

Complex containing the Bridging Formazanido(3-) Ligand. Synthesis and X-Ray Crystal Structure of $[\{WBr(dppe)_2\}_2\{\mu-CH(N_2)_2\}]^+ [Cr(NH_3)_2(NCS)_4]^- \cdot 1/3CH_2Cl_2^\dagger$

By HOWARD M. COLQUHOUN

(I.C.I. Corporate Laboratory, P.O. Box 11, The Heath, Runcorn, Cheshire WA7 4QE)

and KIM HENRICK

(Department of Chemistry, The Polytechnic of North London, Holloway Road, London N7 8DB)

Summary The reaction between $[WBr(dppe)_2N_2H_2]^+Br^-$ and $CHBr_2$, in the presence of $[Ph_2I]^+Br^-$ and aqueous base, yields a cationic, dinuclear complex $[\{WBr(dppe)_2\}_2\{\mu-CH(N_2)_2\}]^+$, which has been isolated as its bromide, hexafluorophosphate, and Reineckate salts; a single crystal X-ray study of the latter confirms that the cation contains a formazanido(3-) ligand $[N=N=CH=N=N]^{3-}$, bridging two tungsten atoms in a fully conjugated, 7-atom chain.

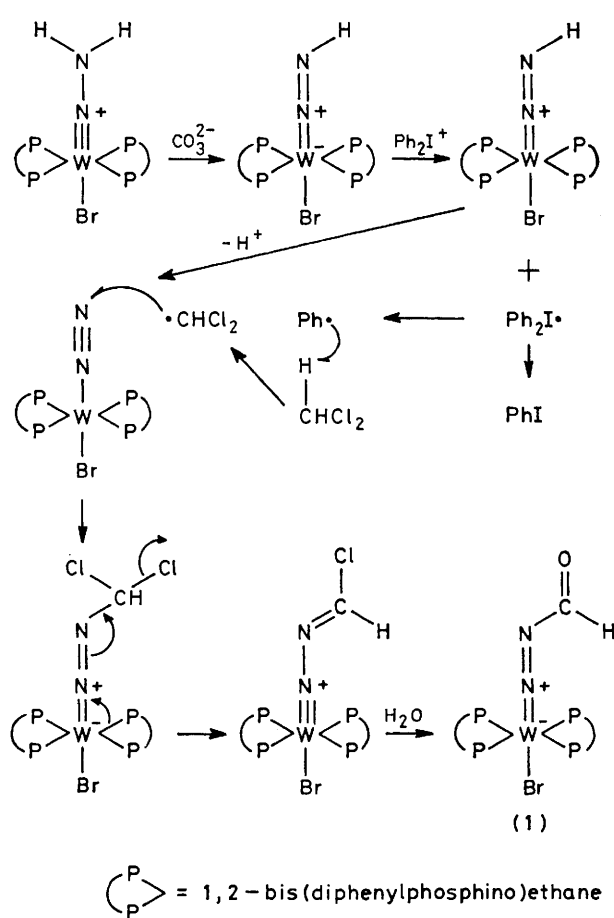
$CBrCl_3$ -5% aqueous K_2CO_3 , has recently been shown² to give a dichlorodiazomethane complex $[WBr(dppe)_2-NN=CCl_2]^+$. The reaction pathway is thought to involve a sequence of ionic and radical steps,² including abstraction of bromine from the solvent by $Ph\cdot$, and attack by the resulting $\cdot CCl_3$ radical on $[WBr(dppe)_2N_2]$ (*cf.* ref. 3). We have now extended this type of reaction to the halogenocarbon solvents $CHBr_3$, CH_2Cl_2 , and $CHBr_2$, with somewhat unexpected results.

REACTION of the hydrazido(2-) complex¹ $[WBr(dppe)_2-N_2H_2]^+Br^-$ with $[Ph_2I]^+Br^-$, in the two-phase system

in the presence of dichloromethane or bromoform, treatment of $[WBr(dppe)_2N_2H_2]^+Br^-$ with $[Ph_2I]^+Br^-$ and 5% aqueous K_2CO_3 gave moderate yields (15-20%) of the yellow

[†] dppe = 1,2-bis(diphenylphosphino)ethane.

formyldiazenido-complex $[\text{WBr}(\text{dppe})_2\text{N}=\text{N}-\text{CHO}]$ (**1**), identified by elemental analysis, its i.r. spectrum [$\nu(\text{CO})$ 1575 and $\nu(\text{N}_2)$ 1323 cm^{-1}], and by an independent synthesis involving the reaction of $[\text{WBr}(\text{dppe})_2\text{N}_2\text{H}_2]^+\text{Br}^-$ with formic acetic anhydride, a known formylation reagent.⁴ A mechanism for the formation of complex (**1**) can be proposed (Scheme). The susceptibility of a C-X



SCHEME

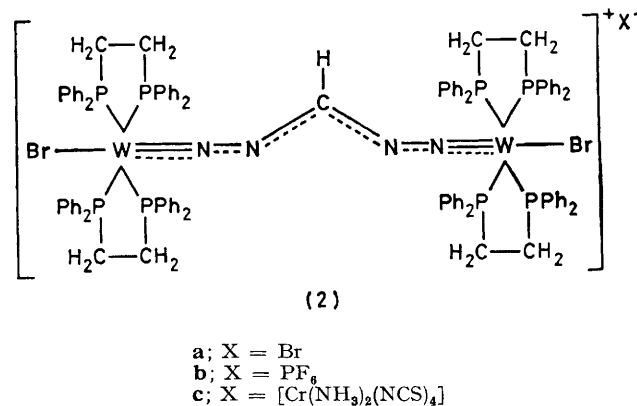
bond to abstraction of X by the phenyl radical decreases in the order⁵ C-Br > C-H > C-Cl > C-F, and thus reaction of CH_2Cl_2 and CHBr_3 with $\text{Ph}\cdot$ would give $\cdot\text{CHCl}_2$ and $\cdot\text{CHBr}_2$, respectively. Combination of these radicals with $[\text{WBr}(\text{dppe})_2\text{N}_2]$ to give the dihalogenomethyl-diazenido-complexes $[\text{WBr}(\text{dppe})_2\text{N}=\text{N}-\text{CHX}_2]$, followed by ionisation, would yield the halogenodiazomethane complexes $[\text{WBr}(\text{dppe})_2\text{N}=\text{N}=\text{CHX}]^+\text{X}^-$ (X = Cl or Br), and hydrolysis of the latter then gives the observed product (**1**).

Dibromofluoromethane as the organic phase also yielded small quantities (<10%) of the complex (**1**), but the

† *Crystal data:* $\text{C}_{108}\text{H}_{108}\text{Br}_2\text{CrN}_{10}\text{P}_8\text{S}_4\text{W}_2 \cdot 1/3 \text{CH}_2\text{Cl}_2$, M 2534.84, monoclinic, space group $P2_1/n$, $a = 19.089(3)$, $b = 44.263(4)$, $c = 13.807(2)$ Å, $\beta = 104.4(1)^\circ$, $U = 11299.5$ Å³, $Z = 4$, $D_c = 1.489$ g cm^{-3} , $\mu(\text{Mo}-K\alpha) = 29.8$ cm^{-1} . 7700 Intensities were collected on a Phillips PW 1100 4-circle diffractometer and merged to give 5918 unique observed reflections [$F > 6\sigma(F)$]. The residuals are R 0.082 and R_w [$= \sum \omega \Delta / \sum \omega \Delta |F^\circ|$] 0.083. The structure was solved by a combination of Patterson and Fourier difference techniques and refined by blocked full-matrix least-squares with the 16 phenyl rings constrained to be rigid bodies with C-C 1.395 Å and C-C-C 120°. Hydrogen atoms were not included.

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

major product in this case (>40% yield) was an intensely yellow-brown material [λ_{max} 475 nm (ϵ 5.5×10^4)] which showed strong i.r. absorptions at 1450 (νCN) and 1325 cm^{-1} (νN_2). This compound (**2a**) proved to be the bromide salt of the cationic complex (**2**), which was also isolated as its hexafluorophosphate (**2b**) and Reineckate $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$



(NCS)₄]⁻ salt (**2c**). The integrated ³¹P n.m.r. spectrum of (**2b**) showed that the cation contained two equivalent $[\text{W}(\text{dppe})_2]$ units per hexafluorophosphate anion [dppe δ 34.5 p.p.m., 8 P, $J(^{185}\text{W}-^{31}\text{P})$ 282 Hz; PF₆⁻ -144.6, 1 P, $J(^{19}\text{F}-^{31}\text{P})$ 710 Hz; $\delta \text{H}_3\text{PO}_4(\text{ext.}) = 0$] and elemental analysis of (**2a**) indicated two nitrogen atoms per tungsten.

On the basis of these results, the cation was provisionally formulated as a dinuclear species in which two $[\text{WBr}(\text{dppe})_2\text{N}_2]$ units are linked by a [CH] group derived from CHFBr_2 ; a single-crystal X-ray study[†] of the Reineckate salt (**2c**) has confirmed this proposal.

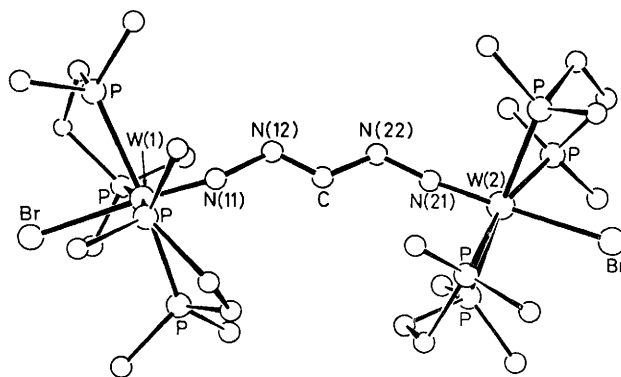
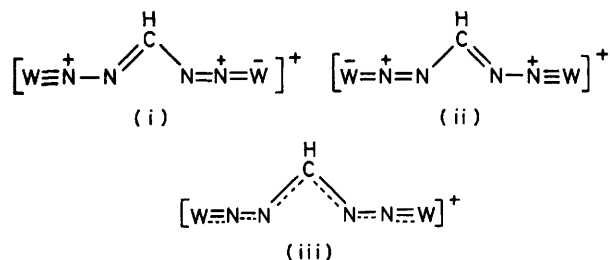
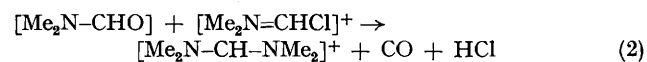
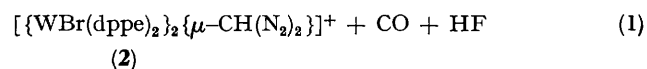
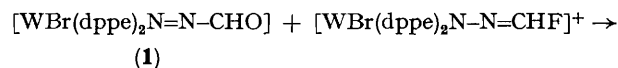


FIGURE. The structure of the cation (**2**). Selected bond lengths and angles: W(1)-N(11) 1.69(2), N(11)-N(12) 1.43(3), N(12)-C 1.29(4), C-N(22) 1.37(4), N(22)-N(21) 1.34(3), and N(21)-W(2) 1.68(2) Å. W(1)-N(11)-N(12) 163(2), N(11)-N(12)-C 120(2), N(12)-C-N(22) 122(2), C-N(22)-N(21) 124(2), and N(22)-N(21)-W(2) 172(2)°. Phenyl groups are omitted for clarity.

The structure of the cation (2), shown in the Figure, reveals an approximately symmetrical $[\text{WN}_2\text{CN}_2\text{W}]^+$ system, for which bond angles in the central $[\text{NCN}]$ fragment are indicative of sp^2 hybridisation (120 , 124° at nitrogen, 122° at carbon). The bridging ligand may thus be regarded as a triply deprotonated derivative of the hypothetical compound formazan ($\text{H}_2\text{N}-\text{N}=\text{CH}-\text{N}=\text{NH}$), and since two completely equivalent canonical structures [(i) and (ii)] can be written for (2), a delocalised description (iii) is perhaps most appropriate. In agreement with this, no atom of the $[\text{WN}_2\text{CN}_2\text{W}]^+$ system lies more than 0.09 \AA from a least-squares plane.



The reaction pathway leading to (2) may well involve coupling of the formyldiazenido-complex (1) with its precursor, the fluorodiazomethane complex $[\text{WBr}(\text{dppe})_2-\text{N}=\text{N}=\text{CHF}]^+\text{Br}^-$ [equation (1)], since an analogous reaction, of dimethylformamide with $[\text{Me}_2\text{N}=\text{CHCl}]^+\text{Cl}^-$, is known to give the symmetrical tetramethylformamidinium ion by decarbonylation and loss of HCl [equation (2)].⁶



We thank Dr. W. Hewertson for valuable discussions, and Miss S. Kilshaw for experimental assistance.

(Received, 15th October 1980; Com. 1116.)

¹ J. Chatt, G. A. Heath, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1974, 2074.

² H. M. Colquhoun and T. J. King, *J. Chem. Soc., Chem. Commun.*, 1980, 879.

³ J. Chatt, R. A. Head, G. J. Leigh, and C. J. Pickett, *J. Chem. Soc., Dalton Trans.*, 1978, 1638.

⁴ C. W. Huffman, *J. Org. Chem.*, 1958, **23**, 727.

⁵ C. Walling, 'Free Radicals in Solution,' Wiley, New York, 1957, p. 255.

⁶ W. Kantlehner and P. Speh, *Chem. Ber.*, 1971, **104**, 3714.