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STRUCTURES OF POLYFLUOROAROMATIC COMPOUNDS. PART VIII.* SYNTHESIS AND CRYSTAL STRUCTURE OF μ-(PERFLUORODIPHENYLETHYNE)-BIS(η⁵-CYCLOPENTADIENYL-NICKEL)

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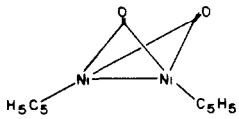
SUMMARY

Reaction of perfluorodiphenylethyne with cyclopentadienylnickel-carbonyl dimer gives μ-(perfluorodiphenylethyne)-bis(η⁵-cyclopentadienylnickel). The crystal structure of this complex has been determined from X-ray data collected by counter methods. The Ni-Ni bond length is 2.329(2) Å. Each end of the bridging ethyne moiety is symmetrically bonded to both nickel atoms with Ni-C distances in the range 1.899(12) - 1.924(10) Å. Angles C≡C-C_6F_5 are 141.2(10) and 142.7(11)° and the formal triple bond is lengthened from *ca.* 1.20 to 1.362(17) Å, the ethyne ligand adopting a cis-bent geometry, characteristic of other complexed ethynes. The cyclopentadienyl rings are essentially planar and are each oriented very nearly perpendicular to the Ni-centre of ring vector. The crystals are monoclinic, space group $P2_1/c$, with a = 17.05(1), b = 8.25(1), c = 15.695(10) Å, β = 99.86(5)° and four molecules in the unit cell. The structure has been refined to R 5.3% for 1324 observed amplitudes.

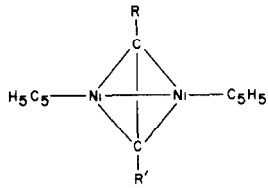
INTRODUCTION

Reaction [1] of $[(\eta^5\text{-}C_5H_5)_2Ni(CO)_2]_2$ (I) or $(\eta^5\text{-}C_5H_5)_2Ni$ with alkynes RC≡CR' (R,R' = H,C_6H_5,CH_3, etc.) results in the formation of ethyne bridged species. The structures of two of these complexes, (II) and (III), and of the analogous compound (IV) have been determined [2-4] by X-ray crystallography.

* Part VII: M.J.Hamor and T.A.Hamor, Acta Cryst., B36 (1980). In the press.



(I)



(II) R = R' = H
(III) R = R' = C_6H_5
(IV) R = CF_3, R' = $P(O)(C_6H_5)_2$
(V) R = R' = C_6F_5

Current theories [5-7] of bonding in transition metal complexes of alkynes are based on the Dewar-Chatt-Duncanson [8] model of bonding in alkene complexes. This involves overlap of a carbon pπ orbital with a hybrid σ-type acceptor orbital of the metal and a synergically related back-donation of electron density from a filled metal dπ orbital into a vacant antibonding pπ^* orbital of the ligand. Ethynes having two sets of π and π^* orbitals orthogonal to each other, permit bonding interaction also between the second set of π orbitals and appropriate metal orbitals, or equivalent bonding to two metal atoms.

The crystallographic studies of the complexes (II) - (IV), and of other metal-alkynes, show [2-4,9] that the ligand is symmetrically disposed with respect to the metal and assumes a cis-bent geometry with a lengthened C≡C bond. Spectroscopic studies [10] indicate that the electron configuration of complexed ethynes resembles that of ethenes, with at least partial rehybridization of the carbon atoms, sp → sp^2. Blizzard and Santry [11] concluded from CNDO calculations that the degree of bending depends on the extent of the dπ - pπ^* back donation. Electronegative substituents attached to the ethyne may therefore influence the bonding and geometry of such complexes by enhancing the metal to ligand back donation, and this effect has been invoked [4] to account for certain features of the structure (IV). Here the bonds between the nickel atoms and the carbon atom bearing the electronegative trifluoromethyl substituent are shorter than those involving the carbon atom bearing the oxodiphenylphosphino group, and the C≡C-CF_3 angle, 141°, is closer to 120° than the C≡C - $P(O)(C_6H_5)_2$ angle at 150°. Comparison of pertinent features of the molecular geometry of $(\eta^5\text{-}C_5H_5Ni)_2C_6F_5C{\equiv}CC_6F_5$ (V), whose synthesis and crystal structure we now report, with those determined for (II) - (IV) will be of relevance in assessing the effect of the electronegative fluoro-substituents on bonding and geometry.

RESULTS AND DISCUSSION

The complex (V) was prepared from perfluorodiphenylethyne [12] and cyclopentadienylnickelcarbonyl dimer as described [1] for the hydrocarbon analogue. Its stereochemistry determined from three-dimensional X-ray counter data is illustrated in Figure 1, which also shows the atomic numbering. Fluorine and hydrogen atoms are assigned the number of the carbon atom to which they are linked. Atomic coordinates are given in Table 1 and bond lengths and valence angles with their estimated standard deviations are given in Table 2.

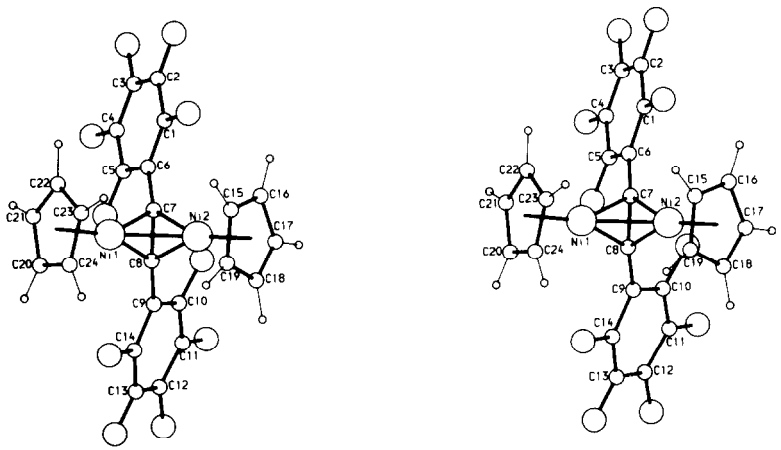


Fig. 1. Stereoscopic view of the molecule (V)

Each nickel atom is coordinated to the two ethynyl carbon atoms, a

C(1) - C(2) - C(3)	117.7(13)	C(10) - C(11) - C(12)	118.9(16)
C(1) - C(2) - F(2)	123.3(14)	C(10) - C(11) - F(11)	120.1(14)
C(3) - C(2) - F(2)	119.0(14)	C(12) - C(11) - F(11)	121.0(13)
C(2) - C(3) - C(4)	120.3(14)	C(11) - C(12) - C(13)	121.3(13)
C(2) - C(3) - F(3)	121.6(13)	C(11) - C(12) - F(12)	118.1(17)
C(4) - C(3) - F(3)	118.1(15)	C(13) - C(12) - F(12)	120.5(16)
C(3) - C(4) - C(5)	121.4(14)	C(12) - C(13) - C(14)	116.6(15)
C(3) - C(4) - F(4)	121.0(13)	C(12) - C(13) - F(13)	120.0(12)
C(5) - C(4) - F(4)	117.6(11)	C(14) - C(13) - F(13)	123.4(15)
C(4) - C(5) - C(6)	120.1(11)	C(13) - C(14) - C(9)	127.5(15)
C(4) - C(5) - F(5)	119.8(11)	C(13) - C(14) - F(14)	115.9(14)
C(6) - C(5) - F(5)	120.2(11)	C(9) - C(14) - F(14)	116.6(11)
C(20) - C(21) - C(22)	106.5(12)	C(15) - C(16) - C(17)	105.4(15)
C(21) - C(22) - C(23)	110.0(12)	C(16) - C(17) - C(18)	110.5(15)
C(22) - C(23) - C(24)	107.1(12)	C(17) - C(18) - C(19)	109.9(15)
C(23) - C(24) - C(20)	106.2(13)	C(18) - C(19) - C(15)	105.0(15)
C(24) - C(20) - C(21)	110.1(11)	C(19) - C(15) - C(16)	109.2(15)

*Cp(1) and Cp(2) are the centres of cyclopentadienyl rings C(20) - (24) and C(15) - (19), respectively.

TABLE 3

Mean plane calculations

(a) Deviations (Å) from least-squares planes

Plane (1): phenyl ring C(1) - (6)

C(1)	0.004,	C(2)	-0.008,	C(3)	0.007,	C(4)	-0.002,
C(5)	-0.003,	C(6)	0.001,	C(7)	-0.066,	F(1)	-0.008,
F(2)	0.000,	F(3)	0.052,	F(4)	-0.009,	F(5)	-0.046

Plane (2): phenyl ring C(9) - (14)

C(9)	-0.013,	C(10)	0.000,	C(11)	0.014,	C(12)	-0.017,
C(13)	0.004,	C(14)	0.011,	C(8)	-0.002,	F(10)	0.053,
F(11)	0.008,	F(12)	-0.006,	F(13)	-0.006,	F(14)	0.002

Plane (3): cyclopentadienyl ring C(15) - (19)

C(15)	0.011,	C(16)	-0.006,	C(17)	-0.001,	C(18)	0.008,
C(19)	-0.011,	Ni(2)	1.736				

Plane (4): cyclopentadienyl ring C(20) - (24)

C(20)	-0.009,	C(21)	0.013,	C(22)	-0.012,	C(23)	0.006,
C(24)	0.002,	Ni(1)	1.716				

Plane (5): ethyne moiety C(6) - (9)

C(6)	-0.018,	C(7)	0.048,	C(8)	-0.049,	C(9)	0.018

(b) Interplanar angles (°)

(1) - (2)	53.1	(2) - (5)	34.8
(1) - (5)	26.8	(3) - (4)	69.4

TABLE 4

Comparison of selected structural parameters in ethyne-bridged Ni complexes (II)-(V)

Values in parentheses are estimated standard deviations; those in square brackets are maximum deviations from mean values. C(ac) denotes an ethyne carbon atom. Cp is the centre of a cyclopentadienyl ring. For the unsymmetrically substituted compound IV, where two values are listed, the first refers to the ethyne carbon atom adjacent to $R(CF_3)$ and the second to that adjacent to $R'[P(O)(C_6H_5)_2]$. Complex I possesses crystallographic C_{2v} symmetry.

	II [ref.2]	III [ref.3]	IV [ref.4]	V [present work]
Distances (Å)				
Ni - Ni	2.345(3)	2.329(4)	2.365(1)	2.329(2)
C(ac) - C(ac)	1.341(6)	1.35(3)	1.353(9)	1.362(17)
Ni - C(ac)	1.884(4)	1.888[18]	1.881[8], 1.915[6]	1.910[14]
Ni - Cp	1.793	1.739[17]	1.724[7]	1.726[10]
Valence angles (°)				
C(ac) - C(ac) - R,R'	148.1(5)	139.9[21]	140.7(6), 150.2(5)	142.0[8]
Ni - C(ac) - C(ac)	69.2(1)	69.0[9]	70.5[6], 67.8[6]	69.1[8]
Ni - C(ac) - Ni	77.0(1)	76.3[3]	77.9(2), 76.3(2)	75.2[1]
Cp - Ni - C(ac)	157.4	154.3[16]	154.2[21], 155.5[31]	154.9[38]
C(ac) - Ni - C(ac)	41.7(2)	42.0[0]	41.8[1]	41.8[1]
Torsion angles (°)				
R - C(ac) - C(ac) - R'	0	-3.6	16.2	19.0
Cp - Ni - Ni - Cp	0	2.6	9.9	8.3
Interplanar angles (°)				
C_5H_5 ^ C_5H_5	73.9	64.7	68.0	69.4
$CpNi_2Cp$ ^ C_5H_5	90	88.5[13]	88.1[1]	89.0[3]
Other angles (°)				
C_5H_5 plane ^ Ni-Cp line	88.0	87.6[9]	89.5[2]	89.6[2]
Ni - Ni ^ C(ac) - C(ac)	90	89.2	89.1	88.9

ethyne ligand [11]. The order of increasing electronegativities of the groups R,R' is P < H < C_6H_5 < C_6F_5 < CF_3 [15,16], i.e. compound IV(P) < II < III < V < IV(CF_3), but with only a small difference between C_6H_5 and C_6F_5 [16].

The Ni - C(ac) distances, apart from those in (IV), do not show the expected trend. On the other hand, the acetylenic bond lengths do increase in the order (II) < (III) < (V), although the differences are not statistically significant, and with the exception of structure (III), the ethynyl bending angles C(ac) - C(ac) - R,R' also show the expected trend.† The C(ac) - C(ac) - P angle of structure (IV) may however be affected to some extent by P - C π-bonding, although this effect cannot be large [4]. Other valence angles at Ni and C(ac) have similar values in the four structures.

Apart from structure (II) with crystallographic C_{2v} symmetry, the ethyne fragments are not accurately planar. The distortions (*cf.* torsion angles R - C(ac) - C(ac) - R' in Table 4) are largest in (IV) and (V), presumably due to the steric effect of the bulky substituents R,R' in these compounds. In general, however, the four structures are quite similar with respect to the mutual orientations of the planes of the cyclopentadienyl rings, the Cp-Ni_2-Cp plane and the Ni - Cp, Ni - Ni and C(ac) - C(ac) vectors.

EXPERIMENTAL

A solution of perfluorodiphenylethyne (60 mg., 0.167 mmol) and the nickel complex (I) (51 mg., 0.167 mmol) in oxygen-free toluene (20 ml) was refluxed under nitrogen for 1.5 hr. The cooled solution was filtered and evaporated to dryness. Crystallization of the residue from n-hexane gave μ-perfluorodiphenylethyne-bis(η^5-cyclopentadienylnickel) as dark green plates (81 mg., 80%), m.p. 218-219 °
(Found: C, 47.9; H, 1.5; F, 31.4%. Calc. for $C_{24}H_{10}F_{10}Ni_2$: C, 47.6; H, 1.65; F, 31.4%). UV(n-hexane) λ_{max} 263, 368, 474 and 660 nm (ε 35860, 24260, 2426 and 1424 respectively).

† It may be noted that the structural parameters of (III) are based on photographically recorded X-ray data and are not quite as accurate as those determined for the other complexes from counter measurements.

Crystallographic measurements.

The crystals were in the form of dark green, diamond shaped thin plates. A crystal of dimensions 0.2 x 0.2 x 0.04 mm was mounted inside a Pantak capillary tube and aligned about the crystallographic y axis, which coincided with one of the edges of the diamond. After initial examination by photographic methods, final cell dimensions and intensities were measured with a Stoe STADI2 two-circle diffractometer using graphite monochromated Mo-Kα radiation. The scan speed was 0.3° min^{-1} in ω with 30 s background counts at each end of the scan. The intensities of four h0ℓ reflections were remeasured after each layer of data collection to monitor the stability of the system. There was a small decrease in the intensities of these reflections during the course of the data collection and appropriate layer scale factors were applied. Of 3518 unique reflections scanned within the range $0.1 < \sin\theta/\lambda < 0.61$ $\AA^{-1}$, 1324 [$I > 2.5\sigma(I)$] were considered to be observed and were used in the analysis. Absorption corrections were not applied.

Crystal data.

$C_{24}H_{10}F_{10}Ni_2$, M = 605.7, monoclinic, a = 17.05(1), b = 8.25(1), c = 15.695(10) $\AA$, β = 99.86(5)°, U = 2175 $\AA^3$, Z = 4, D_c = 1.85 g cm^{-3}, space group $P2_1/c$, λ(Mo-Kα) = 0.71069 $\AA$, μ(Mo-Kα) = 1.74 mm^{-1}.

Structure determination.

The positions of the nickel atoms were determined by direct methods, and these were used to phase an electron density map from which C and F atoms were located. Hydrogen atoms were placed in calculated positions. The structure was refined by least-squares, coordinates and anisotropic thermal parameters being adjusted for the non-hydrogen atoms. Owing to the large number of parameters, the molecule was divided into two blocks which were refined in alternate cycles. One block consisted of the perfluorodiphenylethyne residue and the second block of the two cyclopentadienyl rings with the nickel atoms common to both blocks. Refinement was terminated when all calculated shifts were < 0.1σ and R 5.3% for the 1324 observed amplitudes.[†] The weighting scheme used

[†] Lists of observed and calculated structure factors and thermal parameters have been deposited (N. Goodhand, Thesis, University of Birmingham, 1979).

in the least-squares calculations was $w = 1/\sigma^2(F)$ where $\sigma(F)$ is the estimated standard deviation in the observed amplitudes.

Computations were carried out on the Birmingham University ICL 1906A computer and on the CDC 7600 at the University of Manchester Regional Computer Centre with SHELX [17], together with local ancillary programs.

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