# Perfluoroalkane- and Perfluoroarene-thiolates. Part VI.[1] Reactions of some Cyclopentadienylnickel Derivatives with Hexafluorobut-2-yne †

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The reactions of $CF_3C_2CF_3$ with $[\{Ni(\eta\text{-}C_5H_5)(SCF_3)\}_2]$, $[Ni(\eta\text{-}C_5H_5)_2]$, $[Ni(\eta\text{-}C_5H_5)\{C_5H_6(CF_3C_2CF_3)\}]$, $[Ni(\eta\text{-}C_5H_5)\{C_5H_6(C_2F_3Cl)\}]$, and $[\{Ni(\eta\text{-}C_5H_5)\}_2(CF_3C_2CF_3)]$ have been examined. The new products characterised are $[Ni(\eta\text{-}C_5H_5)\{(CF_3C_2CF_3)_2H\}]$, $[Ni_3(\eta\text{-}C_5H_5)_2(CF_3C_2CF_3)_3]$, $[Ni_2(C_5H_5)_2(CF_3C_2CF_3)_3]$, $[Ni(C_5H_5)_2(CF_3C_2CF_3)_3]$, $[Ni(\eta\text{-}C_5H_5)\{C_5H_5(CF_3C_2CF_3)_2\}]$, $[\{Ni(C_5H_5)(CF_3C_2CF_3)\}_4]$, and $[Ni(C_5H_5)(CF_3C_2CF_3)_2\{C_5H_5(C_2F_3Cl)\}]$.

IN previous papers we have given details of the results of studies on the interactions of some metal perfluorothiolates with acetylenes. In the present paper we describe similar studies with nickel derivatives but, in order to fully characterise the products of the reactions, it was necessary to carry out further studies on the reactions between acetylenes and $[Ni(\eta\text{-}C_5H_5)_2]$ and some other cyclopentadienylnickel derivatives, and the results of this study are also described here. A preliminary account of the latter reactions has been published.[2]

## RESULTS AND DISCUSSION

In our previous studies [1,3] of the reactions between thiolates and acetylenes the products have included π-acetylene complexes, metallated olefin derivatives, and the products of acetylene telomerisation and/or insertion into M–S bonds. In most cases the initial reaction proceeded with retention of the $SR_F$ group within the product, although with excess of acetylene this group is sometimes lost and, for example, $[\{Fe(CO)_3(SR_F)\}_2]$ gives the cyclopentadienone complex $[Fe(CO)_3\{(CF_3C_2CF_3)_2CO\}]$ and $[\{Co(CO)_3(SC_6F_5)\}_2]$ gives $[\{Co(CO)_3\}_2(CF_3C_2CF_3)]$ and $[Co_2(CO)_4(CF_3C_2CF_3)_3]$. Neither the fate of the thiolate group nor the mechanism of the reaction is clear in this type of reaction. In the reactions of nickel thiolates to be described below the thiolate is lost from the metal.

Bis(η-cyclopentadienyl)nickel, $[Ni(\eta\text{-}C_5H_5)_2]$, is a reactive complex and much of its chemistry is dominated by the tendency to achieve a stable 18-electron configuration [4] which may occur by substitution of one of the cyclopentadienyl rings or by 1,2- or 1,4-addition to one of the rings. Relatively few studies of reactions between

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† No reprints available.

[1] Part V, P. S. Braterman, J. L. Davidson, and D. W. A. Sharp, *J.C.S. Dalton*, 1976, 241.

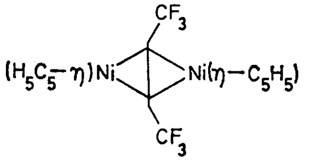
[2] J. L. Davidson, R. Herak, L. Manolovic-Muir, K. W. Muir, and D. W. A. Sharp, *J.C.S. Chem. Comm.*, 1973, 865.

[3] J. L. Davidson and D. W. A. Sharp, *J.C.S. Dalton*, 1975, 2283.

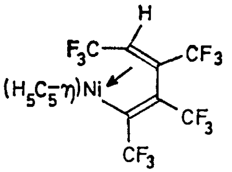
[4] K. W. Barnett, *J. Organometallic Chem.*, 1974, **78**, 139.

hexafluorobut-2-yne and nickel complexes have been reported. Hexafluorobut-2-yne reacts with $[\{Ni(\eta\text{-}C_5H_5)(CO)\}_2]$[5] or $[Ni(\eta\text{-}C_5H_5)_2]$[6] to give the acetylene-bridged species $[\{Ni(\eta\text{-}C_5H_5)\}_2(CF_3C_2CF_3)]$, whilst $[Ni(\eta\text{-}C_5H_5)_2]$ also gives $[Ni(\eta\text{-}C_5H_5)\{C_5H_5(CF_3C_2CF_3)\}]$ in which the acetylene has undergone 1,4-addition to one of the cyclopentadienyl rings. Hexafluorobut-2-yne reacts with many other organonickel derivatives [7] to give products containing trimers of hexafluorobut-2-yne.

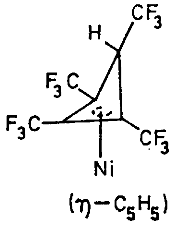
Hexafluorobut-2-yne reacts with $[\{Ni(\eta\text{-}C_5H_5)(SCF_3)\}_2]$ in pentane between 293 and 323 K to give a complex mixture of products from which $[\{Ni(\eta\text{-}C_5H_5)\}_2(CF_3C_2CF_3)]$ (I), $C_6(CF_3)_6$ (II), $[Ni(\eta\text{-}C_5H_5)\{(CF_3C_2CF_3)_2H\}]$ (III), $[Ni_3(C_5H_5)_2(CF_3C_2CF_3)_3]$ (IV), $[Ni_2(C_5H_5)_2(CF_3C_2CF_3)_3]$ (V), and $[Ni(C_5H_5)_2(CF_3C_2CF_3)_3]$ (VI) were separated and identified.



(I)



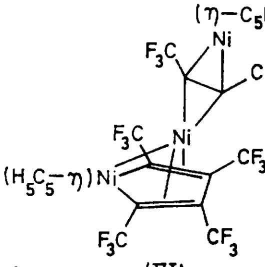
(IIIa)



(IIIc)

The main products, $[\{Ni(\eta\text{-}C_5H_5)\}_2(CF_3C_2CF_3)]$ (I) [5] and hexakis(trifluoromethyl)benzene, $C_6(CF_3)_6$ (II),[5,7] were previously identified as products from the reactions between hexafluorobut-2-yne and nickel complexes. Complex (I) has a bridging acetylene between two nickel atoms; (III) is a volatile brown crystalline solid which is air-stable in the solid state and in solution for a limited time. The mass spectrum and the volatility indicate a monomeric species for (III) and of the possible structures (IIIa), which is formally derived by double insertion of acetylenes into a Ni–H bond, is considered to be the most likely on spectroscopic evidence. The $^{19}F$ n.m.r. spectrum (Table 3) showed four multiplets of equal intensity, thus eliminating a structure containing a cyclobutenyl ring, (IIIc). The broad doublet at δ 53.7 p.p.m. (with respect to $CCl_3F$) had $J_{F-H}$ 6.7 Hz with coupling to the *gem*-4-proton and broadening due to coupling to a *trans*-trifluoromethyl group, and is thus assigned to the 4-trifluoromethyl group. The quartet at δ 56.0 p.p.m. was also broadened as a result of coupling to the *trans*-4-trifluoromethyl group and to the *cis*-4-proton, but shows its main coupling $J_{FF}$ 10.6 Hz to the 2-trifluoromethyl group. The quartet at δ 63.5 p.p.m. is assigned to the 1-trifluoromethyl group and is coupled, $J_{FF}$ 6.7 Hz, only to the 2-trifluoromethyl fluorines. The 2-trifluoromethyl group gave a quartet of quartets at 65.7 p.p.m. The $^{19}F$ n.m.r. spectrum rules out an alternative structure (IIIb) with all of the trifluoromethyl substituents mutually *cis*, as this arrangement would show three complex multiplets and only one quartet as is found for $[Ru(\eta\text{-}C_5H_5)\{(CF_3C_2CF_3)_2H\}(PPh_3)]$.[8] The $^1H$ n.m.r. spectrum showed the 4-proton at τ 5.6 which is a low chemical shift but presumably reflects the exposed position of the proton in the molecule.

The complex $[Ru(\eta\text{-}C_5H_5)(CO)_2H]$ reacts with hexafluorobut-2-yne to give $[Ru(\eta\text{-}C_5H_5)\{(CF_3C_2CF_3)_2H\}(CO)]$ which has a very similar n.m.r. spectrum to that of (III) and is formulated with a similar arrangement of trifluoromethyl substituents.[9] The i.r. spectrum of (III) showed a single C=C stretching mode at 1 661 $cm^{-1}$ which is comparable with that observed at 1 641 $cm^{-1}$ for $[Ru(\eta\text{-}C_5H_5)\{(CF_3C_2CF_3)_2H\}(PPh_3)]$ and at 1 672 $cm^{-1}$ for $[Ru(\eta\text{-}C_5H_5)\{(CF_3C_2CF_3)_2H\}(CO)]$. The mass spectrum of (III) showed a molecular ion and the nickel-containing fragments $[Ni(C_5H_5)F]^+$ and $[Ni(C_5H_5)]^+$ and peaks due to $[C_4(CF_3)_4H]^+$ and its fragmentation products. Also observed were peaks due to $[(C_5H_5)C_4(CF_3)_4H]^+$ and its fragments, corresponding to loss of nickel from a molecular ion or to combination of the major organic portions of the molecule. The hydrogen in this complex probably arises from attack on the solvent; similar reactions have previously been shown to occur when hexafluorobut-2-yne reacts with organometallic derivatives in hexane.[10]



(IV)

Complex (IV), $[Ni_3(C_5H_5)_2(CF_3C_2CF_3)_3]$, is believed from spectroscopic evidence to have the structure shown with a nickelacyclopentadiene ring. The $^1H$ n.m.r. spectrum indicates the presence of two distinct η-cyclopentadienyl groups, whilst the $^{19}F$ n.m.r. spectrum showed three signals of equal intensity one of which was sharper than the other two. The two highly coupled peaks at 51.8 and 54.8 p.p.m. are similar to those observed for other ring systems $[C_4(CF_3)_4X]$ (*e.g.* X =

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[5] J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *J. Chem. Soc.*, 1962, 3488.

[6] D. W. McBride, E. Dudek, and F. G. A. Stone, *J. Chem. Soc.*, 1964, 1752.

[7] J. Browning, C. S. Cundy, M. Green, and F. G. A. Stone. *J. Chem. Soc.* (*A*), 1971, 448; J. Browning, M. Green, J. L, Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 97.

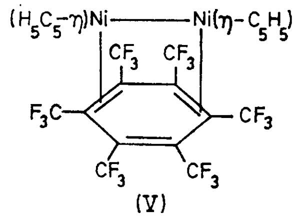
[8] T. Blackmore, M. I. Bruce, F. G. A. Stone, R. E. Davis, and A. Garza, *Chem. Comm.*, 1971, 852; T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 106.

[9] J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, personal communication.

[10] R. E. J. Bichler, M. R. Booth, and H. C. Clark, *J. Organometallic Chem.*, 1970, **24**, 145.

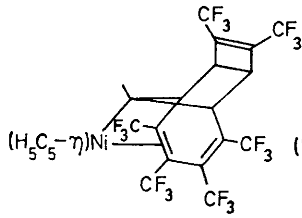
CO,[5] Rh,[11] or $SR_F$[3]) and spectrum is very different from those observed for metal hexakis(trifluoromethyl)benzene derivatives [4] which all give one very broad peak. Further, the mass spectrum gave no species characteristic of a $C_6(CF_3)_6$ group, but did show a molecular ion $[Ni_3(C_5H_5)_2\{C_6(CF_3)_6\}]^+$ which loses $C_4F_6$ to give $[Ni_3(C_5H_5)_2\{C_4(CF_3)_4\}]^+$ with $[Ni_2(C_5H_5)_2\{C_4(CF_3)_4\}]^+$, $[Ni(C_5H_5)(C_8F_{12})]^+$, and $[Ni(C_5H_5)(C_8F_{11})]^+$ also being prominent. The i.r. spectrum had a C≡C mode at 1 591 $cm^{-1}$ which is very similar to the band at 1 597 $cm^{-1}$ for the corresponding mode in $[\{Ni(\eta\text{-}C_5H_5)\}_2(CF_3C_2CF_3)]$: a C≡C stretch near this wavenumber appears to be characteristic of a π-bridging acetylene. Structure (IV) contains the basic structural elements of (I) and $[\{Ni(\eta\text{-}C_5H_5)(CF_3C_2CF_3)\}_4]$ (IX); each nickel atom has attained the 18-electron configuration.

The other products of the reaction between $[\{Ni(C_5H_5)(SCF_3)\}_2]$ and $CF_3C{\equiv}CCF_3$ were only obtained in low yield and characterisation is therefore based mainly on spectroscopic properties. Complex (V) is a dark red crystalline solid. The mass spectrum showed a peak of highest mass at *m/e* 732 with a double nickel-isotope pattern suggesting the molecular formula $Ni_2(C_5H_5)_2(CF_3C_2CF_3)_3$. This ion loses fluorine and then $Ni(C_5H_5)$ to give $[Ni(C_5H_5)(C_{12}F_{17})]^+$, the only other nickel-containing species observed being $[Ni(C_5H_5)]^+$ and $[Ni(C_5H_5)F]^+$. The remainder of the mass spectrum showed organic fragments with a $[C_6(CF_3)_6]^+$ ion at *m/e* 486 which undergoes an almost identical fragmentation process to that observed for hexakis(trifluoromethyl)benzene. The $^1H$ n.m.r. spectrum showed only one signal for the two η-cyclopentadienyl groups; it was not possible to obtain a $^{19}F$ n.m.r. spectrum from the small quantity of sample available. The i.r. spectrum is very simple in the C–F region which rules out a structure with a flyover $C_6(CF_3)_6$ unit similar to that found in $[Co_2(CO)_4\{C_6(CF_3)_6\}]$ [12] as this cobalt complex gives a complex i.r. spectrum. No C=C mode was observed in the i.r. spectrum. The postulated structure (V) is analogous to that found [13] for $[Pt\{C_6(CF_3)_6\}(PEt_3)_2]$ with fluxional behaviour about the ring; the C=C vibrational mode may be i.r. inactive for symmetry reasons.

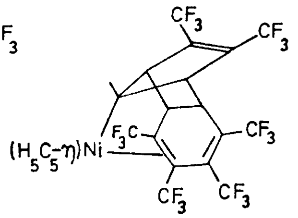


(V)

The other complex (VI) obtained in low yield is also red and the mass spectrum had an ion of highest mass at *m/e* 672 with a single nickel-isotope pattern corresponding to $[Ni(C_5H_5)\{C_6(CF_3)_6\}]^+$. There were no ions corresponding to $C_6(CF_3)_6$ and its fragmentation pattern, but there was an extensive series of organic ions which could be based on $[C_5H_5\{C_6(CF_3)_6\}]^+$ and its fragmentation involving loss of fluorine, hydrogen, and trifluoromethyl groups. The $^1H$ n.m.r. spectrum showed a cyclopentadienyl group and three multiplets of ratio 1 : 2 : 2 at *ca.* τ 6.75. The $^{19}F$ n.m.r. spectrum obtained was not good because of the small sample size, but showed five distinct trifluoromethyl environments, one environment containing two such groups. The coupling is similar to that observed in the butadiene complex (III). The i.r. spectrum in the C–F region is complex as would be expected from the $^{19}F$ n.m.r. spectrum; the spectrum showed a band at 1 711 $cm^{-1}$ suggesting the presence of an unco-ordinated $CF_3C{=}CCF_3$ group $[Ni(\eta\text{-}C_5H_5)\{(C_5H_5)C_4(CF_3)_4\}]$ has a C=C mode at 1 710 $cm^{-1}$). Tentative proposals for the structure of (VI) involve 1,4- or 1,2-addition of a tetrakis(trifluoromethyl)butadiene group to a cyclopentadienyl ring with addition of a further hexafluorobut-2-yne to the remaining olefinic bond or 1,4 to the ring. In $[\{Ni(\eta\text{-}C_5H_5)(CF_3C_2CF_3)\}_4]$ (IX) a tetrakis(trifluoromethyl)butadiene group has undergone 1,2-addition to a cyclopentadiene ring, which suggests that (VIb) may be the appropriate structure.

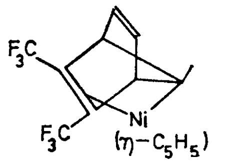


(VIa)

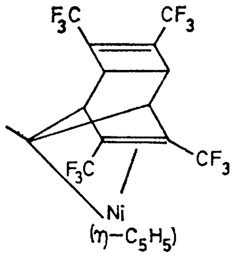


(VIb)

Bis(η-cyclopentadienyl)nickel has been previously reported [6] to react at 293 K with hexafluorobut-2-yne to give (I) and the 1,4-Diels–Alder adduct $[Ni(\eta\text{-}C_5H_5)\{C_5H_5(CF_3C_2CF_3)\}]$ (VII). A new range of products was found by carrying out the reaction at 353 K and those identified were (I), (II), (VII), $[Ni(\eta\text{-}C_5H_5)\{C_5H_5(CF_3C_2CF_3)_2\}]$ (VIII), and $[\{Ni(C_5H_5)(CF_3C_2CF_3)\}_4]$ (IX). The $^1H$ n.m.r. spectrum of (VIII) is comparable with that of complex (VII) formed by 1,4-addition of hexafluorobut-2-yne to one cyclopentadienyl ring of $[Ni(\eta\text{-}C_5H_5)_2]$, and accordingly (VIII) is formulated with a structure derived by 1,2-addition of a further molecule of alkyne to the free olefinic bond of (VII). (Various



(VII)



(VIII)

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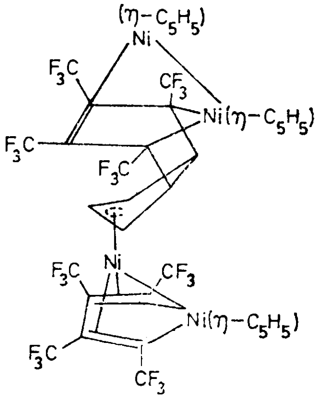
[11] J. T. Mague and G. Wilkinson, *Inorg. Chem.*, **1968**, **7**, 542.

[12] R. S. Dickson and D. B. W. Yawney, *Austral. J. Chem.*, 1969, **22**, 533.

[13] J. Browning, M. Green, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 97; J. Browning, M. Green, B. R. Penfold, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1973, 31.

isomers are possible according to the relative position of the various rings but the product appears to consist of one isomer only.) The mass spectrum showed a molecular ion and ions due to $[(C_5H_5)C_4(CF_3)_4]^+$ and its fragments, and the i.r. spectrum contained a band at 1 710 $cm^{-1}$ which is assigned to the un-co-ordinated double bond. It seems very unlikely, however, that (VIII) is formed by direct attack of hexafluorobut-2-yne on (VII), as this direct reaction gives only low yields of (VIII) whereas good yields of (VIII) are obtained by the action of hexafluorobut-2-yne on $[Ni(\eta\text{-}C_5H_5)_2]$ at 353 K.

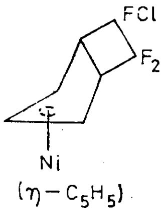
The black crystalline tetramer $[\{Ni(C_5H_5)(CF_3C_2CF_3)\}_4]$ (IX) was only obtained in trace amounts from the reaction between hexafluorobut-2-yne and $[Ni(\eta\text{-}C_5H_5)_2]$, but was formed in good yield (72%) from the reaction between (I) and hexafluorobut-2-yne at 360 K. (This may, in fact, be the only route for formation of this derivative.) Other products formed in trace amounts from this latter reaction were (II) and (IV). The structure of (IX) was established by *X*-ray crystallography [2] and provides an example of the strong tendency of nickel to attain an 18-electron configuration as each nickel, although in a completely different environment, can be considered to attain that configuration. Each nickel is bonded to seven carbon atoms and one other nickel. The attachment of a $[\{Ni(\eta\text{-}C_5H_5)_2\}_2]$ unit to a cyclohexane ring by one $\pi$-olefin and two $\sigma$ bonds is novel, as is the 1,2-addition of a $NiC_4$ unit to a cyclopentadienyl system which then becomes an $\eta^3$-cyclopentenyl group. A complex containing a $Ni(\eta\text{-}C_5H_5)$ group $\pi$-bonded to a cyclopentenyl group has been previously postulated as resulting from the reaction between octafluorocyclohexa-1,3-diene and $[Ni(\eta\text{-}C_5H_5)_2]$.[14] Complex (IX) appears to have been the first complex for which a ($\eta$-nickelacyclopentadienyl)nickel system has been studied by *X*-ray crystallography, although related complexes of other transition metals have been described.[15] The structure lends support to structures postulated in this paper for complexes (IV) and (VIII).



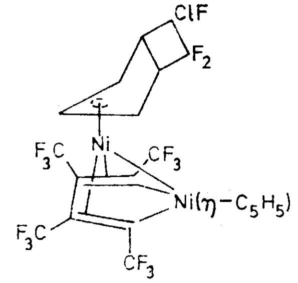
(IX)

The spectroscopic properties of (IX) are in full accord with the crystal structure. There is extensive fragmentation in the mass spectrometer so that the peak of highest mass that could be positively identified occurred at *m/e* 570 corresponding to $[\{Ni(C_5H_5)(CF_3C_2CF_3)\}_2]^+$; although weak ions with a triple-nickel pattern were observed at higher *m/e* values, precise masses could not be assigned. It is not obvious from the structure as to where direct cleavage of the tetramer could easily occur to give a dimer, but this is an example of a retro-Diels–Alder fragmentation which is a common process under the influence of electron impact.[16] The mass spectra of (IV) and $[Ni_2(C_5H_5)_3(CF_3C_2CF_3)(C_2F_3Cl)]$ (XI) also showed ions corresponding to $[\{Ni(C_5H_5)(CF_3C_2CF_3)\}_2]^+$, although the peak in the spectrum of (IV) was weak presumably because of the necessity to transfer the remote cyclopentadienyl group. ($\eta$-Nickelacyclopentadienyl)-nickel systems are postulated in both of these derivatives. The $^1H$ n.m.r. spectrum showed the expected pattern of three magnetically non-equivalent $\eta$-cyclopentadienyl groups together with three lower-intensity resonances of intensity ratio 1 : 2 : 2. The $^{19}F$ n.m.r. spectrum showed only three highly coupled resonances in intensity ratio 1 : 1 : 2, and it must be assumed that two multiplets are accidentally degenerate thus accounting for the lack of fine structure on the more intense peak. No peaks were observed in the i.r. spectrum between 1 500 and 2 000 $cm^{-1}$, in accord with the absence of unco-ordinated olefinic bonds.

In a further attempt to confirm the manner of addition of acetylenes to the cyclopentadienyl rings of $[Ni(\eta\text{-}C_5H_5)_2]$ derivatives, hexafluorobut-2-yne was treated at 340 K with the 1,2-addition product $[Ni(\eta\text{-}C_5H_5)\text{-}\{C_5H_5(C_2F_3Cl)\}]$ (X) from the reaction between $[Ni(\eta\text{-}C_5H_5)_2]$ and chlorotrifluoroethylene.[17] The products of this reaction were small quantities of (I) and a brown crystalline complex $[Ni_2(C_5H_5)(CF_3C_2CF_3)_2\{C_5H_5(C_2F_3\text{-}Cl)\}]$ (XI) formulated with a ($\eta$-nickelacyclopentadienyl) nickel system similar to that found in (IX) and postulated for (IV). The mass spectrum contained a parent ion at *m/e* 628 and the ion $[\{Ni(C_5H_5)(CF_3C_2CF_3)\}_2]^+$ and its fragments as observed in the mass spectra of (IV) and (IX). The $^1H$ n.m.r. spectrum of (XI) is virtually identical to that of the precursor (X), confirming the presence of $\eta$-cyclopentadienyl and $\eta^3$-cyclopentenyl



(X)



(XI)

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[14] R. L. Hunt and G. Wilkinson, *Inorg. Chem.*, 1965, **4**, 1270.

[15] E. F. Epstein and L. F. Dahl, *J. Amer. Chem. Soc.*, 1970, **92**, 502 and refs. therein.

[16] A. Karpati, A. Rave, J. Deutsch, and A. Mandelbaum, *J. Amer. Chem. Soc.*, 1973, **95**, 4244.

[17] D. W. McBride, R. L. Pruett, E. Pitcher, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1962, **84**, 497.

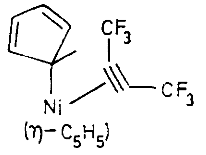
ligands. The $^{19}F$ n.m.r. spectrum showed two highly coupled peaks of the type associated with metallatetrakis(trifluoromethyl)cyclopentadiene systems, but the resonances of the $C_2F_3Cl$ substituent were not clear, partly because of low solubility and partly because of isomerism resulting from the different orientations of the group.[17] The i.r. spectrum showed no C–C modes between 1 500 and 2 000 cm$^{-1}$ which could be attributed to unco-ordinated acetylenic or olefinic bonds.

In an attempt to prepare analogues of (XI) by addition of fluoro-olefins to the unco-ordinated double bond of (VII), this latter complex was treated under thermal and photochemical initiation with chlorotrifluoroethylene and perfluoropropene. No reaction was observed with chlorotrifluoroethylene, but surprisingly perfluoropropene gave a low yield of (VIII). The perfluoropropene was completely free from hexafluorobut-2-yne and the reaction must proceed either by a complex process involving conversion of the olefin into hexafluorobut-2-yne (fluoroacetylenes are known to be formed from fluoro-olefins under the influence of fluoride ion,[18] although there is apparently no precedent for forming a $C_4$ unit from a $C_3$ species), or alternatively by induction of a retro-Diels–Alder reaction in (VIII) by the olefin followed by interaction of the hexafluorobut-2-yne so formed with [Ni($\eta$-$C_5H_5$)$_2$] or (VII). If this latter mechanism is correct, it is remarkable that there are no other identifiable products.

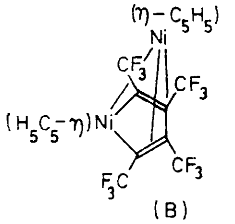
The structural significance of the various products of the reactions between [{Ni($\eta$-$C_5H_5$)($SCF_3$)}$_2$] or [Ni($\eta$-$C_5H_5$)$_2$] and hexafluorobut-2-yne have been mentioned above. It is immediately apparent that although there are common products between the two reactions [particularly (I)] there are products which are specific to each reaction so that metal substituents play an important part in determining the products in reactions with alkynes. Moreover, the reactions were not carried out under precisely similar conditions and by comparison of the products identified from the present study of the reaction between [Ni($\eta$-$C_5H_5$)$_2$] and hexafluorobut-2-yne and those identified from previous studies of this system [6] it is apparent that precise conditions strongly influence the course of the reaction.

Reactions between cyclopentadienylnickel derivatives and acetylenes may proceed through an intermediate (A) of stoicheiometry Ni($\eta$-$C_5H_5$)$_2$($CF_3C_2CF_3$) in which the acetylene interacts initially with the metal and a rearrangement gives an intermediate (A) with a $\eta^1$- or $\eta^3$-$C_5H_5$ group.[4,19] The formation of (X) from [Ni($\eta$-$C_5H_5$)$_2$] and chlorotrifluoroethylene presumably proceeds similarly. As described on page 1126 it is unlikely that (VIII) is formed by way of (VII) as an intermediate, and it is more probable that (VIII) is formed by attack of a further acetylene on the $\sigma$-bonded diene ring of (A) followed by intramolecular attack of the co-ordinated acetylenes to give (VIII) (both steps may take place *via* co-ordinated acetylenes). The other main product of the reaction between [Ni($\eta$-$C_5H_5$)$_2$] and hexafluorobut-2-yne is (I) which is likely to be formed from (A) and a further molecule of [Ni($\eta$-$C_5H_5$)$_2$].

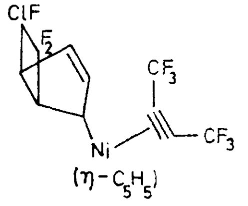
Complex (I) reacts with hexafluorobut-2-yne to give tetramer (IX) as the principle product, and it seems likely that the small quantities of (IX) formed in the reaction between [Ni($\eta$-$C_5H_5$)$_2$] and hexafluorobut-2-yne result from the attack of hexafluorobut-2-yne on (I). Species derived from a dimer, [{Ni($C_5H_5$)($CF_3C_2CF_3$)}$_2$], are very prominent in the mass spectrum of (IX) and such a dimer (B) resulting from further attack of hexafluorobut-2-yne on (I) and containing a nickelacyclopentadiene unit is a plausible precursor by self-dimerisation by Diels–Alder addition for (IX), by reaction with A {or the equivalent of successive reaction of [Ni($\eta$-$C_5H_5$)$_2$] and hexafluorobut-2-yne} to form (IV), and by further insertion of hexafluorobut-2-yne followed by elimination for (II). [The species (B) is written formally with one nickel as a 20-electron species; this could be achieved in several obvious ways or could account for the extreme reactivity of the species.] The conversion of (I) into the double Diels–Alder adduct (VIII) may not be part of this main chain of reactions and may proceed through direct successive intermolecular attack of hexafluorobut-2-yne on a cyclopentadienyl group of (I), or by reversion of (I) to [Ni($\eta$-$C_5H_5$)$_2$], although further attack of hexafluorobut-2-yne on (B) cannot be ruled out.



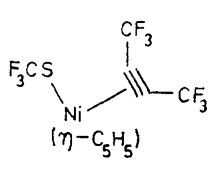
(A)



(B)



(C)



(D)

The products of the reaction between hexafluorobut-2-yne and (X) appear to be formed by a similar sequence of reactions involving intermediate formation of an adduct (C), analogous to (A) and its adduct with a further molecule of acetylene, which reacts with a further molecule of (C) to give (I) or with a further molecule of hexafluorobut-2-yne to give a nickelacyclopentadiene derivative, (XI).

The reactions of [{Ni($\eta$-$C_5H_5$)($SCF_3$)}$_2$] with hexafluorobut-2-yne give some products common to those formed from [Ni($\eta$-$C_5H_5$)$_2$]. Insertion of alkyne into the Ni–S

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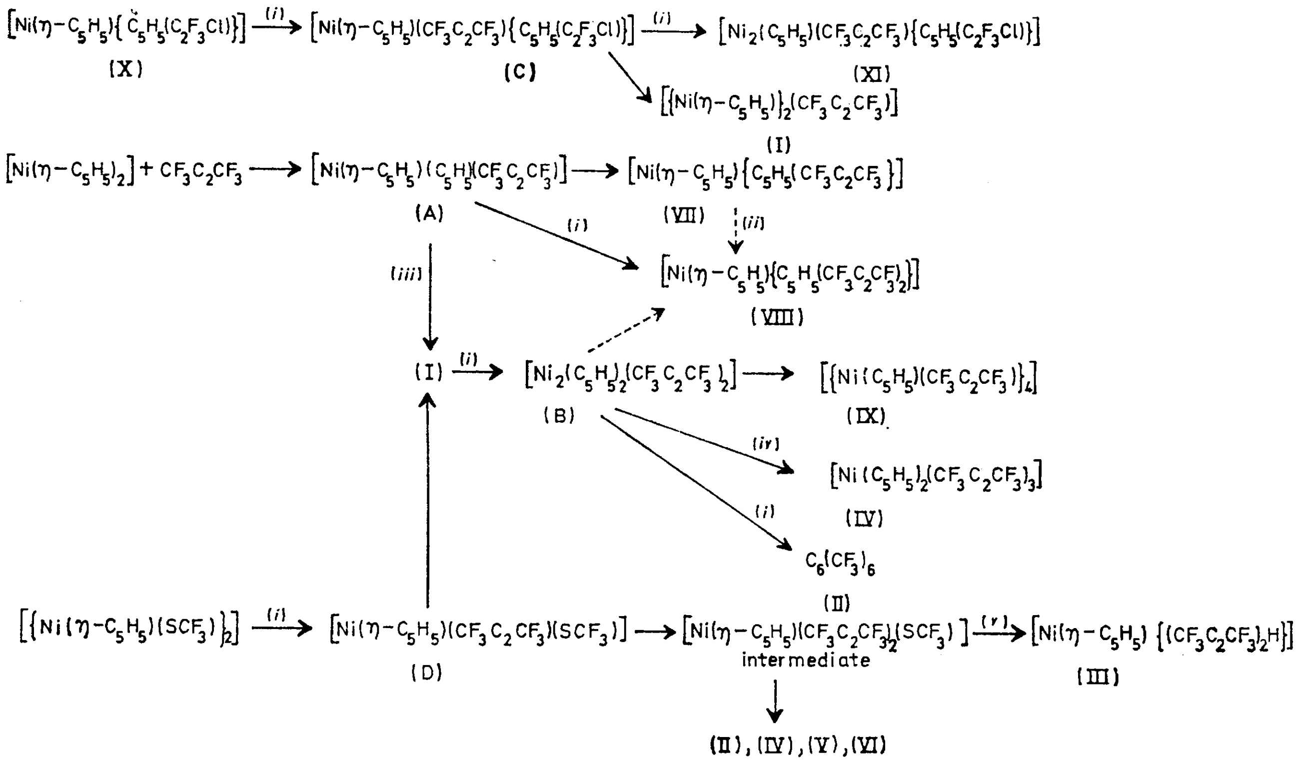
[18] N. A. Bailey, M. R. Churchill, R. Hunt, R. Mason, and G. Wilkinson, *Proc. Chem. Soc.*, 1964, 401; D. M. Roundhill and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 506.

[19] H. C. Clark, D. G. Ibbott, N. C. Payne, and A. Shaver, *J. Amer. Chem. Soc.*, 1975, **97**, 3555.



SCHEME (*i*), $CF_3C_2CF_3$; (*ii*), $C_3F_6$; (*iii*), $[Ni(\eta\text{-}C_5H_5)_2]$; (*iv*), (A); (*v*), solvent.

bond seems unlikely as a mode of reaction since $MC_n$-$(SCF_3)$ derivatives once formed do not appear to undergo subsequent cleavage of the $C\text{-}SCF_3$ bond.[4] The series of reactions can be adequately explained by postulation of an initial alkynecyclopentadienylnickel thiolate monomer intermediate, (D), which can react with a similar intermediate or the starting dimer to give (I). Complex (I) undergoes the sequence of reactions described above to form (II) and (IV), although it is noteworthy that the tetramer (IX) was not identified from these reactions. Addition of further acetylene to (D) could give rise to a nickelacyclopentadiene derivative which should be easily converted into (III) *via* a radical attack on the solvent, whilst further insertion of an acetylene to give a nickelacycloheptatriene would provide an alternative path to (IV)—(VI).

## EXPERIMENTAL

Reactions were carried out as previously described [20] under conditions given in Table 1. Specific separation and purification procedures are given below. Hexafluoropropene and chlorotrifluoroethylene were obtained from P.C.R. Inc., $[Ni(\eta\text{-}C_5H_5)_2]$ from Alpha Inorganics. The complexes $[\{Ni(\eta\text{-}C_5H_5)(SCF_3)\}_2]$,[20] $[Ni(\eta\text{-}C_5H_5)\{C_5H_5(CF_3C_2CF_3)\}]$,[6] $[Ni(\eta\text{-}C_5H_5)\{C_5H_5(C_2F_3Cl)\}]$,[17] and $[\{Ni(\eta\text{-}C_5H_5)\}_2(CF_3C_2CF_3)]$ [5] were prepared by literature methods.

*Reactions of Hexafluorobut-2-yne.—With* $[\{Ni(\eta\text{-}C_5H_5)(SCF_3)\}_2]$. The product was extracted with light petroleum, chromatographed over Florisil, and eluted with light petroleum. The first two bands, red $[Ni_2(C_5H_5)_2(CF_3C_2CF_3)_3]$ (V) and orange $[Ni(C_5H_5)_2(CF_3C_2CF_3)_3]$ (VI), were rechromatographed over activated alumina and the products recrystallised from pentane. The other products were green $[\{Ni(\eta\text{-}C_5H_5)\}_2(CF_3C_2CF_3)]$ (I), yellow $[Ni(\eta\text{-}C_5H_5)\{(CF_3C_2CF_3)_2H\}]$ (III), purified by sublimation at 313

TABLE 1

Reaction conditions and products

| Reactants | $T$/K | $t$/h | Products | Yield (%) |
|---|---|---|---|---|
| $[\{Ni(\eta\text{-}C_5H_5)(SCF_3)\}_2]$ + $CF_3C_2CF_3$ | 318 | 60 | (I) | 28 |
| | | | (II) | 15 |
| | | | (III) | 5 |
| | | | (IV) | 8 |
| | | | (V) | * |
| | | | (VI) | * |
| $[Ni(\eta\text{-}C_5H_5)_2]$ + $CF_3C_2CF_3$ | 358 | 10 | (I) | 25 |
| | | | (II) | * |
| | | | (VII) | * |
| | | | (VIII) | 37 |
| | | | (IX) | * |
| $[Ni(\eta\text{-}C_5H_5)\{C_5H_5(CF_3C_2CF_3)\}]$ + $CF_3C_2CF_3$ | 353 | 70 | (VIII) | 8 |
| $[Ni(\eta\text{-}C_5H_5)\{C_5H_5(CF_3C_2CF_3)\}]$ + $CF_3CF{=}CF_2$ | 358 | 80 | (VIII) | 6 |
| $[Ni(\eta\text{-}C_5H_5)\{C_5H_5(C_2F_3Cl)\}]$ + $CF_3C_2CF_3$ | 343 | 90 | (I) | 6 |
| | | | (XI) | 62 |
| $[\{Ni(\eta\text{-}C_5H_5)\}_2(CF_3C_2CF_3)]$ + $CF_3C_2CF_3$ | 363 | 90 | (II) | * |
| | | | (IV) | * |
| | | | (VIII) | * |
| | | | (IX) | 72 |

* Trace amount.

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[20] J. L. Davidson and D. W. A. Sharp, *J.C.S. Dalton*, 1973, 1957.

K, and purple $[Ni_3(C_5H_5)_2(CF_3C_2CF_3)_3]$ (IV), recrystallised from methylene chloride–hexane.

TABLE 2

Melting points, colours, and analyses (calculated values in parentheses)

| | M.p. (*T*/K) | Analysis (%) C | H | F | Ni | *M* [a] |
|---|---|---|---|---|---|---|
| $[Ni(\eta\text{-}C_5H_5)\{(CF_3C_2CF_3)_2H\}]$ (III) | 327 | 35.3 | 1.5 | 49.8 | 13.4 | 448 |
| | | (34.8) | (1.3) | (50.9) | (13.1) | (448) |
| $[Ni_3(C_5H_5)_2(CF_3C_2CF_3)_3]$ (IV) | 461 (decomp.) | 33.7 | 1.2 | 42.6 | 21.9 | 790 |
| | | (33.3) | (1.3) | (43.1) | (22.2) | (790) |
| $[Ni_2(C_5H_5)_2(CF_3C_2CF_3)_3]$ (V) | 453 | | | | | 732 |
| | | | | | | (732) |
| $[Ni(C_5H_5)_2(CF_3C_2CF_3)_3]$ (VI) | 431—433 | | | | | 674 |
| | | | | | | (674) |
| $[Ni(\eta\text{-}C_5H_5)\{C_5H_5(CF_3C_2CF_3)_2\}]$ (VIII) | 469—470 | 41.2 | 2.1 | 44.3 | 11.5 | 512 |
| | | (40.6) | (2.0) | (44.4) | (11.4) | (512) |
| $[\{Ni(C_5H_5)(CF_3C_2CF_3)\}_4]$ (IX) | 538 (decomp.) | 37.6 | 1.9 | 40.5 | 21.5 | |
| | | (37.5) | (1.9) | (40.0) | (20.4) | |
| $[Ni_2(C_5H_5)(CF_3C_2CF_3)_2\{C_5H_5(C_2F_3Cl)\}]$ (XI) [b] | 461 (decomp.) | 35.2 | 1.5 | 42.5 | 17.5 | 686 |
| | | (34.9) | (1.5) | (41.5) | (17.1) | (686) |

[a] By mass spectrometry. [b] Cl 4.9 (5.2%).

TABLE 3

N.m.r. parameters of cyclopentadienylnickel complexes (measured in $CCl_4$ or cyclohexane solution (indicated *). Relative intensities are in parentheses

| | $^1H$ N.m.r. ($\tau$) | | | | | | $^{19}F$ N.m.r. (p.p.m. with respect to $CCl_3F$) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Complex | $\delta_1$ | $\delta_2$ | $\delta_3$ | $\delta_4$ | $\delta_5$ | $\delta_6$ | $\delta_1$ | $\delta_2$ | $\delta_3$ | $\delta_4$ | $\delta_5$ |
| $[Ni(\eta\text{-}C_5H_5)\{(CF_3C_2CF_3)_2H\}]$ (III) * | 4.24(5) | 5.63(1) | | | | | 53.7(1) | 56.0(1) | 63.5(1) | 65.7(1) | |
| $[Ni_3(C_5H_5)_2(CF_3C_2CF_3)_3]$ (IV) | 4.39(1) | 4.50(1) | | | | | 47.5(1) | 51.8(1) | 54.8(1) | | |
| $[Ni_2(C_5H_5)_2(CF_3C_2CF_3)_3]$ (V) * | 4.55 | | | | | | | | | | |
| $[Ni(C_5H_5)_2(CF_3C_2CF_3)_3]$ (VI) * | 4.36(5) | 6.54(1) | 6.72(2) | 7.02(2) | | | 51.1(1) | 55.4(1) | 56.0(1) | 61.5(1) | 64.0(2) |
| $[Ni(\eta\text{-}C_5H_5)\{C_5H_5(CF_3C_2CF_3)_2\}]$ (VIII) | 4.52(5) | 6.50(2) | 7.05(2) | 7.61(1) | | | 57.8(1) | 66.8(1) | | | |
| $[\{Ni(C_5H_5)(CF_3C_2CF_3)\}_4]$ (IX) | 3.86(1) | 4.20(5) | 4.24(5) | 4.64(5) | 4.91(2) | 7.18(2) | 47.3(1) | 50.0(1) | 55.0(2) | | |
| $[Ni_2(C_5H_5)(CF_3C_2CF_3)_2\{C_5H_5(C_2F_3Cl)\}]$ (XI) | 3.75(1) | 4.40(5) | 5.05(2) | 6.91(2) | | | 49.0(1) | 56.7(1) | | | |

*With* $[Ni(\eta\text{-}C_5H_5)_2]$. The products were sublimed at 318 K, the sublimate extracted with pentane, and the solution chromatographed over Florisil to give yellow $[Ni(\eta\text{-}C_5H_5)\{C_5H_5(CF_3C_2CF_3)_2\}]$ (VIII), yellow $[Ni(\eta\text{-}C_5H_5)\{C_5H_5(CF_3C_2CF_3)\}]$ (VII), and green (I). These were resublimed at 353 (VIII) and 303 K (VII) and (I). The residue from the extraction of the first sublimation, $C_6(CF_3)_6$ (II), was recrystallised from methylene chloride–hexane. The residue from the first sublimation was resublimed at 353 K to give (VIII) which was recrystallised from methylene chloride–hexane. The black solid remaining in the sublimation vessel was dissolved in methylene chloride and hexane was added to give $[\{Ni(C_5H_5)(CF_3C_2CF_3)\}_4]$ (IX) after centrifuging and removal of solvent under nitrogen.

TABLE 4

I.r. spectra (cm$^{-1}$) of cyclopentadienylnickel complexes measured in $CCl_4$ or cyclohexane (*) solution

| Complex | ν(C–C) | ν(C–F) |
|---|---|---|
| (III) * | 1 661w | 1 293s. 1 260s, 1 245s, 1 214w, 1 187s, 1 178s, 1 160s, 1 150(sh) |
| (IV) | 1 589w | 1 265mb, 1 219s, 1 189s, 1 177m, 1 170m, 1 147m, 1 134m |
| (V) * | | 1 296vw, 1 237m, 1 205vs, 1 188s, 1 120vw |
| (VI) | 1 711w | 1 299m, 1 290m(sh), 1 271m, 1 234m, 1 224m, 1 219m, 1 200vs, 1 183m, 1 168s, 1 166s(sh), 1 144s, 1 126m, 1 116w |
| (VIII) | 1 710w | 1 287w, 1 258s, 1 241m, 1 235m, 1 218w, 1 196vs, 1 178m(sh), 1 170m, 1 145vsb, 1 131vs, 1 112m |
| (IX) | | 1 270w(sh), 1 247m, 1 216s, 1 198s, 1 191s, 1 173s(sh), 1 161s, 1 146m, 1 129m |
| (XI) | | 1 297m, 1 294m, 1 274m, 1 260m, 1 247m, 1 219vs, 1 190s, 1 172s, 1 133m |

*With* (VII). The product mixtures were sublimed to remove unchanged (VII), and (VIII) was recrystallised from methylene chloride–hexane. The reaction of the complex with hexafluoropropene was similar.

*With* $[Ni(\eta\text{-}C_5H_5)\{C_5H_5(C_2F_3Cl)\}]$ (X). The product mixture was sublimed at 323 K to leave dark brown $[Ni_2(C_5H_5)(CF_3C_2CF_3)_2\{C_5H_5(C_2F_3Cl)\}]$ (XI) which was recrystallised from methylene chloride–hexane. The sublimate was chromatographed over Florisil and eluted with pentane to give (I) and small quantities of (XI).

*With* $[\{Ni(\eta\text{-}C_5H_5)\}_2(CF_3C_2CF_3)]$. The product mixture was extracted with light petroleum and after removal of solvent it was sublimed at 323 K. The sublimate was extracted with pentane to leave a small quantity of (II). The residue in the sublimation vessel and the pentane-soluble extract were combined and chromatographed over Florisil eluting with pentane to give (I), (IV), (VIII), and (IX). Complex (IX) was recrystallised from methylene chloride–hexane.

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