Organic Chemistry of Dinitrogen and Related Ligands. Part 7.[1] *N*-Vinylation or Oxidative Replacement of the Hydrazido(2−) Ligand in Reactions of $[WX(dppe)_2(NNH_2)]Y$ (dppe = $Ph_2PCH_2CH_2PPh_2$, X = F or Br, Y = BF_4 or Br) with Cyanoalkenes. *X*-Ray Crystal Structure of $[WBr(dppe)_2\{NC(Br)C(CN)C(CN)_2\}]$†

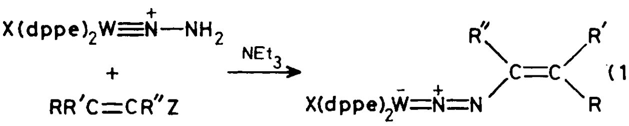
Howard M. Colquhoun *
Imperial Chemical Industries plc, The Heath, Runcorn WA7 4QE
Allan E. Crease and Stephen A. Taylor
Department of Physical Sciences, Trent Polytechnic, Nottingham NG11 8NS
David J. Williams
Department of Chemistry, Imperial College, London SW7 2AY

The dinitrogen-derived hydrazido(2−) complexes $[WX(dppe)_2(NNH_2)]Y$ (dppe = $Ph_2PCH_2CH_2PPh_2$, X = F or Br, Y = BF_4 or Br respectively) react readily with certain polycyanoalkenes such as $(CN)_2C{=}CHCl$ in the presence of base to give vinyldiazenido(1−) complexes, *e.g.* $[WBr(dppe)_2\{NNCH{=}C(CN)_2\}]$. This type of reaction proceeds *via* the neutral diazenido(1−) complex $[WX(dppe)_2(NNH)]$. Some more heavily cyano-substituted alkenes, including tetracyanoethene and tetracyanoquinodimethane react differently however, to give complexes in which the hydrazido(2−) ligand is replaced by a novel type of methyleneamido ligand derived from the cyanoalkene and the bromide counter ion of the starting complex. The structure of one such methyleneamido complex, $[WBr(dppe)_2\{NC(Br)C(CN)C(CN)_2\}]$, has been determined by single-crystal *X*-ray analysis. The compound crystallises in the monoclinic space group $C2/c$, with unit-cell parameters $a = 26.473(5)$, $b = 14.443(4)$, $c = 30.144(4)$ Å, $\beta = 102.51(1)^\circ$, and $Z = 8$. The structure was solved by the heavy-atom method and refined to $R = 0.043$ for 5 021 independent observed reflections.

Dinitrogen-derived diazenido(1−), NNH^-, and hydrazido(2−), NNH_2^{2-}, complexes of tungsten and molybdenum[2] are known to react as nucleophiles with a variety of organic electrophiles including alkyl halides,[3] isocyanates,[4] acyl halides[3] and anhydrides,[5] aldehydes and ketones,[6] and the strongly activated aryl halide 2,4-dinitrofluorobenzene,[7] to give complexes containing nitrogen–carbon bonds. Since cyanoalkenes are also susceptible to attack by nitrogen nucleophiles, as in the 'cyanoethylation' reactions of acrylonitrile with primary and secondary amines, we have examined the reactivity of such alkenes towards the hydrazido(2−) complexes $[WX(dppe)_2(NNH_2)]Y$ (dppe = $Ph_2PCH_2CH_2PPh_2$, X = F or Br, Y = BF_4 or Br respectively) and their diazenido(1−) analogues $[WX(dppe)_2(NNH)]$. Part of this work has been published in preliminary form.[8]

Results and Discussion

Acrylonitrile did not react with the above hydrazido(2−) complexes, even under conditions of acid or base catalysis and at elevated temperatures (up to 100 °C). We did not in fact observe *addition* of the hydrazido(2−) ligand to any alkene in the course of this work, but a number of strongly activated cyanoalkenes, bearing leaving groups such as chloro or ethoxy, underwent *substitution* at ambient temperature, in the presence of mild base, to give high yields of cyanovinyldiazenido(1−) complexes [equation (1)]. The four alkenes which were found to react according to equation (1) were $(CN)_2C{=}CH(OEt)$, $(CN)_2C{=}CHCl$, $(CN)(CO_2Et)C{=}CHCl$, and $(CN)_2C{=}CCl_2$, although a number of apparently only slightly less activated alkenes, including $(CN)(CO_2Et)C{=}CH(OEt)$ and $(CO_2Et)_2C{=}CHCl$, were recovered unchanged, indicating that the success of this type of reaction depends on a rather delicate balance of electronic factors.



(1)

R = R′ = CN , R″ = H or Cl, Z = Cl or OEt
R = CN, R′ = CO_2Et, R″ = H, Z = Cl

In a typical reaction, equimolar amounts of the alkene and hydrazido(2−) complex were dissolved in methanol and a slight molar excess of triethylamine was added to generate the neutral diazenido(1−) complex $[WBr(dppe)_2(NNH)]$[2] which is, as we shall see, the probable nucleophilic species in this system. Vinylation of the complex was indicated by a colour change from yellow-brown to olive-green (X = Br) or red-orange (X = F), and the crystalline product then slowly (15—20 min) precipitated from solution and was filtered off and purified by recrystallisation from dichloromethane–methanol. The vinyldiazenido(1−) complexes were characterised by i.r., n.m.r., and u.v.–visible spectroscopy (Table 1), and by elemental analysis (see Experimental section). All such complexes showed strong i.r. bands at *ca.* 2 200 [ν(C≡N)] and 1 500 cm^{-1} [ν(C=C/C=N/N=N)], together with ^{13}C n.m.r. resonances in the region of 116—118 p.p.m. [δ($SiMe_4$) = 0 p.p.m.], consistent with the presence of nitrile carbon atoms. The ethoxycarbonyl group in $[WBr(dppe)_2\{NNCH{=}C(CN)(CO_2Et)\}]$ gave rise to a set of characteristic ^{13}C resonances at δ 58.9 ($-OCH_2-$), 14.7 ($-CH_3$), and 160.9 (C=O), and a strong i.r. band [ν(C=O)]

---

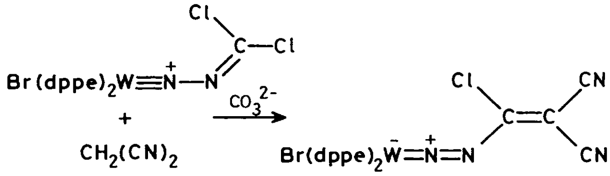
† *trans*-Bis[1,2-bis(diphenylphosphino)ethane]bromo(1-bromo-2,3,3-tricyanoprop-2-en-1-ylideneamido)tungsten.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Spectroscopic data (i.r., n.m.r., and u.v.–visible)

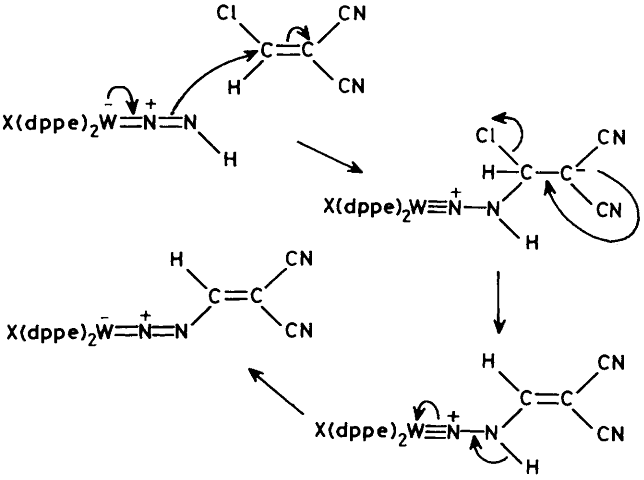
Complex	$\lambda_{max.}$/nm; ε/dm^3 mol^{-1} cm^{-1}	ν/cm^{-1}	δ/p.p.m.
Vinyldiazenido(1 –) complexes			
$[WBr(dppe)_2\{NNCH{=}C(CN)_2\}]$	412; 26 000	2 220s, 2 190m, 1 510s	
$[WF(dppe)_2\{NNCH{=}C(CN)_2\}]$	395; 33 500	2 195s, 1 470vs	118.5, 117.4 ($^{13}C{\equiv}N$) 157.7(q) ($^{19}F–WP_4$)
$[WBr(dppe)_2\{NNC(Cl){=}C(CN)_2\}]$	408; 29 000	2 205s, 2 195m, 1 480s	118.9, 117.1, ($^{13}C{\equiv}N$)
$[WF(dppe)_2\{NNC(Cl){=}C(CN)_2\}]$	390; 30 000	2 190s, 1 490s, br	120.1, 118.6, ($^{13}C{\equiv}N$)
$[WBr(dppe)_2\{NNCH{=}C(CN)(CO_2Et)\}]$	419; 32 000	2 190s, 1 680s, 1 500s,	160.9 ($^{13}CO_2$–) 118.8 ($^{13}C{\equiv}N$) 58.9 ($^{13}CH_2O$–) 14.7 ($^{13}CH_3$–)
$[WF(dppe)_2\{NNCH{=}C(CN)(CO_2Et)\}]$	403; 31 000	2 190s, 1 665m, 1 500s, 1 485s	172.6 ($^{13}CO_2$–) 128.1 ($^{13}C{\equiv}N$) 58.6 ($^{13}CH_2$–) 12.1 ($^{13}CH_3$–) 176.3 (^{19}F–W)
Methyleneamido complex			
$[WBr(dppe)_2\{NC(Br)C(CN)C(CN)_2\}]$	510; 51 000	2 180s, 2 150m, 1 465s,	119.6, 114.6 ($^{13}C{\equiv}N$) 19.9 [$^{31}P_4W$, $J(^{185}W–^{31}P)$ = 278 Hz]

at 1 680 cm^{-1}. Perhaps the most compelling evidence for the formulation of these compounds as vinyldiazenido(1 –) complexes however, is our observation that the physical, chemical, and spectroscopic properties of $[WBr(dppe)_2\{NNC(Cl){=}C(CN)_2\}]$, prepared by the vinylation reaction described in this work, are identical to those of the same complex obtained previously by an entirely independent route, involving condensation of the dichlorodiazomethane complex $[WBr(dppe)_2(NNCCl_2)]^+$ with dicyanomethane [equation (2)], and for which an *X*-ray structure is available.[9]



(2)

The vinylation reactions described here almost certainly proceed *via* the diazenido(1 –) complexes $[WX(dppe)_2(NNH)]$, since preparative reactions using pre-formed diazenido(1 –) complexes, in the absence of base, gave identical results to those in which the corresponding hydrazido(2 –) complexes and a tertiary amine were used. A classical addition–elimination mechanism (Scheme 1) seems very probable for this type of reaction. Scheme 1 suggests the possible existence of a vinyl hydrazido(2 –) intermediate, and indeed such complexes are readily detected spectroscopically in strongly acidic solution, *e.g.* on treatment of a dichloromethane solution of $[WBr(dppe)_2\{NNC(Cl){=}C(CN)_2\}]$ with trifluoroacetic acid. Protonation of the latter complex leads to a marked change in the principal visible absorption band, which moves from 408 to 350 nm, corresponding to the observed colour change from olive-brown to pale green. There is, moreover, a substantial shift to higher frequency of the i.r. $\nu(C{\equiv}N)$ absorption, from 2 205 to 2 235 cm^{-1}. In keeping with the proposed *N*-protonation reaction, these changes are reversed on addition of weak bases (amines or ethers) to the system, and indeed the hydrazido(2 –) complexes are so easily deprotonated that our attempts to isolate them from solution invariably led to their reversion to the starting vinyldiazenido(1 –) complexes.



Scheme 1.

Although protonated derivatives proved difficult to isolate, a *methylated* analogue, $[WBr(dppe)_2\{NN(Me)CH{=}C(CN)_2\}][PF_6]$, was readily obtained by reaction of the corresponding methylhydrazido(2 –) complex with 2-chloro-1,1-dicyanoethene and a tertiary amine. The resulting deep green complex showed a pair of $^{13}C{\equiv}N$ resonances at 111.7 and 110.9 p.p.m. (cyano groups *cis* or *trans* to the *N*-methyl substituent), a $^{13}CH_3$ signal at 45.0 p.p.m., and a characteristic u.v.–visible absorption at 366

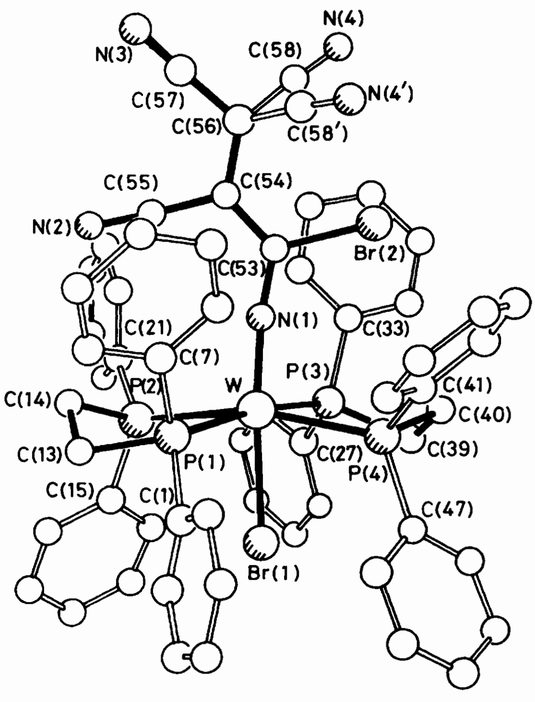
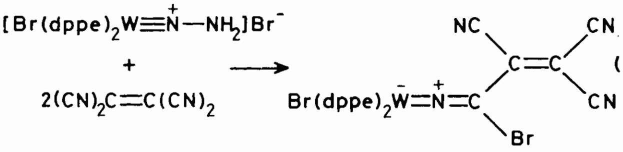


Figure 1. Molecular structure of [WBr(dppe)$_2${NC(Br)C(CN)=C(CN)$_2$}] (hydrogen atoms omitted)

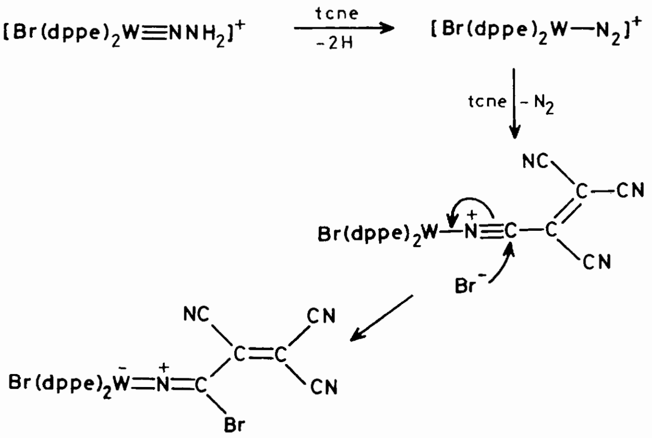
nm, close to that observed at 348 nm for solutions of the analogous protonated complex.

A small number of strongly oxidising cyanoalkenes, in particular tetracyanoethene (tcne) and tetracyanoquinodimethane (tcnq), reacted with the hydrazido(2−) complex [WBr(dppe)$_2$(NNH$_2$)]Br in tetrahydrofuran (thf) or dichloromethane, even in the *absence* of base, to give 'anomalous' products. The expected *N*-vinylation reaction, with loss of one cyano group, would have given products containing substantially more nitrogen than was found analytically, and moreover, *two* molar equivalents of alkene were required for complete conversion of the hydrazido(2−) complex, so that it was evident that a completely different type of reaction was occurring. The product from reaction of [WBr(dppe)$_2$(NNH$_2$)]Br with tcne was a black crystalline complex (dark red in solution) which showed strong i.r. bands at 2 180, 2 150, and 1 465 cm^{-1}. A cyanoalkene residue was thus clearly present, and ^{1}H and ^{13}C n.m.r. indicated that the W(dppe)$_2$ fragment was intact. Elemental analysis suggested that both bromine atoms of the starting complex had been retained, and also that there were only four nitrogen atoms per tungsten, rather than the five expected for a tricyanovinyldiazenido(1−) complex. Finally, a single-crystal *X*-ray study identified the product (Figure 1) as a novel type of methyleneamido complex,[10] in which the dinitrogen-derived NNH$_2$ ligand has been replaced by a ligand derived from tcne and the bromide counter ion of the starting complex [equation (3)].



(3)

Since two moles of tcne are consumed in the formation of this complex, it seems likely that one mole serves to oxidise the hydrazido(2−) ligand back to dinitrogen [a reaction known to occur with other oxidising agents such as silver(I)]^2 and that N$_2$ is then lost from the metal. The residual 14-electron species [WBr(dppe)$_2$]$^+$ is then attacked by a nitrile group of a second tcne molecule, to give a 16-electron intermediate which finally achieves an 18-electron configuration by addition of bromide ion to the co-ordinated cyano group. [This last step converts tcne from a formally neutral two-electron ligand to a formally anionic, four-electron, methyleneamido(1−) ligand.] The proposed mechanism is summarised in Scheme 2, although it should be noted that since tcne is known to form a charge-transfer complex in solution with bromide ion,[11] it is possible that the two final steps shown in this Scheme are in fact concerted. A curious feature of the behaviour of this complex is that the ν(C≡N) bands in its i.r. spectrum (CH$_2$Cl$_2$ solution) disappear entirely on addition of trifluoroacetic acid, the colour of the solution changing from deep red to pale yellow. The colour change is reversed and the ν(C≡N) bands reappear unchanged on neutralisation with triethylamine, so that reversible protonation of the complex is clearly occurring, but at present we have no satisfactory explanation for this extraordinary spectroscopic phenomenon.



Scheme 2.

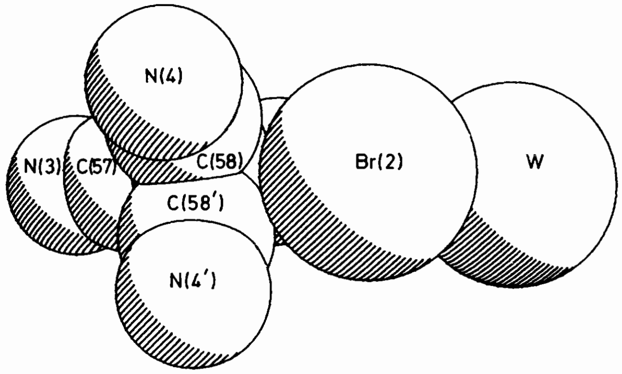


Figure 2. Space-filling representation of the 1-bromo-2,3,3-tricyanopropen-2-en-1-ylideneamido ligand, showing the enforced pyramidalisation of C(56) caused by steric interactions between the bromo- and cyano-substituents

The structure of [WBr(dppe)$_2${NC(Br)C(CN)C(CN)$_2$}] is shown in Figure 1, with a space-filling representation of the tcne-derived ligand in Figure 2. Atomic co-ordinates are given in Table 2 and selected bond lengths and angles are shown in Table 3. The distinct non-planarity of the distal dicyanomethylene group [C(56)] is at first sight rather curious, since the C(56)–C(54) bond would be expected to retain substantial double-bond character in the complex. In fact, although the

Table 2. Atomic co-ordinates (× 10^4)

Atom	*x*	*y*	*z*
W	1 635(1)	494(1)	1 137(1)
Br(1)	1 983(1)	2 029(1)	904(1)
Br(2)	1 941(1)	−1 826(1)	1 975(1)
P(1)	1 431(1)	12(2)	306(1)
P(2)	753(1)	1 272(2)	866(1)
P(3)	1 851(1)	1 186(2)	1 924(1)
P(4)	2 603(1)	136(2)	1 359(1)
N(1)	1 449(2)	−587(4)	1 333(2)
N(2)	240(3)	−1 559(6)	707(3)
N(3)	166(4)	−3 976(7)	1 162(4)
N(4)	1 182(7)	−3 416(13)	2 398(5)
N(4′)	1 763(9)	−3 946(21)	1 574(11)
C(1)	1 841(3)	297(5)	−93(3)
C(2)	1 880(3)	1 195(6)	−226(3)
C(3)	2 206(4)	1 421(7)	−509(3)
C(4)	2 505(4)	766(7)	−656(4)
C(5)	2 459(4)	−133(7)	−527(3)
C(6)	2 130(3)	−380(6)	−248(3)
C(7)	1 304(3)	−1 225(5)	201(3)
C(8)	977(4)	−1 536(7)	−206(3)
C(9)	906(4)	−2 455(8)	−288(4)
C(10)	1 147(4)	−3 095(7)	32(4)
C(11)	1 469(4)	−2 809(7)	424(4)
C(12)	1 547(3)	−1 871(6)	504(3)
C(13)	819(3)	571(6)	30(3)
C(14)	451(3)	632(6)	355(3)
C(15)	710(3)	2 475(6)	676(3)
C(16)	935(3)	3 163(6)	970(3)
C(17)	883(4)	4 064(8)	845(4)
C(18)	622(4)	4 314(7)	420(4)
C(19)	404(4)	3 648(7)	115(3)
C(20)	441(3)	2 730(6)	244(3)
C(21)	272(3)	1 224(6)	1 219(3)
C(22)	51(3)	1 975(7)	1 357(3)
C(23)	−308(4)	1 918(9)	1 635(4)
C(24)	−446(4)	1 051(9)	1 761(4)
C(25)	−241(5)	281(9)	1 624(5)
C(26)	120(4)	377(8)	1 351(4)
C(27)	1 628(3)	2 330(6)	2 051(3)
C(28)	1 159(4)	2 427(7)	2 165(3)
C(29)	962(4)	3 288(8)	2 217(4)
C(30)	1 224(5)	4 056(8)	2 148(4)
C(31)	1 696(4)	3 992(8)	2 038(4)
C(32)	1 900(4)	3 114(7)	1 989(3)
C(33)	1 683(3)	473(7)	2 371(3)
C(34)	1 222(4)	−5(7)	2 279(4)
C(35)	1 060(6)	−590(9)	2 590(5)
C(36)	1 398(7)	−664(11)	2 995(6)
C(37)	1 858(6)	−168(12)	3 115(4)
C(38)	1 996(5)	409(9)	2 800(3)
C(39)	2 551(3)	1 260(6)	2 082(3)
C(40)	2 780(3)	340(6)	1 973(3)
C(41)	2 852(3)	−1 020(6)	1 295(3)
C(42)	3 111(4)	−1 564(8)	1 656(3)
C(43)	3 290(4)	−2 421(8)	1 580(4)
C(44)	3 236(4)	−2 754(7)	1 159(4)
C(45)	2 994(4)	−2 249(8)	790(4)
C(46)	2 797(4)	−1 379(7)	860(3)
C(47)	3 072(3)	827(6)	1 140(3)
C(48)	3 054(3)	842(7)	677(3)
C(49)	3 432(4)	1 287(7)	501(4)
C(50)	3 825(4)	1 742(9)	781(4)
C(51)	3 839(4)	1 749(9)	1 240(4)
C(52)	3 467(4)	1 298(8)	1 410(4)
C(53)	1 384(3)	−1 420(6)	1 506(3)
C(54)	983(4)	−2 029(6)	1 370(3)
C(55)	577(3)	−1 750(6)	999(3)
C(56)	922(3)	−2 926(7)	1 539(4)
C(57)	490(4)	−3 502(7)	1 323(4)
C(58)	1 052(7)	−3 168(12)	2 031(4)
C(58′)	1 395(8)	−3 518(20)	1 569(12)
X(1)	−537(10)	−5 673(13)	1 079(11)
X(2)	−159(12)	−4 608(29)	2 269(9)
X(3)	−1(85)	−2 619(37)	2 498(85)

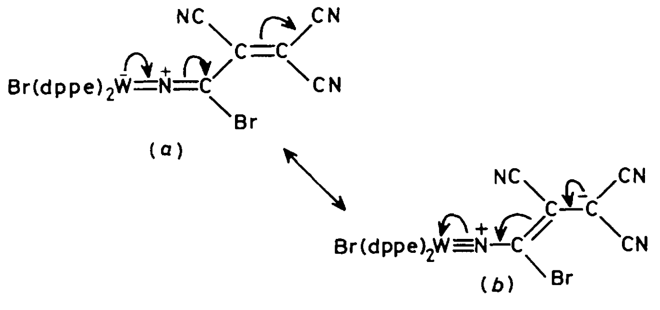
Table 3. Selected bond lengths (Å) and angles (°)

W–Br(1)	2.558(1)	W–P(1)	2.543(2)
W–P(2)	2.561(2)	W–P(3)	2.523(2)
W–P(4)	2.558(2)	W–N(1)	1.777(6)
Br(2)–C(53)	1.902(8)	N(1)–C(53)	1.337(11)
N(2)–C(55)	1.144(11)	N(3)–C(57)	1.118(15)
N(4)–C(58)	1.144(24)	N(4′)–C(58′)	1.203(50)
C(53)–C(54)	1.366(12)	C(54)–C(55)	1.432(11)
C(54)–C(56)	1.428(16)	C(56)–C(57)	1.366(17)
C(56)–C(58)	1.533(22)	C(56)–C(58′)	1.728(38)
Br(1)–W–P(1)	88.8(1)	Br(1)–W–P(2)	83.7(1)
P(1)–W–P(2)	79.7(1)	Br(1)–W–P(3)	83.8(1)
P(1)–W–P(3)	172.4(1)	P(2)–W—P(3)	97.5(1)
Br(1)–W–P(4)	81.2(1)	P(1)–W–P(4)	100.9(1)
P(2)–W–P(4)	164.8(1)	P(3)–W–P(4)	79.9(1)
Br(1)–W–N(1)	174.8(2)	P(1)–W–N(1)	94.1(2)
P(2)–W–N(1)	101.1(2)	P(3)–W–N(1)	93.4(2)
P(4)–W–N(1)	94.1(2)	W–N(1)–C(53)	171.4(5)
Br(2)–C(53)–N(1)	115.0(5)	Br(2)–C(53)–C(54)	116.8(7)
N(1)–C(53)–C(54)	128.1(7)	C(53)–C(54)–C(55)	117.2(8)
C(53)–C(54)–C(56)	130.8(9)	C(55)–C(54)–C(56)	112.0(8)
N(2)–C(55)–C(54)	177.2(10)	C(54)–C(56)–C(57)	123.4(10)

Table 4. Deviations (Å) from the least-squares plane through N(1), C(53), C(54), C(55), C(56), N(2), and Br(2)

Atom	Deviation from plane (Å)
W	0.14
Br(2)	0.03
N(1)	0.00
N(2)	0.02
N(3)	0.24
N(4)	−1.31
N(4′)	1.92
C(53)	−0.03
C(54)	−0.03
C(55)	0.01
C(56)	0.00
C(57)	0.12
C(58)	−0.80
C(58′)	1.07

cyano group C(58)N(4) shows positional disorder, the cyano-carbon atom [C(58)/C(58′)] is quite unambiguously located some 1.0 Å either above or below the mean plane of the methyleneamido ligand (Table 4). A probable explanation is to be found in the steric interaction between adjacent bromo [Br(2)] and cyano [C(58)N(4)] substituents. Such an interaction is, as depicted in Figure 2, sufficient to force the cyano group out of plane, and the resulting distortion emphasises the potentially carbanionic character of C(56) conferred on it by delocalisation of electron density from the metal (Scheme 3). Canonical form (*b*) would in fact allow substantial pyramidalisation at C(56), and this form therefore probably contributes very significantly to the actual electronic structure of the complex. This conclusion is in good agreement with the observed bond lengths of 1.37(1) Å for C(53)–C(54) [the formal double bond in canonical form (*b*)], and 1.43(2) Å for the formal single bond C(54)–C(56).



Scheme 3.

Further evidence for serious steric hindrance between Br(2) and C(58)N(4) is provided by the opening up of the angle C(53)–C(54)–C(56) from a conventional trigonal value of *ca.* 120° to 131(1)°. The tungsten–nitrogen distance of 1.777(6) Å is very similar to the corresponding distances in a wide range of related hydrazido(2−) and diazenido(1−) complexes, and seems to represent a W–N bond order of between 2.5 and 3.[12] The bulky nature of the methyleneamido ligand as a whole is reflected in the distortions from octahedral geometry about the tungsten atom, which lies some 0.25 Å above the mean plane of the phosphorus atoms, with Br–W–P angles in the range 81—89°.

Experimental

The starting hydrazido(2−) complexes[2] and cyanoalkenes[13] (other than tcne and tcnq, which were purchased from Aldrich) were prepared according to literature procedures. Solvents were dried and distilled from appropriate reagents, and reactions were carried out under dry dinitrogen, although neither the vinyldiazenido(1−) nor methyleneamido complexes isolated as products proved to be particularly air-sensitive, even in solution. Melting points were determined in air and are uncorrected. Infrared spectra were obtained using Perkin-Elmer 157G and PE683 instruments, and u.v.–visible spectra were recorded on a PE402 spectrometer. N.m.r. spectra were run on a JEOL FX 100 instrument at 100 [^{1}H, δ(SiMe$_4$) = 0], 94 [^{19}F, δ(CFCl$_3$) = 0], 40.3 [^{31}P, δ(H$_3$PO$_4$, external) = 0], or 25.1 MHz [^{13}C, δ(SiMe$_4$) = 0]. Elemental analyses were by the Characterisation and Measurement Group of I.C.I. Mond Division.

trans-*Bis[bis(1,2-diphenylphosphino)ethane]bromo[2-(2′,2′-dicyanovinyl)diazenido]tungsten (Method 1).*—A stirred solution of [WBr(dppe)$_2$(NNH$_2$)]Br (3.0 g, 3.51 mmol) in methanol (250 cm^3 was treated with 1,1-dicyano-2-ethoxyethene (0.39 g, 3.51 mmol), and when this had dissolved, triethylamine (1 cm^3) was added dropwise over *ca.* 5 min. The reaction mixture was stirred at room temperature for a further 30 min and the resulting brown, crystalline precipitate was filtered off, washed with diethyl ether, and recrystallised from dichloromethane–methanol to give 2.52 g (84% yield) of [WBr(dppe)$_2${NNCH=C(CN)$_2$}]·0.5CH$_2$Cl$_2$, m.p. 190 °C (decomp.) (Found: C, 55.8; H, 4.0; N, 4.6. Calc. for C$_{56}$H$_{49}$BrN$_4$P$_4$W·0.5CH$_2$Cl$_2$: C, 56.2; H, 4.1; N, 4.6%).

trans-*Bis[bis(1,2-diphenylphosphino)ethane]bromo[2-(1′-chloro-2′,2′-dicyanovinyl)diazenido]tungsten (Method 2).*—To a solution of [WBr(dppe)$_2$(NNH$_2$)]Br (1.17 g, 1.00 mmol) in dichloromethane (100 cm^3) was added 1,1-dichloro-2,2-dicyanoethene (0.15 g, 1.02 mmol), followed by dropwise addition of triethylamine (0.5 cm^3) with stirring. After stirring for 30 min, the solution was washed with water (2 × 100 cm^3), separated, dried over 3A molecular sieves, and treated with methanol (50 cm^3). Evaporation under reduced pressure to *ca.* 60 cm^3 total volume afforded dark olive-brown crystals of [WBr(dppe)$_2${NNC(Cl)=C(CN)$_2$}]·CH$_2$Cl$_2$ (1.10 g, 88% yield), m.p. 210 °C (decomp.) (Found: C, 53.8; H, 3.8; N, 4.3. Calc. for C$_{56}$H$_{48}$BrClN$_4$P$_4$W·CH$_2$Cl$_2$: C, 53.3; H, 3.9; N, 4.4%).

trans-*Bis[bis(1,2-diphenylphosphino)ethane][2-(2′,2′-dicyanovinyl)diazenido]fluorotungsten.*—This compound was prepared, using Method 1, by reaction of [WF(dppe)$_2$(NNH$_2$)][BF$_4$] (1.12 g, 1.00 mmol) and 2-chloro-1,1-dicyanoethene (0.12 g, 1.06 mmol). The bright orange product was recrystallised from dichloromethane–methanol to give 1.00 g (91% yield) of [WF(dppe)$_2${NNCH=C(CN)$_2$}]·0.5CH$_2$Cl$_2$, m.p. 139 °C (decomp.) (Found: C, 58.6; H, 4.2; N, 4.7. Calc. for C$_{56}$H$_{49}$FN$_4$P$_4$W·0.5CH$_2$Cl$_2$: C, 59.2; H, 4.4; N, 4.9%).

trans-*Bis[bis(1,2-diphenylphosphino)ethane][2-(1′-chloro-2′,2′-dicyanovinyl)diazenido]fluorotungsten.*—This was obtained, using Method 1, by reaction of [WF(dppe)$_2$(NNH$_2$)][BF$_4$] (1.12 g, 1.00 mmol) and 1,1-dichloro-2,2-dicyanoethene (0.15 g, 1.02 mmol). The dark red precipitate was recrystallised from dichloromethane–methanol to give 1.03 g (88% yield) of [WF(dppe)$_2${NNC(Cl)=C(CN)$_2$}]·CH$_2$Cl$_2$, m.p. 174 °C (decomp.) (Found: C, 56.6; H, 4.3; N, 4.4. Calc. for C$_{56}$H$_{48}$ClFN$_4$P$_4$W·CH$_2$Cl$_2$: C, 55.9; H, 4.1; N, 4.6%).

trans-*Bis[bis(1,2-diphenylphosphino)ethane]bromo[2-(2′-cyano-2′-ethoxycarbonylvinyl)diazenido]tungsten.*—This was prepared, *via* Method 1, from [WBr(dppe)$_2$(NNH$_2$)]Br (1.00 mmol) and 2-chloro-1-cyano-1-ethoxycarbonylethene (1.00 mmol) which gave, after recrystallisation, 0.98 g (81% yield) of dark brown crystalline [WBr(dppe)$_2${NNCH=C(CN)(CO$_2$Et)}]·0.5CH$_2$Cl$_2$, m.p. 255 °C (decomp.) (Found: C, 56.4; H, 4.5; N, 3.5. Calc. for C$_{58}$H$_{54}$BrN$_3$O$_2$P$_4$W·0.5CH$_2$Cl$_2$: C, 56.1; H, 4.3; N, 3.2%).

trans-*Bis[bis(1,2-diphenylphosphino)ethane][2-(2′-cyano-2′-ethoxycarbonylvinyl)diazenido]fluorotungsten.*—This was obtained using Method 1, from [WF(dppe)$_2$(NNH$_2$)][BF$_4$] (1.00 mmol) and 2-chloro-1-cyano-1-ethoxycarbonylethene (1.00 mmol) which gave, after recrystallisation, 1.10 g (95%) of red, crystalline [WF(dppe)$_2${NNCH=C(CN)(CO$_2$Et)}]·0.5CH$_2$Cl$_2$, m.p. 189 °C (decomp.) (Found: C, 59.0; H, 4.4; N, 3.4. Calc. for C$_{58}$H$_{54}$FN$_3$O$_2$P$_4$W·0.5CH$_2$Cl$_2$: C, 58.8; H, 4.6; N, 3.5%).

trans-*Bis[bis(1,2-diphenylphosphino)ethane]bromo[2-(2′,2′-dicyanovinyl)-2-methylhydrazido]tungsten Hexafluorophosphate.*—A solution of [WBr(dppe)$_2${NNH(Me)}][BF$_4$] (0.12 g, 0.10 mmol) and 2-chloro-1,1-dicyanoethene (0.012 g, 0.106 mmol) in dichloromethane (10 cm^3) was treated with triethylamine (0.3 cm^3), and the resulting dark green solution was stirred for 30 min and then washed with water (2 × 30 cm^3), separated, and dried over 3A molecular sieves. Addition of hexane to the filtered solution yielded a dark green oil which was taken up in methanol (5 cm^3), and a solution of ammonium hexafluorophosphate (1.0 g) in methanol (10 cm^3) was added dropwise with stirring. The green microcrystalline precipitate was filtered off, washed with diethyl ether (20 cm^3), and dried, to give 0.08 g (60%) of [WBr(dppe)$_2${NN(Me)CH=C(CN)$_2$}][PF$_6$]·CH$_2$Cl$_2$, m.p. 179 °C (decomp.) (Found: C, 48.4; H, 4.2; N, 4.2. Calc. for C$_{57}$H$_{52}$BrF$_6$N$_4$P$_5$W·CH$_2$Cl$_2$: C, 49.4; H, 3.8; N, 4.0%).

trans-*Bis[bis(1,2-diphenylphosphino)ethane]bromo(1-bromo-2,3,3-tricyanoprop-2-en-1-ylideneamido)tungsten.*—A suspension of [WBr(dppe)$_2$(NNH$_2$)]Br (1.17 g, 1.00 mmol) in tetrahydrofuran (100 cm^3) was stirred and treated with 0.26 g (2.00 mmol) of tetracyanoethene. After stirring for 20 min, the solvent was removed under reduced pressure and the residue taken up in dichloromethane (100 cm^3) to give a dark red solution which was washed with water (3 × 100 cm^3), separated, and dried over 3A molecular sieves. This solution was filtered and treated with acetonitrile (50 cm^3), and then evaporated under reduced pressure to *ca.* 50 cm^3 total volume to give greenish-black crystals of $[\mathrm{WBr(dppe)_2\{NC(Br)C(CN){=}C(CN)_2\}}]\cdot\mathrm{CH_2Cl_2}$, which were filtered off, washed with acetonitrile and diethyl ether, and dried. The yield was 0.65 g (71%), m.p. 210 °C (decomp.) (Found: C, 52.8; H, 3.7; Br, 12.0; Cl, 2.7; N, 4.4; P, 9.1; W, 14.0. Calc. for $\mathrm{C_{58}H_{48}Br_2N_4P_4W\cdot CH_2Cl_2}$: C, 53.5; H, 3.7; Br, 12.2; Cl 2.6; N, 4.3; P, 9.5; W, 14.2%).

trans-*Bis*[*bis*(1,2-*diphenylphosphino*)*ethane*]*bromo*{1-*bromo*-2-*cyano*-2-[4′-(*dicyanomethylene*)*cyclohexa*-2′,5′-*dienylidene*]-*ethylideneamido*}*tungsten*.—A suspension of $[\mathrm{WBr(dppe)_2(NNH_2)}]\mathrm{Br}$ (1.17 g, 1.00 mmol) in thf (100 cm^3) was stirred with tetracyanoquinodimethane (0.41 g, 1.00 mmol) for 1 h, and the dark red solution was then filtered and evaporated to dryness under reduced pressure. Recrystallisation of the residue from methanol afforded 0.76 g (57%) of dark green $[\mathrm{WBr(dppe)_2\{NC(Br)C(CN)C_6H_4C(CN)_2\}}]$, m.p. 190 °C (decomp.) (Found: C, 57.1; H, 3.9; N, 4.1. Calc. for $\mathrm{C_{64}H_{52}Br_2N_4P_4W}$: C, 57.1; H, 3.8; N, 4.0%).

Crystal Structure Determination of $[\mathrm{WBr(dppe)_2\{NC(Br)C(CN){=}C(CN)_2\}}]$.—Single crystals were obtained by slow evaporation of a dichloromethane–acetonitrile solution.

Crystal data. $\mathrm{C_{58}H_{48}Br_2N_4P_4W\cdot 1.25X}$*, M = 1 283.6,† monoclinic, a = 26.473(5), b = 14.443(4), c = 30.144(4) Å, β = 102.51(1)°, U = 11 252 Å^3, space group $C2/c$, Z = 8, D_c = 1.51 g cm^{-3}. Crystal dimensions 0.10 × 0.12 × 0.17 mm, μ(Cu-K_α) = 69 cm^{-1}, λ = 1.541 78 Å, F(000) = 5 083.

Data collection and processing. Nicolet $R3m$ diffractometer, ω-scan method ($2\theta \leqslant 100°$), graphite-monochromated Cu-K_α radiation; 5 021 independent observed reflections $[|F_o| > 3\sigma(|F_o|)]$, corrected for Lorentz and polarisation factors; numerical absorption correction (face indexed crystal) applied.

Structure analysis and refinement. The structure was solved by the heavy-atom method and the non-hydrogen atoms refined anisotropically. A ΔF map revealed disorder in one of the terminal cyano groups attached to C(56) resulting from a tetrahedral distortion at this atom, the two alternative positions for C(58)—N(4) having estimated occupancies of 0.65 and 0.35. The major occupancy atoms were refined anisotropically and the minor isotropically. All three terminal cyano groups were refined subject to common, but refinable, distance constraints for both their C–C and C–N bonds. The ΔF map also revealed unidentified and disordered fractional solvent atoms, two in general positions which were refined anisotropically as 0.5 weight carbon atoms and a third lying on one of the two-fold axes, which was refined isotropically as a 0.25 weight carbon atom. The positions of the hydrogen atoms were idealised (C–H 0.96 Å), assigned isotropic thermal parameters U(H) = 1.2 U_{eq} (C) and allowed to ride on their parent carbons. Refinement was by block-cascade full-matrix least squares to R = 0.043, R' = 0.045 $[w^{-1} = \sigma^2(F) + 0.0008F^2]$. The maximum residual electron density in the final ΔF map was 0.91 e Å^{-3}. The mean and maximum shift/error ratios in the final refinement cycle were 0.01 and 0.08 respectively. Computations were carried out on an Eclipse S140 computer using the SHELXTL program[14] system and published scattering factors.[15]

Additional material available from the Cambridge Crystallographic Data Centre comprises the H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.[15]

Acknowledgements

We thank the S.E.R.C. and Imperial Chemical Industries plc for the award of a co-operative research grant (to A. E. C.).

References

1 Part 6, H. M. Colquhoun and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1984, 1675.

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

3 J. Chatt, A. J. Pearman, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1976, 1520.

4 K. Iwanami, Y. Mizobe, T. Takahashi, T. Kodama, Y. Uchida, and M. Hidai, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1773.

5 H. M. Colquhoun, *Transition Met. Chem.*, 1981, **6**, 57.

6 M. Hidai, Y. Mizobe, and Y. Uchida, *J. Am. Chem. Soc.*, 1976, **98**, 7824.

7 H. M. Colquhoun, *J. Chem. Res.*, 1979, (*S*) 325; (*M*) 3677.

8 H. M. Colquhoun, A. E. Crease, and S. A. Taylor, *J. Chem. Soc., Chem. Commun.*, 1982, 738.

9 H. M. Colquhoun and T. J. King, *J. Chem. Soc., Chem. Commun.*, 1980, 879; H. M. Colquhoun, *J. Chem. Res.*, 1981, (*S*) 276; (*M*) 3416.

10 J. Chatt, R. J. Dosser, F. King, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1976, 2435 and refs. therein.

11 G. Briegleb, W. Liptay, and R. Fick, *Z. Phys. Chem.*, (*Frankfurt am Main*), 1962, **33**, 181.

12 K. Dehnicke and J. Strähle, *Angew. Chem., Int. Edn. Engl.*, 1981, **20**, 413 and refs. therein.

13 A. D. Josey, C. L. Dickinson, K. Dewhurst, and B. C. McKusick, *J. Org. Chem.*, 1967, **32**, 1941; K. Friedrich and H. K. Thieme, *Chem. Ber.*, 1970, **103**, 1982; O. Diels, H. Gartner, and R. Kaack, *ibid.*, 1922, **55B**, 3439.

14 G. M. Sheldrick, SHELXTL, An Integrated Program for Solving, Refining, and Displaying Crystal Structures from Diffraction Data, University of Göttingen, Federal Republic of Germany, 1978; revised version, 1984.

15 ‘International Tables for *X*-Ray Crystallography,’ Kynoch Press, Birmingham, 1974, vol. 4, pp. 9—149.

Received 19*th November* 1987; *Paper* 7/2052

---

* X = Unidentified solvent fragment.

† Assigns X = carbon.