Journal of Organometallic Chemistry, 141 (1977) 141—148
© Elsevier Sequioa S.A., Lausanne — Printed in The Netherlands

(PENTAPHENYL)ALUMINACYCLOPENTADIENE AS A COMPLEXING LIGAND. THE MOLECULAR STRUCTURE OF (PENTAPHENYL)ALUMINACYCLOPENTADIENE AND ITS COMPLEX WITH 1,5-CYCLOOCTADIENENICKEL

CARL KRÜGER *, JANINE C. SEKUTOWSKI *, HEINZ HOBERG and REINHILD KRAUSE-GÖING

Max-Planck-Institut für Kohlenforschung, 4330 Mülheim a.d. Ruhr, Lembkestr. 5 (B.R.D.)

(Received June 27th, 1977)

Summary

The molecular conformations of a (pentaphenyl)aluminacyclopentadiene ligand (I) and its complex with 1,5-cyclooctadienenickel (II) have been determined from single crystal X-ray data collected at room temperature with counter methods. The free ligand crystallizes in the monoclinic space group *Cc* with 4 molecules in a unit cell of dimensions *a* 10.5598(5), *b* 22.7089(12), *c* 13.3417(4) Å, β 98.064(3)°; its (COD)Ni complex crystallizes in the monoclinic space group $P2_1/n$ with 4 molecules in a unit cell of the dimensions *a* 11.9948(8), *b* 16.9758 (13), *c* 18.7721(14) Å, β 97.958(3)°. Both structures have been refined anisotropically to *R* values of 0.0577 and 0.0493, respectively. Upon complexation of I to the nickel atom the planarity of the ring system is distorted, with the aluminum being bent away from the nickel. A direct metal—metal interaction in II (Ni—Al: 2.748(1) Å) cannot be ruled out.

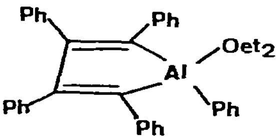
Stereochemical information about nickel compounds containing main group metals is of interest because of the importance of the so-called nickel-effect [1] in the catalytic chemistry of the main group metal series. The discovery of the latter led to the development of the numerous Ziegler-type catalysts. It is also well known that for nickel catalysts carrying various stereochemically controlling and/or accelerating ligands there is a marked dependence in the product distribution on the nature of the ligand. Thus, the cyclotrimerisation of 1,3-butadiene by a nickel catalyst may be shifted towards cyclodimerisation by adding a ligand, usually a phosphine or phosphite, at the reactive center. Alterations of reaction pathways are numerous, and are understood to some extent [2].

Recently a new metallacyclopentadienyl-system became available [3]. It was

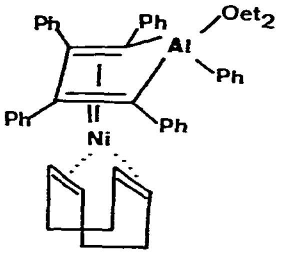
---

* X-ray structural analysis.

of immediate interest to prepare transition metal complexes of this ligand and to test the catalytic activities of these new compounds. In this paper we describe the preparation and the molecular structure of a compound obtained from the reaction of (pentaphenyl)aluminacyclopentadiene (I) with dicyclooctadienylnickel. This is part of our series of investigations on the structure of "mixed-metal compounds". In order to gain more information about the nature of the complex formation, we include a structural study of the starting material I. The molar composition of the nickel complex II was proven by analyses as well as by spectroscopic methods. Crystal data and details of the structure determinations of I and II are given in Table 1 [4]. Lists of structure factors, atomic positonal and thermal parameters are available from the authors (C.K.) on request.



I



The structure of (pentaphenyl)aluminacyclopentadiene (I) is showed in Fig. 1. The five-membered ring is completely planar as seen in Table 2, with the alumi-

TABLE 1

CRYSTAL DATA AND DETAILS OF STRUCTURE DETERMINATIONS OF COMPOUNDS I AND II

I	II
$C_{38}H_{35}AlO$, Mol.wt. 534.7	$C_{46}H_{47}AlNiO$, Mol.wt. 701.58
a 10.5598(5) Å	a 11.9948(8) Å
b 22.7089(12) Å	b 16.9758(13) Å
c 13.3417(4) Å	c 18.7721(14) Å
β 98.06-(3)°	β 97.958(3)°
V 3167.7 Å^3	V 3785.61 Å^3
$Z = 4$	$Z = 4$
d_c 1.12 g cm^{-3}	d_c 1.23 g cm^{-3}
μ(Cu-K_α) 7.28 cm^{-1}	μ(Cu-K_α) 11.84 cm^{-1}
Systematic absences:	Systematic absences:
hkl for $h + k = 2n + 1$	$h0l$ for $h + l = 2n + 1$
$h0l$ for $l = 2n + 1$	$0k0$ for $k = 2n + 1$
Space group: $C2/c$ or Cc	Space group: $P2_1/n$
Nonius diffractometer CAD-4	Nonius diffractometer CAD-4
λ(Cu-$K_{\bar{\alpha}}$) 1.54178 Å	λ(Cu-$K_{\bar{\alpha}}$) 1.54178 Å
Ni filtered	Ni filtered
4359 reflections hkl, $\bar{h}kl$ measured; averaged to give 3247 unique reflections of which 1430 were considered unobserved($I/\delta(I) < 2.0$)	8286 reflections hkl, $\bar{h}kl$ measured; averaged to give 7758 unique reflections of which 2984 were considered unobserved ($I/\delta(I) < 2.0$)
Both structures were solved by direct methods and subsequent Fourier and difference Fourier techniques.	
Full matrix least squares refinement including isotropic refinement of H atoms converged at $R = 0.0577$, $R_w = 0.0797$	Blockdiagonal least squares refinement including isotropic refinement of H atoms converged at $R = 0.0493$, $R_w = 0.0614$

$R = \Sigma\Delta/\Sigma|F_0|$ and $R_w = [\Sigma w \cdot \Delta^2/\Sigma w \cdot |F_0|^2]^{1/2}$, $\Delta = ||F_0| - |F_c||$

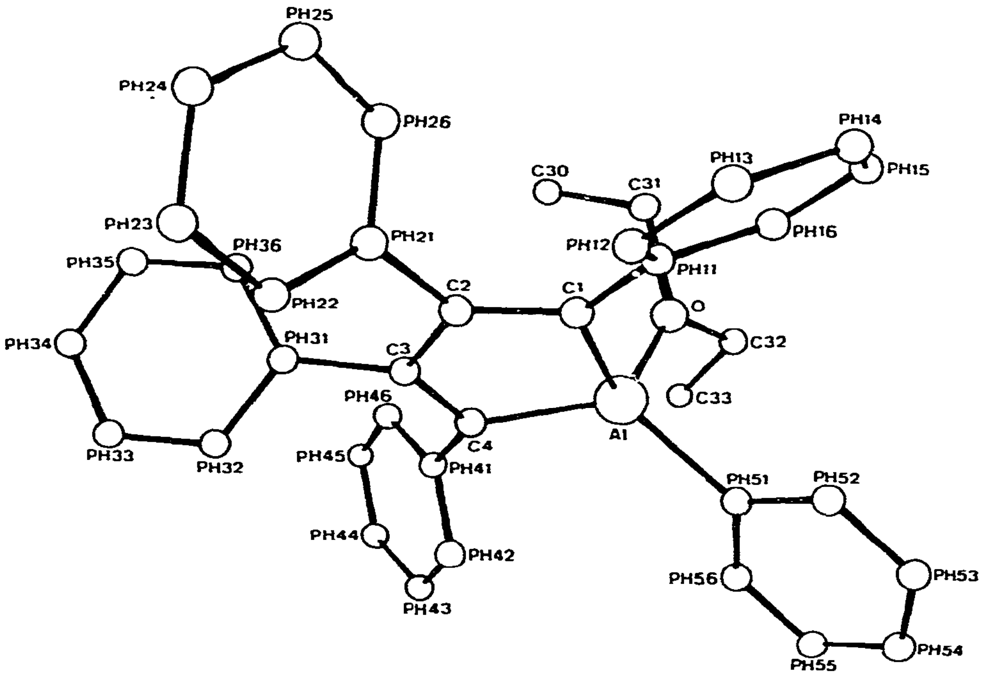


Fig. 1. Molecular structure of (pentaphenyl)aluminacyclopentadiene (I).

num atom showing the greatest out-of-plane deviation of only 0.039(15) Å. The dihedral angle between the plane C(1)—C(2)—C(3)—C(4) and the plane C(1)—Al—C(4) is 1.1°. The aluminum bonds to the butadiene moiety in a symmetrical manner, the average Al—C distance being 1.966(6) Å (see Tables 3 and 4 for bond distances and angles). Furthermore, it is linked with a phenyl group (1.979(6) Å), and, to complete its coordination sphere, with one molecule of diethyl ether. The aluminium—oxygen distance of 1.907(5) Å is shorter than that, viz 2.02 Å, found in the dioxane adduct of trimethylaluminum [5]. However, in the trimethylaluminum case, the Al—O bond is expected to be elongated, since oxygen is more electronegative than the methyl carbons, thus shortening the aluminum—carbon bonds

TABLE 2

OUT-OF-PLANE DEVIATIONS IN THE C_4Al RING OF COMPOUNDS I AND II

I best plane		II best plane	
Al	0.039(15)	Al	−0.49(2)
C(1)	0.006(15)	C(1)	0.005(18)
C(2)	−0.012(15)	C(2)	−0.009(18)
C(3)	0.012(15)	C(3)	0.009(18)
C(4)	−0.006(15)	C(4)	−0.005(18)

TABLE 3

BOND LENGTHS (A) WITH STANDARD DEVIATIONS IN PARENTHESES

Compound I

Al—C(1)	1.965(6)	C(1)—Ph(11)	1.479(9)
Al—C(4)	1.968(6)	C(2)—Ph(21)	1.501(9)
Al—Ph(51)	1.979(6)	C(3)—Ph(31)	1.491(8)
Al—O	1.907(5)	C(4)—Ph(41)	1.471(9)
C(1)—C(2)	1.363(8)	C(2)—C(3)	1.516(9)
C(3)—C(4)	1.358(9)		

Compound II

Al—Ni	2.748(1)	Ni—C(3)	2.094(3)
Al—C(1)	1.960(3)	Ni—C(1)	2.204(3)
Al—C(4)	1.954(3)	Ni—C(4)	2.220(3)
Al—Ph(51)	1.975(3)	Ni—C(2)	2.100(3)
Al—O	1.977(3)	Ni—C(11)	2.110(4)
C(1)—C(2)	1.405(4)	Ni—C(10)	2.083(3)
C(2)—C(3)	1.498(4)	Ni—C(14)	2.100(3)
C(3)—C(4)	1.409(4)	Ni—C(15)	2.091(3)
C(1)—Ph(11)	1.488(4)	C(10)—C(11)	1.374(5)
C(2)—Ph(21)	1.502(4)	C(11)—C(12)	1.522(5)
C(3)—Ph(31)	1.497(4)	C(12)—C(13)	1.537(6)
C(4)—Ph(41)	1.491(4)	C(13)—C(14)	1.508(5)
C(14)—C(15)	1.385(5)	C(16)—C(17)	1.531(5)
C(15)—C(16)	1.525(5)	C(17)—C(10)	1.522(5)

TABLE 4

VALENCY ANGLES (DEG.) WITH STANDARD DEVIATIONS IN PARENTHESES

Compound I

C(4)—Al—O	104.5(2)		
C(1)—Al—C(4)	91.6(3)		
C(1)—Al—O	106.8(2)		
C(1)—Al—Ph(51)	122.4(3)	C(2)—C(1)—Ph(11)	126.7(6)
C(4)—Al—Ph(51)	126.4(3)	C(1)—C(2)—Ph(21)	124.4(6)
O—Al—Ph(51)	103.2(2)	C(3)—C(2)—Ph(21)	117.5(5)
Al—C(1)—C(2)	105.8(4)	C(2)—C(3)—Ph(31)	118.6(5)
Al—C(1)—Ph(11)	127.4(5)	C(4)—C(3)—Ph(31)	122.1(6)
Al—C(4)—C(3)	105.3(4)	C(3)—C(4)—Ph(41)	122.9(5)
Al—C(4)—Ph(41)	131.1(5)		

Compound II

C(4)—Al—O	108.0(1)	C(2)—C(1)—Ph(11)	120.9(3)
C(1)—Al—C(4)	88.1(1)	C(1)—C(2)—Ph(21)	122.7(3)
C(1)—Al—O	106.0(1)	C(3)—C(2)—Ph(21)	120.7(3)
C(1)—Al—Ph(51)	125.3(1)	C(2)—C(3)—Ph(31)	120.1(3)
C(4)—Al—Ph(51)	129.7(1)	C(4)—C(3)—Ph(31)	124.2(3)
O—Al—Ph(51)	98.1(1)	C(3)—C(4)—Ph(41)	121.5(3)
Al—C(1)—C(2)	107.4(2)	O—Al—Ni	146.9(1)
Al—C(2)—Ph(11)	72.7(1)	Ph(51)—Al—Ni	114.8(1)
Al—C(4)—C(3)	108.1(2)	C(1)—Ni—C(4)	75.9(1)
Al—C(4)—Ph(41)	130.1(2)	C(1)—Ni—C(2)	38.0(1)
Ni—C(1)—Al	82.4(1)	C(1)—Ni—C(3)	69.9(1)
Ni—C(4)—Al	82.1(1)	C(2)—Ni—C(3)	41.9(1)
Ni—C(1)—C(2)	67.0(2)	C(2)—Ni—C(4)	69.3(1)
Ni—C(2)—C(3)	68.9(2)	C(3)—Ni—C(4)	38.0(1)
Ni—C(2)—C(1)	75.0(2)	C(14)—Ni—C(15)	38.6(1)
Ni—C(3)—C(2)	69.3(2)	C(10)—Ni—C(11)	38.2(1)
Ni—C(3)—C(4)	75.9(2)	Ni—C(10)—C(11)	71.9(2)
Ni—C(4)—C(3)	66.2(2)	Ni—C(11)—C(10)	69.8(2)
		Ni—C(14)—C(15)	70.3(3)
		Ni—C(15)—C(14)	71.1(2)

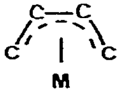
and elongating the more polar Al—O bond. The opposite effect is evident in I. Due to the electron-withdrawing phenyl groups at the butadiene moiety and at the aluminum, the aluminum—oxygen bond is shortened. The coordination around the aluminum is distorted tetrahedral; the distortion results from participation of the aluminum in a five-membered ring. As seen in Table 4 the Ph(51)—Al—C(1) and Ph(51)—Al—C(4) angles are opened up, probably because of steric interactions of the phenyl ring on aluminum with the phenyl groups on C(1) and C(4). The phenyl substituents on the carbon atoms are arranged in a propeller-like fashion about the five-membered ring, the angles between their planes ranging from 50° to 61°.

Bonds C(1)—C(2) and C(3)—C(4) (av. 1.360(8) Å) may be compared with the double bond lengths found in 1,2,3,4-tetraphenyl-*cis,cis*-butadiene (1.36 Å) [6]. However, the central carbon—carbon bond length of 1.516(9) Å is slightly longer than the 1.49 Å found in the butadiene compound. This lengthening may be attributed to steric interactions between the phenyls on carbons C(2) and C(3), as these groups are constrained to a cisoid geometry by the participation of the butadiene moiety in the five-membered ring.

The complexation of I to the (COD)Ni moiety takes place through the butadiene sub-unit of the five-membred ring. The interaction of butadienes with transition metals can be described by three basic bonding schemes [7]:

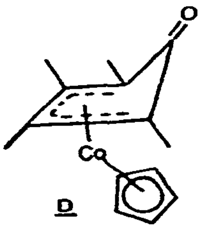
A

B

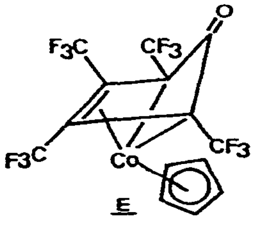


C

In structure A the electrons are localized as in butadiene, and so the metal—butadiene interaction can be considered as composed of two localized metal—olefin bonds. In B the metal is σ-bonded to the terminal carbons and π-bonded to C(2)—C(3), and in structure C the butadiene π-electrons are completely delocalized. These idealized bonding schemes can be extended to five-membered ring ligands bonding to the metal atom through a butadiene moiety. For example, bonding mode C was found in cyclopentadienyltetramethylcyclopentadienone-



D



E

cobalt(0) (D) [8]. The carbon—carbon bond lengths of the butadiene moiety are equal (1.43 Å), indicating delocalization of the electrons as in structure type C. Upon replacing the methyl groups by electron-withdrawing trifluoromethyl groups (E) the structure is indicative of two σ bonds and one π bond [9] as in structure type B.

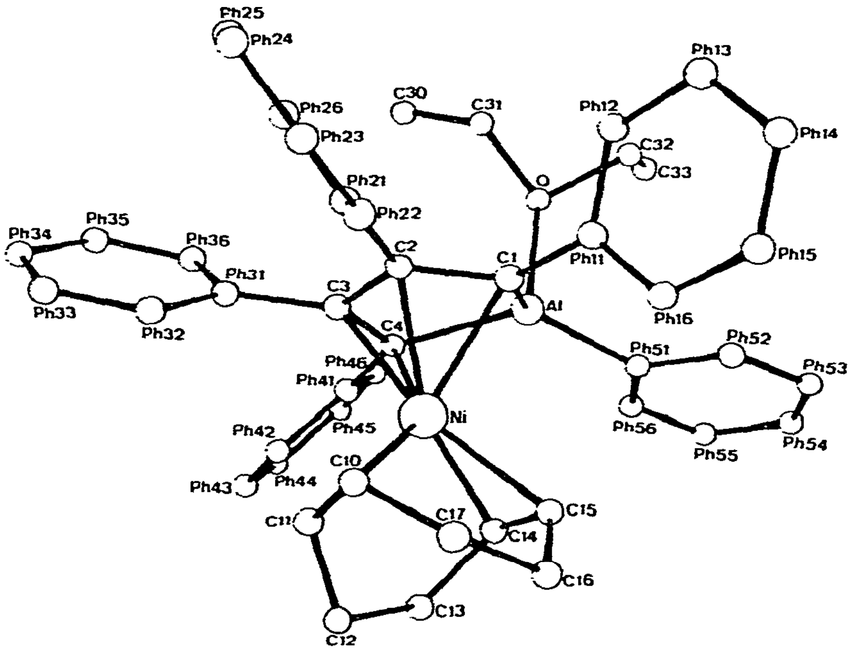
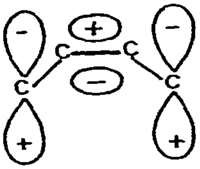


Fig. 2. Molecular structure of the complex of (pentaphenyl)aluminacyclopentadiene with 1,5-cyclopentadienenickel.

Complex II can be considered ideally to have bonding of type A. The central carbon—carbon bond (C(2)—C(3) 1.498(4) Å) is longer than the other two carbon—carbon bonds (C(1)—C(2), C(3)—C(4) av. 1.407(4) Å), indicative of two localized nickel—olefin bonds (see Fig. 2).

Surprisingly the central carbon—carbon bond distance (C(2)—C(3) 1.498(4) Å) is slightly shorter than that in the free ligand (1.516(9) Å). The olefinic bonds (C(1)—C(2), C(3)—C(4) av. 1.407(4) Å) have lengthened from those found in the free ligand (av. 1.360(4) Å) as is usually observed for other metal olefinic complexes [10]. The aluminum atom is bent out of the ring and away from the nickel (Ni — — — Al 2.748(1) Å). A best plane calculation (see Table 2) shows the aluminum to be 0.49(2) Å out of the C(1)—C(2)—C(3)—C(4) plane with a dihedral angle of 20.44° between the plane containing C(1)—C(2)—C(3)—C(4) and the plane containing C(1)—Al—C(4). This distortion from planarity suggests a partial rehybridization of C(1) and C(4) from sp^2 to sp^3, as is also indicated by the increase in the bond lengths C(1)—C(2) and C(3)—C(4). The greater sp^3 character of the C(1) and C(4) orbitals should lead to longer C—Al bonds, for two reasons: first, the covalent radius of an sp^3 carbon is larger than that of an sp^2 carbon [11], and, second, the electronegativity of an sp^3 carbon is less than that of an sp^2 carbon [12]. However, the exact opposite is found here. The aluminum—carbon distances decrease slightly upon complexation (av. 1.957(3) Å vs. av. 1.966(6) Å in the free ligand) and are now shorter than the aluminum oxygen distance (1.977(3) Å) which has increased from that in the free ligand (1.907(5) Å).

This observed effect can be explained in simplified terms by considering the interaction of the (COD)Ni moiety with the π orbitals of the diene unit. π-Back-bonding from the electron-rich nickel(0) to the lowest π^* orbital of butadiene



[13], which is of the appropriate symmetry, can increase the interaction of the outer carbons with the $d(x^2-y^2)$ and dxy orbitals on the nickel. This increases the electron density of the π^* orbital, which, in turn, can interact with the sp^3 orbitals on the aluminum. The result is a shortening of the Al—C bonds. This contraction of the aluminum—carbon bonds suggests a nickel—aluminum interaction. The nickel—aluminum distance of 2.748(1) Å is slightly less than the sum of the covalent radii of nickel (1.32 Å) and aluminum (1.43 Å) [14]. Such an interaction would explain the slight decrease of the central carbon—carbon bond length upon complexation. The increase of electron density in this orbital imparts double bond character to the central carbon—carbon bond. Two of the nickel—carbon distances (Ni—C(1) 2.204(3) Å, Ni—C(4) 2.220(3) Å) are considerably longer than the Ni—C(2) (2.100(3) Å) and Ni—C(3) (2.094(3) Å) distances. Such a phenomenon has been observed in similar systems, such as butadieneiron tricarbonyl [15].

The COD ring is linked to the nickel through two π-bonds with an average Ni—C distance of 2.096(3) Å, similar to the bonding found in $(COD)_2Ni$ [16]. The average carbon—carbon double bond length is 1.379(5) Å and the average carbon—carbon single bond length is 1.524(5) Å. There is no apparent difference between the two double bonds and their bonding modes with nickel. However, both the ^1H NMR and ^{13}C NMR spectra show inequivalencies. In the ^1H NMR spectrum the olefinic COD protons appear as two signals (τ 4.78, 5.50 ppm). The olefinic carbons in the ^{13}C NMR spectrum exhibit two signals at 91.3 and 86.2 ppm, which can be compared to the single signal at 89.74 ppm found for $(COD)_2Ni$. These inequivalencies in the NMR spectra can be explained as being due to the different environments of the olefinic bonds with respect to the (pentaphenyl)aluminacyclopentadiene ligand.

Experimental

Preparation of (pentaphenyl)aluminacyclopentadiene-1,5-cyclooctadienylnickel

(1) As the tetrahydrofuran adduct. 2.6 g (9.46 mmol) of $(COD)_2Ni$ [17] are added to a stirred solution of 10.1 g (18.89 mmol) (pentaphenyl)aluminacyclopentadiene (I) [3] in 120 ml absolute THF at 40°C. After 5 days the red mixture is filtered. From the filtrate a red precipitate is obtained by cooling, and recrystallized from THF (2.4 g, 36.8% yield with respect to $(COD_2)Ni$, decomposition above 90°C, diamagnetic). Analysis: Found: Al, 3.88; Ni, 8.33. $C_{46}H_{47}AlNiO$ calcd.: Al, 3.87; Ni, 8.40%. Mass spectrum: with increasing evapo-

TABLE 5

^{13}C NMR ANALYSIS (C_6D_5, 100 MHz, room temperature)

Compound	σ10,11,14,15	$\Delta\sigma$10,11,14,15	σ12,13,16,17	$\Delta\sigma$12,13,16,17
COD	128.7		28.5	
$(COD)_2Ni$	89.7	−39.0	30.9	+2.4
II	91.3 86.2	−37.4 −42.5	31.2 30.2	+2.7 +1.7

ration the following decomposition products are observed: THF, benzene, COD, tetraphenylbutadiene, tetraphenylbutene, and (pentaphenyl)aluminacyclopentadiene-1,5-cyclooctadienylnickel.

(2) As the diethyl ether adduct. A suspension of 5.4 g (10.2 mmol) I and 1.4 g (5.1 mmol) $(COD)_2Ni$ in 120 ml diethyl ether is stirred at room temperature for 15 days. The suspension is then warmed to 35°C and filtered warm. On cooling, red crystals of II crystallize (1.2 g, 33.3% yield with respect to $(COD)_2Ni$, decomposition above 90°C, diamagnetic). 60 MHz ^{1}H NMR analysis: (II in C_6D_6, TMS as external standard) 8.00, 7.56, 7.21, 6.98 ppm (m, 25 phenyl protons); 5.20 ppm (br s, 2 C=CH protons); 4.52 ppm (br s, 2 C=CH) protons); 3.5 ppm (q, 4 CH_2 protons (ether)); 2.13 ppm (m, 8 CH_2 protons (COD)); 0.84 ppm (t, 6 CH_3 protons (ether)).

The principal ^{13}C NMR data are given in Table 5.

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft. We thank Dr. R. Mynott for the ^{13}C NMR analysis.

References

1 K. Fischer, K. Jonas, P. Misbach, R. Stabba and G. Wilke, Angew. Chem., 85 (1973) 1002.
2 P.W. Jolly and G. Wilke, The Organic Chemistry of Nickel, Vol. II, Academic Press, New York, 1975.
3 H. Hoberg and R. Krause-Göing, J. Organometal. Chem., 127 (1977) C29.
4 D.J. Brauer, C. Krüger, P.J. Roberts and Y.-H. Tsay, Chem. Ber., 107 (1974) 3706.
5 J.L. Atwood and G.D. Stucky, J. Amer. Chem. Soc., 89 (1967) 5362.
6 I.L. Karle and K.S. Dragonette, Acta Cryst., 19 (1965) 500.
7 G.E. Coates, M.L.H. Green and K. Wade, Organometallic Compounds, Vol. II, Methuen, London, 1968.
8 L.F. Dahl and D.L. Smith, J. Amer. Chem. Soc., 83 (1961) 752.
9 N.A. Bailey, M. Gerloch and R. Mason, Nature, 201 (1964) 72.
10 S.D. Ittel and J.A. Ibers, Advan. Organometal. Chem., 14 (1976) 33.
11 L. Pauling, The Nature of the Chemical Bond, Cornell Univ. Press, New York, 1948.
12 A.D. Walsh, Dis. Faraday Soc., 2 (1947) 18.
13 W.L. Jorgensen and L. Salem, The Organic Chemists Book of Orbitals, Academic Press, London, 1973, p. 179.
14 R.W.G. Wykoff, Crystal Structures, Vol. I, Interscience, New York, 1948—1960.
15 O.S. Mills and G. Robinson, Acta Cryst., 16 (1963) 758 and ref. therein; C. Krüger and Y.-H. Tsay, J. Organometal. Chem., 33 (1971) 59.
16 H. Dierks and H. Dietrich, Z. Kristallogr., 122 (1965) 1; C. Krüger, unpublished results.
17 B. Bogdanović, M. Kröner and G. Wilke, Liebigs Ann. Chem. 699 (1966) 1.