Synthesis, Structure, and Chemistry of Ligating Dichlorodiazomethane. The Crystal and Molecular Structures of $[WBr(dppe)_2N_2CCl_2]^+[PF_6]^-$ and $[WBr(dppe)_2\{N_2C(Cl)C(CN)_2\}]\cdot CH_2Cl_2$†

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Summary A complex of dichlorodiazomethane, $[WBr(dppe)_2N_2CCl_2]^+$ $[PF_6]^-$, which is formed by reaction of $[WBr(dppe)_2N_2H_2]^+Br^-$ with $CXCl_3$ (X = Br or H) in the presence of a diphenyl iodonium salt and aqueous base, undergoes rapid reaction with nucleophiles to give a range of novel organodinitrogen complexes; the molecular structures of the parent dichlorodiazomethane complex, and its reaction product with dicyanomethanide ion (a vinyl diazenido complex), were determined by single-crystal *X*-ray analysis.

LIGATING dinitrogen, in the molybdenum and tungsten complexes *trans*-$[M(N_2)_2(dppe)_2]$, undergoes a variety of reactions with organic halides to yield derivatives containing alkyl-, acyl-, or aroyl-diazenido ligands.[1] With alkylidene dihalides, diazoalkane complexes are formed,[2] though the latter are equally accessible by condensation of dinitrogen-derived hydrazido(2−) complexes with aldehydes or ketones.[3] Such hydrazido(2−) complexes also condense with 2,4-dinitrofluorobenzene in the presence of base, giving complexes of the 2,4-dinitrophenyldiazenido ligand,[4] and we have attempted analogous arylation reactions with diphenyliodonium salts in an effort to prepare corresponding phenyl diazenido complexes.

When carried out in the two-phase system $CHCl_3$– aq. 5% w/v K_2CO_3, reaction between equimolar quantities of $[WBr(dppe)_2N_2H_2]^+Br^-$ and $Ph_2I^+Cl^-$ yielded, not the anticipated product, but a complex of the previously unknown molecule dichlorodiazomethane. This cationic complex, formulated as $[WBr(dppe)_2(NN{=}CCl_2)]^+$, was isolated in low (<5%) yield as its hexafluorophosphate salt, and showed strong i.r. bands at 1535 (νC=N) and 962 cm^{-1} (νCCl). Its structure was confirmed by a single-crystal *X*-ray study [Figure, (a)] which revealed *inter alia* that the *endo*-chlorine lies in a sterically crowded position among the phenyl groups of a diphosphine ligand. As in the corresponding 2-diazopropane complex,[5] this steric crowding results in a bending of some 11° from linearity at the metal-bound nitrogen.

Crystal data: $C_{53}H_{48}BrCl_2F_6N_2P_5W$, M = 1316·5, tetragonal, space group $I4$, $a = b$ = 21·415(5), c = 25·034(6) Å, U = 11480·6 $Å^3$, D_c = 1·524, D_m = 1·51 g cm^{-3}, Z = 8, $\mu(\text{Mo-}K_\alpha)$ = 31·6 cm^{-1}. The structure was solved by heavy-atom methods, and refined by least-squares to R = 0·074 for 4722 independent observed reflections $[I \geqslant 3\sigma(I)]$, collected on a Hilger-Watt four-circle diffractometer.‡

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† dppe = $Ph_2PCH_2CH_2PPh_2$.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

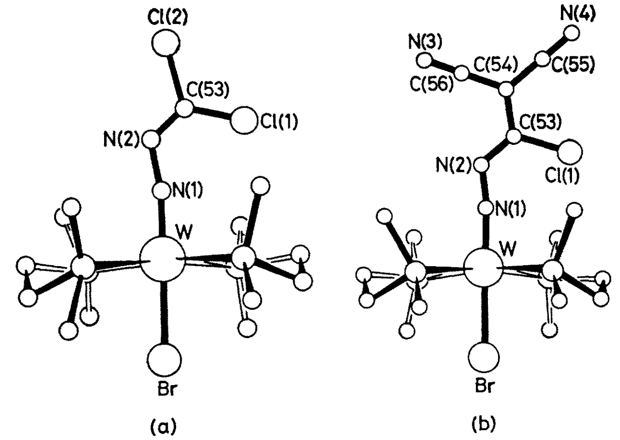
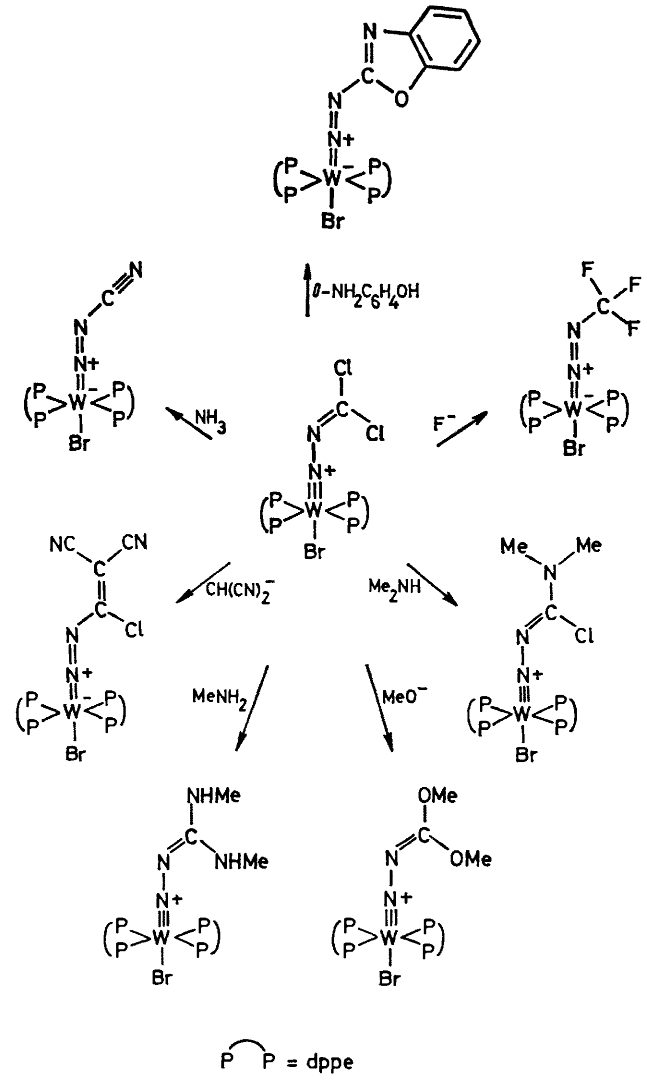


FIGURE (a), The structure of the $[WBr(dppe)_2(N_2CCl_2)]^+$ cation. Bond lengths and angles W–N(1), 1·75(2), N(1)–N(2), 1·35(3), N(2)–C(53), 1·28(3), C(53)–Cl(2), 1·75(3), C(53)–Cl(2), 1·70(3) Å, W–N(1)–N(2), 169(2), N(1)–N(2)–C(53), 122(2)°. (b), The structure of $[WBr(dppe)_2\{N_2C(Cl)C(CN)_2\}]$. Bond lengths and angles W–N(1), 1·783(5), N(1)–N(2), 1·289(8), N(2)–C(53), 1·300(8), C(53)–Cl(1), 1·726(7), C(53)–C(54), 1·40(1), C(54)–C(55), 1·38(1), C(54)–C(56), 1·40(1), C(55)–N(4), 1·16(1), C(56)–N(3), 1·16(1) Å, W–N(1)–N(2), 171·5(5), N(1)–N(2)–C(53), 124·9(6)°. Phenyl groups are omitted for clarity.

In order to rationalise formation of the dichlorodiazomethane complex, we suggest the following sequence of reactions (i) deprotonation of the hydrazido(2–) complex,[6] (ii) one-electron oxidation of the resulting diazenido complex $[WBr(dppe)_2N_2H]$ (which may be regarded as a W^0 complex, containing Br^- and $[N_2H]^+$ ligands) by Ph_2I^+, giving the W^I-dinitrogen complex $[WBr(dppe)_2N_2]$, a proton, and diphenyl iodine $Ph_2I\cdot$, (iii) decomposition of the latter[7] to iodobenzene, and a phenyl radical which abstracts hydrogen from the solvent, (iv) combination of the trichloromethyl radical thus formed with $[WBr(dppe)_2N_2]$ by attack at dinitrogen,[8] and (v) ionisation of the resulting trichloromethyl diazenido complex to give the observed cation. In agreement with this mechanism, replacing chloroform by bromotrichloromethane (an excellent source of trichloromethyl radicals) increases the yield of dichlorodiazomethane complex to *ca* 60%. An analogous mechanism has in fact been recently proposed for the formation of a trichloromethyl isocyanide complex in a reaction involving $[Cr(CO)_5CN]^-$ and PhN_2^+ in chloroform.[9]

Despite its hydrolytic stability (being prepared in the presence of aqueous base) dichlorodiazomethane is otherwise a highly reactive ligand, undergoing rapid reaction with a variety of nucleophiles (fluoride, ammonia, amines, alkoxides, and carbanions) to give a range of novel organonitrogen ligands.§ These reactions are summarised in the Scheme, and appear to be governed in part by steric factors, so that primary amines for example yield disubstituted products whereas the bulkier secondary amines afford only *exo*-monosubstituted derivatives.

In the reaction with dicyanomethanide ion, monosubstitution is followed by deprotonation at carbon, so that the product constitutes the first example of a vinyl diazenido complex. The structure of this compound [Figure, (b)] was determined by *X*-ray methods, which showed all three C–C bonds in the vinyl fragment to be essentially the same length (1·38—1·40 Å) implying extensive delocalisation of electron density within the planar metal–ligand π-system.



SCHEME Reactions of ligating dichlorodiazomethane (Cationic complexes were isolated and characterised as hexafluorophosphate salts).

Crystal data $C_{56}H_{48}BrClN_4P_4W\cdot CH_2Cl_2$, $M = 1285·05$, monoclinic, space group $P2_1/c$, $a = 12·202(3)$, $b = 20·818(5)$, $c = 21·435(5)$ Å, $\beta = 100·8(1)°$, $U = 5348·5$ Å^3, $D_c = 1·596$, $D_m = 1·59$ g cm^{-3}, $Z = 4$, $\mu(\text{Mo-}K_\alpha) = 33·9$ cm^{-1}. The structure was solved as above, and refined to $R = 0·047$ for 7376 independent observed reflections $[I \geqslant 3\sigma(I)]$.‡

The chemistry of ligating dichlorodiazomethane closely parallels that of the iminium ion $[Me_2N{=}CCl_2]^+$, though the

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§ Satisfactory analytical and spectroscopic data have been obtained for all new complexes.

latter is more reactive, and the results described here suggest that the dichlorodiazomethane complex should prove as versatile a reagent as its organic analogue has been shown to be in more conventional areas of organic synthesis.[10]

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