X-Ray Diffraction Studies on Catalysis: Crystal Structure of Di-μ-trifluoroacetato-bis[(2-methylallyl-3-norbornyl)nickel(II)] and Comparison with Related Nickel(II) and Palladium(II) Complexes

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The crystal structure of the title compound (III) has been determined from diffractometer data (1 888 non-zero reflections) by the heavy-atom method and refined by least-squares to R 0.070. Crystals are monoclinic, space group $P2_1/c$, a = 16.431(3), b = 9.954(2), c = 16.614(3) Å, β = 92° 32′(2′), Z = 4. The structure is compared with those of the related nickel [(I) and (II)] and palladium complexes, (IV), in view of their relevance to norbornene polymerization catalysed by π-allyl nickel carboxylates. The molecular configuration is considered to be a key factor in the formation of mononuclear species, which are the active intermediates in the propagation reaction.

RECENTLY [1-3] we have investigated the crystal structures of a palladium(II) and of two nickel(II) methylallylnorbornyl complexes of general formula $[\{(C_{11}H_{17})M(OAc)\}_2]$ (M = Ni or Pd),[4] in order to establish the stereochemistry of the insertion reaction of olefins into the metal–allyl bond. We considered especially the nickel complexes since they can be considered as model products of the norbornene insertion reaction which initiates the propagation step in the polymerization catalysed by π-allylnickel halides and carboxylates.[5]

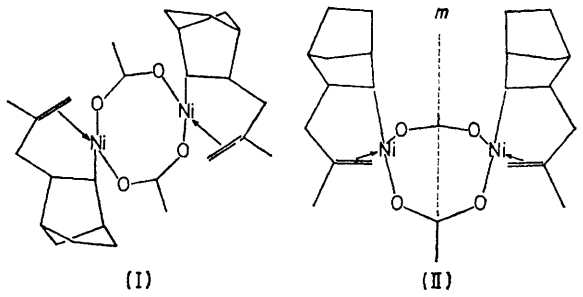
Dawans and Teyssié found[6] these carboxylates to be also very efficient catalysts for the 1,4-stereospecific polymerization of buta-1,3-diene, and observed a strong increase in catalytic activity associated with the electron-withdrawing properties of the co-ordinated anions. In view of their findings and of similar observations [5] for norbornene polymerization, we have extended our investigations to fluoroacetate complexes, in order to correlate catalytic activity and molecular structure.

We now report the crystal structure of, (III), di-μ-trifluoroacetato-bis[(2-methylallyl-3-norbornyl)nickel(II)], and compare it with the structures of the two aforementioned nickel complexes [2,3], (I) and (II), which were crystallized from the same solution under slightly different experimental conditions and were found [7] to be configurational isomers.

Complex (I), which is isostructural with the already studied palladium complex, (IV), has a two-fold symmetry axis perpendicular to the metal–metal axis while (II) has a non-crystallographic mirror plane passing through the carbon atoms of the bridging acetate groups. This means that in (II) the two hydrocarbon ligands are enantiomorphous to each other. In the crystal of (I)

[1] M. Zocchi, G. Tieghi, and A. Albinati, *J.C.S. Dalton*, 1973, 883.
[2] G. Tieghi and M. Zocchi, *Cryst. Struct. Comm.*, 1973, **2**, 557.
[3] G. Tieghi and M. Zocchi, *Cryst. Struct. Comm.*, 1973, **2**, 561.
[4] M. C. Gallazzi, T. L. Hanlon, G. Vitulli, and L. Porri, *J. Organometallic Chem.*, 1971, **33**, C45.
[5] M. C. Gallazzi, personal communication.
[6] F. Dawans and Ph. Teyssié, *J. Polymer Sci.*, 1969, **B7**, 111.
[7] G. Tieghi and M. Zocchi, *J. Organometallic Chem.*, 1973, **57**, C90.

(space group *Pbcn*), owing to the presence of the inversion centres, all the dimeric molecules are coupled by enantio-



(I) (II)

morphism relations, *i.e.* for every molecule of type *dd* there is another one of type *ll*. In the crystal of (II) (space group $P2_1/c$) all the dimeric molecules are of type *dl*. We have suggested[7] that (I) and (II) coexist in solution and that the exchange between the two forms is based on the dissociation of the nickel–acetate bonds by a mechanism similar to that postulated[8] for the interchange process of two configurational isomers in an allylic palladium acetate system. We have also shown that in (II), because of its configuration, the *trans*-effect of the carbon atoms σ-bonded to the metal ions gives rise to a substantial weakening of the bonds formed by one of the two acetate bridging groups. We now further develop this point and relate the weakening to the formation of catalytically active intermediates in the polymerization of norbornene.

EXPERIMENTAL

Crystals of (III) are much less stable than those of (I), (II), and (IV) and some decomposition was observed even after they had been sealed under inert gas in glass capillaries. The only way out of this difficulty was to measure the diffraction intensities at the highest speed compatible with a reasonable precision.

Crystal Data.—(III), $C_{26}H_{34}Ni_2F_6O_4$, Monoclinic, a = 16.431(3), b = 9.954(2), c = 16.614(3) Å, β = 92° 32′(2′), U = 2 714.6 Å^3, Z = 4 dimers, D_c = 1.30 g cm^{-3}. Space group $P2_1/c$. Mo-K_α radiation, λ = 0.71069 Å; μ (Mo-K_α) = 14.1 cm^{-1}.

The intensities of 1 888 non-zero independent reflections up to 2θ 50° (graphite-monochromatized Mo-K_α radiation) were measured on a Philips four-circle automated diffractometer by the ω-scan technique and by averaging two background counts for each reflection. The intensities of three standard reflections were monitored every hour. The scanning speed was 2.4° min^{-1} so that the total number of 4 780 reflections (observed and non-observed) could be measured in only 2 days. Since in this period the intensities of the standard reflections decreased by <8%, it appears that the general accuracy of the data set was not badly impaired by decomposition.

Data were corrected for Lorentz and polarization factors, but not for absorption since the crystal was approximately cube-shaped with an edge of *ca.* 0.03 cm and the linear absorption coefficient is small.

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

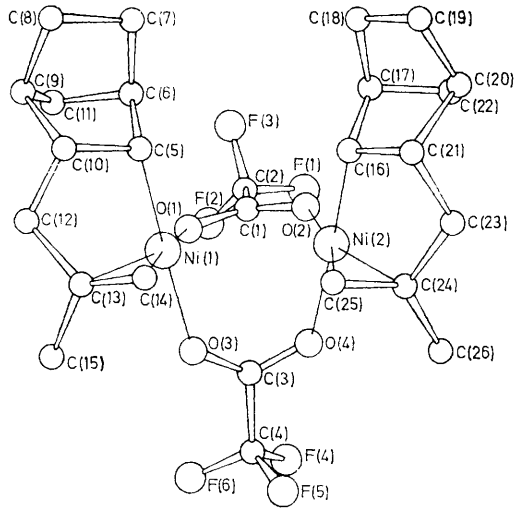
Structure Determination.—Since the cell parameters and the intensity distribution of (III) were so close to those of (II), the nickel atoms were positioned as in (II). A Fourier map based on this assumption showed the most important features of the structure. Refinement was carried out by Fourier and isotropic least-squares methods. A final least-squares refinement based on anisotropic temperature parameters, in the block-diagonal approximation, resulted in R 0.070. Dirac–Slater atomic scattering factors[9] for nickel and Hartree–Fock factors[10] for carbon, oxygen, and fluorine were used in the refinement.

The refined atomic positional and thermal parameters and their estimated standard deviations are given in Table 1. The exceptionally high values for the thermal parameters of the fluorine atoms indicate positional disorder or hindered rotation of the CF_3 groups and, together with the observed slight decomposition of the sample, explain the higher value of R for (III), compared with that for (I) and (II).

Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21257 (29 pp., 1 microfiche).*

DISCUSSION

The molecular configuration of (III) (Figure) is like that of (II), with a non-crystallographic mirror plane



Molecular structure of (III), showing the atom numbering system used in the analysis

passing through the carbon atoms of the bridging trifluoroacetate groups and with an approximately square-planar co-ordination about each nickel ion. Some interatomic distances, together with the corresponding values for (II), are given in Table 2.

As in (II), the two carboxylate groups are differently bonded to the nickel ions as a consequence of the *trans*-effect exerted by the σ-bonded carbon atoms of the norbornyl moieties. In both cases the farthest anion is asymmetrically bound to the metal, as shown by the fact that Ni(2)–O(4) is significantly longer than Ni(1)–O(3).

[8] J. Powell, *J. Chem. Soc.* (*A*), 1971, 2233.
[9] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.
[10] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

TABLE 1

Atomic positional ($\times 10^5$) and thermal * parameters for (III), with estimated standard deviations in parentheses

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni(1)	20 435(8)	10 998(14)	15 504(14)	4.47(6)	4.65(6)	4.65(6)	−0.26(10)	1.43(9)	0.72(10)
Ni(2)	33 192(8)	1 252(13)	3 152(8)	5.14(6)	4.34(6)	4.05(5)	−0.05(10)	1.29(9)	0.12(9)
O(1)	25 508(43)	27 040(72)	12 001(43)	5.00(34)	5.54(36)	5.75(36)	0.58(58)	1.88(55)	−0.71(59)
O(2)	33 192(44)	20 342(66)	1 921(40)	6.44(38)	4.14(31)	4.68(32)	−1.11(56)	0.19(55)	1.18(50)
O(3)	30 517(44)	7 444(88)	22 243(46)	5.12(36)	7.97(48)	5.46(36)	0.28(69)	0.56(57)	1.70(70)
O(4)	40 144(48)	4 567(84)	13 423(42)	6.43(42)	7.27(44)	4.21(32)	0.40(71)	−0.28(57)	−0.06(63)
F(1)	38 737(99)	44 911(106)	1 037(104)	22.5(13)	7.3(5)	26.8(15)	−9.4(14)	34.4(24)	−5.9(15)
F(2)	33 981(93)	50 216(87)	10 970(54)	27.8(14)	6.8(5)	7.2(5)	−15.6(13)	6.2(13)	−2.4(7)
F(3)	27 650(96)	49 297(106)	893(115)	20.3(12)	8.0(6)	31.9(18)	−10.9(14)	−31.8(25)	17.8(17)
F(4)	50 333(60)	13 360(138)	25 468(59)	8.6(5)	21.2(11)	8.1(5)	−13.0(13)	−2.8(8)	1.3(12)
F(5)	47 145(87)	−5 373(125)	28 091(84)	18.5(11)	11.7(8)	17.5(11)	2.7(15)	−23.6(19)	3.5(15)
F(6)	41 540(55)	10 059(156)	33 781(50)	7.6(5)	27.9(14)	5.7(4)	−0.9(14)	−0.8(7)	−8.3(13)
C(1)	30 214(62)	28 937(96)	6 444(59)	5.3(5)	3.8(4)	4.5(5)	0.1(7)	−0.4(7)	−1.2(7)
C(2)	32 665(78)	43 029(115)	5 098(70)	8.1(7)	4.5(5)	5.7(6)	1.6(10)	−1.1(10)	−1.5(9)
C(3)	37 428(64)	6 257(109)	20 224(60)	5.2(5)	5.1(5)	4.2(5)	−0.1(8)	0.7(8)	1.8(8)
C(4)	44 124(73)	6 580(138)	27 057(69)	5.6(6)	8.1(7)	5.0(5)	−0.1(11)	−1.1(9)	1.9(11)
C(5)	10 586(67)	13 734(121)	8 451(62)	5.3(5)	6.4(6)	4.5(5)	−0.2(9)	2.2(8)	−0.5(9)
C(6)	9 200(68)	27 414(118)	4 427(67)	5.4(5)	6.1(6)	5.2(5)	0.3(9)	−0.2(8)	3.0(9)
C(7)	2 333(75)	25 722(142)	−2 011(76)	6.1(6)	8.3(8)	6.2(6)	4.4(12)	0.4(10)	2.6(12)
C(8)	−5 414(75)	24 565(130)	2 870(80)	5.7(6)	6.9(7)	7.0(7)	2.0(11)	−0.7(10)	1.0(11)
C(9)	−1 769(69)	25 433(136)	11 762(74)	4.7(5)	7.8(7)	6.3(6)	1.5(10)	1.7(9)	0.5(11)
C(10)	2 829(60)	11 955(110)	13 412(67)	3.7(4)	5.6(5)	6.1(5)	0.0(8)	1.7(8)	1.7(9)
C(11)	4 989(76)	35 282(122)	10 696(80)	6.3(6)	5.4(6)	8.0(7)	−1.2(10)	−1.1(11)	−3.7(11)
C(12)	4 925(73)	10 413(122)	22 297(68)	6.0(6)	6.3(6)	5.1(5)	−1.5(10)	2.2(9)	0.8(9)
C(13)	12 927(65)	2 698(110)	23 999(65)	4.9(5)	5.3(5)	5.2(5)	−1.2(8)	2.0(8)	1.6(8)
C(14)	15 491(79)	−7 027(115)	18 647(66)	7.7(7)	5.0(5)	4.9(5)	−2.4(10)	0.9(10)	1.7(9)
C(15)	16 503(72)	3 992(135)	32 360(69)	5.4(6)	8.6(7)	5.4(5)	−1.7(11)	0.0(9)	4.0(10)
C(16)	26 131(60)	−1 416(99)	−6 499(61)	4.3(4)	4.5(5)	4.9(5)	−0.1(8)	1.1(7)	−1.2(8)
C(17)	26 167(73)	9 402(110)	−13 098(64)	6.9(6)	5.0(5)	4.5(5)	0.8(9)	−2.2(9)	−1.9(8)
C(18)	18 427(80)	6 968(140)	−18 552(82)	6.4(7)	7.0(7)	7.4(7)	1.4(11)	−3.1(11)	−3.3(12)
C(19)	20 509(74)	−6 045(149)	23 089(70)	6.0(6)	9.0(8)	4.8(5)	−2.2(12)	−1.8(9)	−2.5(11)
C(20)	29 134(71)	−9 290(122)	−19 919(64)	5.9(6)	6.6(6)	4.4(5)	−0.7(10)	0.8(8)	−2.3(9)
C(21)	28 558(62)	−14 534(104)	−11 085(58)	5.0(5)	4.9(5)	4.1(4)	0.6(8)	1.2(7)	−1.1(7)
C(22)	32 742(74)	4 505(124)	−18 662(70)	6.3(6)	6.1(6)	5.5(6)	−2.4(10)	−0.8(9)	1.7(10)
C(23)	36 747(74)	−20 014(119)	−7 955(63)	7.2(7)	5.8(6)	4.3(5)	1.9(10)	2.7(9)	−0.3(9)
C(24)	37 863(72)	−17 957(103)	1 156(72)	6.6(6)	3.8(4)	6.8(6)	2.9(9)	3.3(10)	3.3(9)
C(25)	31 138(82)	−18 044(117)	5 901(66)	9.7(8)	5.3(6)	4.6(5)	−2.9(11)	−1.0(10)	7.5(9)
C(26)	46 215(96)	−19 461(152)	4 472(93)	9.0(9)	7.4(8)	8.7(9)	5.5(14)	0.7(14)	−0.9(13)

* Temperature factors in the form $\exp -\frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)$.

The Ni(2)–C(16) distance appears to be shorter than Ni(1)–C(5) in both (II) and (III), which means that the shorter Ni–C σ bond is *trans* to the longer Ni–O distance.

TABLE 2

Comparison of some interatomic distances (Å) in (III) and (II), with estimated standard deviations in parentheses

	(III)	(II)
Ni(1)–Ni(2)	3.151(2)	3.079(1)
Ni(1)–O(1)	1.904(7)	1.895(5)
Ni(2)–O(2)	1.911(7)	1.904(5)
Ni(1)–O(3)	1.989(8)	1.969(5)
Ni(2)–O(4)	2.038(8)	2.001(5)
Ni(1)–C(5)	1.974(11)	1.971(6)
Ni(2)–C(16)	1.955(10)	1.952(5)
Ni(1)–C(14)	2.047(12)	2.023(7)
Ni(1)–C(13)	2.086(11)	2.079(6)
Ni(2)–C(25)	2.006(12)	2.013(7)
Ni(2)–C(24)	2.092(11)	2.068(7)
C(13)–C(14)	1.392(15)	1.371(9)
C(24)–C(25)	1.386(17)	1.392(9)

While the standard deviations on the Ni–C distances are comparatively large, this effect must be real since it is observed in both complexes.

In (III) the distances Ni(1)–Ni(2) and Ni(2)–O(4) are longer than in (II), clearly indicating that in (III) there is a further weakening of the bond between the two halves of the dimeric molecule. The electron-withdrawing properties of the fluorine substituents in (III) apparently act in the sense of reducing the tendency of the most weakly bound anion to occupy two co-ordination sites. This effect may allow an easier cleavage, in solution, of the carboxylate bridges, with production of mononuclear species of both types (*d* and *l*), as required [7] by the fact that both (I) and (II) are obtained from the same solution. If no appreciable quantity of molecules of (I) is formed, the concentration of mononuclear species may be substantial.

It has been shown [11-13] that similar mononuclear species are responsible for the propagation reaction in the polymerization of butadiene catalysed by π-allyl-nickel and -palladium halides and carboxylates. We now suggest that mononuclear molecules are also the active species in the polymerization of norbornene and that the existence of molecules of type (II) in the reacting solution greatly helps their formation.

It has been stated [13] that in the polymerization of butadiene, the position of the equilibrium between bi- and mono-nuclear complexes, and therefore the concentration of the active mononuclear species, depends on three factors: (i) the nature of a substitutent in the vinyl

[11] F. Dawans, J. C. Marechal, and Ph. Teyssié, *J. Organometallic Chem.*, 1970, **21**, 259.

[12] V. N. Sokolov, G. M. Khvostic, I. Ya. Poddubnyi, and G. P. Kondratenkov, *J. Organometallic Chem.*, 1971, **29**, 313.

[13] R. P. Hughes, T. Jack, and J. Powell, *J. Organometallic Chem.*, 1973, **63**, 451.

end of the hydrocarbon ligand, (ii) the nature of the halogen substituents in the carboxylate ligand, and (iii) the solvent. We consider that, at least in the polymerization of norbornene, there is a fourth factor of possibly greater importance, *i.e.* the molecular configuration of the binuclear insertion product.

In view of the greater stability of type (I) complexes, it it possible that the mechanism of their formation may compete with that for production of mononuclear species. In fact, in these complexes, besides the already mentioned symmetry of the bridging function of the two carboxylate groups, there is a further stabilizing factor resulting from the easier packing of the two hydrocarbon ligands allowed by the two-fold symmetry axis. Moreover, in some cases, additional stability may be given to this type of complex by a direct interaction between the two metal ions in the dimeric molecules, as appears to be the case for (IV).[1] Such interactions are more difficult in type (II) complexes because of the steric hindrance between the bulky hydrocarbon ligands, mutually related by the operation of the mirror plane.

The shift of the double-bond ends of the hydrocarbon ligands from their 'normal' positions, previously observed in (IV) [2] and in (I) and (II),[7] is also present in (III). This shift is defined by the angle δ (lying in the plane Ni–C–C) between the C=C bond axis and the normal to the average co-ordination plane, and by the distance (d) of the end olefinic carbon atom from this plane. In the 'normal' position of a co-ordinated olefin this angle is zero and the co-ordination plane passes through the C=C bond at equal distances from the two atoms. The values of the shift angles and the deviations from the co-ordination plane observed in the complexes (I)—(III) are listed in Table 3. In (II) the shift for C(24)–C(25) is smaller than for C(13)–C(14).

TABLE 3

Shift of the $CH_2{:}CH\cdot$ group from its 'normal' position in the Ni complexes studied. Columns (A) and (B) refer to the groups C(13)–C(14) and C(24)–C(25)

		(II)		(III)	
	(I)	(A)	(B)	(A)	(B)
δ	11.95°	13.80°	5.29°	15.13°	5.38°
d/Å	0.19	0.11	0.45	0.09	0.38

We have already [1,7] interpreted this shift in terms of an asymmetry induced by the substituents into the π^* orbital of the olefinic group. The fact that, for (II), the shift is smaller for one of the two C=C bonds can be rationalized by considering that the stability of a μ bond depends heavily on the electron density on the metal, and that the effective charges must be different for the two nickel ions in view of the significant difference between the distances Ni(1)–O(3) and Ni(2)–O(4).

Bond distances and angles in the norbornyl moieties in (III) are in agreement with those in (I), (II), (IV), and in a norbornane–methallyl–carboxylic acid.[14] Comparison of the relevant bond lengths shows that the bond between the carbon atoms, which had olefinic character before insertion, is systematically longer than the other bonds in the bicyclic system and that, as a consequence, this difference is significant in spite of the relatively large estimated standard deviations. Thus, there is direct evidence of relief of strain in the bicyclic ligand following the insertion reaction.

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[14] A. Albinati, M. Zocchi, G. Germain, and J. P. Declerq, *Cryst. Struct. Comm.*, 1973, **2**, 585.