

## Reactions of Cyanoalkenes with a Tungsten Hydrazido(2-) Complex: the X-Ray Crystal Structure of $[\text{WBr}(\text{dppe})_2\{\text{NC}(\text{Br})\text{C}(\text{CN})\text{C}(\text{CN})_2\}]^{\dagger}$ , a Bromotricyanoprop-2-enylideneamino-complex

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Cyanoalkenes react with the dinitrogen-derived hydrazido(2-) complex  $[\text{WBr}(\text{dppe})_2\text{N}_2\text{H}_2]^+ \text{Br}^-$  (**1**) to form either vinyl diazenido-complexes or, after loss of the hydrazido(2-) ligand, to form nitrile-derived methyleneamino-complexes; the product of reaction with tetracyanoethylene is a bromotricyanoprop-2-enylideneamino-complex which has been characterised by single-crystal X-ray analysis.

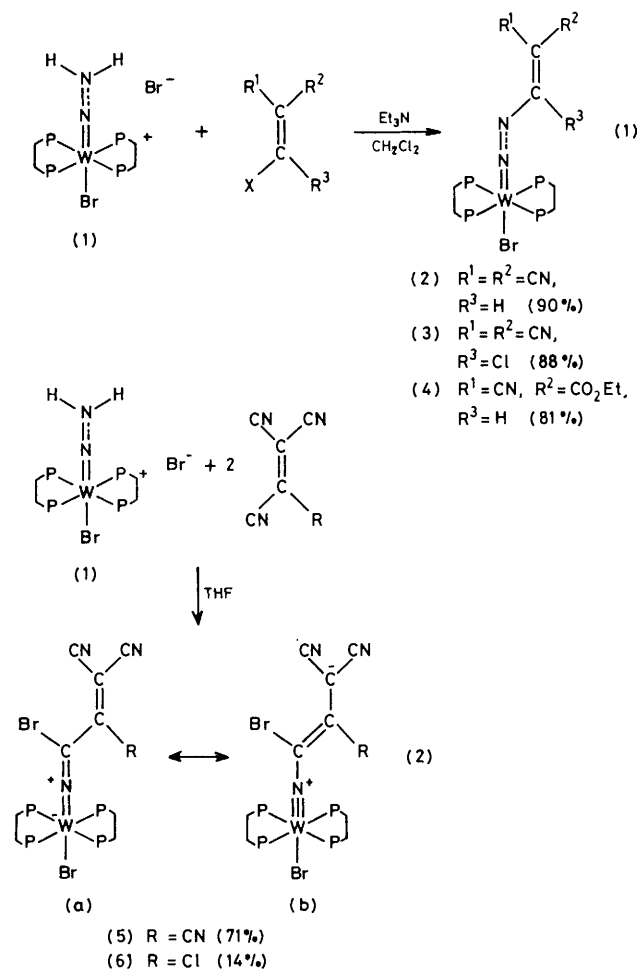
Dinitrogen-derived hydrazido(2-) complexes of molybdenum and tungsten<sup>1</sup> have been shown to undergo condensations with aldehydes, ketones,<sup>2</sup> and in the presence of base, with 2,4-dinitrofluorobenzene,<sup>3</sup> to give complexes of organodinitrogen ligands. Here we report the results of a study employing the hydrazido(2-) ligand in reactions with alkenes activated by electron-withdrawing substituents. This work not only provides the first examples of carbon-nitrogen bond formation resulting from reactions of alkenes with a dinitrogen-derived

ligand, but also shows that the hydrazido(2-) ligand is susceptible to oxidative substitution by certain cyanoalkenes.

In a typical reaction leading to C-N bond formation [equation (1)], the alkene (1 mmol) was added to a solution of (**1**) (1 mmol) in dichloromethane at room temp. under dinitrogen. Triethylamine (0.5 cm<sup>3</sup>) was added dropwise, resulting in an immediate colour change, and the solution was washed with water, dried, evaporated to dryness, and the residue recrystallised from dichloromethane-methanol. ‡ Yields were generally

† dppe =  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ .

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

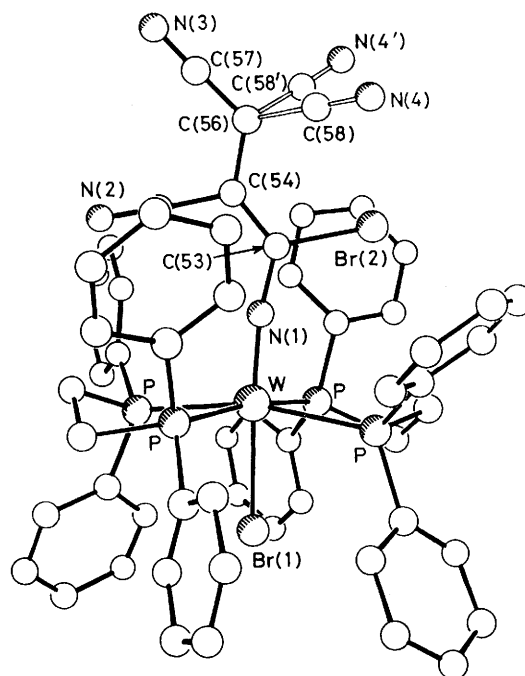


**Table 1.** Alkenes ( $R^1R^2C:CR^3X$ ) which react according to equation (1).

$R^1$	$R^2$	$R^3$	X
CN	CN	H	Cl
CN	CN	Cl	Cl
CN	$\text{CO}_2\text{Et}$	H	Cl
CN	CN	H	OEt

>90%. The resulting complexes (2), (3), and (4) showed strong i.r. bands around 2200 ( $\nu \text{C}\equiv\text{N}$ ) and 1500  $\text{cm}^{-1}$  ( $\nu \text{C}=\text{C}/\text{N}=\text{N}$ ), as well as  $^{13}\text{C}$  n.m.r. resonances in the range 116–118 p.p.m. ( $\delta \text{Me}_3\text{Si}$  0 p.p.m.) assigned to nitrile carbon atoms. Complex (4) showed  $^{13}\text{C}$  n.m.r. resonances characteristic of the ethoxycarbonyl group at 58.09 ( $-\text{OCH}_2-$ ), 14.7 ( $-\text{CH}_3$ ), and 160.9 p.p.m. ( $-\text{CO}-$ ), and perhaps most conclusively, the physical and chemical properties of complex (3) were identical with those of the compound prepared independently from  $[\text{WBr}(\text{dppe})_2\text{N}_2\text{CCl}_2]^+$  and  $[\text{CH}(\text{CN})_2]^-$ , for which an X-ray crystal structure is available.<sup>4</sup> We therefore believe complexes (2) and (4) to have analogous structures.

Table 1 lists those alkenes which react according to equation (1). However, several other apparently similar alkenes failed to react, and there appears to be a dependence on (i), the degree of electron withdrawal provided by  $R^1$  and  $R^2$ , (ii), the nature of the potential leaving group X, and (iii), the nature of  $R^3$ . Thus, when  $R^1 = R^2 = \text{CN}$ , reaction occurs readily for X = Cl or OEt, whereas when  $R^1 = R^2 = \text{CO}_2\text{Et}$ , no reaction is observed. Alternatively, X = Cl successfully acts as a leaving



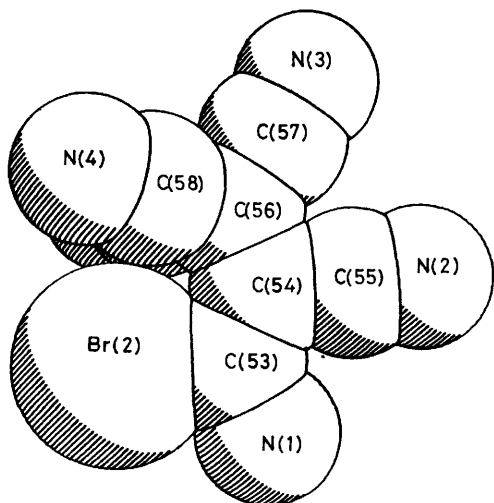
**Figure 1.** The molecular structure of (5). The W atom is displaced 0.25 Å from the mean plane of the four P atoms. Selected bond lengths and angles: W–P 2.523(2)–2.561(2), W–Br(1) 2.558(1), W–N(1) 1.777(6), N(1)–C(53) 1.34(1), C(53)–Br(2) 1.902(8), C(53)–C(54) 1.37(1), C(54)–C(56) 1.43(2), and C(56)–C(57) 1.37(2) Å; W–N(1)–C(53) 171.4(5) and Br(1)–W–N(1) 174.8(2)°.

group when  $R^1 = \text{CN}$  and  $R^2 = \text{CO}_2\text{Et}$ , though X = OEt fails to react when the same substituents are present.

In a different type of reaction [equation (2)] involving tetracyanoethylene (TCNE) (2 mmol) and complex (4) in tetrahydrofuran at room temp. in the absence of base, loss of the hydrazido(2–) ligand resulted. The product (5) gave strong i.r. bands at 2180, 2150 ( $\nu \text{C}\equiv\text{N}$ ), and 1465  $\text{cm}^{-1}$  ( $\nu \text{C}=\text{C}/\text{C}=\text{N}$ ), the  $^{13}\text{C}$  n.m.r. spectrum contained resonances at 119.6 (CN), 114.6 (CN), and 135.3 p.p.m. (C=C), and the visible spectrum had an absorption centred at 510 nm ( $\epsilon = 51\ 000$ ).

A single crystal X-ray study§ (Figure 1) revealed the structure of this product (5), which appears to be formed by addition of a bromide ion to a co-ordinated TCNE molecule.<sup>5</sup> Presumably the first mole of TCNE oxidatively deprotonates the hydrazido(2–) ligand to give an unstable dinitrogen complex  $[\text{WBr}(\text{dppe})_2\text{N}_2]^+$  which loses  $\text{N}_2$ , thereby providing a vacant site for co-ordination of a second mole of TCNE. Addition of bromide to the co-ordinated nitrile results in an 18-electron configuration for the complex. Chlorotricyanoethylene undergoes a similar reaction to give an analogous product (6).

§ **Crystal data:** Crystals of (5) are monoclinic,  $a = 26.473(5)$ ,  $b = 14.443(4)$ ,  $c = 30.144(4)$  Å,  $\beta = 102.51(1)^\circ$ ,  $U = 11\ 251$  Å<sup>3</sup>, space-group  $C2/c$ ,  $Z = 8$ . Of the 5770 independent reflections ( $\theta \leq 50^\circ$ ), measured on a diffractometer using  $\text{Cu-K}\alpha$  radiation, 749 were classified as unobserved. The structure was solved by the heavy-atom method and refined anisotropically using absorption-corrected data to give  $R = 0.042$ . 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.



**Figure 2.** Space-filling model of the bromotricyanoprop-2-enylideneamino-ligand showing the steric interaction between bromo- and cyano-substituents.

The structure of (5) shows disorder in the distant  $\text{C}(\text{CN})_2$  group which undergoes a tetrahedral distortion with the cyano-carbon atom C(58), C(58') displaced approximately 1 Å either above or below the mean plane of the alkene. This apparently results from a steric interaction between the

cyanide [C(58)–N(4)] and the adjacent bromine atom which prevents the alkene achieving coplanarity of all its substituents. This can be seen in Figure 2 which gives a space-filling representation of this region of the structure. A charge-distribution which would permit the observed pyramidal distortion at C(56) is shown in equation (2) [canonical form (5b)].

The very similar bond lengths C(53)–C(54), C(54)–C(56), and C(56)–C(57) do in fact indicate substantial delocalisation within the ligand, in keeping with the proposed contribution of the two canonical forms (5a) and (5b) to the actual structure.

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