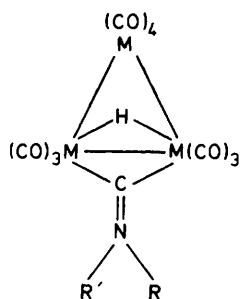


Synthesis and Fluxional Character of Complexes of the Type $[\text{Fe}_3\text{H}(\text{CO})_{10}(\mu\text{-CNR}_2)]$ and $[\text{Fe}_3\text{H}(\text{CO})_9(\mu_3\text{-CH=NR})]$

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Sequential room-temperature carbonyl substitution of $[\text{N}(\text{PPh}_3)_2][\text{Fe}_3\text{H}(\text{CO})_{11}]$ with isocyanides CNR ($\text{R} = \text{Me, Et, or Pr}^i$) yields the substituted anions $[\text{N}(\text{PPh}_3)_2][\text{Fe}_3\text{H}(\text{CO})_{11-x}(\text{CNR})_x]$ ($x = 1$ or 2), which on alkylation using $\text{R}'_3\text{OBF}_4$ ($\text{R}' = \text{Me or Et}$) or acidification using $\text{CF}_3\text{SO}_3\text{H}$ yield the complexes $[\text{Fe}_3\text{H}(\text{CO})_{10}(\text{CNR}'\text{R}')]$ ($\text{R} = \text{R}' = \text{Et}$; $\text{R} = \text{Pr}^i$, $\text{R}' = \text{Me or Et}$; $\text{R} = \text{Me, R}' = \text{H}$) and $[\text{Fe}_3\text{H}(\text{CO})_9(\text{CNR}'\text{R}')(\text{CNR})]$ ($\text{R} = \text{R}' = \text{Et}$). At higher temperatures, an insertion of isocyanide into the M-H-M bond is observed to yield, after acidification, the complex $[\text{Fe}_3\text{H}(\text{CO})_9(\text{CH=NR}^i)]$. The fluxional properties of these molecules are discussed.

THERE is currently some interest in the chemistry of transition-metal clusters containing carbene, carbyne, and carbide species because of their possible relevance as simple models for the catalytic hydrogenation of carbon monoxide.¹ In recent years, several examples of the preparation of complexes containing the dialkylamino-carbyne (CNR_2) bound in a terminal μ or μ_3 fashion have been reported. Thus, the complexes *trans* $[\text{MBr}(\text{CO})_4(\text{CNEt}_2)]$ ($\text{M} = \text{Cr or W}$) have been prepared by classic Fischer^{2a,b} methods while Chatt *et al.*^{3a,b} have recently shown that protonation of terminal isocyanides in electron-rich complexes such as *trans* $[\text{M}(\text{CNR})_2(\text{dppe})_2]$ [$\text{dppe} = 1,2$ -bis(diphenylphosphino)ethane] yields both the mono- and di-protonated derivatives *trans* $[\text{M}(\text{CNHR})(\text{CNR})(\text{dppe})_2]\text{X}$ and *trans* $[\text{M}(\text{CNHR})_2(\text{dppe})_2]\text{X}_2$ ($\text{M} = \text{Mo or W}$). Complexes containing $\mu\text{-CNR}_2$ species have been prepared by a variety of methods. Thus, alkylation or protonation of derivatives of the type $[\text{M}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_3(\text{CNR})]$ ($\text{M} = \text{Ru or Fe}$) yields salts of structure $[\text{M}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CNR}'\text{R}')]\text{X}$ ($\text{R}' = \text{H or alkyl}$)^{4,5} while a similar alkylation of $[\text{Fe}_2(\text{CNEt})_9]$ yields a salt of formula $[\text{Fe}_2(\text{CNEt})_6(\mu\text{-CNEt})(\mu\text{-CNEtR})_2]\text{X}_2$ ($\text{R} = \text{Me or Et}$).⁶ Complex (1a) has been prepared by a cleavage reaction of $\text{Me}_2\text{NCH}_2\text{SnMe}_3$ with $[\text{Ru}_3(\text{CO})_{12}]$,⁷ while reaction of $[\text{Os}_3(\text{CO})_{12}]$ with $\text{PhCH}_2\text{-NMe}_2$ results in elimination of H_2 to give (1b).⁸ The analogous complexes (1c) may be prepared by thermolysis of the isocyanide adducts $[\text{Os}_3\text{H}_2(\text{CO})_{10}(\text{CNR})]$.^{9a,b}



- (1a) $\text{M} = \text{Ru}, \text{R} = \text{R}' = \text{Me}$
 (1b) $\text{M} = \text{Os}, \text{R} = \text{Me}, \text{R}' = \text{CH}_2\text{Ph}$
 (1c) $\text{M} = \text{Os}, \text{R} = \text{Bu}^t, \text{Me}, \text{ or Ph}, \text{R}' = \text{H}$
 (1d) $\text{M} = \text{Fe}, \text{R} = \text{R}' = \text{alkyl}$

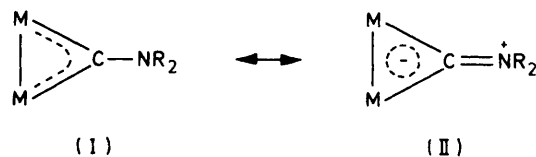
Cleavage of the $\text{C}\equiv\text{C}$ bond is observed on reaction of $[\text{Fe}_2(\text{CO})_9]$ with $\text{Et}_2\text{NC}\equiv\text{CNEt}_2$ to give $[\text{Fe}_2(\text{CO})_6(\mu\text{-CNEt}_2)_2]$, and a similar reaction with $[\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$ ($\text{M} = \text{Co or Rh}$) yields the face-bridged complexes $[\text{M}_3(\eta\text{-C}_5\text{H}_5)_3(\mu_3\text{-CNEt}_2)_2]$.^{10a,b}

We wish to report here a method of potential utility in the synthesis of neutral clusters containing the CNR_2 moiety, namely the alkylation of isocyanide substituted anionic metal clusters. Herein, we describe the preparation and fluxional properties of derivatives of structure (1d). The complex where $\text{R} = \text{R}' = \text{Me}$ has previously been isolated from the reaction of $[\text{Fe}_3(\text{CO})_{12}]$ with benzoyl chloride in dimethylformamide,^{11a,b} and from the (probably related) reaction of $[\text{Fe}_3(\text{CO})_{12}]$ with $[\text{Me}_2\text{N=CHCl}]\text{Cl}$;¹² a crystal structure determination has recently been reported.¹³ Part of this work has been the subject of a preliminary communication.¹⁴

DISCUSSION

Reaction of $[\text{N}(\text{PPh}_3)_2][\text{Fe}_3\text{H}(\text{CO})_{11}]$ (2) with a four-fold molar excess of CNR ($\text{R} = \text{Me, Et, or Pr}^i$) at room temperature in dichloromethane followed by alkylation with $\text{R}'_3\text{OBF}_4$ ($\text{R}' = \text{Et or Me}$) and purification yields the complexes (4a—d) as red-purple solids (Scheme 1). Microanalytical and i.r. data are given in Tables 1 and 2.

Crystallographic determinations of the complexes $[\text{CrBr}(\text{CO})_4(\text{CNEt}_2)]$,^{2b} $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_3(\text{CNHMe})]$ -



$[\text{BF}_4]$,⁴ $[\text{M}_3\text{H}(\text{CO})_{10}(\text{CNMe}_2)]$ ($\text{M} = \text{Fe or Ru}$)^{7,13} $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{CNHtBu}^t)]$,^{9b} and $[\text{Fe}_2(\text{CO})_6(\text{CNEt}_2)_2]$ ^{10a} have shown that the C-N bond length (1.28—1.30 Å) is typical of a C=N double bond. In addition, n.m.r. data on (1b)⁸ and on the complex salts $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_3(\text{CNR}'\text{R}')]\text{X}^5$ have shown that C-N bond rotation is slow, at least on the n.m.r. time-scale. These data have been interpreted primarily in terms of the immonium structure (II).

We find, however, that restricted C-N bond rotation

variable-temperature ^{13}C n.m.r. spectra, which show that the inequivalence of the two axial carbonyls of the unique $\text{Fe}(\text{CO})_4$ group is maintained in spectra taken at temperatures significantly higher than those of the fast-exchange proton spectrum. While a rotation of the complete CNR_2 ligand cannot be ruled out, this process seems unlikely.

Infrared spectral data support these conclusions. The $\nu(\text{C-N})$ value observed for (4b) ($1\,540\text{ cm}^{-1}$, Nujol) is intermediate between accepted values for $\nu(\text{C=N})$ of

the static structure is obtained at $-70\text{ }^\circ\text{C}$. On the basis of intensities, the resonances at 218.3 and 216.5 may be assigned to carbons C^e, C^f , while C^d, C^d' may be associated with the resonance at 207.3 p.p.m. which is the only peak of intensity two not to show proton coupling (Table 4). The $\text{Fe}(\text{CO})_3$ resonances may be assigned according to the magnitude of the difference in chemical shift of the pairs $\text{C}^x, \text{C}^{x'}$ ($x = a, b, c$) when $\text{R} \neq \text{R}'$ as in (4b—d). The previously determined crystal structures of $[\text{M}_3\text{H}(\text{CO})_{10}(\text{CNMe}_2)]$ ($\text{M} = \text{Fe}$ and Ru)^{7,13} indicate

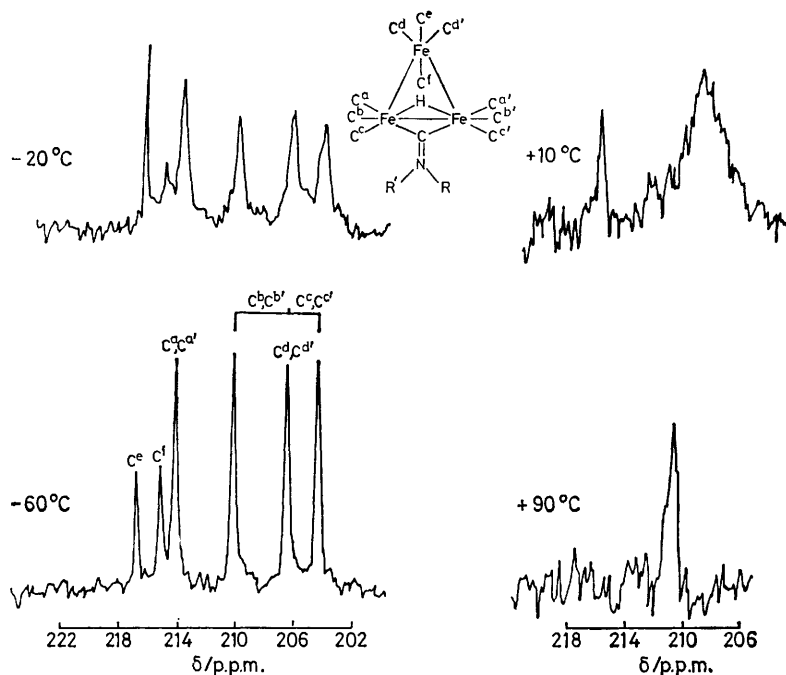


FIGURE 2 Variable-temperature ^{13}C n.m.r. spectra of (4a) ($\text{R} = \text{R}' = \text{Et}$)

$1\,640$ — $1\,690\text{ cm}^{-1}$ for imines, oximes,¹⁷ or immonium salts ($[\text{R}_2\text{CHCR}=\text{NR}_2]\text{X}$ ¹⁸) and accepted values for $\nu(\text{C-N})$ of $1\,360$ — $1\,310\text{ cm}^{-1}$ for tertiary amines.¹⁹ The complex $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CNMeEt})][\text{BF}_4]$ exhibits an analogous absorption at $1\,595\text{ cm}^{-1}$,⁵ the shift to higher frequency being consistent with the cationic nature of the complex.

Protonation of (3a—c) using $\text{CF}_3\text{SO}_3\text{H}$ yields the expected complexes (5a—c). Only (5a) has been isolated in a reasonable state of purity, as these compounds decompose in the solid state over a period of hours to give $[\text{Fe}_3(\text{CO})_{11}(\text{CNR})]$. It is known that protonation of (2) at $-80\text{ }^\circ\text{C}$ yields the analogous $[\text{Fe}_3\text{H}(\text{CO})_{10}(\text{COH})]$ which decomposes above $-30\text{ }^\circ\text{C}$ to give $[\text{Fe}_3(\text{CO})_{12}]$.²⁰ Although the N-H proton itself could not be detected in the n.m.r. spectrum of (5a), its presence is evident in the coupling observed to both the methyl and M-H resonances, and in $\nu(\text{N-H})$, observed at $3\,330\text{ cm}^{-1}$ in the i.r. spectrum (Nujol mull).¹⁷

An independent fluxional process is apparent from the ^{13}C spectra (Figure 2). For (4a), a six-line carbonyl spectrum in the ratio of 1 : 1 : 2 : 2 : 2 : 2 consistent with

that the order of difference in chemical shifts should be $\text{C}^e, \text{C}^f > \text{C}^b, \text{C}^{b'} \gg \text{C}^a, \text{C}^{a'}$. As the lowest field resonance at ca. 215 p.p.m. occurs as a singlet in both (4b) and (4c), this is assigned to the $\text{C}^a, \text{C}^{a'}$ pair. An unambiguous

TABLE 1

Analytical data (%) *

| Complex | C | H | N |
|---------|-------------|-------------|-------------|
| (2) | 55.7 (55.6) | 3.00 (3.05) | 1.40 (1.40) |
| (4a) | 33.7 (33.8) | 2.05 (2.05) | 2.65 (2.65) |
| (4b) | 32.5 (32.4) | 1.70 (1.75) | 2.65 (2.70) |
| (4c) | 35.0 (35.2) | 2.45 (2.40) | 2.80 (2.55) |
| (4d) | 34.0 (33.8) | 2.05 (2.05) | 2.80 (2.65) |
| (5a) | 30.7 (29.3) | 1.15 (1.00) | 2.65 (2.85) |
| (7) | 36.8 (36.4) | 3.05 (2.85) | 5.05 (5.00) |
| (8a) | 31.7 (31.8) | 1.70 (1.85) | 2.75 (2.85) |

* Calculated values are in parentheses.

assignment of $\text{C}^b, \text{C}^{b'}$ and $\text{C}^c, \text{C}^{c'}$ is not possible, since the relevant resonances show a reversed order of chemical shift difference in (4b) as compared to (4c). This uncertainty is reflected in the contrasting assignments for the analogous carbons in the $[\text{M}_3\text{H}(\text{CO})_{10}(\text{COMe})]$ ($\text{M} = \text{Fe}, \text{Ru}, \text{and Os}$) series.^{15,16} As $\text{C}^a, \text{C}^{a'}$ occur at

lower field than C^e, C^{e'} the lower of the two resonances belonging to the axial Fe(CO)₄ carbons is assigned to C^e.

On initial warming, two fluxional processes are observed to occur at approximately equal rates: (a) a polytopal rearrangement of the Fe(CO)₃ carbonyls, and (b) a polytopal rearrangement of three of the four Fe(CO)₄ carbonyls (C^d, C^{d'}, C^f). This preferential exchange of three carbonyls can be explained by a trigonal twist mechanism involving the triangular C^dC^{d'}C^f face (Scheme 2). On further warming, the resonance due to C^e also broadens, implying a higher activation energy for the trigonal twist involving the C^dC^{d'}C^e face. At +90 °C, only a single, broadened resonance is observed, consistent with complete carbonyl scrambling over the cluster.

TABLE 2

| Infrared spectral data (2 200—1 700 cm ⁻¹) | |
|--|--|
| Complex | $\nu(\text{CO})/\text{cm}^{-1}$ |
| (2) ^a | 2 000s, 1 971m, 1 723w |
| (4a) ^b | 2 082m, 2 035s, 2 023s, 2 004m, 1 994m, 1 989 (sh), 1 974m, 1 958m |
| (4b) ^b | 2 082m, 2 035s, 2 023s, 2 004m, 1 994m, 1 989 (sh), 1 974m, 1 958m |
| (4c) ^b | 2 082m, 2 035s, 2 023s, 2 004m, 1 994m, 1 989s, 1 974m, 1 958m |
| (4d) ^b | 2 082m, 2 035s, 2 023s, 2 004m, 1 994m, 1 989s, 1 974m, 1 958m |
| (5a) ^b | 2 083w, 2 039s, 2 028s, 2 010s, 1 999s, 1 987m, 1 979m, 1 963m |
| (7) ^b | 2 058m, 2 016s, 2 008s, 2 000m, 1 993m, 1 990m, 1 982m, 1 976s, 1 972 (sh), 1 966 (sh), 1 960m, 1 950w, 1 938w |
| (8a) ^b | 2 083w, 2 051s, 2 021s, 2 011s, 1 995m, 1 987w, 1 967w, 1 959w |

^a CH₂Cl₂ solution. ^b Hexane solution.

Polytopal carbonyl rearrangement at cluster M(CO)₃ units is a well established process. Rearrangement at an M(CO)₄ moiety may proceed *via* a pseudo-four-fold or pseudo-three-fold mechanism; the number of examples

which provide definitive evidence are rare, but recent results are most consistent with the pseudo-three-fold (trigonal twist) mechanism which is evident here.²¹

More prolonged reaction of [Fe₃H(CO)₁₁]⁻ with CNEt, followed by alkylation and purification, yields the mono-substituted complex [Fe₃H(CO)₉(CNEt₂)(CNEt)] (7), presumably *via* the intermediacy of the disubstituted anion (6). The complexity of the i.r. spectrum (Table 2) indicates the presence of isomers and at -65 °C in the ¹H n.m.r. spectrum, three M-H resonances of unequal intensity are observed (Figure 3). The temperature dependence of the three resonances is most consistent with the three isomers (7a—c) (Figure 4). Initial warming to -25 °C results in broadening and coalescence of the highest and lowest field resonances, while further warming yields eventually a single resonance at +75 °C. The results imply an initial exchange of two of the three possible isomers, and can be explained in terms of the trigonal twist mechanism previously outlined. Thus, an initial twist about the C^aC^bCNEt face of (7a) or the C^dCNEtC^{d'} face of (7b) results in exchange between (7a) and (7b); a similar twist about the C^fC^eC^{f'} face of (7c) results in axial \rightleftharpoons equatorial site exchange, but not in isomer interchange. At higher temperatures, rotation about the alternate faces *cis* to the M-H-M bridge [C^aC^cCNEt, C^dC^eC^{d'}, and C^fC^{f'}CNEt] results in exchange between all three isomers. The resonance of greatest intensity at δ -17.4 may thus be assigned to (7c), and it is of interest to note that in the related complex [Os₃H(CO)₉(COMe)(CNBu^t)] only the isomer of analogous structure is observed in the solid state and in solution.¹⁵ Unambiguous assignment of (7a) and (7b) is not possible, although steric considerations would lead one to predict a lower population for the axially substituted (7b). Variable-temperature ¹³C n.m.r. spectra in the region of

TABLE 3
Hydrogen-1 n.m.r. spectral data ^a

| Complex | Temperature/°C | M-H | Other |
|-------------------|----------------|-----------------|--|
| (2) | +25 | -15.0(s) | N(PPh ₃) ₂ 7.33—7.50 (m) |
| (4a) | -60 | -18.0(s) | CH ₂ CH ₃ 4.32 (q, J 7.5) |
| | | | CH ₂ CH ₃ 1.42 (t) |
| (4b) | -60 | -18.0(s) | CH ₂ CH ₃ 4.26 (q, J 7.3) |
| | | | CH ₂ CH ₃ 1.48 (t) |
| | | | CH ₃ 3.88 (s) |
| (4c) | -60 | -18.0(s) | CH ₂ CH ₃ 4.13 (m) |
| | | | CH ₂ CH ₃ 1.51 (t, J 7.5) |
| | | | CH(CH ₃) ₂ 1.51 (d, J 6.6) |
| | | | CH(CH ₃) ₂ 1.41 (d, J 6.8) |
| (4d) | -60 | -18.0(s) | CH(CH ₃) ₂ 4.99 (sept) |
| | | | CH(CH ₃) ₂ 1.37 (d, J 6.8) |
| | | | CH(CH ₃) ₂ 1.50 (d, J 6.8) |
| | | | CH(CH ₃) ₂ 4.92 (sept) |
| | | | CH ₃ 3.72 (s) |
| (5a) ^b | +25 | -18.0(d, J 2.5) | CH ₃ 2.71 (d, J 4.6) |
| (7) | -65 | -17.2 (s) | CN(CH ₂ CH ₃) ₂ 4.29 (m) |
| | | -17.4 (s) | CNCH ₂ CH ₃ 3.55—3.97 (m) |
| | | -17.5 (s) | CNCH ₂ CH ₃ 1.38 (m) |
| | | | CN(CH ₂ CH ₃) ₂ 1.38 (m) |
| (8a) ^b | -50 | -26.7(s) | CHNCH(CH ₃) ₂ 8.10 (s) |
| | | | CHNCH(CH ₃) ₂ 2.38 (sept) |
| | | | CHNCH(CH ₃) ₂ 0.61 (d, J 6.8) |
| | | | CHNCH(CH ₃) ₂ 0.35 (d, J 6.8) |

^a CD₂Cl₂ solution unless otherwise indicated; values in p.p.m. from SiMe₄. s = Singlet, d = doublet, t = triplet, q = quartet, sept = septet. Coupling constants J in Hz. ^b C₆D₆CD₃ solution.

the CNEt and CNEt₂ resonances (Figure 5) agree with this interpretation, showing, at -60 °C, three resonances of unequal intensity. On warming to -30 °C, exchange of two of the isomers is evident, while at +25 °C, single broadened resonances are found, consistent with exchange between all three isomers.

It is of interest to compare these results with those for the initial isonitrile substitution of [Fe₃H(CO)₁₁]⁻. Because of the sequential substitution, pure samples of (3a—c) cannot be obtained. However, the position of substitution may be demonstrated by n.m.r. techniques. In the ¹H n.m.r. spectrum, reaction of (2) over 30 min at room temperature with a 4 : 1 excess of CNEt results in replacement of the M-H resonance of (2) (δ -15.0) with a new resonance at δ -14.5 assignable to (3b), which on cooling to -65 °C yields three resonances of unequal intensity at δ -14.0, -14.6, and -14.8 (Figure 3). The similarity in pattern to (7a—c) may be noted, and we assign the resonances tentatively to the analogous isomers (3bi—iii) (Figure 4). In contrast, however, only one isomer is present in reasonable abundance, and on the basis of the previous discussion, this resonance

may be assigned to (3biii). Carbon-13 n.m.r. spectra conclusively demonstrate the axial substitution. The spectrum of [N(PPh₃)₂][Fe₃H(CO)₁₁] at -120 °C²² (Table 4) exhibits two resonances of unit intensity at 223.8 and 221.3 p.p.m. due to the axial carbonyls (C^e, C^f); in the spectrum of [N(PPh₃)₂][Fe₃H(CO)₁₀(CNEt)] taken at -70 °C, only one axial resonance is observed, together with the appearance of a terminal isonitrile resonance at 160.5 p.p.m. Resonances due to the two minor isomers are not observed.

Chemically, the results imply an alkylation of (3a—c) at the terminal isonitrile rather than bridging carbonyl, followed by structural rearrangement; the presence of a small amount of a bridging isonitrile isomer cannot be discounted, however.

If the solvent and excess isonitrile are removed from a sample of (3c), and it is heated in tetrahydrofuran (thf), protonation yields complex (8a) instead of the carbyne derivative (5c). This complex is clearly derived from initial insertion of co-ordinated isonitrile into the M-H-M bond, as the n.m.r. spectrum of the complex obtained on deuteration shows >90% incorporation of hydrogen

TABLE 4
Carbon-13 n.m.r. spectral data^a

| Complex | Temperature/°C | Terminal carbonyls ^b | Other |
|------------------|----------------|---|---|
| (2) ^c | -120 | 223.8(1) 221.3(1) 219.3(2) 215.8(2) 210.4(2) 208.9(2) | μ-CO 285.7 |
| (3b) | -70 | 222.9(1) 220.4(2) 217.4(2) 211.7(2) 208.9(2) | μ-CO 279.4 CNEt 160.5 |
| (4a) | -70 | (C ^a , C ^{a'}) 215.6(2) (<i>J</i> 10.4) (C ^b , C ^{b'}) } 204.8(2) (<i>J</i> 5.2) (C ^c , C ^{c'}) } 211.2(2) (<i>J</i> 3.4) (C ^d , C ^{d'}) 207.3(2) (C ^e) 218.3(1) (C ^f) 216.5(1) (<i>J</i> 3.5) | CN 317.3 (<i>J</i> 13.7) (CH ₂ CH ₃) ₂ 57.4 (CH ₂ CH ₃) ₂ 11.2 |
| (4c) | -70 | (C ^a , C ^{a'}) 214.9(2) (C ^b , C ^{b'}) } 204.2, 204.4(2) (C ^c , C ^{c'}) } 210.6, 210.1(2) (C ^d , C ^{d'}) 206.5, 205.7(2) (C ^e) 217.6(1) (C ^f) 216.1(1) | CN 318.4 CH ₂ CH ₃ <i>d</i> CH ₂ CH ₃ 13.4 CH(CH ₃) ₂ <i>d</i> CH(CH ₃) ₂ 20.47, 19.0 |
| (4b) | -70 | (C ^a , C ^{a'}) 214.6(2) (C ^b , C ^{b'}) } 204.1, 203.7(2), (C ^c , C ^{c'}) } 210.5(2) (C ^d , C ^{d'}) 206.5(2) (C ^e) 217.4(1) (C ^f) 215.6(1) | CN 316.6 CH ₃ 48.6 CH ₂ CH ₃ 62.1 CH ₂ CH ₃ 11.2 |
| (7) | -60 | 205.1 (s) 207.5—209.9 (m) 211.7—213.4 (m) 216.3—218.1 (m) 219.0—219.9 (m) | CN(CH ₂ CH ₃) ₂ 318.1, 319.6, 322.3 CNCH ₂ CH ₃ 150.7, 154.7, 157.8 CNCH ₂ CH ₃ 39.8—40.7 (m) CN(CH ₂ CH ₃) ₂ <i>d</i> CN(CH ₂ CH ₃) ₂ } 11.9—14.6 (m) CNCH ₂ CH ₃ |
| (8a) | -60 | 203.1(1) (<i>J</i> 9.4) 204.8(1) (<i>J</i> 5.4) 206.5(2) (m) 207.9(1) (<i>J</i> 9.2) 209.5(1) (<i>J</i> 13.6) 210.9(3) (broad) | CH=N[CH(CH ₃) ₂] 173.8 CH=N[CH(CH ₃) ₂] 69.7 CH=N[CH(CH ₃) ₂] 23.3, 26.1 |

^a CD₂Cl₂/CH₂Cl₂ solution; values in p.p.m. from SiMe₄. ^b Coupling constants *J* in Hz. ^c Relative intensities and coupling constants in parentheses; C^a—^f refer to Figure 2. ^d Data from ref. 22. ^e Not detected; may be under solvent resonance at 53.8 p.p.m.

into the $CHNPr^i$ position. Several isostructural examples have been recently prepared and characterized. Thus, reaction of $[Os_3(CO)_{12}]$ with NMe_3 yields (8b),⁸ while hydrogenation of $[Ru_3(CO)_{11}(CNBu^t)]$ yields (8c).²³ Reaction of $[Os_3H_2(CO)_{10}]$ with CNR yields the

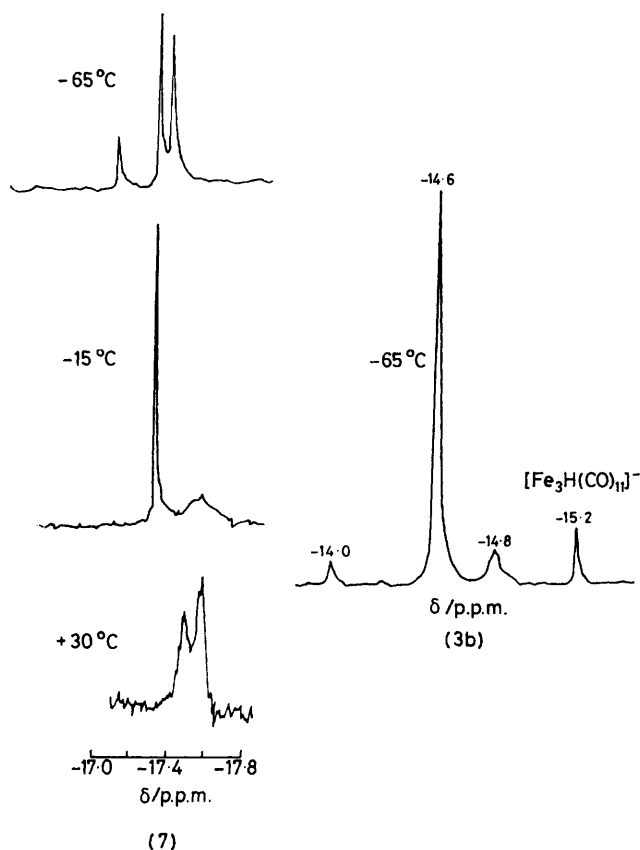
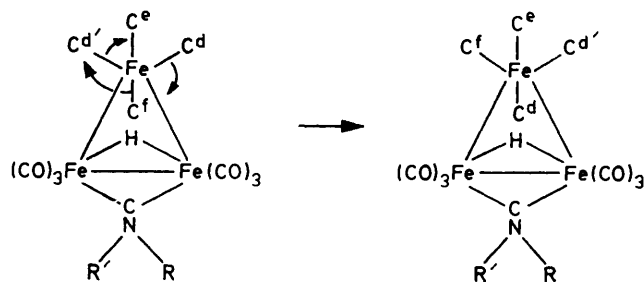


FIGURE 3 Variable-temperature 1H n.m.r. spectra of (7) and (3b) (Fe-H region only)

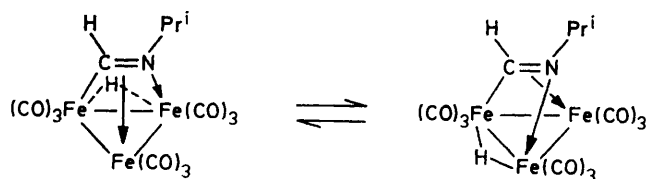
substituted complexes $[Os_3H_2(CO)_{10}(CNR)]$ and $[Os_3H_2(CO)_9(CNR)]$ ($R = Me, Ph,$ or Bu^t) which on further heating in poor donor solvents ($R = Me$ or Ph only) yield edge-bridging $[Os_3H(CO)_{10}(\mu-CH=NR)]$ and face-bridging (8d) complexes.^{9a,24} Reaction of $[Fe_3H(CO)_{11}]^-$ with moist acetonitrile followed by protonation yields (8c), isomeric with the complex reported herein.²⁵ Interestingly, (8e) isomerizes on heating to the complex $[Fe_3H(CO)_9(\mu_3-N=CHMe)]$. Deuteration studies were



SCHEME 2

not conclusive as to whether the N-H or the M-H proton is transferred to carbon. Complex (8a), however, does not exhibit such an isomerization, implying that it is the N-H proton which is transferred.

Complex (8a) is also fluxional. Thus, the 1H n.m.r. spectrum at $-50^\circ C$ exhibits the two doublets expected for the $CH(CH_3)_2$ group on the basis of a static structure.



SCHEME 3

On warming, broadening and coalescence yield eventually a single sharp doublet at $0^\circ C$. The mechanism most likely responsible involves a concurrent flipping of the hydride ligand and twisting of the $CH=NPr^i$ group (Scheme 3), thus generating an apparent plane of symmetry through the isopropyl moiety. From the coalescence temperature of the isopropyl resonance, an activation energy of 52 kJ mol^{-1} may be calculated.

An independent fluxional process is apparent from the ^{13}C n.m.r. spectra. On the basis of a static structure, all nine carbonyls are inequivalent. At $-60^\circ C$, the ^{13}C

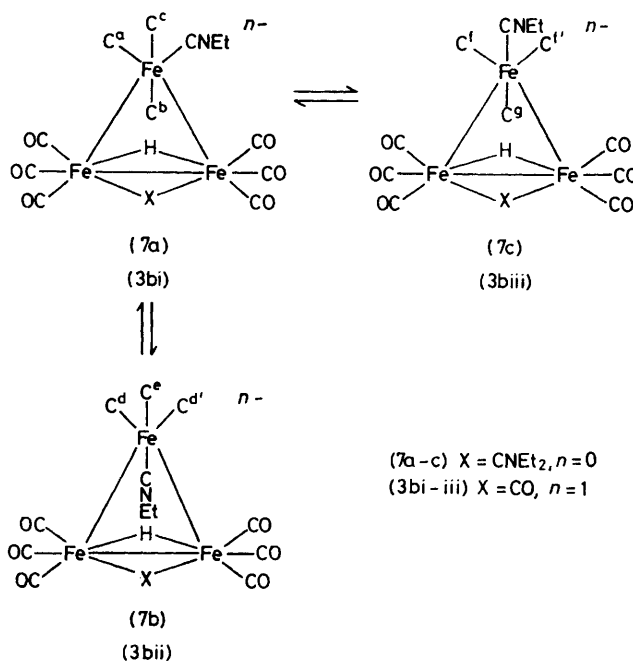


FIGURE 4 Possible isomers of $[Fe_3H(CO)_9(CNEt_2)_2(CNEt)]$ (7) and $[Fe_3H(CO)_{10}(CNEt)]^-$ (3b)

spectrum exhibits five sharp resonances at 209.5, 207.9, 206.5, 204.8, and 203.1 p.p.m. in the ratio of 1 : 1 : 2 : 1 : 1, together with a much broader resonance at 210.9 p.p.m. which broadens further on cooling to $-90^\circ C$. The proton-coupled spectrum shows that all the sharp resonances exhibit proton coupling, and that the reso-

nance of intensity two is in fact two coincident resonances. Thus, the broad peak at 210.9 p.p.m. is assigned to the $\text{Fe}(\text{CO})_3$ moiety not involved in the M-H-M bridge. The broadness indicates a significantly lower barrier for polytopal rearrangement of the carbonyl ligands at this iron atom. Warming to room temperature results in broadening and coalescence to yield two signals in the ratio of 2 : 1 at 207.8 and 206.2 p.p.m.,

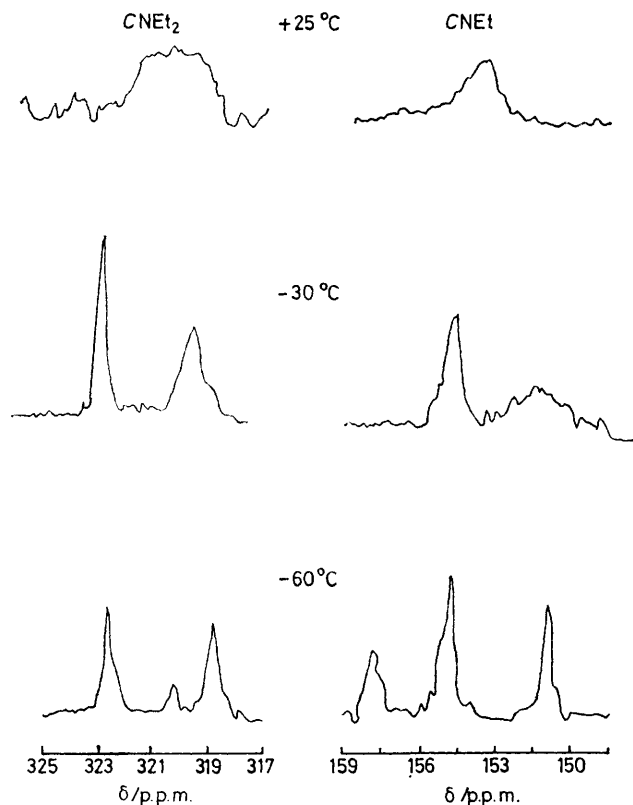


FIGURE 5 Variable-temperature ^{13}C n.m.r. spectra of (7) in the regions of the CNet and CNet₂ resonances

consistent with polytopal exchange of carbonyls at each iron atom, accompanied by the flipping of the metal hydride and $\text{CH}=\text{NPr}^i$ ligand described earlier. Carbonyl exchange between the iron atoms is not evident. Throughout the $\text{CH}=\text{NPr}^i$ resonance at 174.9 p.p.m. remains sharp.

Conclusion.—The results thus demonstrate the partial reduction of the $\text{R}-\overset{\ominus}{\text{N}}\equiv\overset{\oplus}{\text{C}}$ bond on an anionic cluster by alkylation or M-H insertion. We are currently exploring the generality of the synthetic method, and the reactivity of the $\mu\text{-CNR}_2$ and $\mu\text{-CHNR}$ ligands.

EXPERIMENTAL

All reactions were performed in dry solvents under nitrogen. The isonitriles,²⁶⁻²⁸ $[\text{NH}(\text{Et})_3][\text{Fe}_3\text{H}(\text{CO})_{11}]$,²⁹ $[\text{N}(\text{PPh}_3)_2]\text{Cl}$,³⁰ and Et_3OBF_4 ³¹ were prepared as described in the literature. All other chemicals were purchased commercially. Light petroleum refers to that fraction boiling in the range 30–40 °C. Infrared and n.m.r. spectra were

run on Perkin-Elmer 257 and JEOL FX-100 instruments respectively. Proton-decoupled ^{13}C n.m.r. spectra were run in the presence of $[\text{Cr}(\text{acac})_3]$ (acac = acetylacetonate); coupled spectra were run without $[\text{Cr}(\text{acac})_3]$ at low temperature (< -50 °C) using slightly longer pulse intervals. Spectra at or below room temperature were run in CD_2Cl_2 ; those above room temperature were run in $\text{C}_6\text{D}_5\text{CD}_3$.

(a) $[\text{N}(\text{PPh}_3)_2][\text{Fe}_3\text{H}(\text{CO})_{11}]$ (2).—This compound has been reported,²² but details of its preparation have not been given. To a solution of $[\text{NH}(\text{Et})_3][\text{Fe}_3\text{H}(\text{CO})_{11}]$ (36 g, 62 mmol) in CH_2Cl_2 (200 cm^3) was added $[\text{N}(\text{PPh}_3)_2]\text{Cl}$ (50 g, 87 mmol) and the mixture was stirred at room temperature for 3 h. The solvent was removed to give a red oily mass which solidified on addition of light petroleum (20 cm^3). The crude product was washed several times with warm water and dried *in vacuo* to give, after recrystallization from CH_2Cl_2 -light petroleum, dark red-purple crystals (45 g, 72%).

(b) $[\text{Fe}_3\text{H}(\text{CO})_{10}(\text{CNet}_2)]$ (4a).— $[\text{N}(\text{PPh}_3)_2][\text{Fe}_3\text{H}(\text{CO})_{11}]$ (5g, 5 mmol) and CNet (1.80 cm^3 , 20 mmol) were stirred in CH_2Cl_2 (100 cm^3) at room temperature. The reaction was monitored by reaction of 1- cm^3 aliquots of the reaction mixture with Et_3OBF_4 , followed by thin-layer chromatography (t.l.c.) to detect the product $[\text{Fe}_3\text{H}(\text{CO})_{10}(\text{CNet}_2)]$. When monosubstitution of the anion was complete (*ca.* 2 h) the CH_2Cl_2 and the excess CNet were removed *in vacuo*. The purple-red residue was dissolved in dichloromethane, and 1.2 g (5.5 mmol) of Et_3OBF_4 was added. The mixture was stirred at room temperature for 10 min, the solvent was evaporated off, and the residue was chromatographed on a silica-gel column. Elution with light petroleum-benzene (9 : 1) yielded a trace of red $[\text{Fe}_3\text{H}(\text{CO})_{10}(\text{COEt})]$ followed by purple $[\text{Fe}_3\text{H}(\text{CO})_{10}(\text{CNet}_2)]$ (0.7 g, 26%). Further elution with light petroleum-benzene (2 : 8) yielded a small amount of the substituted complex $[\text{Fe}_3\text{H}(\text{CO})_9(\text{CNet})(\text{CNet}_2)]$ (7). This complex can be isolated as the major product if a larger excess of isonitrile is used, and the reaction is left for a longer period of time. The reaction is monitored by the method described above.

Complexes (4b) and (4c) were prepared in an analogous manner, while (4d) was prepared similarly using Me_3OBF_4 . Derivatives (4b–d) were purified by sublimation (0.1 mmHg, * 80 °C) or by crystallization from light petroleum. $[\text{Fe}_3\text{H}(\text{CO})_9(\text{CNet})(\text{CNet}_2)]$ would not crystallize and was purified by preparative t.l.c. $[\text{Fe}_3\text{H}(\text{CO})_{10}(\text{COEt})]$ may be prepared in 79% yield by an analogous alkylation of $[\text{N}(\text{PPh}_3)_2][\text{Fe}_3\text{H}(\text{CO})_{11}]$.

(c) $[\text{Fe}_3\text{H}(\text{CO})_{10}(\text{CNMeH})]$ (5a).— $[\text{N}(\text{PPh}_3)_2][\text{Fe}_3\text{H}(\text{CO})_{11}]$ (2.0 g, 2 mmol) and CNMe (0.22 cm^3 , 4 mmol) were stirred in CH_2Cl_2 (50 cm^3) at room temperature until titration of an aliquot with Et_3OBF_4 indicated that monosubstitution was complete. Solvent and excess isonitrile were evaporated off, and the residue was dissolved in diethyl ether. $\text{CF}_3\text{-SO}_3\text{H}$ (0.4 cm^3 , 2 mmol) dissolved in diethyl ether (10 cm^3) was added and the mixture stirred at room temperature for 10 min. After evaporation of solvent, the residue was chromatographed on a silica-gel column. Elution with light petroleum yielded a trace of $[\text{Fe}_3(\text{CO})_{12}]$, after which purple $[\text{Fe}_3\text{H}(\text{CO})_{10}(\text{CNMeH})]$ was eluted with light petroleum-benzene (9 : 1). The product was purified by preparative t.l.c.

(d) $[\text{Fe}_3\text{H}(\text{CO})_9(\text{CHNPr}^i)]$ (8a).—A mixture of $[\text{N}(\text{PPh}_3)_2][\text{Fe}_3\text{H}(\text{CO})_{11}]$ (7.5 g, 7.5 mmol) and CNPr^i (2.7 cm^3 , 29 mmol) was stirred in CH_2Cl_2 (150 cm^3) at room

* Throughout this paper: 1 mmHg = (101 325/760) N m⁻².

temperature until titration with Et_3OBF_4 indicated that monosubstitution was complete. Solvent and excess isonitrile were removed, and the residue was dissolved in thf and heated at 40 °C for 2 h. $\text{CF}_3\text{SO}_3\text{H}$ (2 g, 10 mmol) dissolved in diethyl ether (30 cm^3) was added at room temperature and the mixture was stirred for 30 min. After removal of solvent, the residue was chromatographed on a silica-gel column. A trace of $[\text{Fe}_3(\text{CO})_{12}]$ was eluted by using light petroleum, while further elution using light petroleum-benzene (9:1) yielded orange $[\text{Fe}_3\text{H}(\text{CO})_9(\text{CHNPr}^1)]$ which was recrystallized from light petroleum (1.5 g, 41%).

Deuteriation in the same manner using $\text{CF}_3\text{CO}_2\text{D}$ yielded the deuteriated analogue $[\text{Fe}_3\text{D}(\text{CO})_9(\text{CHNPr}^1)]$.

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REFERENCES

- ¹ E. L. Muetterties and J. Stein, *Chem. Rev.*, 1979, **79**, 479.
- ² (a) E. O. Fischer, G. Kreis, F. R. Kreissel, W. Kalbfus, and E. Winkler, *J. Organomet. Chem.*, 1974, **65**, C53; (b) E. O. Fischer, G. Huttner, W. Kleine, and A. Frank, *Angew. Chem. Int. Ed.*, 1975, **14**, 760.
- ³ (a) J. Chatt, A. J. L. Pombiero, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1980, 492; (b) J. Chatt, A. J. L. Pombiero, R. L. Richards, G. H. D. Royston, K. W. Muir, and R. Walker, *J. Chem. Soc., Chem. Commun.*, 1975, 708.
- ⁴ S. Willis, A. R. Manning, and F. S. Stephens, *J. Chem. Soc., Dalton Trans.*, 1979, 23.
- ⁵ J. A. S. Howell and A. J. Rowan, *J. Chem. Soc., Dalton Trans.*, 1980, 503.
- ⁶ F. G. Stone, J. M. Bassett, G. K. Barker, M. Green, J. A. K. Howard, and W. C. Wolsey, *J. Chem. Soc., Dalton Trans.*, 1981, 219.
- ⁷ M. R. Churchill, B. G. de Boer, E. W. Abel, E. F. Rotella, and R. J. Rowley, *J. Am. Chem. Soc.*, 1975, **97**, 7158.
- ⁸ C. Choo Yin and A. J. Deeming, *J. Organomet. Chem.*, 1977, **133**, 123.
- ⁹ (a) R. D. Adams and N. M. Golembenski, *J. Am. Chem. Soc.*, 1979, **101**, 2579; (b) R. D. Adams and N. M. Golembenski, *Inorg. Chem.*, 1979, **18**, 2255.
- ¹⁰ (a) G. G. Cash, R. C. Petterson, and R. B. King, *J. Chem. Soc., Chem. Commun.*, 1977, 30; (b) R. B. King and C. A. Harmon, *Inorg. Chem.*, 1976, **15**, 879.
- ¹¹ (a) I. Rhee, M. Ryang, and S. Tsutsumi, *Chem. Commun.*, 1968, 455; (b) R. Greatrex, N. N. Greenwood, I. Rhee, M. Ryang, and S. Tsutsumi, *Chem. Commun.*, 1970, 1193.
- ¹² J. Altman and M. Welcman, *J. Organomet. Chem.*, 1979, **165**, 353.
- ¹³ F. H. Herbstein, *Acta Crystallogr., Sect. B*, 1981, **37**, 339.
- ¹⁴ J. A. S. Howell and P. Mathur, *J. Chem. Soc., Chem. Commun.*, 1981, 263.
- ¹⁵ P. D. Gavens and M. J. Mays, *J. Organomet. Chem.*, 1978, **162**, 389.
- ¹⁶ B. F. G. Johnson, J. Lewis, A. G. Orpen, P. R. Raithby, and G. Suss, *J. Organomet. Chem.*, 1979, **173**, 187.
- ¹⁷ I. Fleming and D. H. Williams, 'Spectroscopic Methods in Organic Chemistry,' McGraw-Hill, London, 1966, p. 65.
- ¹⁸ P. A. S. Smith, 'Open Chain Nitrogen Compounds,' W. A. Benjamin, New York, 1965, p. 865.
- ¹⁹ R. M. Silverstein and G. C. Bassler, 'Spectrometric Identification of Organic Compounds,' John Wiley, New York, 1967, p. 96.
- ²⁰ H. A. Hodali, D. F. Shriver, and C. A. Ammlung, *J. Am. Chem. Soc.*, 1978, **100**, 5239.
- ²¹ E. L. Muetterties and E. Band, *Chem. Rev.*, 1978, **78**, 639.
- ²² J. R. Wilkinson and L. J. Todd, *J. Organomet. Chem.*, 1976, **118**, 199.
- ²³ M. I. Bruce and R. C. Wallace, *J. Organomet. Chem.*, 1979, **164**, C6.
- ²⁴ R. D. Adams and N. M. Golembenski, *Inorg. Chem.*, 1979, **18**, 1909.
- ²⁵ (a) M. A. Andrews and H. D. Kaesz, *J. Am. Chem. Soc.*, 1979, **101**, 7238; (b) M. A. Andrews, G. van Buskirk, C. B. Knobler, and H. D. Kaesz, *J. Am. Chem. Soc.*, 1979, **101**, 7245; (c) M. Andrews and H. D. Kaesz, *J. Am. Chem. Soc.*, 1977, **99**, 6763.
- ²⁶ R. E. Schuster, J. E. Scott, and J. Casanova, *Org. Synth.*, 1966, **46**, 75.
- ²⁷ I. Ugi, R. Meyr, M. Lipinski, F. Bodensheim, and F. Rosen-dahl, *Org. Synth.*, 1961, **41**, 13.
- ²⁸ W. P. Weber and G. W. Gokel, *Tetrahedron Lett.*, 1972, 1637.
- ²⁹ J. R. Case and M. C. Whiting, *J. Chem. Soc.*, 1960, 4632.
- ³⁰ J. K. Ruff and W. J. Schlientz, *Inorg. Synth.*, 1974, **15**, 84.
- ³¹ H. Meerwein, *Org. Synth. Coll. Vol.*, **5**, 1080.