# Chemistry of Hydrogen Isocyanide. Part 1. Reactions of $[M(CO)_5(CNH)]$ (M = Cr or W) with Epoxides†

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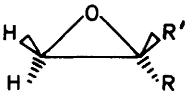
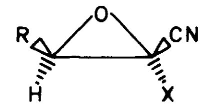
The hydrogen isocyanide complexes $[M(CO)_5(CNH)]$ (M = Cr or W) have been treated with a total of eleven epoxides to give 2-hydroxyalkyl isocyanide or oxazolin-2-ylidene complexes, respectively. In general, regiospecific ring opening occurred except with 2,2-dimethyloxirane which gave rise to a mixture of regioisomers. The silyl derivatives $[M(CO)_5(CNSiMe_3)]$ (M = Cr or W) react similarly. I.r., $^1H$ n.m.r., $^{13}C$ n.m.r., and mass spectra of the new compounds are reported and discussed.

Hydrogen isocyanide which has recently been detected as a major constituent in certain interstellar clouds[1] is highly unstable with respect to its isomerization to hydrogen cyanide under terrestrial conditions. Its stabilization by co-ordination in metal complexes such as $[M(CO)_5(CNH)]$ (M = Cr, Mo, or W)[2,3] and $[Mn(\eta\text{-}C_5H_5)(CO)_2(CNH)]$[4] has therefore attracted much attention, however without stimulating further spectroscopic and structural investigations. In particular, no chemistry of this species has been reported, except in a paper dealing with the preparation of γ-oxoisocyanides from $H_4M(CN)_6$(M = Fe or Ru) and α,β-unsaturated carbonyl compounds.[5]

Our interest in functional isocyanides prompted us to explore the synthetic potential of organometallic CNH complexes. In this paper we describe the reactions of pentacarbonyl(hydrogen isocyanide)-chromium and -tungsten with two different kinds of epoxides (**1**) [including 1,2-epoxycyclohexane (**1a**) and 2,3-epoxynorbornane (**1b**)] and (**2**) to give either 'open-chain' 2-hydroxyalkyl isocyanide or cyclic oxazolin-2-ylidene metal complexes.


(**1**)


(**2**)

(**a**), (**b**) : see text

R = H, R' = Me (**c**), Et (**d**), $CH_2OPh$(**e**), $CH_2Cl$(**f**), or Ph(**g**); R = R' = Me (**h**)

X = CN, R = 4 - $MeC_6H_4$ (**a**) or 4 - $ClC_6H_4$ (**b**); X = $CO_2Et$, R = 4 - $ClC_6H_4$ (**c**)

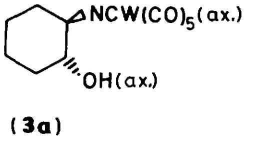
## Results and Discussion

*2-Hydroxyalkyl Isocyanide Complexes.*—Type (**1**) epoxides have been treated with either $[W(CO)_5(CNH)]$ or, more economically, $[W(CN)(CO)_5]^-$ followed by addition of $HBF_4$ to give low to moderate yields of the compounds (**3a**)—(**3h**) (Scheme 1). No particular effort was made to improve yields, except in the case of (**3c**) where a more elaborate work-up procedure was applied to exemplify that the reaction was almost quantitative (see Experimental section). Analytical and selected i.r. data for the white crystalline products (**3a**)—(**3h**) are summarized in Table 1. Each compound exhibits three characteristic i.r. absorptions corresponding to the ν(OH), ν(NC), and ν(CO) stretching vibrations. As expected, the frequency and intensity pattern of the last two closely resembles that of hexacarbonylmetal derivatives of *non*-functional alkyl isocyanides.[6] The mass spectra show the required parent peaks along with five equidistant lines corresponding to the successive loss of carbon monoxide. At various stages, fragmentation of the isocyanide ligands occurs with loss of methyl, hydrogen, and, most characteristically, HCN (or CN) and OH (or $H_2O$) (Table 2).

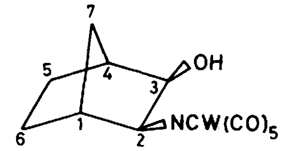
$$(1)\xrightarrow[\text{or }(ii)]{(i)}\begin{cases}\text{(3a), (3b): see below}\\ W(CO)_5(CNCH_2CRR'OH)\ (3c)\text{—}(3f),\ (3h_1)\\ W(CO)_5(CNCRR'CH_2OH)\ (3g),\ (3h_2)\end{cases}$$

**Scheme 1.** (*i*) $[W(CO)_5(CNH)]$; (*ii*) $NEt_4[W(CN)(CO)_5]$, $HBF_4$

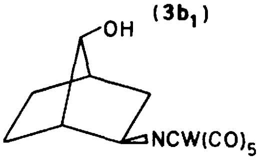
The ring-opening reactions presumably proceed by nucleophilic attack of the cyano N atom at the O-protonated heterocycle, *i.e.* by a mechanism which is well established for other HX additions to oxiranes.[7] Cyclohexane oxides are known to ring open to give invariably *trans*-diaxial products[7,8] which fixes the stereochemistry of complex (**3a**). Norbornyl systems, on the other hand, are preferentially (if not exclusively) approached from the *exo* side,[9a] suggesting that (**3b**) has the *cis*-(**3b$_1$**) or (due to some rearrangement of an intermediate carbenium ion) *syn*-related structure (**3b$_2$**). Though at present



(**3a**)



(**3b$_1$**)



(**3b$_2$**)

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† *Non S.I. unit employed:* eV ≈ 1.6 × $10^{-19}$ J.

Table 1. Analytical and i.r. data

| Compound | Analysis (%)[a] | | | $M^{a,b}$ | M.p./°C | I.r. data (cm$^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|
| | C | H | N | | | ν(CN)[c] | ν(CO)[c] | Other[d] |
| (**3a**)[e] | 32.0<br>(31.9) | 2.4<br>(2.4) | 3.1<br>(3.1) | 449<br>(449) | 95 | 2 155m–s | 2 064s ($A_1$)<br>1 954vs ($E$)<br>1 923w ($A_1'$) | 3 175m,br [ν(OH)] |
| (**3b**)[e] | 34.1<br>(33.7) | 2.4<br>(2.4) | 3.0<br>(3.0) | 461<br>(461) | 119 | 2 172m–s | 2 067s ($A_1$)<br>1 949vs($E$)<br>1 920w ($A_1'$) | 3 315w,br [ν(OH)] |
| (**3c**) $[W(CO)_5\{CNCH_2CH(Me)OH\}]$ | 26.3<br>(26.3) | 1.7<br>(1.7) | 3.4<br>(3.4) | 409<br>(409) | 56 | 2 163m–s | 2 066s ($A_1$)<br>1 955vs ($E$)<br>1 925w ($A_1'$) | 3 319m,br [ν(OH)] |
| (**3d**) $[W(CO)_5\{CNCH_2CH(Et)OH\}]$ | 28.7<br>(28.4) | 2.1<br>(2.1) | 3.2<br>(3.3) | 423<br>(423) | 57 | 2 163m–s | 2 067s ($A_1$)<br>1 955vs ($E$)<br>1 925w ($A_1'$) | 3 421m,br [ν(OH)] |
| (**3e**) $[W(CO)_5\{CNCH_2CH(CH_2OPh)OH\}]$ | 35.8<br>(35.8) | 2.2<br>(2.2) | 2.8<br>(2.8) | 501<br>(501) | 92.5 | 2 172m–s | 2 068s ($A_1$)<br>1 952vs ($E$)<br>1 923w ($A_1'$) | 3 471m [ν(OH)] |
| (**3f**) $[W(CO)_5\{CNCH_2CH(CH_2Cl)OH\}]$ | 24.1<br>(24.3) | 1.5<br>(1.4) | 3.4<br>(3.2) | 443<br>(443) | 54 | 2 168m–s | 2 067s ($A_1$)<br>1 952vs ($E$)<br>1 924w ($A_1'$) | 3 369m,br [ν(OH)] |
| (**3g**) $[W(CO)_5\{CNCH(Ph)CH_2OH\}]$ | 35.5<br>(35.5) | 1.9<br>(1.9) | 3.0<br>(3.0) | 471<br>(471) | 78.5 | 2 152m–s | 2 062s ($A_1$)<br>1 956vs ($E$)<br>1 926w ($A_1'$) | 3 436s,br [ν(OH)] |
| (**3h**) $[W(CO)_5(CNCMe_2CH_2OH)]$<br>+ isomer[e] | 28.5<br>(28.4) | 2.2<br>(2.1) | 3.4<br>(3.3) | 423<br>(423) | 89—94 | 2 161m<br>2 147m–s | 2 065(sh)<br>2 062s ($A_1$)<br>1 954vs ($E$)<br>1 925m ($A_1'$) | 3 453m,br [ν(OH)] |
| (**4h**) $[Cr(CO)_5(CNCMe_2CH_2OH)]$<br>+ isomer[e] | 41.5<br>(41.3) | 3.2<br>(3.1) | 4.8<br>(4.8) | —<br>(291) | | 2 145s,br[f] | 2 040m ($A_1$)[f]<br>1 930vs,br ($E$)[f] | 3 380vs,br [ν(OH)] |
| (**5h**) $[Cr(CO)_5(CNCMe_2CH_2OSiMe_3)]$<br>+ isomer[e] | 42.8<br>(43.0) | 5.6<br>(4.7) | 4.0<br>(3.9) | —<br>(363) | | 2 135s | 2 045m($A_1$)<br>1 935vs,br ($E$) | 1 250s [δ(SiMe$_3$)] |
| (**6h**) $[W(CO)_5(CNCMe_2CH_2OSiMe_3)]$<br>+ isomer[e] | | | | | | 2 150s,br[d] | 2 065w ($A_1$)[d]<br>1 910vs,br ($E$)[d] | 1 245w [δ(SiMe$_3$)] |
| (**10a**) $[Cr(CO)_5\{\overline{CNHCR{=}C(CN)O}\}]$[g] | | | 7.4<br>(7.5) | 376<br>(376) | 230<br>(decomp.) | | 2 067s ($A_1$)[f]<br>1 942vs ($E$)[f] | 3 210m,br [ν(NH)]<br>2 231m–s [ν(CN)]<br>1 449[ν$_{asym}$ (N⩦C⩦O)] |
| (**10b**) $[Cr(CO)_5\{\overline{CNHCR{=}C(CN)O}\}]$[h,i] | 45.2<br>(45.3) | 1.5<br>(1.5) | 7.3<br>(7.0) | 395.915<br>(395.924) | 230<br>(decomp.) | | 2 068s ($A_1$)[f]<br>1 942vs ($E$)[f] | 3 215[ν(NH)]<br>2 232m–s [ν(CN)]<br>1 447[ν$_{asym}$ (N⩦C⩦O)] |
| (**11**) $[Cr(CO)_5\{CNCHRC(CN)(CO_2Et)OH\}]$[h] | 45.8<br>(46.0) | 2.0<br>(2.3) | 5.7<br>(6.0) | 469.9609<br>(469.9585) | 112 | 2 147s[f] | 2 058s ($A_1$)[f]<br>1 963vs ($E$)[f] | 3 442m [ν(OH)]<br>1 749m–s [ν(CO$_2$Et)] |

[a] Calculated values are given in parentheses. [b] Mass spectrometrically determined, $^{184}W$. [c] In n-pentane. [d] In KBr. [e] See text. [f] In $CH_2Cl_2$. [g] R = 4-$MeC_6H_4$. [h] R = 4-$ClC_6H_4$. [i] Cl 8.8 (8.9%).

no clear decision can be made between these (or other plausible) structures, the $^{13}C$ n.m.r. pattern of (**3b**) slightly favours the 2-*exo*-7-*syn* isomer.[*] This is not unreasonable in the light of HBr addition to compound (**1b**) which gave 2-*exo*-bromo-7-*syn*-norbornanol as the major product.[11] A further complication arises in the case of the unsymmetrical oxiranes (**1c**)—(**1g**) which in principle offer two non-equivalent sites for nucleophilic attack. According to the literature, however, ring-opening of monoalkyl oxiranes occurs almost exclusively at the less-branched C atom.[7]

In order to ascertain the regiochemistry of the above reactions (Scheme 1), we synthesized 2-hydroxypropyl isocyanide and its pentacarbonyltungsten derivative by an independent route (Scheme 2). The product was identical to (**3c**), which shows that, contrary to recent speculations,[12] cyano transition-metal complexes enter the same positions in the oxiranes as $CN^-$, $SiMe_3CN-AlCl_3$,[13,†] and most ordinary nucleophiles (however, see below).

$$HCONH-CH_2CHMeOH \xrightarrow{(i)} CN-CH_2CHMeOH \xrightarrow{(ii)} (OC)_5WCN-CH_2CHMeOH$$

Scheme 2. (*i*) $COCl_2$, $NEt_3$; (*ii*) $[W(CO)_5(thf)]$ (thf = tetrahydrofuran)

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[*] *Note added in proof*: The $^{13}C$ chemical shifts calculated for this isomer from the values of the newly prepared pentacarbonyl(2-*exo*-isocyanonorbornane)tungsten are in excellent agreement with the experimental data of (**3b**) (*cf.* Table 3 and ref. 10) (E. Bär and W. P. Fehlhammer, unpublished work).

[†] In the $ZnI_2$-catalysed addition of trimethylsilyl cyanide to 1-methylcyclohexene oxide, however, a reversal of regiochemistry was firmly established.[14]

**Table 2.** Major fragments in the mass spectra (*m*/*z*, relative intensity in %; 100 defines base peak) of 2-hydroxy- and 2-trimethylsiloxy-alkyl isocyanide metal complexes (M = $^{52}$Cr or $^{184}$W)

| Ion | (3a) | (3b) | (3c)[a] | (3d) | (3e) | (3f)[b] | (3g) | (3h)[c] | (4h)[d] | (5h)[e] | (11) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $M(CO)_5L^+$ | 449(67) | 461(55) | 409(*100*) | 423(62) | 501(58) | 443(75) | 471(6) | 423(*100*) | 291(49) | 363(7) | 470(19) |
| $[M(CO)_5L - HCN]$ | | | | | | | | | | | 443(8) |
| $M(CO)_4L^+$ | 421(17) | 433(14) | 381(22) | 395(9) | | | 443(4) | 395(13) | 263(5) | 335(1) | |
| $[M(CO)_4L - Me]$ | | | | | | | | 380(5) | 248(5) | 320(2) | |
| $M(CO)_3L^+$ | 393(*100*) | 405(*100*) | 353(76) | 367(50) | | | 415(1) | 367(33) | 235(13) | 307(2) | |
| $[M(CO)_3L - Me]$ | | | | | | | | | 220(17) | 292(4) | |
| $[M(CO)_3L - OH]$ | | | 336(13) | | | | | | | | |
| $M(CO)_2L^+$ | 365(21) | 377(32) | 325(37) | 339(23) | 417(85) | 359(38) | 387(6) | 339(50) | 207(17) | 279(2) | 386(8) |
| $[M(CO)_2L - Me]$ | | | | | | | | | 192(8) | 264(4) | |
| $[M(CO)_2L - OH]$ | | | | 322(5) | | | | | | | |
| $[M(CO)_2L - HCN]$ | | | | | | | | | 180(29) | | |
| $M(CO)L^+$ | 337(13) | 349(26) | 297(46) | 311(61) | 389(85) | 331(65) | 359(9) | 311(86) | 177(63) | 251(18) | 358(25) |
| $[M(CO)L - Me]$ | | | | | | | | | 164(2) | 236(1) | |
| $[M(CO)L - OH]$ | | | | 294(9) | | 315(*100*) | | | | | |
| $[M(CO)L - HCN]$ | | | | | | | | | 152(46) | | |
| $ML^+$ | 309(48)[f] | 321(75) | 269(73) | 283(98) | 361(27) | 303(34) | 331(20) | 283(73) | 151(*100*) | 223(90) | 330(*100*) |
| $(ML - 2H)$ | | | | 281(*100*) | | | | | | | |
| $(ML - Me)$ | | | | | | | | | 136(14) | 208(4) | |
| $(ML - OH)$ | | | | 266(16) | | | | | | | |
| $(ML - HCN)$ | | | | | 334(8) | | | | 124(48) | 196(18) | 303(45) |
| $(ML - H_2CN)$ | 281(23)[f] | 293(36)[f] | | 255(49)[f] | | | 302(23)[g] | | | | |
| $M(CNH)^+$ | 211(10) | 211(8) | | | | | | 211(27) | | | |
| $M(CN)^+$ | 210(12) | 210(9) | 210(27) | 210(13) | 210(9) | 210(30) | 210(11) | 210(32) | | | |
| $(L - CN)$ | | 111(12) | 59(19) | | 151(6) | | 121(43) | 73(13) | | | |
| $(L - CN - H_2O)$ | 81(67) | 93(31) | | 55(22) | 133(35) | | 103(*100*) | 55(29) | | | |
| | | | | | 94(*100*)[h] | | 77(48)[i] | | | 73(*100*)[j] | |

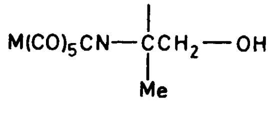
[a] Additional peaks: *m*/*z* 311(40), 283(80), and 255(40) $[W(CO)_n(CNC_2H_4OH)]^+$ (*n* = 2—0); 225[30%, $W(CNMe)^+$]. [b] Also: *m*/*z* 315[100, $W(C)L^+$], 222[29, $WC(CN)^+$], and 196(12%, $WC^+$). [c] Additional lines: *m*/*z* 351(25), 323(88), and 295(37)$[W(CO)_n(C)L]^+$ (*n* = 2—0); 267[49, $W(CNCMe_3)^+$], and 252[42%, $W(CNCMe_2)^+$]. [d] Additional lines: *m*/*z* 260(2), 232(17), 204(11), 176(10), 148(12), and 120(23) $[Cr(CO)_n(CNCMe_2)]^+$ (*n* = 5 – 0). Metastable peaks: m* [ = (mass of final fragment)$^2$/(mass of initial ion)] 237.7(291 ⟶ 263), 127.3(177 ⟶ 152), and 101.8(151 ⟶ 124). [e] m* 172.3 (223 ⟶ 196). Also: *m*/*z* 151[58%, $Cr(CNCMe_2CH_2OH)^+$ + $Cr(CNCH_2CMe_2OH)^+$]. [f] Together with further H abstractions. [g] (WL – HCN – 2H). [h] $PhOH^+$. [i] $Ph^+$. [j] $SiMe_3^+$.

In the $^{13}$C n.m.r. spectra of complexes **(3b)**—**(3d)** (Table 3) the *cis* and *trans* carbonyl carbon atoms appear at the expected low-field position as do the very weak and broad signals of the isocyano carbon atoms which were not sufficiently resolved to allow observation of $^{13}$C–$^{183}$W or $^{13}$C–$^{14}$N coupling, respectively. The assignment of signals to the carbon atoms of the alkyl side chains was made on the basis of H coupling and, in the case of **(3b)**, by comparison with the calculated $^{13}$C chemical shifts of the 2-*exo*-NH$_2$-substituted 3-*exo*- and 7-*syn*-norbornanols.[10]

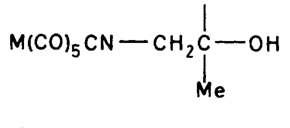
The shifts of the α- and β-carbon atoms of the isocyanide ligand in complex **(3d)** are very similar to those of the 2-hydroxypropyl isocyanide complex **(3c)**, suggesting a structure with the ethyl group in the β position. In complex **(3g)**, however, the CH$_2$ triplet has been considerably shifted downfield to even below the CH doublet, which clearly indicates a reverse ring opening of the epoxide **(1g)** to give the α-phenyl derivative. The same substitution pattern has been ascertained by *X*-ray analysis for the heterocyclic ligand in $[Au(CN)\{\overline{CNHCH(Ph)CH_2O}\}]$, the product of cyclization of an intermediate 2-hydroxyalkyl isocyanide complex of the type **(3g)**; along with other oxazolidinylideneplatinum and hydroxyalkyl isocyanidegold complexes, this compound has recently been prepared by a similar approach from styrene oxide and $HAu(CN)_2$.[15] There is also a report on a 2-hydroxyalkyl isocyanideruthenium complex which was obtained similarly.[16]

Further evidence in support of the assumed molecular structures of complexes **(3a)**—**(3g)** comes from the $^1$H n.m.r. spectra (Table 3). The signals of the OH protons have been identified by their disappearance on addition of D$_2$O; their positions proved to be highly solvent dependent. The chemically non-equivalent CH$_2$ protons together with the chiral CH groups of compounds **(3c)**—**(3g)** give rise to complicated patterns of partly overlapping multiplets at 90 MHz; in the 270-MHz spectra of **(3c)** and **(3d)**, however, a total of eight lines appears per CH$_2$ group as expected for the AB part of an ABX system.

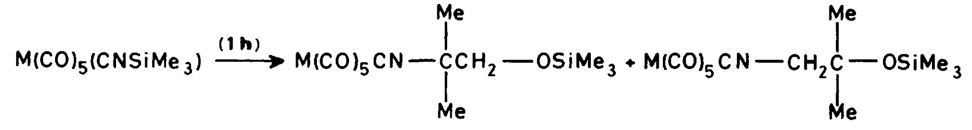
The reaction of $[W(CN)(CO)_5]^-$ and HBF$_4$ with **(1h)** differs from the ones discussed so far in that a mixture of two isomers [**(3h$_1$)** and **(3h$_2$)**] is obtained. No attempts were made to separate the isomers. In view of the presence of a tertiary carbon in compound **(1h)** and the results of the ZnI$_2$-catalysed addition of SiMe$_3$CN to 1-methylcyclohexene oxide,[14] the 3:1 preponderance of the (supposed) $S_N1$ product **(3h$_1$)** is not unexpected.[9b] On the other hand, this regiochemistry sharply contrasts with that reported for the aluminium trichloride-promoted reaction of isobutylene oxide and SiMe$_3$CN,[13] indicating that in this case different mechanisms are operating depending on which end of the ambivalent cyanide, nitrogen or carbon, is available for attack at the protonated epoxide. The assignments of the i.r. (Table 1) and n.m.r. data (Table 3) to either **(3h$_1$)** or **(3h$_2$)** have been made on the basis of the relative band intensities and estimated donor strengths of the two


$M(CO)_5CN{-}C(Me)_2CH_2{-}OH$

**(3h$_1$)** M = W
**(4h$_1$)** M = Cr


$M(CO)_5CN{-}CH_2C(Me)_2{-}OH$

**(3h$_2$)** M = W
**(4h$_2$)** M = Cr



$$M(CO)_5(CNSiMe_3) \xrightarrow{(1h)} M(CO)_5CN{-}CMe_2CH_2{-}OSiMe_3 + M(CO)_5CN{-}CH_2CMe_2{-}OSiMe_3$$

(**5h**$_1$) M = Cr (**5h**$_2$) M = Cr

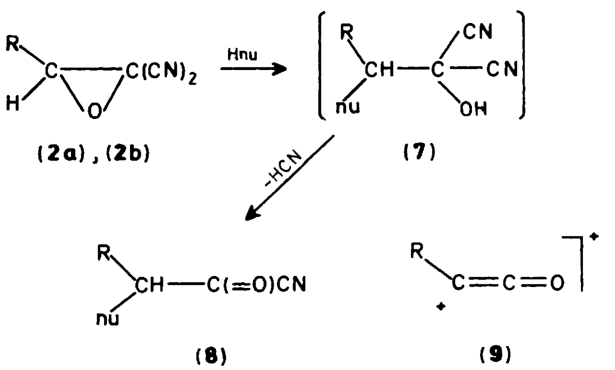
(**6h**$_1$) M = W (**6h**$_2$) M = W

Scheme 3.

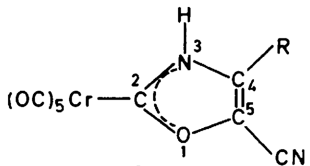
isomeric ligands, as well as by comparison with other 2-hydroxyalkyl isocyanides. The markedly lower CN stretching frequency of complex (**3h**$_1$) as compared to that of (**3h**$_2$) is thought to reflect the decreased electron-withdrawing ability and the increased bulkiness of the tertiary alkyl substituent. Such valuable correlations have been established for some 50 'free' non-conjugated aliphatic isocyanides.[17]

Interestingly, in the above reactions the hydrogen isocyanide ligand can be replaced by isocyanotrimethylsilane[2,18,19] without much alteration of the isomer distribution (Scheme 3). Treatment at room temperature of [$Cr(CO)_5(CNSiMe_3)$] with the epoxide in excess followed by chromatography gave two bands each of which contained a yellow liquid. Fraction 1, (**5h**), was extremely sensitive towards moisture, immediately hydrolysing to the isomeric mixture, (**4h**), which is identical with fraction 2. In the tungsten case, only the hydroxy species (**3h**) could be isolated in an analytically pure state.

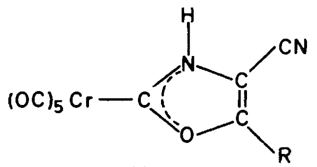
*Oxazolin-2-ylidene(carbene) Complex.*—Type (**2**) oxiranes have been shown to react with nucleophiles very selectively (Scheme 4). Since the resulting acyl cyanide (**8**) easily takes up a second molecule of the nucleophile, these 'dielectrophilic' oxiranes (**2a**) and (**2b**) have been regarded as equivalent to the ketene cations (**9**).[20] Their reactions with [$Cr(CO)_5(CNH)$] to give pentacarbonyl(oxazolin-2-ylidene)chromium complexes (**10**) require reflux conditions; when [$Cr(CO)_5(CNH)$] was replaced by [$Cr(CN)(CO)_5$]$^-$ and $HBF_4$, however, no products could be isolated. The reactions are likely to proceed *via* an intermediate (**7**) [nu = $Cr(CN)(CO)_5$] which then undergoes intramolecular cycloaddition and HCN elimination thereby attaining aromaticity.* This last step has its precedent in the spontaneous elimination of toluene-*p*-sulphinic acid from the primary cyclization product of metal-co-ordinated $CNCH_2SO_2C_6H_4Me$-4 and aldehydes.[21,22] However, it cannot be excluded that HCN is eliminated prior to cyclization, *i.e.* an intermediate (**8**) is involved.



**Scheme 4.** General reaction of dicyano epoxides with nucleophiles (Hnu)



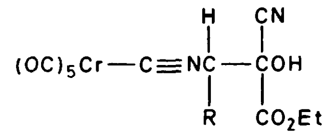
(**I**)



(**II**)

The spectroscopic data of complexes (**10a**) and (**10b**) (*cf.* Tables 1 and 3 and Experimental section) suggest structure (**I**). Thus, in the mass spectrum of (**10b**) a peak emerges at *m*/*z* 137 which is attributable to 4-$ClC_6H_4C{\equiv}N^{\cdot+}$, though there is no evidence that this fragment is derived directly from the molecular ion. On the other hand, there is clearly no line corresponding to a fragment $RCO^+$ of the alternative regioisomer (**II**). Likewise, the $^{13}C$ chemical shifts of the $C^4$ and $C^5$ carbon atoms are more in accord with structure (**I**) than (**II**); for the latter, one would expect both a more shielded $C^4$ (between NH and CN) and a more deshielded $C^5$ (between O and R).

We have demonstrated previously[23] that the readiness for intramolecular cycloaddition of a given 2-hydroxyalkyl isocyanide is strongly dependent on the metal to which it is attached. According to these studies, $M(CO)_5$ (M = Cr, Mo, or W) fragments generally stabilize the 'open-chain' isocyanide form which is in accord with our present results for the 2-hydroxy isocyanide complexes, yet contrasts with the above findings. Thus one's attention is drawn to other factors such as the presence of electron-withdrawing substituents in the side chain of the hydroxy isocyanide intermediates (**7**) [nu = $Cr(CN)(CO)_5$] which, to a lesser extent, also contribute to the activity of the metal-co-ordinated isocyano group towards nucleophilic attack by the OH group. That the factors controlling this hydroxyalkyl isocyanide to N,O-carbene isomerization are even more complex (and not fully understood), however, becomes apparent in the reaction of [$Cr(CO)_5(CNH)$] with (**2c**) which, in spite of an almost identical set of α and β substituents, does not proceed beyond the hydroxyalkyl isocyanide stage (**11**).



$$(OC)_5Cr{-}C{\equiv}NC(H)(R){-}C(CN)(OH)CO_2Et$$

(**11**)

## Experimental

All reactions were carried out under an atmosphere of pure argon using conventional Schlenk-tube techniques. Solvents were dried, distilled, and stored under argon. The starting

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* A similar heterocyclization has been reported to account for the formation of 1,3-oxaselenoles from *gem*-dicyanoepoxides.[20]

**Table 3.** $^1H$ and $^{13}C$ n.m.r. data[a]

| Compound | |
|---|---|
| **(3a)**[b] | 1.1—2.3[c, 9 H, $(CH_2)_4$ + OH], 2.01 (s, OH), 3.53—3.78 (c, 2 H, C*H*OH + CHNC) |
| **(3b)**[b,c] | 1.0—2.5 (c, 9 H, norbornyl envelope and OH), 1.69 (s, OH),[d] 3.71 (m, 1 H, CHNC), 4.18 (br s with fine structure, 1 H, C*H*OH)<br>[e] 23.6 (t, $C^6$), 24.6 (t, $C^5$), 37.8 (t, $C^3$), 40.4 (d, $C^4$), 47.7 (d, $C^1$), 56.0 (d, $C^2$), 79.3 (d, $C^7$), 140.0 (s, CN), 194.5 [s, *cis*-CO, *J*(W–C) = 128.0], 196.9 (s, *trans*-CO) |
| **(3c)**[f] | 1.28 (d, 3 H, $CH_3$, *J* = 7.0), 2.93 (s, 1 H, OH), 3.62[g] (2 H, $CH_2$), 4.08 (m, 1 H, CH)<br>[e] 20.1 (q, $CH_3$), 51.1 (t, $CH_2$), 65.7 (d, CH), 143.7 (s, CN), 194.1 [s, *cis*-CO, *J*(W–C) = 126.0], 196.1 (s, *trans*-CO) |
| **(3d)**[f] | 1.00 (t, 3 H, $CH_3$, *J* = 6.8), 1.55 (q, 2 H, $CH_3CH_2$, *J* = 6), 2.42 (s, 1 H, OH), 3.66[g] (2 H, $CNCH_2$), 3.77 (m, 1 H, C*H*OH)<br>9.1 (q, $CH_3$, *J* = 130.6), 27.1 (t, $CH_3CH_2$, *J* = 128.2), 49.6 (t, $CNCH_2$, *J* = 146.5), 70.8 (d, CHOH, *J* = 141.6), 143.8 (s, CN), 194.1 [s, CO, *J*(W–C) = 125.7], 196.1 (s, CO) |
| **(3e)**[h] | 2.74 (d, 1 H, OH, *J* = 5.1), 4.1—4.5 (c, 5 H, $CH_2CHCH_2$), 7.34 (m, 5 H, $C_6H_5$) |
| **(3f)**[h] | 2.29 (s, 1 H, OH), 3.5—4.8 (c, 5 H, $CH_2CHCH_2$) |
| **(3g)** | 2.38 (t, 1 H, OH, *J* = 5.7),[i] 4.16 (c, 2 H, $CH_2$), 5.29 (t, 1 H, CH, *J* = 6), 7.66 (m, 5 H, $C_6H_5$)<br>62.8 (d, CH, *J* = 153.0), 66.7 (t, $CH_2$, *J* = 145.0), 126.0, 128.4, 129.1, 133.4 ($C_6H_5$), 146.2 (s, CN), 194.0 (s, *cis*-CO), 195.9 (s, *trans*-CO) |
| **($3h_1$)**[i] | 1.46 (s, 6 H, $CH_3$), 2.00 (s, 1 H, OH), 3.60 (s, $CH_2$)<br>24.9 (q, $CH_3$), 61.7 (s, CN*C*$Me_2$), 69.4 (t, $CH_2$), 142.1 (s, CN), 194.1 [s, *cis*-CO, *J*(W–C) = 124.5], 196.3 (s, *trans*-CO) |
| **($3h_2$)**[j] | 1.36 (s, 6 H, $CH_3$), 1.77 (s, 1 H, OH), 3.60 (s, $CH_2$)<br>26.4 (q, $CH_3$), 55.3 (t, $CH_2$), 70.2 (s, *C*$Me_2$OH), 144.0 (s, CN), 194.0 (*cis*-CO), 196.0 (*trans*-CO) |
| **(4h)** + isomer[b,k] | 1.11—1.35 ($CH_3$), 3.49 (s, $CH_2$) |
| **(5h)** + isomer[b,k] | −0.05 [$Si(CH_3)_3$], 1.18—1.26 [$C(CH_3)_2$], 3.38, 3.41 ($CH_2$) |
| **(6h)** + isomer[b,k] | −0.08 [$Si(CH_3)_3$], 1.25, 1.39 [$C(CH_3)_2$], 3.39, 3.51 ($CH_2$) |
| (**10a**; R = 4-$MeC_6H_4$)[f,h,l] | 1.5 (s, 3 H, $CH_3$), 7.6 (m, 4 H, $C_6H_4$), 10.95 (s, 1 H, NH) |
| (**10b**; R = 4-$ClC_6H_4$)[f,h] | 7.67 (m, 4 H, $C_6H_4$), 11.3 (s, 1 H, NH)<br>110.5 (s, CN), 122.0, 129.8, 130.9, 138.9 ($C_6H_4$), 125.7 (s, *C*CN), 140.7 (*C*$C_6H_4$), 217.0 (*cis*-CO), 222.0 (*trans*-CO), 233 [C(carbene)?] |
| (**11**; R = 4-$ClC_6H_4$)[h] | 1.46 (t, 3 H, $CH_3$, *J* = 6), 4.3 (s, 1 H, OH), 4.32 (q, 2 H, $CH_2$), 4.5 (s, 1 H, CH), 7.43 (s, 4 H, $C_6H_4$) |

[a] Spectra were measured in $CDCl_3$ at 90 MHz; δ scale; coupling constants, *J*, are in Hz; c = complex. [b] See text. [c] Calculated $^{13}C$ values for 2-*exo*-amino-7-*syn*-norbornanol: 23.9 ($C^6$), 25.8 ($C^5$), 38.9 ($C^3$), 40.0 ($C^4$), 49.3 ($C^1$), 51.8 ($C^2$), 75.1 ($C^7$). [d] δ(OH): in [$^2H_6$]dimethyl sulphoxide, 5.16(s); in [$^2H_6$] acetone, 4.33(s). [e] $^{13}C$ N.m.r., off-resonance. [f] $^1H$ N.m.r.: Bruker WH 270. [g] AB part of an ABX system, eight lines. [h] External $SiMe_4$. [i] δ(OH) in [$^2H_6$]dimethyl sulphoxide: 5.72 (t, *J* = 5.3 Hz). [j] Isomer distribution (from integrated intensities): (**$3h_1$**) 73, (**$3h_2$**) 27%. [k] Isomer distribution *ca.* 1:1. [l] In [$^2H_6$]acetone.

complexes [$Cr(CO)_5(CNH)$], [$Cr(CO)_5(CNSiMe_3)$], Na[$W(CN)(CO)_5$], $NEt_4$[$W(CN)(CO)_5$], [$W(CO)_5(CNH)$], and [$W(CO)_5(CNSiMe_3)$] were prepared as described in the literature.[2,24] The epoxides (**1a**)—(**1g**) were commercial products (Fluka) while (**1h**)[25] and (**2a**)—(**2c**) were prepared as described earlier.[16,26]

Infrared spectra were recorded on a Perkin-Elmer model 983 spectrometer, hydrogen-1 and carbon-13 n.m.r. spectra on JEOL FX 90 Q and Bruker WH 270 instruments with the solvent ($CHCl_3$) as internal standard. Mass spectra were measured on Varian MAT 711 [electron impact (e.i.), 80 eV] and CH 5 (e.i., 70 eV) instruments, melting or decomposition points (uncorrected) using a Gallenkamp melting-point MFB-595 apparatus. Microanalyses were carried out on a Heraeus CHN-Rapid.

*Pentacarbonyl(2-hydroxyalkyl isocyanide)tungsten Complexes* (**3a**)—(**3h**).—In a typical experiment, the epoxide (1 $cm^3$) was added to an ice-cold solution of [$W(CO)_5(CNH)$] (0.8 g, 2.3 mmol) in $CH_2Cl_2$ (5 $cm^3$) or, alternatively, $HBF_4$ (2 $cm^3$) (35% in water) was syringed dropwise onto a cooled mixture of Na[$W(CN)(CO)_5$] (1.5 g, 4.0 mmol) {or $NEt_4$[$W(CN)(CO)_5$]} and the epoxide (2 $cm^3$) in $CH_2Cl_2$ (5 $cm^3$). The dark brown solution which resulted immediately was stirred overnight at room temperature, diluted with $CH_2Cl_2$ (30 $cm^3$), dried over $Na_2SO_4$, filtered, and evaporated to dryness *in vacuo*. A mixture of light petroleum (b.p. 40—60 °C) and diethyl ether (1:1, 10 $cm^3$) was added to the green-black oily residue and the solution obtained was chromatographed on Florisil (Merck) (2 × 20 cm) using light petroleum as eluant. The first 200 $cm^3$ of the eluate were concentrated to *ca.* 1/10 of the volume under reduced pressure, and the white precipitate was filtered off and dried *in vacuo* (*ca.* 30% yield).

Complex (**3c**) was obtained in an almost quantitative yield using pure diethyl ether for both the extraction and chromatographic processes. Concentration of the eluate gave an oily solid, the purification of which required repeated recrystallization from hot light petroleum.

*Preparation of the Trimethylsiloxyalkyl Isocyanide Complexes of Chromium*, (**5h**).—The complex [$Cr(CO)_5(CNSiMe_3)$] (1.20 g, 4.0 mmol) was dissolved in toluene (25 $cm^3$). 2,2-Dimethyloxirane (**1h**) (0.9 $cm^3$, 10.0 mmol) was syringed into the solution. The solution was stirred for 2 d at room temperature, after which the solvent and excess of epoxide were removed under vacuum to leave an oily residue which was redissolved in n-hexane. This solution was then chromatographed on Florisil (1 × 5 cm, n-hexane) and evaporated to dryness. The resultant yellow oil [(**5h**); 0.61 g, 41%] was purified by high-vacuum microdistillation (60—70 °C, *ca.* 0.13 Pa). Elution with $CH_2Cl_2$ gave a second fraction which was identified as the hydrolysed species [$Cr(CO)_5(CNCMe_2CH_2OH)$] + its regioisomer [(**4h**), 17%].

*Preparation of the Trimethylsiloxyalkyl Isocyanide Complexes of Tungsten*, (**6h**).—In a manner analogous to that described above, [$W(CO)_5(CNSiMe_3)$] (1.30 g, 3.1 mmol) was treated with an excess of 2,2-dimethyloxirane in toluene for 3 d. Chromatography on Florisil (2 × 10 cm, n-hexane) yielded a 3:1 isomer mixture of complex (**6h**) which was contaminated with some [$W(CO)_5(CNCMe_2CH_2OH)$] + [$W(CO)_5(CNCH_2CMe_2OH)$] (**3h**). The latter product (0.40 g, 27%) was obtained as white crystalline needles by elution with $CH_2Cl_2$, concentration of the solution, addition of n-hexane, and cooling to −20 °C for several hours.

*(4-Aryl-5-cyanooxazolin-2-ylidene)pentacarbonylchromium Complexes*, (**10a**) *and* (**10b**).—A solution of [$Cr(CO)_5(CNH)$]

(0.33 g, 1.51 mmol) and compound (**2a**) (0.28 g, 1.51 mmol) or (**2b**) (0.31 g, 1.51 mmol) in toluene (20 $cm^3$) was heated to 100 °C. After *ca.* 2 h the solvent was removed *in vacuo*, and the remaining red-brown oil was stirred in light petroleum until it had solidified. The yellow solid was washed with light petroleum (50 $cm^3$) three or four times, or chromatographed on Florisil (2 × 20 cm, ether) to give 0.34 g (60%) [0.44 g (74%)] of analytically pure complex (**10a**) [(**10b**)]. Mass spectra: (**10a**), *m/z* 376 ($M^+$, 18), 320 (9), 292 (7), 264 (24), 236 (100) $[Cr(CO)_nL]^+$ ($n$ = 3—0), 193 (21, CrL − HNCO), 184 (45, $L^+$), 156 (24, L − CO); (**10b**) *m/z* 396 ($M^+$, 17), 340 (6), 312 (8), 284 (30), 256 (100) $[Cr(CO)_nL]^+$ ($n$ = 3—0), 213 (16, CrL − HNCO), 204 (41, $L^+$), 176 (21, L − CO), and 137 (2%, 4-$ClC_6H_4CN^+$?).

$[Cr(CO)_5\{CNC(H)(C_6H_4Cl\text{-}4)C(CN)(CO_2Et)OH\}]$ (**11**).—This compound was prepared in a 45% yield by a procedure analogous to that used for (**10a**) and (**10b**).

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