Diazoalkane Complexes and Related Compounds from Reactions of Dinitrogen Complexes of Tungsten and Molybdenum with *gem*-Dibromides, and from Condensation of Hydrazido(2−)-complexes with Aldehydes

By **Raphael Ben-Shoshan, Joseph Chatt, G. Jeffery Leigh,*** and **Wasif Hussain,** A.R.C. Unit of Nitrogen Fixation and School of Molecular Sciences, The University of Sussex, Brighton BN1 9RQ

The reactions of *trans*-[W(N_2)$_2$($Ph_2PCH_2CH_2PPh_2$)$_2$] with *gem*-dibromides lead to new diazoalkane complexes. These do not react with protonic acids, but the unique diazoalkane carbons are attacked by nucleophiles, such as LiMe, to yield diazenido-complexes, some of which cannot be obtained by conventional means. Other nucleophiles, such as Bu^{t}O$^-$, cleave the nitrogen–carbon bond. The reactions of *trans*-[Mo(N_2)$_2$($Ph_2PCH_2CH_2PPh_2$)$_2$] with *gem*-dibromides are more complex, and diazoalkane complexes are, at best, minor products.

DIAZOALKANE complexes of transition metals are not yet well known. The reaction of diazoalkanes with transition-metal complexes usually leads to decomposition reactions in which the methylene radical is trapped. The use of diazoalkanes in organometallic synthesis has been particularly well documented by Herrmann.[1] To synthesise a diazoalkane complex, it is frequently necessary to assemble the diazoalkane *in situ*, from a dinitrogen complex or a derivative of a dinitrogen complex. We achieved the first syntheses of diazoalkane complexes from the reaction of dinitrogen complexes with *gem*-dibromides [2] and by chance from reactions of alkyl halides and dinitrogen complexes in tetrahydrofuran.[3] Subsequently we developed an alternative synthesis by the condensation of hydrazido(2−)-complexes with aldehydes or ketones. This route was initially restricted to hydrazido(2−)-complexes of molybdenum and tungsten of the form *trans*-[MBr(NNH_2)(dppe)$_2$]$^+$ [M = Mo or W, dppe = 1,2-bis(diphenylphosphino)ethane] and was developed independently on related complexes by Hidai *et al.*[4] We have since in collaboration [5] extended this to hydrazido(2−)-complexes of the type *trans*-[WX_2(NNH_2)(PR_3)$_3$] (X = Cl or Br, PR_3 = monotertiary phosphine) to yield diazoalkane complexes which are not attainable by the *gem*-dibromide route. Here we report our results on the *gem*-dibromide route in detail.

In general, at least two alternative valence-bond structures (A) and (B) can be written for the diazoalkane, which in our complexes confer upon the metal an oxidation state of II or IV, respectively. *X*-Ray structure determinations indicate that the actual structures approximate more closely to (B) than to (A), in which

$$\underset{\text{(A)}}{\mathrm{BrM{-}\overset{-}{N}{=}\overset{+}{N}{=}CRR'}} \longleftrightarrow \underset{\text{(B)}}{\mathrm{BrM{=}N{-}N{=}CRR'}}$$

case the nitrogenous ligand would be named according to its closest approximate structure as an alkylidenehydrazido(2−)-ligand, but in the spirit of I.U.P.A.C. nomenclature [6] we shall name the ligand as if it were neutral, *i.e.* as a diazoalkane.

RESULTS AND DISCUSSION

Preparation and Structure.—The complex *trans*-[W(N_2)$_2$(dppe)$_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$) reacts with $R^1R^2CBr_2$ in benzene solution under tungsten-filament irradiation to yield the green or grey diazoalkane complexes as detailed in Table 1 [method (a)]. The condensation reaction [method (b)] was found to be generally less useful, and not to proceed with ketones, except, as shown by Hidai *et al.*,[4] under protic acid catalysis.

$$trans\text{-}[\mathrm{W(N_2)_2(dppe)_2}] + \mathrm{Br_2CR^1R^2} \longrightarrow trans\text{-}[\mathrm{WBr(N_2CR^1R^2)(dppe)_2}]\mathrm{Br} + \mathrm{N_2} \quad \text{(a)}$$

$$trans\text{-}[\mathrm{WBr(NNH_2)(dppe)_2}]\mathrm{Br} + \mathrm{OCR^1R^2} \longrightarrow trans\text{-}[\mathrm{WBr(N_2CR^1R^2)(dppe)_2}]\mathrm{Br} + \mathrm{H_2O} \quad \text{(b)}$$

The structures of three related diazoalkane complexes have been determined, *trans*-[WBr(N_2CMe_2)(dppe)$_2$]Br (3),[7] *trans*-[WBr{$N_2CH(CH_2)_3OH$}(dppe)$_2$][PF_6],[8] and *trans*-[WF{$N_2CMe(CH_2COMe)$}(dppe)$_2$][BF_4].[4] They have similar structures, with the smaller group on the

TABLE 1

Diazoalkane complexes of tungsten

Complex	Colour	M.p. (θ_c/°C)	Conductivity Λ [a] (ohm^{-1} cm^2 mol^{-1})	Method of preparation	Analysis (%) [b] C	H	N
(1) *trans*-[WBr(N_2CH_2)(dppe)$_2$]Br·0.5 CH_2Cl_2 [c]	Green	206—208	60	(a)	52.5 (52.9)	4.25 (4.10)	2.25 (2.30)
(2) *trans*-[WBr(N_2CHMe)(dppe)$_2$]Br·1.5 CH_2Cl_2	Grey	224	86	(a), (b)	50.6 (50.3)	4.65 (4.20)	2.25 (2.10)
(3) *trans*-[WBr(N_2CMe_2)(dppe)$_2$]Br·CH_3OH [d]	Grey	228—230	76	(a)	54.2 (54.1)	4.25 (4.70)	2.45 (2.25)
(4) *trans*-[WBr(N_2CHPh)(dppe)$_2$]Br	Green	156—157		(b)	56.2 (56.3)	4.40 (4.30)	2.25 (2.20)

[a] In nitromethane solution. [b] Calculated values are given in parentheses. [c] Bromine analysis 12.7 (13.0)%. [d] Bromine analysis 13.0 (12.9)%.

TABLE 2

Spectral data of diazoalkane complexes

	I.r. (cm^{-1})[a]			
Complex	ν(C=N)	ν(N=N)	^1H n.m.r. (τ)[b]	^{13}C n.m.r.[b,c]
(1)	Not assignable	Not assignable	3.04 (d, 1), 4.48 (d, 1, NCH_2)	155.27 (NCH_2)
(2)	1 575m, br	1 325w (sh) 1 225w (sh)	4.5 (q, 1, NCH), 9.07 (d, 3, NCH_3)	168.66 (NCH_2), 19.96 ($NCCH_3$)
(3)	1 580m, br	1 375m, br 1 310w (sh)	8.87 (s, 3), 10.75 [s, 3, $NC(CH_3)_2$]	174.54 ($NCCH_2$), 20.33, 24.9 [$NCC(CH_3)_2$]
(4)	1 530m, br	1 310w, br	3.92 (s, 1, NCH)[d]	

[a] KBr disc. [b] In CD_2Cl_2. [c] In p.p.m., downfield from $SiMe_4$. [d] Ph resonance masked by Ph of dppe.

diazo-carbon (Me or H) occupying a ' sandwich ' position between two phenyl groups of the dppe ligands, whereas the larger group on the end of the W–N–N–C chain, which is essentially linear except for a NNC angle of *ca.* 120°, points away from any other groups and is free of steric interactions. The limited space of the ' sandwich ' position undoubtedly explains why we were unable to make a derivative by method (b), even with acid catalysis, from diphenyl or methyl phenyl ketone. The tungsten–nitrogen bonds are all multiple (*ca.* 1.75 Å), the nitrogen–nitrogen bonds have an order rather less than two (*ca.* 1.32 Å), and the N–C bonds are also multiple (*ca.* 1.29 Å).

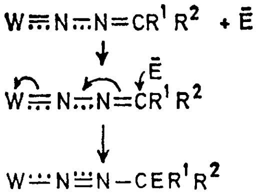
This structure is reflected by the spectral properties (Table 2). Generally there is a band at *ca.* 1 550 cm^{-1} assignable to ν(C=N), but ν(N=N) is difficult to assign and the figures quoted in Table 2 are the only significant bands we noted in the region which presumably relates to ν(N=N). This has been observed by Hidai *et al.*[4] and ourselves.[2]

The mechanism of formation of the diazenido-complexes from *gem*-dibromides has been discussed in detail elsewhere.[9]

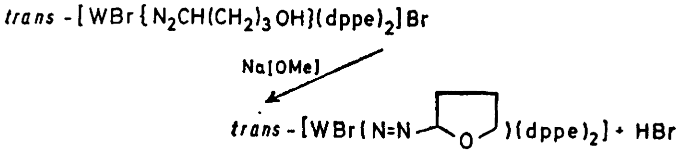
Reactions.—The complexes *trans*-[$WBr(N_2CR^1R^2)(dppe)_2]^+$ do not react with HBr in solution in benzene but they react with nucleophiles E^-. Thus, using methyl-lithium in diethyl ether we were able to convert [(1), Table 1] into the known ethyldiazenido-complex *trans*-[$WBr(N_2Et)(dppe)_2$] and [(3), Table 1] to the known complex *trans*-[$WBr(N_2Pr^i)(dppe)_2$] using Li[AlH_4]. We have already reported[9] the synthesis of [$WBr\{N_2CH_2\overline{CH(CH_2)_3CH_2}\}(dppe)_2$] from (1) and Li[$\overline{CH(CH_2)_3CH_2}$]. Perhaps more interestingly, (1) and phenyl-lithium yield the benzyldiazenido-complex *trans*-[$WBr(N_2CH_2Ph)(dppe)_2$] (5). This complex cannot be synthesised from *trans*-[$W(N_2)_2(dppe)_2$] and $PhCH_2Br$ because the benzyl radical generated in the initial stages of this reaction [equation (1)] is not sufficiently reactive to attack the bound N_2, and eventually dimerises.[9] The benzyldiazenido-complex is perfectly stable and similar

$$trans\text{-}[W(N_2)_2(dppe)_2] + PhCH_2Br \longrightarrow trans\text{-}[WBr(N_2)(dppe)_2] + PhCH_2{\cdot} + N_2 \quad (1)$$

to all the other diazenido-complexes; it protonates to give a hydrazido(2—)-complex (6). In similar fashion, (1) and Li[AlH_4] yield *trans*-[$WBr(N_2Me)(dppe)_2$].

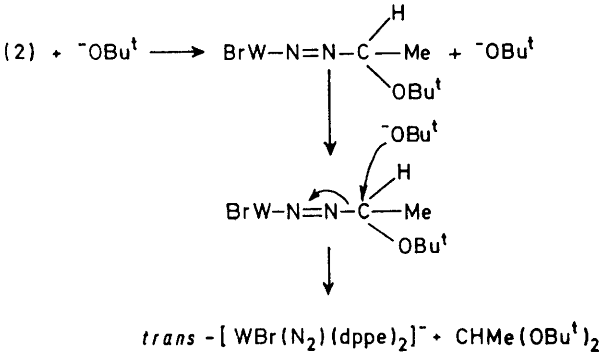


The reactions with alkoxide ions are more complex. Complex (1) and Na[OMe] react to give the novel methoxymethyldiazenido-complex *trans*-[$WBr(N_2CH_2OMe)(dppe)_2$] (7). However (3) was recovered unchanged from an attempted reaction with Na[OMe], possibly for steric reasons. The reaction of (1) and Na[OBu^t] in Bu^tOH under N_2 yielded some bis(dinitrogen) complex [$W(N_2)_2(dppe)_2$] but also in the reaction mixture was a product we could not adequately purify, but which appeared to be [$WBr(N_2CH_2OBu^t)(dppe)_2$] on the basis of its i.r. spectrum [ν(N=N) at 1 490 cm^{-1}]. The reaction of (2) and Na[OBu^t] under N_2 gave even more [$W(N_2)_2(dppe)_2$] (*ca.* 35%) and an intractable mixture. Under argon, however, we obtained *no* dinitrogen complex, a small amount of what is apparently [$WBr(N_2CHMeOBu^t)(dppe)_2$] (8) [ν(N=N) at 1 450 cm^{-1}] and an unidentified major product. An analogous generation of a dinitrogen complex under N_2 had already been observed during the attempted deprotonation of a diazobutanol complex using sodium ethoxide [reaction (2)].



(2)

The generation of *trans*-[$W(N_2)_2(dppe)_2$] is puzzling. The fact that it does not occur under Ar shows that N_2 is taken up from the gas phase. The reaction of *trans*-[$WBr(^{15}N_2CHMe)(dppe)_2$]Br with Na[$OBu^t$] under $^{14}N_2$ gave *trans*-[$W(^{14}N_2)(^{15}N_2)(dppe)_2$] in *ca.* 40% yield, showing that only one N_2 is picked up from the gas. Hence nitrogen–carbon bond cleavage takes place rather than generation of free diazoalkane. At present we favour the general sequence of reactions shown below. The organic product has not been detected, but the complex (C) is known to dissociate[10] to give $[W(N_2)(dppe)_2]$ and Br^-, and thence, under N_2 *trans*-$[W(N_2)_2(dppe)_2]$.



(C)

Finally, it is worth noting, in contrast, that complexes such as $[WBr_2(N_2CMe_2)(PMe_2Ph)_3]$ can be reduced to amines by $Li[AlH_4]$, and are also reactive with protic acids.[5] This greater reactivity must be associated with the lability of systems containing monotertiary phosphines as opposed to the chelating ditertiary phosphines.

Reactions of trans-$[Mo(N_2)_2(dppe)_2]$.—We have already described how complexes of both molybdenum and tungsten with unidentate phosphines do not yield isolable complexes when allowed to react with CH_2Br_2.[5] If *trans*-$[Mo(N_2)_2(dppe)_2]$ is treated with CH_2Br_2 in benzene solution under the conditions which yield tungsten diazoalkane complexes (8 h irradiation with tungsten filament light) no organonitrogen complexes can be isolated. However if the reaction is allowed to proceed in the laboratory for 48 h with no special irradiation conditions (exposure to daylight or laboratory illumination), then a green solid (9) separates from the solution. Its ^1H n.m.r. spectrum shows that it is not a diazoalkane complex (compare Table 1 and the data below), and there is no ν(N=N) band in the i.r. spectrum. Hence it is not a diazenido-complex. In the ^1H n.m.r. spectrum in solution in CD_2Cl_2 there is a broad singlet (τ 8.73, intensity 2) which we associate with methylene protons. On addition of D_2O, this sharpens, suggesting that the broadening of the singlet is due to coupling to exchangeable protons (N*H* or O*H*, probably the former). A broad singlet (τ 0.05, intensity 2) disappears on deuteriation. The only other proton signals can be assigned to dppe. In the ^{13}C n.m.r. spectrum in solution, all the signals arise from dppe, save one at 48.35 p.p.m. downfield from tetramethylsilane, which we assign to a single carbon adjacent to electronegative atoms. The analytical and spectral data are all consistent with (9) being *trans,trans*-$[(dppe)_2BrMo(N{-}NHCH_2NH{-}N)MoBr(dppe)_2]Br_2$. On treatment with NEt_3 in CH_2Cl_2 it yields *trans,trans*-$[(dppe)_2BrMo(N_2CH_2N_2)MoBr(dppe)_2]$ (10), which has diagnostic bands at 1 500 cm^{-1} [ν(N=N)] and 1 290 cm^{-1}, but is too insoluble for n.m.r. spectroscopy.

A further complex separated from the mother-liquor from the preparation of (9), after addition of HBr. This is apparently *trans*-$[MoBr(N_2HCH_2CH_2Br)(dppe)_2]Br$ (6) which cannot be prepared directly from $[Mo(N_2)_2(dppe)_2]$ and $BrCH_2CH_2Br$ due to the extreme instability of the radical $BrCH_2CH_2\cdot$.[9] In the ^1H n.m.r. spectrum in CD_2Cl_2 solution we observed a broad multiplet at τ 7.87—8.19 (intensity 2) which became a triplet upon adding D_2O, and which we assign to $NHCH_2$. Coupled to it is a triplet at τ 7.43 (CH_2Br). In the ^{13}C n.m.r. spectrum there is a single peak at 46.92 p.p.m. downfield from $SiMe_4$, which we assign to NCH_2, the CH_2Br signal probably being obscured by the phosphine methylenes.

It is difficult to explain how these different products arise, particularly because *trans*-$[Mo(N_2)_2(dppe)_2]$ and Br_2CMe_2 yield a normal diazoalkane complex *trans*-$[MoBr(N_2CMe_2)(dppe)_2]Br$ (12), albeit in low yield. Complex (10) presumably arises because the intermediate $[MoBr(N_2CH_2Br)(dppe)_2]$ which ionises to give a diazoalkane complex for M = W attacks another molecule of *trans*-$[Mo(N_2)_2(dppe)_2]$ preferentially. The formation of (11) strongly suggests that a diazoalkane complex is also formed, but breaks down to yield a carbene which inserts into the C–Br bond of the intermediate *trans*-$[MoBr(N_2CH_2Br)(dppe)_2]$. In any case, the isolation of both (11) and (5) unattainable by more conventional routes[9] emphasises the dangers of prognosticating about the thermodynamic stability of compounds on the basis of their unexpected non-appearance in a given chemical reaction.

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. G. Olney in the School of Molecular Sciences, the University of Sussex. For spectroscopic studies the following instruments were used: i.r., Perkin-Elmer 577; ^1H n.m.r., JEOL PS100; ^{13}C n.m.r., JEOL PFT100. Melting points were determined in air using a Reichert hot-stage microscope. Conductivities were measured with a Portland Electronics bridge in nitromethane solutions.

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*(*diazomethane*)*tungsten Bromide–Dichloromethane* (2/1), (1).—To a solution of $[W(N_2)_2(dppe)_2]$[11] (2.0 g, 2 mmol) in benzene (60 cm^3), was added CH_2Br_2 (0.3 cm^3, 4 mmol) and the solution was stirred for 12 h under tungsten-filament irradiation. A bright yellow solid separated, which was filtered off, washed with benzene (4 × 10 cm^3), and dried *in vacuo* for 1 h. It was then extracted with tetrahydrofuran (thf) (30 cm^3) and filtered. Crystallisation from a dichloromethane–diethyl ether–hexane mixture afforded green crystals (yield 1.3 g, 55%).

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*(*diazoethane*)*tungsten Bromide–Dichloromethane* (2/3), (2).—A solution containing *trans*-$[W(N_2)_2(dppe)_2]$ (1.5 g, 1.5 mmol) and $MeCHBr_2$ (0.27 cm^3) in benzene (70 cm^3) was stirred under irradiation for 12 h. A grey solid separated which was filtered off, washed with benzene (3 × 10 cm^3), and extracted with methanol (30 cm^3). The methanolic solution was reduced to dryness *in vacuo*, and the residual solid was crystallised from a dichloromethane–hexane mixture to yield grey crystals (yield 0.80 g, 45%).

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*(2-*diazopropane*)*tungsten Bromide–Methanol* (1/1), (3).—A mixture of [W(N$_2$)$_2$(dppe)$_2$] (1.2 g, 1.2 mmol) and Me$_2$CBr$_2$ (0.27 cm^3, 2.5 mmol) was stirred in benzene (60 cm^3) under irradiation for 8 h. A grey solid separated, which was filtered off, washed with benzene (3 × 10 cm^3), and crystallised from a methanol–diethyl ether–hexane mixture as bright grey crystals (yield 0.60 g, 43%).

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*(*diazotoluene*)*tungsten Bromide*, (4).—Into a dichloromethane solution of [WBr(N$_2$H$_2$)(dppe)$_2$][BPh$_4$] [12] (0.39 g, 0.28 mmol) and C$_6$H$_5$CHO (0.28 cm^3, 2.8 mmol) was distilled HBr gas (1.5 mmol) on a vacuum line. Immediately the colour of the reaction solution turned from orange-brown to green. The solution was stirred for 6 h. On removal of the solvent *in vacuo* a sticky green solid was obtained. Crystallisation from a methanol–diethyl ether–hexane mixture afforded bright green crystals (yield 0.17 g, 49%).

trans-*Benzyldiazenidobis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromotungsten*, (5).—To a suspension of [WBr(N$_2$CH$_2$)(dppe)$_2$]Br (0.4 g, 0.33 mmol) in diethyl ether, was added LiPh (0.005 g, 0.66 mmol in 1.0 cm^3 ether) and the mixture was stirred for 2 h. An orange-yellow solid was obtained, which was extracted with benzene (20 cm^3) and filtered. The solvent was removed *in vacuo* and the residue stirred in hexane (20 cm^3), the orange-yellow solid thus obtained being washed with water (3 × 5 cm^3), methanol (3 × 5 cm^3), and pentane (2 × 3 cm^3), and dried *in vacuo* for 1 h, yield 0.26 g, 70%; m.p. 147—150 °C (decomp.) (Found: C, 59.8; H, 6.20; Br, 6.60; N, 2.15. C$_{59}$H$_{55}$BrN$_2$P$_4$W requires C, 60.0; H, 4.70; Br, 6.75; N, 2.35%). In the n.m.r. spectrum in CD$_2$Cl$_2$ a singlet at τ 6.64 (intensity 2) was assigned to the NCH_2 protons. In the i.r. spectrum a band at 1 482 cm^{-1} was assigned to ν(N=N).

trans-*Benzylhydrazido*(2—)*bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromotungsten Bromide*, (6).—Into a benzene solution of (5) (0.20 g, 0.17 mmol) was distilled HBr gas (1.5 mmol) on a vacuum line and the solution was stirred for 1 h. The brown solid was filtered off, and crystallised from a methanol–diethyl ether–hexane mixture to give red crystals, yield 0.14 g, 70% (Found: C, 55.4; H, 4.65; Br, 14.7; N, 2.20. C$_{59}$H$_{56}$Br$_2$N$_2$P$_4$W requires C, 56.2; H, 4.45; Br, 12.7; N, 2.20%). The NCH_2 resonance was found at τ 7.28 (d) in the ^{1}H n.m.r. spectrum (CDCl$_3$).

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*(*methoxymethyldiazenido*)*tungsten–Methanol* (1/1), (7).—To a suspension of (1) (0.29 g, 0.23 mmol) was added Na[OMe] (0.013 g, 0.25 mmol) and the mixture was stirred for 2 h. The orange solid was filtered off, washed with methanol (2 × 5 cm^3) and pentane (2 × 3 cm^2), and dried *in vacuo* for 1 h, yield 0.17 g, 70%; m.p. 141—145 °C (decomp.) (Found: C, 56.3; H, 4.70; Br, 7.30; N, 2.35. C$_{55}$H$_{57}$BrN$_2$OP$_4$W requires C, 57.7; H, 5.00; Br, 5.20; N, 2.45%). The NCH_2 resonance was found at τ 6.53 (s) in the ^{1}H n.m.r. spectrum (CD$_2$Cl$_2$), and the OCH_3 at τ 7.21 (s).

trans,trans-μ-{*Methylenebis*[*hydrazido*(2—)-N′]}-*bis*{*bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromomolybdenum*} *Dibromide*, (9).—A solution of *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] [11] (2.0 g, 2.1 mmol) and CH$_2$Br$_2$ (0.16 cm^3, 2.0 mmol) in benzene (120 cm^3) was stirred for 48 h. A light green solid separated, which was filtered off, washed with benzene (3 × 5 cm^3), and dried *in vacuo* for 1 h. Repeated crystallisation (three times) from a dichloromethane–hexane mixture gave green needles, yield 1.4 g, 68%; m.p. 195—198 °C; Λ 71 ohm^{-1} cm^2 mol^{-1} (Found: C, 58.2; H, 5.30; Br, 13.1; N, 2.55. C$_{105}$H$_{100}$Br$_4$Mo$_2$N$_4$P$_8$ requires C, 58.0; H, 4.70; Br, 14.7; N, 2.55%).

trans,trans-μ-[*Methylenebis*(*diazenido*)]-*bis*{*bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromomolybdenum*}, (10).—To a dichloromethane solution of (9) (0.1 g, 0.04 mmol) was added NEt$_3$ (0.04 cm^3, 0.4 mmol) and the solution was stirred for 1 h. Removal of the solvent *in vacuo* and stirring in methanol (15 cm^3) gave a solid, which, on crystallisation from CH$_2$Cl$_2$, afforded orange crystals. The crystals were washed with water (2 × 3 cm^3), methanol (2 × 3 cm^3), and pentane (2 × 2 cm^3) and dried *in vacuo* for 1 h, yield 0.06 g, 80%; m.p. 265—267 °C (decomp.) (Found: C, 62.7; H, 5.05; Br, 7.95; N, 2.85. C$_{105}$H$_{98}$Br$_2$Mo$_2$N$_4$P$_8$ requires C, 62.6; H, 4.90; Br, 7.9; N, 2.8%).

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*[2-*bromoethylhydrazido*(2—)-N′]*molybdenum Bromide*, (11).—The benzene mother-liquor remaining after the isolation of (9) was treated with gaseous HBr (2 mmol) and the mixture was stirred for 0.5 h. The cloudy solution was concentrated to dryness *in vacuo* and the residual solid extracted with methanol (40 cm^3). The insoluble yellow solid was filtered off. Removal of the solvent from the methanolic solution *in vacuo* gave a solid which on crystallisation from a methanol–diethyl ether–hexane mixture gave dark brown plates. Yield 0.20 g, 4%; m.p. 179—181 °C (decomp.); Λ 75 ohm^{-1} cm^2 mol^{-1} (Found: C, 54.3; H, 4.70; Br, 18.0; N, 2.40. C$_{54}$H$_{53}$Br$_3$MoN$_2$P$_4$ requires C, 54.5; H, 4.50; Br, 20.1; N, 2.35%).

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*(2-*diazopropane*)*molybdenum*, (12).—This compound was obtained only in trace amounts from the reaction of [Mo(N$_2$)$_2$(dppe)$_2$] and Br$_2$CMe$_2$ in benzene under irradiation overnight, and was recrystallised from methanol–diethyl ether–pentane. The i.r. spectrum was similar to that of (3), and the ^{1}H n.m.r. spectrum in CD$_2$Cl$_2$ shows singlets of τ 8.79(3), assignable to the C(CH_3)$_2$ protons (*cf.* Table 2). There was not enough material for any analyses.

Reactions with Na[OBu^t].—(*i*). A solution of (2) (0.32 g, 0.26 mmol) and Na[OBu^t] (0.026 g, 0.28 mmol) in Bu^{t}OH (20 cm^3) was stirred under N$_2$ at 45 °C for 8 h. The orange-brown solid was filtered off, washed with Bu^{t}OH (2 × 5 cm^3), and dried *in vacuo* for 1 h. The solid was stirred in methanol (40 cm^3) and filtered. Recrystallisation from a benzene–methanol mixture gave orange-red crystals (yield 0.094 g, 35%) {Found: C, 61.0; H, 4.90; N, 4.25. *trans*-[W(N$_2$)$_2$(dppe)$_2$], C$_{52}$H$_{48}$N$_4$P$_4$W requires C, 60.2; H, 4.65; N, 5.40%}; ν(N$_2$) at 1 946 cm^{-1}, agreeing with the literature value.[11]

(*ii*). *Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*bromo*(1-*t*-*butoxyethyldiazenido*)*tungsten*, (8). Complex (2) was allowed to react as in (*i*) with Na[OBu^t] but under argon. The only characterisable product isolated from this reaction was an orange-brown solid, the diazenido-derivative [WBr{NNCH(OBu^t)CH$_3$}(dppe)$_2$] (8) as inferred by its microanalyses and i.r. spectrum, yield 15% (Found: C, 59.9; H, 5.20; N, 2.00. C$_{58}$H$_{61}$BrN$_2$OP$_4$W requires C, 59.6; H, 5.25; N, 2.40%).

(*iii*). The reaction was repeated using (2) labelled with ^{15}N, under ^{14}N$_2$. Work-up as under (*i*) yielded *trans*-[W(^{14}N$_2$)(^{15}N$_2$)(dppe)$_2$], as inferred by analysis and its i.r. spectrum (Found: C, 59.6; H, 4.80; N, 4.20. C$_{52}$H$_{48}$N$_4$-

P_4W requires C, 60.2; H, 4.65; N, 5.40%) [ν(N_2) at 1 982, 1 945, 1 895, and 1 810 cm^{-1}].

(*iv*). The reaction of (1) and Na[OBu^t] was carried out as under (*i*). This reaction gave, in addition to *trans*-[W(N_2)$_2$(dppe)$_2$] (yield 10%), a solid which was difficult to purify but probably contains the diazenido-derivative [WBr{N=NCH$_2$(OBu^t)}(dppe)$_2$] as indicated by the i.r. spectrum [ν(N=N) at 1 490 cm^{-1}].

We acknowledge the award of a Royal Society Fellowship to R. B.-S.) and support from the S.R.C. (to W. H.). We thank Dr. F. P. Terreros for the synthesis of complex (12).

[9/816 *Received, 24th May,* 1979]

REFERENCES

[1] W. A. Herrmann, *Angew. Chem. Internat. Edn.*, 1978, **17**, 800.

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

[3] P. C. Bevan J. Chatt, A. A. Diamantis, R. A. Head, G. A. Heath, and G. J. Leigh, *J.C.S. Dalton*, 1977, 1711, and refs. therein.

[4] M. Hidai, Y. Mizobe, M. Sato, T. Kodama, and Y. Uchida, *J. Amer. Chem. Soc.*, 1978, **100**, 5740.

[5] P. C. Bevan, J. Chatt, M. Hidai, and G. J. Leigh, *J. Organometallic Chem.*, 1978, **160**, 165.

[6] Provisional Nomenclature, 'Hydrides of Nitrogen and Derived Cations, Anions and Ligands,' *IUPAC Inf. Bull.*, 1978, no. 2, p. 151.

[7] J. Chatt, R. A. Head, P. B. Hitchcock, W. Hussain, and G. J. Leigh, *J. Organometallic Chem.*, 1977, **133**, C1.

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

[9] J. Chatt, R. A. Head, G. J. Leigh, and C. J. Pickett, *J.C.S. Dalton*, 1978, 1638.

[10] J. Chatt, H. Neukomm, G. J. Leigh, C. J. Pickett, and D. R. Stanley, *J.C.S. Dalton*, 1980, 121.

[11] J. R. Dilworth and R. L. Richards, *Inorg. Synth.*, in the press.

[12] J. Chatt, G. A. Heath, and R. L. Richards, *J.C.S. Dalton*, 1974, 2074.