ-[1,10-*Bis*{*hydrazido*(2—)-N′}*decane*]-*bis*[*bis*{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromotungsten*] *Bis*(*tetrafluoroborate*)-*Dichloromethane* (1/0.25) (20).—The reaction solution containing [$W(N_2)_2$(dppe)$_2$] (1.0 g, 1.0 mmol) and $Br(CH_2)_{10}Br$ (0.31 g, 1.0 mmol) was stirred under irradiation for 8 h. The products in the reaction solution were protonated with an excess of $HBF_4{\cdot}OEt_2$. Removal of the solvent *in vacuo* and stirring in diethyl ether (30 cm^3) gave a light brown solid which was stirred in methanol (50 cm^3) at 50 °C for 0.5 h. The insoluble solid was filtered off. The methanolic solution was reduced *in vacuo* to *ca.* 25 cm^3 and stored at 0 °C for 12 h. A yellow-brown *solid* separated, which was isolated and crystallised from dichloromethane–hexane to give (20) as light pink crystals, yield 0.56 g, 45%.

To the methanolic filtrate obtained after the isolation of (20), diethyl ether (10 cm^3) and hexane (5 cm^3) were added, and the mixture was stored at 0 °C for 12 h. From this solution (19) separated as light brown crystals, yield 0.3 g, 21%.

Attempts to synthesise the molybdenum analogues of (19) and (20) were hampered by very low yields. A sample of the mononuclear complex was unequivocally identified by its ^{1}H n.m.r. spectrum, but not enough material was obtained for characterisation by normal methods. The dinuclear species (21) was isolated in 15% yield.

Bis{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*{11-*bromoundecylhydrazido*(2—)-N′}*tungsten Tetrafluoroborate* (22) *and* μ-[1,11-*Bis*{*hydrazido*(2—)-N′}*undecane*]-*bis*[*bis*{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromotungsten*] *Bis*(*tetrafluoroborate*) (23).—The complex [$W(N_2)_2$(dppe)$_2$] (1.0 g, 1.0 mmol) and $Br(CH_2)_{11}Br$ (0.32 g, 1.0 mmol) were stirred in benzene (60 cm^3) under irradiation for 8 h. Addition of an excess of $HBF_4{\cdot}OEt_2$ followed by removal of the solvent and stirring in diethyl ether (30 cm^3) gave a buff coloured solid. Extraction with methanol (80 cm^3) gave a brown solution and an insoluble solid which was filtered off. The methanolic solution was reduced *in vacuo* to *ca.* 40 cm^3 and stored at 0 °C for 12 h. The pink *crystals* of (23) were filtered off, washed with pentane (2 × 3 cm^3), and dried *in vacuo* for 1 h, yield 0.32 g, 26%.

The filtrate from the above product was reduced *in vacuo* to *ca.* 20 cm^3 and the solution was kept at 0 °C for 48 h. Complex (22) separated as brown *leaflets*, yield 0.4 g, 29%.

The molybdenum analogues were prepared by an essentially similar method, but with 4 h irradiation. The yields were 15% (24) and 20% (25).

μ-[1,12-*Bis*{*hydrazido*(2—)-N′}*dodecane*]-*bis*[*bis*{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromotungsten*] *Bis*(*tetrafluoroborate*) (26).—The complex [$W(N_2)_2$(dppe)$_2$] (1.0 g, 1.0 mmol) was dissolved in benzene (60 cm^3) and the solution was stirred under irradiation for 8 h. An excess of $HBF_4{\cdot}OEt_2$ was added and the solution was stirred for 0.5 h. Reducing the volume to dryness *in vacuo* followed by stirring in diethyl ether (30 cm^3) afforded a buff coloured *solid*. Crystallisation from a methanol–diethyl ether–hexane mixture gave light brown crystals. From the filtrate more product was isolated, yield 0.48 g, 38%.

The molybdenum analogue was obtained by an essentially similar method [complex (27)]. In neither molybdenum nor tungsten series was a clean mononuclear complex obtained. The following are specific examples of the general synthesis of tungsten diazenido-complexes by the deprotonation of the corresponding hydrazido(2—)-complexes.

Bis{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*(7-*bromoheptyldiazenido*)*tungsten* (28).—Potassium carbonate (0.096 g, 0.7 mmol) was added to a methanolic solution of (11) (0.1 g, 0.07 mmol). Immediately an orange-yellow solid separated; the mixture was stirred for 0.5 h. The reaction solution containing the orange-yellow solid was reduced to dryness *in vacuo*, the resultant solid was extracted with benzene (8 cm^3), and filtered off. Removal of the solvent *in vacuo* gave a red oil, which was dissolved in benzene (0.2 cm^3), diethyl ether (5 cm^3) and hexane (1 cm^3) were added, and the mixture was stored at 0 °C for 48 h. A pale yellow *solid* separated, which was filtered off. Finally, removal of the solvent *in vacuo* and stirring in hexane gave an orange solid, yield 0.05 g, 60%.

{μ-1,7-*Bis*(*diazenido*)*heptane*}-*bis*[*bis*{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromotungsten*] (29).—A solution of (12) (0.175 g, 0.07 mmol) and $K_2[CO_3]$ (0.096 g, 0.7 mmol) in methanol (30 cm^3) was stirred for 0.5 h. The solution containing the orange solid was evaporated to dryness *in vacuo*, the residue was extracted with benzene (10 cm^3) and filtered off. The filtrate was concentrated to *ca.* 5 cm^3 *in vacuo*, diethyl ether (4 cm^3) and hexane (1 cm^3) were added, and the volume reduced to *ca.* 6 cm^3 *in vacuo*, when some orange *crystals* appeared. The sample was stored at 0 °C for 12 h. The product separated as orange-red needles, yield 0.096 g, 60%.

The following complexes were prepared by essentially similar methods in almost identical yields (see also Table 4); (31) from (13), (32) from (14), (34) from (16), and (35) from (17).

The molybdenum complexes were more difficult to obtain because of significantly smaller yields and greater sensitivity to air. Often we obtained impure materials which, principally on ^{1}H n.m.r. evidence, apparently contained the required product, but could not be purified. Compounds (33) and (39) were obtained by deprotonation of (15) and (27), respectively. Compound (30) was obtained directly from the reaction of $[Mo(N_2)_2(dppe)_2]$ with $Br(CH_2)_7Br$ in benzene. The major product was $[MoBr_2(dppe)_2]$, and (30) was eventually obtained by recrystallisation of the residue from the evaporated mother-liquors from isopropanol. Complexes (37) and (38) were obtained analogously with recrystallisation from benzene–isopropanol. Finally, (36) was also obtained in this way, with recrystallisation from ethanol.

Analyses and spectra were frequently complicated by the tendency of all these compounds to retain solvent molecules in the crystal lattice, and by a reluctance to crystallise.

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