The Formation of Diazoalkane and Diazenido-complexes from the Reaction of Methyl Bromide with *trans*-Bis[1,2-bis(diphenylphosphino)ethane]bis(dinitrogen)tungsten in Various Solvents

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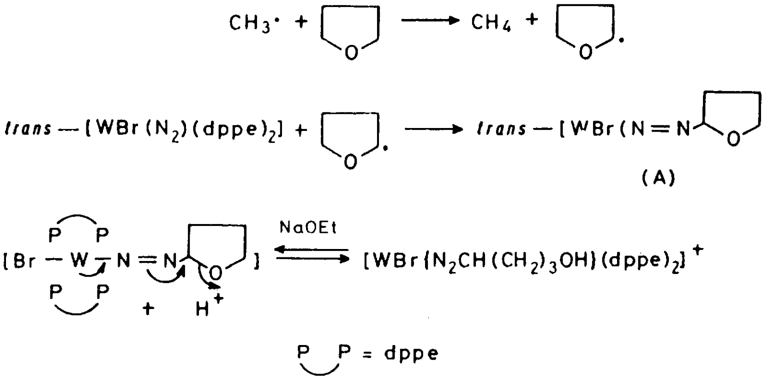
The reaction of *trans*-[$W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2$] with MeBr in solvents such as tetrahydrofuran, 2-methyltetrahydrofuran, and tetrahydropyran leads to new diazenido-complexes *via* a route which is now well understood. These new complexes undergo reversible ring opening with protic acids to yield substituted-diazoalkane complexes. *N*-Methylpyrrolidine and tetrahydrothiophen similarly form diazenido-derivatives, which react with acids to form hydrazido(2−)-compounds and do not undergo ring opening.

We have recently shown that the reaction of MeBr with *trans*-[$W(N_2)_2(dppe)_2$] [dppe = 1,2-bis(diphenylphosphino)ethane] in both benzene[1] and tetrahydrofuran (thf)[2] proceeds *via* rate-determining loss of N_2, co-ordination of MeBr to *trans*-[$W(N_2)(dppe)_2$], and homolysis of the carbon–bromine bond to form a methyl radical and [$WBr(N_2)(dppe)_2$].[3] In thf, the methyl radical attacks the solvent and the solvent radical then reacts to give a diazenido-complex, and, upon subsequent protonation, a diazobutanol complex [reaction sequence (1)].[2,3] This paper reports on the general reactions of MeBr and *trans*-[$W(N_2)_2(dppe)_2$] in a range of solvents containing hydrogen atoms susceptible to abstraction by free radicals.



(1)

RESULTS AND DISCUSSION

(a) *Ethers*.—(i) *Preparative reactions*. Reactions of *trans*-[$W(N_2)_2(dppe)_2$] with methyl bromide or iodide have been attempted in trimethylene oxide, tetrahydrofuran, methyltetrahydrofuran, dihydropyran, and 1,4-dioxan. The trimethylene oxide reaction failed owing to lack of solubility of [$W(N_2)_2(dppe)_2$] in the oxide and dihydropyran gave methane but no identifiable solid product. The reactions in thf and methyltetrahydrofuran have been described earlier.[2] We have now prepared analogous diazoalkanol products from tetrahydropyran and 1,4-dioxan [compounds (II), (III), and (IV) in Tables 1 and 2]. During the preparative reactions CH_4 was evolved, which is consistent with methyl radical attack on the solvent.

Presumably, intermediates such as (A) in reaction sequence (1) [(V) in Table 2] or its analogues are formed prior to protonation in all three cases. We isolated the intermediates from reactions involving tetrahydropyran and 1,4-dioxan and also by treatment of the diazoalkanol complexes with sodium ethoxide. They are

Table 1

Diazenido- and diazoalkane complexes of tungsten

	Complex	Colour	M.p. (°C)	Analysis (%) C	H	N
(III)	[$WBr\{N_2CH(CH_2)_4OH\}(dppe)_2$][$BF_4$]	Green	217	53.8 (54.3)	4.92 (4.63)	2.15 (2.22)
(IV)	[$WBr\{N_2CHCH_2O(CH_2)_2OH\}(dppe)_2$][$PF_6$]·$0.5CH_2Cl_2$	Brown	217	49.1 (49.8)	4.35 (4.22)	2.13 (2.06)
(VI)	[$WBr\{N_2CHO(CH_2)_3CH_2\}(dppe)_2$]	Orange	184—186	58.2 (58.5)	4.85 (5.13)	2.37 (2.35)
(VII)	[$WBr\{N_2CHO(CH_2)_2OCH_2\}(dppe)_2$]	Orange	188	55.8 (56.7)	4.79 (4.89)	2.16 (2.32)
(IX)	[$WBr\{N_2H(CH_2)_5OH\}(dppe)_2$]Br	Rose	218	55.2 (55.2)	5.21 (4.84)	2.26 (2.26)
(X)	[$WBr\{N_2H(CH_2)_2O(CH_2)_2OH\}(dppe)_2$]Br·2MeOH	Brown	231—233	52.7 (52.7)	5.06 (5.03)	2.27 (2.17)
(XI)	[$WBr\{N_2HCHS(CH_2)_2CH_2\}(dppe)_2$][$BF_4$]	Brown	149—152	53.5 (53.3)	4.80 (4.44)	1.81 (2.22)
(XII)	[$WF\{N_2HCHNMe(CH_2)_2CH_2\}(dppe)_2$]Br	Tan	167—169	53.0 (53.9)	5.05 (4.84)	2.52 (3.25)

TABLE 2

Selected spectral data of new complexes

	Solvent	¹H n.m.r.*				¹³C n.m.r.†					Solvent	I.r. (cm⁻¹) ‡
(I) $[\mathrm{WBr(N{-}N{=}\overset{a}{C}H\overset{b}{C}H_2\overset{c}{C}H_2\overset{d}{C}H_2OH)(dppe)_2]Br}$	$CDCl_3$	a 4.38t	b 8.96m	c 8.68m	d 6.58t	a 171.4	b 32.0	c 31.6	d 61.3		$CDCl_3$	1 572s, 1 315w (Nujol)
(II) $[\mathrm{WBr(N{-}N{=}\overset{a}{C}Me\overset{b}{C}H_2\overset{c}{C}H_2\overset{d}{C}H_2OH)(dppe)_2]Br}$	CD_2Cl_2	Me 10.73m	b 8.70m	c 8.70m	d 6.39t	a 171.8	b 35.4	c 28.4	d 61.7	Me 19.2	CD_2Cl_2	1 570s, 1 310m (Nujol)
(III) $[\mathrm{WBr(N{-}N{=}\overset{a}{C}H\overset{b}{C}H_2\overset{c}{C}H_2\overset{d}{C}H_2\overset{e}{C}H_2OH)(dppe)_2]Br}$	CD_2Cl_2	a 4.27t	b,c,d: 8.92—8.66m,br		e 6.38t	a 171.0	b,c,d: 33.4	21.0	31.8	e 61.7	CD_2Cl_2	1 570s, 1 308w (Nujol)
(IV) $[\mathrm{WBr(N{-}N{=}\overset{a}{C}H\overset{b}{C}H_2O\overset{c}{C}H_2\overset{d}{C}H_2OH)(dppe)_2]}$-$[\mathrm{PF_6}]\cdot0.5\mathrm{CH_2Cl_2}$	CD_2Cl_2	a 4.32t	b,c,d: 7.07d, 6.88t, 6.69t, 6.38t		d	a 167.2	b,c: 78.5, 72.8, 70.0, 66.8, 65.3, 63.7		d 61.6		CD_2Cl_2	1 578s, 1 565m, 1 308m (Nujol)
(V) $[\mathrm{WBr(N_2\overset{a}{C}HO\overset{d}{C}H_2\overset{c}{C}H_2\overset{b}{C}H_2)(dppe)_2]}$	$CDCl_3$	a 5.91t	b,c: 9.03m, 8.70m §		d 6.87m, 6.4m	a 88.7	b,c: 29.7, 25.4		d 66.8		C_6D_6	1 460s, 1 310w (KBr)
(VI) $[\mathrm{WBr(N_2\overset{a}{C}HO\overset{e}{C}H_2\overset{d}{C}H_2\overset{c}{C}H_2\overset{b}{C}H_2)(dppe)_2]}$	C_6D_6	a 6.11dd J = 2 Hz, 4 Hz	b,c,d: 9.27—8.34m, 7.91m		e 6.63d, 7.13d J = 11 Hz	a 85.4	b,c,d: 30.2	25.9	22.3	e 64.3	C_6D_6	1 455s, 1 315w, 1 330w (KBr)
(VII) $[\mathrm{WBr(N_2\overset{a}{C}HO\overset{d}{C}H_2\overset{c}{C}H_2O\overset{b}{C}H_2)(dppe)_2]}$	C_6D_6	a 6.08dd J = 3 Hz, 9 Hz	b,c: 9.62—7.68m, 7.94m		d 6.56dd, J = 3 Hz, 9 Hz 6.82dd, J = 3 Hz, 3 Hz							1 450s, 1 310m (KBr)
(VIII) $[\mathrm{WBr(N_2H\overset{a}{C}H_2\overset{b}{C}H_2\overset{c}{C}H_2\overset{d}{C}H_2OH)(dppe)_2]Br}$	CD_2Cl_2	a 8.06dt ¶	b,c: 9.10m, 9.22m		d 6.59t	a 46.6	b 29.4	c 24.3	d 60.5		CD_2Cl_2	1 338m, 1 310w (Nujol)
(IX) $[\mathrm{WBr(N_2H\overset{a}{C}H_2\overset{b}{C}H_2\overset{c}{C}H_2\overset{d}{C}H_2\overset{e}{C}H_2OH)(dppe)_2]Br}$	CD_2Cl_2	a 8.24dt ¶	b,c: 9.36m,br		d 8.77m, e 6.56t	a 47.0	b 27.2	c 23.0	d 32.3	e 61.2	CD_2Cl_2	1 332m, 1 310w (Nujol)
(X) $[\mathrm{WBr(N_2H\overset{a}{C}H_2\overset{b}{C}H_2O\overset{c}{C}H_2\overset{d}{C}H_2OH)(dppe)_2]Br}$	CD_2Cl_2	a 8.12dt ¶	b 7.27t	c 6.39t	d 6.35t	a 45.4	b,c,d: 72.6	67.0	60.7		CD_2Cl_2	1 330m, 1 310m (Nujol)
(XI) $[\mathrm{WBr(N_2H\overset{a}{C}HS\overset{d}{C}H_2\overset{c}{C}H_2\overset{b}{C}H_2)(dppe)_2][BF_4]}$	CD_2Cl_2	a 5.99m	b 8.98m	c 8.55m	d 6.66m, 6.43m	a 100.4	b 37.1	c 28.3	d 65.3		$CDCl_3$	1 312w, 1 286w (KBr)
(XII) $[\mathrm{WF(N_2H\overset{a}{C}HNMe\overset{d}{C}H_2\overset{c}{C}H_2\overset{b}{C}H_2)(dppe)_2]Br}$	CH_2Cl_2	a 5.82m	b 8.46m	c 8.07m	d 6.52m, Me 6.35s	a 99.5	b,c: *ca.* 31.5		d 65.2	Me 46.7	CH_2Cl_2	1 310w (Nujol)

* In τ, d = doublet, t = triplet, m = multiplet, br = broad. † In p.p.m. downfield from tetramethylsilane. ‡ Regions ν(N=N) or ν(C=N) and ν(N–N) or ν(C–N). § Overlap with phosphine methylene. ¶ Upon addition of CD_3OD, dt ⟶ t; also for (X), broad singlet at τ = 6.00 disappears (N*H*), N*H* not unambiguously identified for (VIII) and (IX).

analogous to the thf product (V) [compounds (VI) and (VII)].

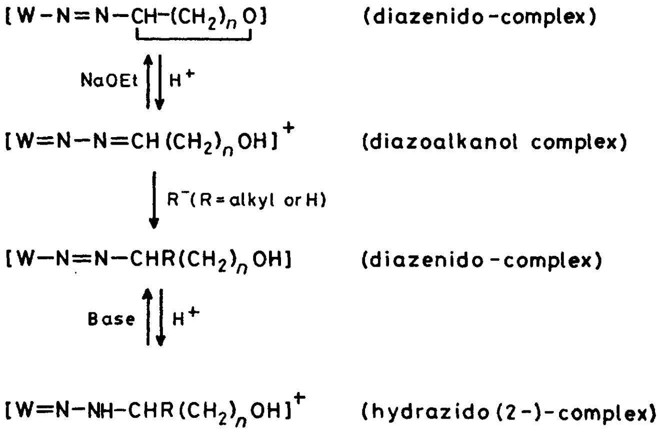
We also attempted similar hydrogen abstraction reactions using styrene oxide and cyclohexane, both of which should be reactive to judge from their established[4] reactivities towards hydrogen abstraction by $Me_3CO\cdot$. Lack of solubility hindered experiments in cyclohexane, and even from a mixture of benzene–cyclohexane (2 : 1) only a trace of methane was detected and the ' normal ' diazenido-product *trans*-$[WBr(N_2Me)(dppe)_2]$ was isolated. Reaction in styrene oxide gave no detectable CH_4 and a stable product could not be isolated.

(ii) *Spectral properties.* The i.r., ^1H n.m.r., and ^{13}C n.m.r. spectra are summarised in Table 2, which also includes data for the compounds derived from thf.[2] The diazoalkanol complexes generally show a band in the i.r. spectrum at *ca.* 1 570 cm^{-1} which we assign to ν(C=N) and another at *ca.* 1 310 cm^{-1} assigned to ν(N=H). The OH group produces a band at *ca.* 3 300 cm^{-1}. Each diazoalkanol complex except (II) has a triplet pattern in the ^1H n.m.r. spectrum at τ = *ca.* 4.3 characteristic of the unique –N=C*H*, and each of the complexes gives rise to a resonance in the ^{13}C n.m.r. spectrum at 170—178 p.p.m. downfield from tetramethylsilane (tms) which is characteristic of the unique carbon of diazoalkane complexes. The proton resonance at τ = *ca.* 6.4 (^{13}C n.m.r. resonance at *ca.* 61 p.p.m. downfield from tms) is assigned to the CH_2–OH group. We were generally unable to see OH in the ^1H n.m.r. spectra. The spectra are summarised in Table 2 and n.m.r. assignments were made on the basis of decoupling measurements.

The ^1H n.m.r. spectrum of complex (IV) contains more resonances than expected. The analysis is good, and the i.r. and ^{13}C n.m.r. spectra are consistent with the formulation as a diazoalkanol complex. The triplet at τ = 4.32 in the n.m.r. spectrum (which is coupled to the doublet at τ = 7.07) suggests that only one complex is present. However, the CH_2–OH resonance appears as two triplets (τ = 6.69 and 6.88). This may be due to isomerism about the N=C bond which does not, however, occur in the solid state. *X*-Ray structural analysis[5] shows that one of the substituents on the carbon in these compounds is forced between phenyl groups of the dppe, and experiences considerable steric repulsion. Only small groups can take up this position, and we have been unable to synthesise complexes $[WBr(N_2CR^1R^2)(dppe)_2]^+$ unless at least one of the substituents R^1 and R^2 is hydrogen or methyl.[6,7]

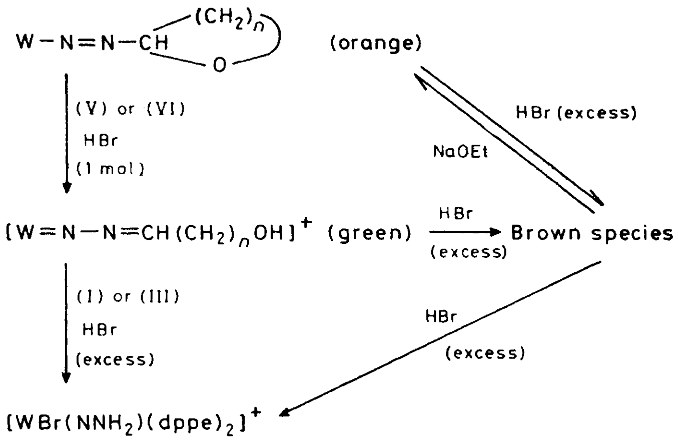
The spectra of the diazenido-complexes which are precursors of the diazoalkanol complexes [compounds (V), (VI), and (VII) in Table 1] are also in Table 2. The complexes are characterised by i.r. bands at *ca.* 1 450 cm^{-1}, which we assign to ν(N=N), although this is some 60 cm^{-1} lower than the comparable band in the alkyldiazenido-complexes. In the ^1H n.m.r. spectra, the unique C*H* of the ring is easily assigned to the resonance at τ = *ca.* 6. The other resonances are assigned on the basis of decoupling experiments. The shapes of the phenyl resonances, with a low field multiplet, are characteristic of the diazenido-complexes in general, and quite distinct from those of the diazoalkane complexes or hydrazido(2—)-complexes. They are, in fact, diagnostic of compound type. The ^{13}C n.m.r. spectra are quite consistent with our structural assignment.

The open-chain hydrazido(2—)-complexes (IX) and (X) have spectra very similar to those of (VIII) which have been previously described (see Table 2) and they will not be discussed further.



SCHEME 1

(iii) *Reactions.* The diazenido-, hydrazido(2—)-, and diazoalkane complexes have reactions with acids, bases, and nucleophilic reagents which are characteristic of each class of compounds (see Scheme 1). Nevertheless, there are interesting complications. For example, unsubstituted diazoalkane complexes such as $[WBr(N_2CMe_2)(dppe)_2]Br$ and $[WBr(N_2CHMe)(dppe)_2]Br$ are unreactive towards an excess of hydrogen bromide at room temperature, and can be removed unchanged from solutions in dichloromethane after several days.[6,7] The thf and tetrahydropyran derivatives (I), (III), (V), and (VI) react with hydrogen bromide in a more complex fashion (Scheme 2).



SCHEME 2

Complexes (I) and (III) react with a ten-fold excess of hydrogen bromide in dichloromethane at room temperature, turning from green to brown. The reaction of (I) is very slow, whereas that of (III) is complete within 30 min. In both cases [WBr(NNH$_2$)(dppe)$_2$]Br is formed ultimately. This suggests that the acid-catalysed condensation route [reaction (2)] to diazoalkane complexes is reversible.[6-8] The reactions of the diazenido-complexes (V) and (VI) with acid can also yield the hydrazido(2—)-complex. A comparable decomposition

$$\text{M=N-NH}_2 + \text{OCR}^1\text{R}^2 \rightleftharpoons \text{M=N-N=CR}^1\text{R}^2 + \text{H}_2\text{O} \quad (2)$$

of the unsubstituted diazoalkane complex *trans*-[WBr(N$_2$CHMe)(dppe)$_2$]Br takes several hours in a sealed tube at 80 °C. Among the products are MeCHBr$_2$ and (Hdppe)Br. Under these conditions *trans*-[WBr(NNH$_2$)(dppe)$_2$]Br decomposes [equation (3)]. The easy de-

$$[\text{WBr(NNH}_2\text{)(dppe)}_2]\text{Br} \xrightarrow[\text{80°C, 15 h}]{\text{HBr, CH}_2\text{Cl}_2} \text{` W species '} + \text{NH}_3\text{(0.40 mol)} + \text{N}_2\text{H}_4\text{ (0.44 mol)} + \text{(Hdppe)Br} \quad (3)$$

gradation with an excess of HBr seems confined to the diazoalkanol complexes.

We attempted to isolate the brown species indicated in Scheme 2 by rapid removal of volatiles after the initial colour change occurred upon addition of an excess of HBr to (V) and (VI). In both cases, some [WBr(NNH$_2$)(dppe)$_2$]Br was obtained, together with a new dark brown material. The brown materials both show ν(C=N) in their i.r. spectra, at the same positions as in (I) and (III). The ^{13}C and ^{1}H n.m.r. spectra are virtually superimposable upon those of the green diazoalkanol complexes. The compounds analyse for the same stoicheiometric formulae as the green diazoalkanol complexes, (I) and (III), and they are converted by base into the same diazenido-complexes (V) and (VI). They are apparently isomers of the green diazoalkanol complexes.

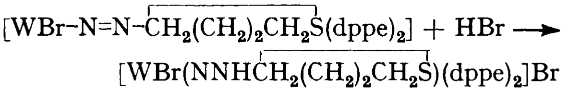
The 1,4-dioxan derivatives (IV) and (VII) also react with an excess of gaseous HBr at room temperature to give a new tan-coloured material (XIII) which is a 1 : 1 electrolyte in MeNO$_2$. This has spectra quite distinct from the diazoalkanol analogues. There is no triplet at τ = *ca.* 4.3, characteristic of N=C*H*–, though there is one at τ = 5.82 (intensity $\frac{1}{2}$). The other resonances are at τ = 6.35s,br (intensity 2), 6.49m,br (intensity 1), 6.9t (intensity 2), 8.08m (intensity 1), 8.52m (intensity 1), and 4.23s,br (intensity $\frac{1}{2}$). These resonances change upon adding CD$_3$OD to the test solution, those at τ = 4.23 and 6.49 disappearing and those at 8.08 and 8.52 sharpening. The lost resonances are assigned to OH and NH, and there are 6—7 protons on an organonitrogen chain. In the ^{13}C n.m.r. spectrum, there are resonances at —65.5 and —60.0 p.p.m. only. This implies considerable symmetry in the organonitrogen ligand. Elemental analysis shows that (XIII) contains only one bromine atom per tungsten.

Treatment of (XIII) with NaOEt generates a new diazenido-complex [ν(N=N) = 1 508 cm^{-1}] to judge from the i.r. spectrum, but the phenyl region in the ^{1}H n.m.r. spectrum is atypical. Evidently we are observing some new transformation of the organonitrogen ligand, and its precise nature is currently under investigation.

Diazoalkane complexes have been shown to be susceptible to attack by nucleophiles at the unique diazoalkane carbon.[6] Thus, the diazoalkanol compounds (III) and (IV) react with Li[AlH$_4$] to yield diazenido-complexes which then protonate at the diazenido-nitrogen to yield the hydrazido(2—)-complexes (IX) and (X).

Non-substituted diazoalkane complexes react with alkoxide ions OR$^-$ either to yield alkoxydiazenido-complexes, or to cleave the =N–N=C carbon–nitrogen bond, depending upon R and the substituents on the diazoalkane carbon.[6,7] We find here [7,9] that this cleavage is particularly easy, and that the deprotonation reactions of (I) to yield (V) are always accompanied by the formation of *trans*-[W(N$_2$)$_2$(dppe)$_2$] when these reactions are carried out under N$_2$. That this is a direct reaction and not some product of generalised decomposition was proved by reaction of (I) enriched with ^{15}N when we isolated [W(^{14}N$_2$)(^{15}N$_2$)(dppe)$_2$]. The mechanism apparently involves nucleophilic attack by alkoxide on the diazoalkane carbon, and will be discussed elsewhere.[7]

(b) *Cyclic Sulphides.*—The reaction of [W(N$_2$)$_2$(dppe)$_2$] with methyl bromide in tetrahydrothiophen followed by treatment with HBF$_4$ affords the yellow-brown complex (XI). This is not a diazoalkane complex (no ^{1}H n.m.r. signal at τ = *ca.* 4.3), but there is a broad triplet centred at τ = 5.99 in the ^{1}H n.m.r. spectrum suggesting that the ring is still intact. Similarly, in the ^{13}C n.m.r. spectrum there is no resonance at *ca.* 170 p.p.m. downfield from tms, where we expect to find the unique diazoalkane carbon resonance. Evidently, the ring structure, analogous to that of (V), is retained, and the diazenido-complex simply protonates on the nitrogen remote from the metal [reaction (4)].



$$[\text{WBr-N=N-CH}_2\text{(CH}_2\text{)}_2\text{CH}_2\text{S(dppe)}_2] + \text{HBr} \longrightarrow [\text{WBr(NNHCH}_2\text{(CH}_2\text{)}_2\text{CH}_2\text{S)(dppe)}_2]\text{Br} \quad (4)$$

(c) *Cyclic Amines.*—The reactions of *trans*-[W(N$_2$)$_2$(dppe)$_2$] with cyclic amines were inhibited by the lack of solubility of the tungsten complex. The use of mixed solvents was not markedly more successful. However, *N*-methylpyrrolidine did react yielding a complex after protonation, which on the basis of its analysis and spectra, must be the ring compound (XII). Addition of acid again does not open the ring. We attempted to convert this material into the tetrafluoroborate salt by reaction with Ag[BF$_4$]. The crude material contained the [BF$_4$]$^-$ ion (i.r. spectrum) but the recrystallised material did not. The ^{31}P n.m.r. spectrum of the pure product showed a singlet resonance (112.7 p.p.m. downfield from trimethyl phosphite) characteristic of four equivalent phosphorus atoms, together with tungsten satellites ($|^1J_{\text{WP}}|$ = 297.4 Hz) further split into a doublet ($|^2J_{\text{FP}}|$ = 42.7 Hz) which other workers[10] have shown to be characteristic of co-ordinated fluoride. This new product is apparently $[\mathrm{WF\{N_2H\overline{CNMe(CH_2)_2CH_2}\}(dppe)_2]Br}$ and is of interest because metathesis of anions in tungsten *trans*-bis(dppe) complexes is normally a very slow process.

We have shown that abstraction of hydrogen atoms by radicals generated from $[\mathrm{W(N_2)_2(dppe)_2}]$ and MeBr can lead to novel products, diazenido-complexes containing a cyclic ether, sulphide, or amine in place of the more usual alkyl group. Treatment of the ether products with acid leads to ring opening and the formation of new diazoalkane complexes. The cyclic sulphides and amines do not undergo ring-opening. We are now intending to extend these abstraction reactions to open-chain compounds.

EXPERIMENTAL

All manipulations were carried out under pure, dry dinitrogen, using standard Schlenk-tube and vacuum-line techniques. Solvents were purified before use by distillation from suitable drying agents under N_2. All protonation reactions and additions of alkyl halide were carried out using a vacuum line. Spectra were generally obtained as follows: i.r., Perkin-Elmer 457; ^{1}H n.m.r., JEOL PS-100; ^{13}C n.m.r., JEOL PFT-100. Conductivities were measured using a Portland Electronics bridge and melting points were obtained using a Reichert hot-stage microscope in air, and are uncorrected.

The complexes were prepared according to published techniques: $[\mathrm{W(N_2)_2(dppe)_2}]$,[11] (I),[2] (V),[2] and (VIII).[2]

trans-*Bis*{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*(5-*diazo-pentan*-1-*ol*-N^2)*tungsten Bromide and Tetrafluoroborate* (III).—A mixture of *trans*-$[\mathrm{W(N_2)_2(dppe)_2}]$ (0.87 g, 0.87 mmol) and MeBr (0.086 g, 0.90 mmol) dissolved in tetrahydrofuran (200 cm^3) was stirred at room temperature for 15.5 h under irradiation.* The resultant yellow solution was reduced to *ca.* 50 cm^3 *in vacuo* and HBr (0.90 mmol) added by vacuum line at −196 °C. On warming to room temperature a grey precipitate formed. This was filtered off, washed with thf and ether, and dried (yield 0.91 g, 0.73 mmol, 84%). Methane was produced during the reaction. The compound was converted quantitatively into the fluoroborate salt as follows: *ca.* 0.5 g of product was dissolved in MeOH (15 cm^3) and an equimolar amount of $\mathrm{Ag[BF_4]}$ added. The precipitate was rejected, and the filtrate reduced in volume to *ca.* 10 cm^3 *in vacuo*. Addition of ether and hexane gave green *crystals* which were filtered off, washed with hexane (3 × 10 cm^3), and dried *in vacuo*.

trans-*Bis*{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*(5-*diazo*-3-*oxapentan*-1-*ol*-N^2)*tungsten Hexafluorophosphate–Dichloromethane* (1/0.5) (IV).—The complex *trans*-$[\mathrm{W(N_2)_2(dppe)_2}]$ (1.00 g, 0.99 mmol) was dissolved in freshly distilled 1,4-dioxan and MeBr (0.096 g, 1.0 mmol) added at −196 °C on a vacuum line. The mixture was warmed to room temperature and irradiated for 19.5 h, during which time methane was evolved. The solution was reduced to dryness *in vacuo* affording an orange oil, which was dissolved in thf (50 cm^3) and HBr (1.5 mmol) added on a vacuum line. On warming to room temperature the solution became dark brown, and was stirred for 10 min before the solvent was removed *in vacuo*. The resultant brown oil was extracted with MeOH (3 × 10 cm^3), the extract filtered, reduced *in vacuo* to 10 cm^3, and ether and hexane added to produce an oily *product* which was washed well with hexane and dried (yield *ca.* 1.1 g, 1.0 mmol).

The crude product was dissolved in MeOH (15 cm^3) and an equimolar amount of $\mathrm{Ag[PF_6]}$ added. The mixture was filtered, the filtrate reduced to dryness *in vacuo*, and extracted with MeOH (3 × 10 cm^3). The extracts were reduced *in vacuo* to *ca.* 12 cm^3, and brown crystals produced with ether and hexane. Subsequent recrystallisation from $\mathrm{CH_2Cl_2}$–hexane produced the product as large brown *crystals*. The tetrafluoroborate salt was prepared analogously using $\mathrm{Ag[BF_4]}$: m.p. 196 °C (*in vacuo*) (Found: C, 53.5; H, 4.47; Br, 6.3; N, 2.25. $\mathrm{C_{56}H_{56}BBrF_4N_2O_2P_4W}$ requires C, 53.2; H, 4.47; Br, 6.3; N, 2.22%.

trans-*Bis*{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*(N-*tetrahydropyran*-2-*yldiazenido*-N′)*tungsten* (VI).—Compound (III) ($\mathrm{PF_6}$ salt) (0.31 g, 0.24 mmol) was dissolved in MeOH (10 cm^3) and an excess of NaOEt added. The solution became green-yellow, and was evaporated to dryness *in vacuo*. The residue was extracted with benzene (3 × 10 cm^3) and reduced *in vacuo* to 5 cm^3; addition of MeOH (8 cm^3) and hexane (5 cm^3) and reduction in volume produced large orange needle-like *crystals* (0.24 g, 84%).

trans-*Bis*{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*(N-*dioxan*-2-*yldiazenido*-N′)*tungsten* (VII).—This compound was prepared similarly from (IV) ($\mathrm{PF_6}$ salt), and recrystallised from benzene–MeOH as orange needle-like *crystals* (92%).

trans-*Bis*{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*{N-5-*hydroxypentanylhydrazido*(2−)-N′}*tungsten Bromide* (IX).—Compound (III) (bromide salt) (0.30 g, 0.24 mmol) was suspended in ether (40 cm^3) and an excess of $\mathrm{Li[AlH_4]}$ added. After 1.5 h, water was added dropwise until effervescence ceased, and the solution was reduced to dryness *in vacuo*. The product was extracted with benzene (2 × 20 cm^3), the extracts reduced to 15 cm^3 *in vacuo*, and HBr (0.5 mmol) added to produce rose-coloured *crystals* (0.29 g, 96%).

trans-*Bis*{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*{N-5-*hydroxy*-3-*oxapentanylhydrazido*(2−)-N′}*tungsten Bromide–Methanol* (1/2) (X).—This compound was prepared as (IX) above from (IV) (bromide salt), except that protonation produced a red, oily precipitate. This was recrystallised from MeOH–ether–hexane to give large brown crystals (yield 80%).

trans-*Bis*{1,2-*bis*(*diphenylphosphino*)*ethane*}*bromo*{N-*thiolan*-2-*ylhydrazido*(2−)-N′}*tungsten Tetrafluoroborate* (XI).—This compound was prepared similarly to (III) from *trans*-$[\mathrm{W(N_2)_2(dppe)_2}]$ (0.68 g, 0.68 mmol) and MeBr (0.066 g, 0.70 mmol) in tetrahydrothiophen (200 cm^3). The mixture was irradiated for 17 h, and protonated with $\mathrm{HBF_4}$–ether. The *product* was purified by recrystallisation from MeOH–ether–hexane; chromatography on silica gel with EtOH eluant (which gave an orange fraction), and crystallisation after addition of ether and hexane (yield 0.19 g, 27%).

trans-*Bis*{1,2-*bis*(*diphenylphosphino*)*ethane*}*fluoro*[N-{2-(N-*methylpyrrolidinyl*)}*hydrazido*(2−)-N′]*tungsten Bromide* (XII).—The compound *trans*-$[\mathrm{W(N_2)_2(dppe)_2}]$ (0.90 g, 0.90 mmol), MeBr (0.086 g, 0.90 mmol), and *N*-methylpyrrolidine (180 cm^3) were irradiated for 4 d, during which time some methane was evolved. The mixture was filtered, reduced to dryness *in vacuo*, dissolved in benzene, and $\mathrm{HBF_4}$–ether added. Removal of volatiles *in vacuo* gave a brown oil. This was extracted with MeOH (3 × 20 cm^3) and the extracts gave a brown oil (0.52 g) on addition of ether and hexane. The oil contained $[\mathrm{BF_4}]^-$ (i.r.). Chromatography

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* The light source was two tungsten-filament bulbs (150 W) placed about 30 cm from the flask.

on silica gel using ethanol as an eluant gave an orange-brown fraction. This was reduced to 10 cm^3 *in vacuo*, and yielded tan *crystals* upon addition of ether–hexane (0.32 g, 30%).

The ^{31}P n.m.r. spectrum in CH_2Cl_2 showed a doublet at 112.7 p.p.m. (reference trimethyl phosphite) $|^2J_{\mathrm{FP}}| = 41.5$ Hz, and tungsten satellites $|^1J_{\mathrm{WP}}| = 278.3$ Hz. This confirms the formulation.

Reactions were also attempted as follows.

trans-$[W(N_2)_2(dppe)_2]$ + MeBr + $\mathrm{Ph}\overline{\mathrm{CH{\cdot}O{\cdot}CH}}_2$, which gave no complex products.

trans-$[W(N_2)_2(dppe)_2]$ + MeBr + C_6H_6 + cyclo-C_6H_{12} (2:1 by volume), which gave *trans*-$[WBr(N_2HMe)(dppe)_2]Br$.

trans-$[W(N_2)_2(dppe)_2]$ + MeBr + C_6H_6 + thf (50 : 1 by volume) which gave *trans*-$[WBr(N_2HMe)(dppe)_2]Br$.

trans-$[W(N_2)_2(dppe)_2]$ + MeI + dihydropyran, which gave no identifiable products.

trans-$[W(N_2)_2(dppe)_2]$ + MeBr + toluene, which gave *trans*-$[WBr(N_2Me)(dppe)_2]$ + *trans*-$[WBr_2(dppe)_2]$.

trans-$[W(N_2)_2(dppe)_2]$ + MeBr + *N*-ethylpiperidine, which gave no identifiable products.

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