Reaction of Hexafluorobut-2-yne with Nickelocene and the Crystal Structure of $[C_5H_5NiCF_3CCCF_3]_4$

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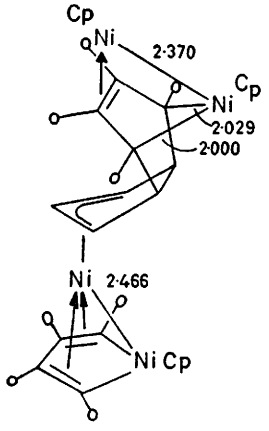
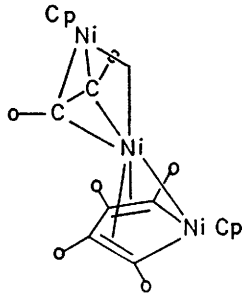
Summary Reaction of CF_3CCCF_3 with $(\pi\text{-}C_5H_5)_2Ni$ gives $C_6(CF_3)_6$, $C_5H_5Ni[C_5H_5(CF_3CCCF_3)_2]$, $[C_5H_5NiCF_3CCCF_3]_4$, and $C_5H_5)_2Ni_3(CF_3CCCF_3)_3$ in addition to known products; the molecular structure of $[C_5H_5NiCF_3CCCF_3]_4$ has been determined by *X*-ray analysis.

HEXAFLUOROBUT-2-YNE has been previously reported[1,2] to react with nickelocene at room temperature to give $(CpNi)_2CF_3CCCF_3$ (**1**) and $CpNi[C_5H_5{\cdot}CF_3CCCF_3]$ (**2**) (Cp = cyclopentadienyl). We now report that at 358 K the range of products is extended to include hexakis(trifluoromethyl)benzene (**3**), $CpNi[C_5H_5(CF_3CCCF_3)_2]$ (**4**), and $[C_5H_5NiCF_3CCCF_3]_4$ (**5**). Complex (**1**) reacts with CF_3CCCF_3 at 363 K to give (**4**) and (**5**) together with some $(C_5H_5)_2Ni_3(CF_3CCCF_3)_3$ (**6**). Complex (**2**) reacts with CF_3CCCF_3 to give a low yield of (**4**). All the complexes have been fully characterised analytically and spectroscopically.



(5)

Complex (**4**) is formulated as an adduct of $CF_3{\equiv}CCF_3$ to the free olefinic bond of (**2**) and although several structural isomers are possible only one appears to be formed. The presence of h^1, h^2, h^3, h^4, and h^5 carbon donor units in (**5**) has been shown by *X*-ray analysis. Each of the four nickel atoms is chemically unique, although all attain noble gas electronic configurations by formation of one Ni–Ni and seven Ni–C bonds. The attachment of a $[(\pi\text{-}C_5H_5)Ni]_2$ unit to a cyclohexene ring by one π-olefin and two σ bonds is novel, as is the 1,2 addition of a NiC_4 unit to a cyclopenta-



(6)

dienyl system which then becomes a π-cyclopentenyl group. (A similar arrangement has been postulated for the product of the reaction between Cp_2Ni and octafluorocyclohexa-1,3-diene.)[2] There also appears to be no previous structure determination of a (π-nickelacyclopentadienyl)nickel system, although related complexes of iron, rhodium, and osmium have been described.[3] From spectroscopic evidence and by analogy with (**5**), (**6**) is formulated as shown being similar to $(CpNi)_2CF_3CCCF_3$ with a nickelacyclopentadienyl ring in place of one cyclopentadienyl group.

The full mechanism of formation of these species is not clear but is consistent with reaction of (**1**) and $CF_3C{:}CCF_3$ to give an intermediate $Cp_2Ni_2(CF_3CCCF_3)_2$ which can dimerise to (**5**) and thus allow each nickel atom to attain a noble gas electronic configuration. The reaction of $CF_3C{:}CCF_3$ with nickelacyclopentadienyl rings provides a ready route to hexakis(trifluoromethyl)benzene.

Crystal data: $[C_9H_5F_6Ni]_4$, $M = 1143{\cdot}3$; triclinic, $a = 9{\cdot}322$, $b = 16{\cdot}520$, $c = 12{\cdot}727$ Å, $\alpha = 103{\cdot}76°$, $\beta = 97{\cdot}83°$, $\gamma = 85{\cdot}89°$, $U = 1884{\cdot}4$ Å^3, space group $P\bar{1}$, $D_c = 2{\cdot}014$ for $Z = 2$. The intensities of 3526 independent reflection were measured on a four-circle diffractometer. All atoms except hydrogens were located by Patterson and Fourier methods. $R = 0{\cdot}09$ currently after block-diagonal least-squares refinement of the positional and anisotropic thermal

parameters of all atoms. The molecular geometry leads unambiguously to the formulation (**5**). Noteworthy features of the structure include the non-equivalence of the Ni–Ni bond lengths [see (**5**)] and of the Ni–C σ-bond lengths; the mean lengths of the Ni–C(nickelacyclopentadienyl) and Ni–C(cyclohexene) σ-bonds ar **1·91** (1) and **2·01** (1) Å respectively. All other bond lengths are normal.

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