THE MOLECULAR CONFIGURATION OF TWO COMPLEXES WITH σ AND π NICKEL—CARBON BONDS:

(π-PENTENYL)(DIISOPROPYLPHENYLPHOSPHINE)METHYLNICKEL(II) AND (π-PENTENYL)(DIMENTHYLMETHYLPHOSPHINE)METHYL-NICKEL(II)

BOBBY L. BARNETT and CARL KRÜGER

Max-Planck-Institut für Kohlenforschung 433 Mülheim-Ruhr, Lembkestrasse 5 (Germany)

Summary

The molecular conformation of two square planar π-pentenylnickel(II) complexes with σ and π nickel—carbon bonds, (π-pentenyl)(diisopropylphenyl-phosphine)methylnickel(II) and (π-pentenyl)(dimenthylmethylphosphine)-methylnickel(II), have been determined from single crystal X-ray data collected at room temperature with counter methods. Molecule I crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of the dimensions a 8.927(3), b 26.031(9), c 8.718(2)Å, β 110.88(2)°; II crystallizes in the orthorhombic system, space group $P2_12_12_1$, with four molecules in a cell a 14.446(1), b 13.727(1), c 11.895(1) Å. Both structures have been refined anisotropically to R values of 6.26 and 3.65%, respectively. The absolute configuration of II has been determined to be R on a 99.5% confidence level. Comments are made on the bonding situation of the π-allylic fragments as well as on the steric conformation of the phosphine ligands. The Ni—C(σ) bond distances were found to be 1.99(1) in compound I and 1.975(4)Å in compound II.

Introduction

Olefins are dimerized catalytically in the presence of low-valent nickel compounds. Investigations of intermediates in these processes suggest π-allyl nickel complexes play an essential role initially in the transformation of olefins in catalytic reactions [1—3]. In many of these catalysis systems the products can be selectively controlled, apparently by the steric nature of the ligands at-

tached to the nickel catalyst. Organic phosphine ligands have been particularly useful in obtaining preferential products, even to the extent of producing stereospecific, optically active compounds in the codimerization of specific olefins [1].

Because of the postulated importance of the steric influence of phosphine ligands in homogenous catalysis, a series of structural investigations on model compounds and possible intermediates of nickel catalysis systems is being undertaken. Forms A and B are general types of model complexes that are related directly to known intermediates formed during the dimerization of olefins. Complexes of type A (Ni^{II}) contain both σ and π-Ni—C bonds, whereas molecules of type B (Ni^0) have only Ni—C(σ) bonds. In this present study structural details of complexes I and II, similar to type A, are reported.

X—Ni—R'
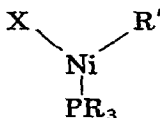|
PR₃
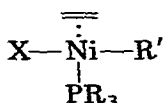
R = alkyl
R' = H, alkyl
X = halogen or $AlX_{3-n}R_n$

(A)

X   R'
 \   /
  Ni
  |
 PR₃

R = alkyl
R' = H, alkyl

(B)

Our choice of these examples was prompted by ambiguous NMR spectroscopic evidence for a series of these compounds [4], and the opportunity to observe σ and π systems in the same molecule. The latter is considered an important feature in catalytic mechanisms. Establishment of the coordination about the nickel atoms in I and II and the absolute configuration of II by X-ray diffraction techniques should enhance our understanding of the nature of catalytic transformations of olefins.

Experimental

Suitable crystals of both complexes were kindly supplied by Drs. Bönnemann and Schenkluhn of this Institute. The complexes were prepared according to the method described by Schenkluhn [5], in which pentenylnickel bromide was treated with CH_3MgCl (in ether) to form pentenylmethylnickel.
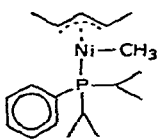
(I)
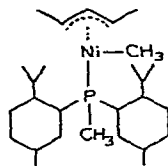
(II)

This was treated with the desired phosphine, and the resulting monomeric adduct was recrystallized from toluene. Crystals of complex II investigated in this study have a lower solubility than the corresponding diastereomer, thereby allowing separation by repeated fractional crystallizations. Crystals of both complexes were mounted in glass capillaries and sealed under argon. Preliminary X-ray in-

TABLE 1

Complex I	Complex II
(π-Pentenyl)(diisopropylphenylphosphine)-methylnickel(II)	(π-Pentenyl)(dimenthenylmethylphosphine)-methylnickel(II)
$C_{18}H_{31}NiP$; mol. wt. 337.13	$C_{27}H_{53}NiP$; mol. wt. 467.41
Color: red-orange	yellow
Crystal system: monoclinic	orthorhombic
a 8.927(3), b 26.031(9),	a 14.446(1), b 13.727(1),
c 8.718(2) Å, β 110.88(2)°	c 11.895(1) Å
V 1892.8 Å^3	V 2847.4 Å^3
Systematic absences: $h0l$,	$h00, h = 2n + 1; 0k0, k = 2n + 1;$
$l = 2n + 1; 0k0, k = 2n + 1$	$00l, l = 2n + 1$
Space group: $P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)
d(calc.): 1.183 g/cm^3	1.091 g/cm^3
λ: Cu-$K\alpha$ mean 1.5418 Å	Cu-$K\alpha$ mean 1.5418 Å
Orientation of crystal: [001]	[010] parallel to ϕ axis
parallel to ϕ axis	negligible
Decomposition: 30%	max. 1.67, min. 1.22
Absorption correction: none	θ max. 65°; 2865 reflections
θ max. 60°; 2614 reflections	2689 observed
1404 observed	

vestigations were carried out by Weissenberg and precession photographic techniques. Cell dimensions, given in Table 1 with other pertinent experimental details, were determined by least-squares methods of 2θ values that were carefully measured on the diffractometer with a narrow receiving slit. The molecular formulas were determined by mass spectroscopic methods.

Three-dimensional single-crystal intensity data were collected by the 5-step $\theta/2\theta$ scan technique [6] on a Siemens diffractometer, controlled by a PDP-8 computer. Intensities of reflections sufficiently above background $I_o > 2\sigma(I_o)$ were considered observable. For intense reflections Ni attenuators were introduced into the primary beam along with the Ni-β filter. After every 20 reflections measured, a monitoring reflection was remeasured and subsequently used to scale the data approximately for decomposition and slight alignment variations. In complex I considerable loss of intensity (28%) during data collection was observed. Because the crystal of I changed colour and frequent realignment minimized orientation errors, the intensity drop was attributed to decomposition and corrected empirically on the basis of the monitor reflection. In complex II the variation of the monitor intensity varied only randomly (5%), indicating this complex did not suffer significantly from radiation effects or thermal decomposition. For this reason the structure of complex I is certainly less accurate than that of complex II. Lorentz and polarization corrections were applied and an absorption correction based on crystal shape* was made for crystal II. Standard deviations of the observed structure factor amplitudes were based solely on counting statistics.

---

* Computer programs used in this investigation are local modifications of standard crystallographic programs and have been described elsewhere [6].

Solution and refinement of the structures

Solution of the structures was accomplished by obtaining Ni and P atom positions from the respective sharpened Patterson maps. Subsequent Fourier synthesis, using phases based on the corresponding heavy atoms and observed amplitudes, revealed all of the non-hydrogen atom positions in the respective structures. Weights equal to $1.0/\sigma^2(|F_o|)$ were used in the least-squares calculations, employing the block-diagonal approximation to the least-squares method. Atomic scattering factors used were those of Stewart, Davidson and Simpson [7] for hydrogen and Cromer and Waber [8] for the remaining atoms. The anomalous dispersion corrections for Ni and P [9] were included in the F_c calculations.

Complex I

Least-squares isotropic refinement for these 20 non-hydrogen atoms reduced the residual index R from 0.32 to 0.11 in six cycles. Converting to anisotropic factors, the refinement converged to 0.098 in seven cycles. A difference density Fourier revealed peaks corresponding to chemically reasonable hydrogen atom positions for the organic part of the phosphine ligand, but were not well defined for hydrogen positions of the methyl and pentenyl groups bonded to the nickel. Apparently this was due to the combination of decomposition effects suffered by the crystal and by high thermal motion in these groups. Calculated hydrogen atom positions were used whenever necessary. Keeping the hydrogen positions fixed and temperature factors constant ($U = 0.06$ Å), all remaining positional parameters, anisotropic temperature factors and the overall scale factor were refined using statistical weights until all shifts were less than 0.5 for all parameters.

Final atomic parameters are given in Tables 2 and 3. The estimated standard deviations were calculated from the inverse matrices of the final least-squares cycle. The final R value for these parameters was 0.0626 (0.0456 for weighted R) for the observed reflections only*.

Complex II

Least-squares isotropic refinement for these 29 non-hydrogen atoms reduced the residual index R from 0.31 to 0.097 in seven cycles. Converting to anisotropic temperature factors, the refinement converged at R 0.0798 in eight cycles. Instead of continuing the refinement the imaginary part of the scattering factors for Ni and P [9] were included in the structure factor calculations. For the assumed structure the R value dropped to 0.0782, while in the enantiomorphic structure the R value rose to 0.0817. Application of the Hamilton significance test [10] showed the expected ratio of R values ($R_{1, 2437, 0.005}$) to be 1.002, while the observed ratio was found to be 1.045 ($wR/wR = 1.027$). The observed ratio is significantly larger and is sufficient to establish the absolute configuration of the complex at a 99.5% confidence level.

---

* The observed and calculated structure factor amplitudes may be obtained from the authors on request (C. K.).

TABLE 2

POSITIONAL AND THERMAL PARAMETERS FOR [(C$_6$H$_5$)(C$_3$H$_{10}$)$_2$P]NiCH$_3$(π-C$_5$H$_9$) COMPLEX I

Atom	x	y	z	U_{11}[a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0.0986 (2)	0.1509 (?)	0.0934 (2)	0.052 (1)	0.048 (1)	0.066 (1)	0.001 (1)	0.021 (1)	−0.001 (1)
P	0.2860 (3)	0.0940 (1)	0.1370 (3)	0.051 (1)	0.047 (1)	0.050 (2)	0.001 (1)	0.024 (1)	−0.001 (1)
C1	−0.0827 (8)	0.1015 (3)	0.0123 (9)	0.040 (5)	0.054 (5)	0.046 (6)	−0.009 (4)	0.014 (4)	−0.005 (5)
C2	−0.2130 (12)	0.2152 (3)	0.0049 (16)	0.077 (8)	0.067 (7)	0.298 (16)	0.027 (6)	0.036 (9)	−0.050 (9)
C3	−0.0563 (12)	0.2107 (3)	0.0773 (18)	0.078 (8)	0.026 (6)	0.440 (21)	0.020 (6)	0.055 (11)	0.008 (9)
C4	0.0882 (10)	0.2267 (3)	0.0954 (11)	0.072 (6)	0.032 (5)	0.118 (9)	0.008 (5)	0.021 (6)	0.019 (6)
C5	0.2325 (12)	0.2171 (3)	0.1514 (21)	0.057 (7)	0.032 (6)	0.603 (29)	−0.009 (6)	0.067 (13)	0.037 (11)
C6	0.3801 (10)	0.2336 (3)	0.1583 (13)	0.082 (8)	0.043 (6)	0.180 (12)	−0.008 (6)	0.009 (7)	0.017 (7)
C7	0.2061 (10)	0.0373 (3)	0.3704 (10)	0.083 (7)	0.072 (6)	0.050 (7)	−0.012 (5)	0.027 (5)	0.003 (5)
C8	0.2482 (8)	0.0309 (3)	0.2150 (9)	0.043 (5)	0.049 (5)	0.063 (7)	0.002 (4)	0.011 (5)	0.009 (5)
C9	0.3785 (9)	−0.0087 (3)	0.2354 (10)	0.017 (7)	0.055 (6)	0.083 (8)	0.020 (5)	0.023 (6)	0.005 (6)
C10	0.1910 (10)	0.0468 (3)	−0.1671 (11)	0.075 (8)	0.119 (8)	0.071 (8)	−0.024 (6)	0.024 (6)	−0.057 (6)
C11	0.3268 (9)	0.0756 (3)	−0.0499 (10)	0.056 (6)	0.075 (6)	0.054 (7)	0.000 (5)	0.035 (5)	0.000 (5)
C12	0.3625 (11)	0.1251 (3)	−0.1299 (11)	0.094 (8)	0.127 (9)	0.088 (9)	−0.016 (7)	0.062 (7)	−0.014 (7)
C21	0.4821 (9)	0.1101 (3)	0.2920 (9)	0.055 (5)	0.048 (5)	0.051 (6)	0.000 (4)	0.023 (5)	0.003 (5)
C22	0.4836 (9)	0.1328 (3)	0.4352 (10)	0.061 (6)	0.056 (6)	0.063 (7)	−0.003 (4)	0.027 (5)	−0.009 (5)
C23	0.6255 (9)	0.1443 (3)	0.5587 (10)	0.076 (7)	0.085 (7)	0.061 (7)	−0.006 (6)	0.016 (5)	−0.004 (6)
C24	0.7688 (10)	0.1346 (3)	0.5413 (11)	0.068 (6)	0.082 (7)	0.071 (8)	−0.015 (5)	0.005 (6)	−0.008 (6)
C25	0.7719 (10)	0.1123 (3)	0.4004 (12)	0.044 (6)	0.129 (9)	0.105 (9)	−0.007 (6)	0.022 (6)	−0.016 (7)
C26	0.6300 (10)	0.1001 (3)	0.2746 (11)	0.067 (7)	0.090 (7)	0.086 (8)	0.003 (6)	0.038 (6)	−0.023 (6)

[a] The form of the anisotropic thermal ellipsoid is: exp[−2π²($U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*$)]

TABLE 3

POSITIONAL PARAMETERS FOR HYDROGEN[a] ATOMS IN COMPLEX I

Atom	x	y	z
H1A	−0.210	0.110	−0.065
H1B	−0.125	0.075	0.075
H1C	−0.100	0.110	0.115
H2A	−0.305	0.180	0.010
H2B	−0.230	0.250	0.085
H2C	−0.270	0.240	−0.010
H3	−0.028	0.183	0.159
H4	0.080	0.259	0.019
H5	0.215	0.190	0.241
H6A	0.480	0.210	0.185
H6B	0.365	0.260	0.135
H6C	0.445	0.245	0.230
H7A	0.280	0.050	0.470
H7B	0.105	0.070	0.345
H7C	0.165	−0.005	0.365
H8	0.135	0.020	0.135
H9A	0.480	0.000	0.355
H9B	0.335	−0.045	0.299
H9C	0.430	−0.015	0.115
H10A	0.115	0.030	−0.200
H10B	0.200	0.035	−0.270
H10C	0.090	0.080	−0.220
H11	0.440	0.055	−0.010
H12A	0.460	0.155	−0.040
H12B	0.425	0.110	−0.180
H12C	0.240	0.145	−0.155
H22	0.379	0.142	0.452
H23	0.626	0.160	0.666
H24	0.876	0.144	0.628
H25	0.881	0.113	0.390
H26	0.631	0.083	0.168

[a] Hydrogen atoms were not refined and a constant isotropic thermal parameter of U 0.06Å^2 was used.

A difference density map revealed positive electron density of well resolved peaks corresponding to chemically reasonable hydrogen atom positions. An additional seven cycles of least-squares calculations, varying overall scale factor, all positional parameters, non-hydrogen anisotropic temperature factors and hydrogen isotropic temperature factors served to complete the refinement. Shifts in the final cycle were less than 0.05 σ for all parameters.

Final atomic parameters are given in Tables 4 and 5. The estimated standard deviations were derived from the inverse matrices of the final least-squares cycle. The final R value for these parameters was 0.0365 (0.0455 for weighted R) for the observed reflections only*.

---

* A list of structure factors may be obtained from the authors (C. K.).

TABLE 4

POSITIONAL AND THERMAL PARAMETERS FOR [(C$_{10}$H$_{19}$)$_2$CH$_3$P]NiCH$_3$(π-C$_5$H$_9$), COMPLEX II

Atom	x	y	z	$U_{11}{}^a$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0.4622 (0)	−0.0089 (0)	0.5135 (0)	0.053 (0)	0.059 (0)	0.047 (0)	0.002 (0)	−0.004 (0)	−0.002 (0)
P	0.5077 (0)	0.1095 (1)	0.6146 (1)	0.041 (0)	0.048 (0)	0.044 (0)	0.003 (0)	0.003 (0)	0.004 (0)
C1	0.4908 (2)	−0.1143 (2)	0.6184 (3)	0.081 (3)	0.049 (2)	0.060 (2)	0.001 (2)	−0.005 (2)	0.000 (2)
C2	0.4558 (3)	0.1428 (4)	0.3050 (3)	0.110 (3)	0.114 (4)	0.051 (2)	0.014 (3)	0.004 (3)	0.018 (3)
C3	0.4162 (2)	0.0708 (3)	0.3785 (3)	0.074 (3)	0.089 (3)	0.055 (2)	0.006 (2)	−0.017 (2)	0.003 (3)
C4	0.4240 (2)	−0.0323 (3)	0.3574 (3)	0.083 (3)	0.098 (3)	0.056 (2)	0.016 (2)	−0.026 (2)	−0.017 (2)
C5	0.3911 (2)	−0.1036 (3)	0.4273 (3)	0.096 (3)	0.086 (3)	0.072 (3)	−0.003 (3)	−0.021 (3)	−0.021 (3)
C6	0.3999 (3)	−0.2085 (3)	0.4098 (5)	0.105 (4)	0.087 (3)	0.145 (5)	−0.010 (3)	−0.017 (4)	−0.041 (4)
C7	0.4898 (2)	0.2346 (3)	0.5674 (3)	0.054 (2)	0.060 (2)	0.064 (2)	0.000 (2)	−0.003 (2)	0.011 (2)
C11	0.4689 (2)	0.1127 (2)	0.7622 (3)	0.044 (2)	0.056 (2)	0.046 (2)	0.002 (2)	0.007 (2)	−0.004 (2)
C12	0.3840 (2)	0.0805 (3)	0.7678 (3)	0.043 (2)	0.066 (3)	0.056 (2)	−0.004 (2)	0.008 (2)	−0.003 (2)
C13	0.3557 (2)	0.0825 (3)	0.8901 (3)	0.053 (2)	0.104 (3)	0.066 (3)	−0.000 (2)	0.013 (2)	0.004 (3)
C14	0.4046 (2)	0.0235 (3)	0.9673 (3)	0.076 (2)	0.096 (3)	0.056 (2)	−0.005 (2)	0.010 (2)	0.006 (2)
C15	0.4869 (2)	0.0567 (3)	0.9664 (3)	0.056 (2)	0.081 (3)	0.050 (2)	−0.009 (2)	0.007 (2)	−0.006 (2)
C16	0.5163 (2)	0.0518 (2)	0.8443 (3)	0.048 (2)	0.063 (2)	0.045 (2)	0.004 (2)	0.005 (2)	0.003 (2)
C17	0.3141 (2)	0.2388 (3)	0.7250 (4)	0.087 (3)	0.086 (3)	0.105 (4)	0.025 (3)	−0.012 (3)	−0.014 (3)
C18	0.3306 (2)	0.1376 (3)	0.6877 (3)	0.044 (2)	0.078 (3)	0.067 (3)	0.004 (2)	0.000 (2)	−0.005 (2)
C19	0.2540 (2)	0.0832 (3)	0.6711 (4)	0.061 (3)	0.109 (4)	0.104 (4)	−0.009 (3)	−0.011 (3)	0.006 (3)
C20	0.5381 (2)	−0.0026 (3)	1.0425 (3)	0.092 (3)	0.100 (3)	0.046 (2)	0.003 (3)	−0.007 (2)	0.008 (3)
C21	0.6138 (2)	0.1133 (2)	0.6331 (3)	0.049 (2)	0.045 (2)	0.050 (2)	0.002 (2)	0.005 (2)	0.007 (2)
C22	0.6613 (2)	0.1056 (2)	0.5233 (3)	0.047 (2)	0.059 (2)	0.050 (2)	0.000 (2)	0.007 (2)	0.000 (2)
C23	0.7472 (2)	0.1084 (3)	0.5537 (3)	0.047 (2)	0.088 (3)	0.060 (2)	0.003 (2)	0.010 (2)	−0.003 (2)
C24	0.7705 (2)	0.1976 (3)	0.6185 (4)	0.045 (2)	0.110 (3)	0.073 (3)	−0.012 (2)	0.006 (2)	−0.005 (3)
C25	0.7243 (2)	0.2064 (3)	0.7265 (3)	0.048 (2)	0.079 (3)	0.069 (3)	−0.006 (2)	−0.004 (2)	−0.006 (2)
C26	0.6383 (2)	0.2040 (2)	0.6983 (3)	0.050 (2)	0.057 (2)	0.065 (2)	−0.002 (2)	0.005 (2)	−0.007 (2)
C27	0.6700 (2)	0.0345 (3)	0.3264 (3)	0.079 (3)	0.107 (4)	0.055 (2)	0.002 (3)	0.016 (2)	−0.016 (2)
C28	0.6425 (2)	0.0157 (3)	0.4482 (3)	0.056 (2)	0.087 (3)	0.054 (2)	−0.000 (2)	0.014 (2)	−0.012 (2)
C29	0.6717 (2)	−0.0804 (3)	0.4913 (4)	0.093 (3)	0.062 (2)	0.088 (3)	0.015 (2)	0.017 (3)	0.000 (3)
C30	0.7443 (2)	0.2998 (3)	0.7924 (4)	0.065 (3)	0.113 (4)	0.116 (4)	−0.029 (3)	0.000 (3)	−0.033 (4)

^{a} The form of the anisotropic thermal ellipsoid is: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

TABLE 5

POSITIONAL PARAMETERS FOR HYDROGEN ATOMS IN COMPLEX II

Atom	x	y	z	U_{iso}
H1A	0.506 (1)	−0.154 (2)	0.584 (3)	0.09 (1)
H1B	0.522 (2)	−0.094 (2)	0.679 (3)	0.10 (1)
H1C	0.438 (2)	−0.132 (3)	0.660 (3)	0.14 (2)
H2A	0.437 (2)	0.214 (3)	0.344 (3)	0.18 (2)
H2B	0.426 (2)	0.141 (2)	0.223 (3)	0.13 (2)
H2C	0.515 (2)	0.107 (3)	0.301 (3)	0.18 (2)
H3	0.357 (2)	0.091 (3)	0.411 (4)	0.15 (2)
H4	0.470 (2)	−0.065 (2)	0.298 (3)	0.12 (1)
H5	0.343 (2)	−0.083 (2)	0.467 (3)	0.11 (1)
H6A	0.360 (2)	−0.250 (2)	0.388 (3)	0.13 (1)
H6B	0.442 (1)	−0.207 (2)	0.373 (3)	0.10 (1)
H6C	0.397 (1)	−0.244 (2)	0.491 (3)	0.11 (1)
H7A	0.505 (1)	0.284 (2)	0.622 (2)	0.07 (1)
H7B	0.432 (1)	0.250 (2)	0.541 (2)	0.07 (1)
H7C	0.528 (1)	0.248 (2)	0.512 (2)	0.07 (1)
H11	0.466 (1)	0.186 (2)	0.789 (2)	0.07 (1)
H12	0.383 (1)	0.014 (2)	0.745 (2)	0.07 (1)
H13A	0.362 (1)	0.156 (2)	0.922 (2)	0.10 (1)
H13B	0.296 (1)	0.051 (1)	0.889 (2)	0.08 (1)
H14A	0.409 (2)	−0.000 (2)	1.037 (3)	0.14 (1)
H14B	0.412 (1)	−0.049 (2)	0.948 (2)	0.10 (1)
H15	0.484 (1)	0.125 (2)	0.978 (2)	0.06 (1)
H16A	0.563 (1)	0.082 (2)	0.845 (2)	0.08 (1)
H16B	0.523 (1)	−0.012 (2)	0.812 (2)	0.07 (1)
H17A	0.374 (1)	0.263 (2)	0.737 (2)	0.11 (1)
H17B	0.316 (1)	0.264 (2)	0.796 (3)	0.15 (1)
H17C	0.293 (1)	0.284 (2)	0.682 (3)	0.15 (2)
H18	0.360 (1)	0.138 (1)	0.610 (2)	0.04 (1)
H19A	0.264 (1)	0.009 (2)	0.640 (3)	0.12 (1)
H19B	0.224 (1)	0.120 (2)	0.624 (3)	0.10 (1)
H19C	0.223 (2)	0.085 (3)	0.737 (4)	0.15 (2)
H20A	0.545 (1)	−0.076 (2)	1.014 (2)	0.09 (1)
H20B	0.525 (1)	0.002 (2)	1.120 (2)	0.10 (1)
H20C	0.585 (1)	0.027 (2)	1.056 (2)	0.10 (1)
H21	0.617 (1)	0.057 (1)	0.666 (2)	0.05 (1)
H22	0.646 (1)	0.178 (1)	0.470 (2)	0.06 (1)
H23A	0.758 (1)	0.043 (1)	0.610 (2)	0.06 (1)
H23B	0.770 (1)	0.096 (2)	0.488 (2)	0.07 (1)
H24A	0.763 (1)	0.253 (2)	0.569 (2)	0.08 (1)
H24B	0.836 (1)	0.197 (2)	0.640 (2)	0.08 (1)
H25	0.734 (1)	0.135 (2)	0.769 (3)	0.10 (1)
H26A	0.606 (1)	0.216 (2)	0.773 (2)	0.05 (1)
H26B	0.629 (1)	0.269 (1)	0.653 (2)	0.05 (1)
H27A	0.667 (2)	−0.008 (3)	0.274 (3)	0.12 (2)
H27B	0.655 (2)	0.111 (2)	0.292 (3)	0.13 (2)
H27C	0.732 (1)	0.034 (2)	0.323 (2)	0.08 (1)
H28	0.577 (1)	0.012 (2)	0.445 (2)	0.06 (1)
H29A	0.650 (2)	−0.138 (2)	0.458 (3)	0.12 (2)
H29B	0.660 (2)	−0.103 (2)	0.565 (2)	0.09 (1)
H29C	0.721 (1)	−0.078 (2)	0.501 (3)	0.09 (1)
H30A	0.795 (2)	0.320 (3)	0.810 (4)	0.15 (2)
H30B	0.739 (2)	0.360 (3)	0.732 (4)	0.17 (2)
H30C	0.717 (2)	0.292 (2)	0.854 (4)	0.16 (2)

Results and discussion

Complex I

Interatomic distances and angles are given in Fig. 1, which also includes the numbering scheme. A stereoscopic drawing of the molecule is shown in Fig. 2. Although the formal standard deviations in bond lengths and angles calculated from the estimated errors in positional coordinates are 0.003 to 0.007 Å for distances and 0.2 to 0.4° for angles involving Ni and P atoms and 0.01 to 0.02 Å and 1° for distances and angles respectively which involve only C atoms, the unrealistic distances and angles observed in the pentenyl group suggest these are severe underestimates. However, in view of the reasonable geometry displayed by the organic phosphine ligand (described below), the pentenyl ligand was probably the principal site of the observed decomposition in the crystal. Although this is unfortunately the prime region of interest in this complex, useful information about gross features of the complex are considered available and are sufficient to describe probable trends in similar complexes.

As mentioned above the phosphorus ligand has no unusual features. The observed C—P—C angles (105° av.) remain unchanged upon coordination from
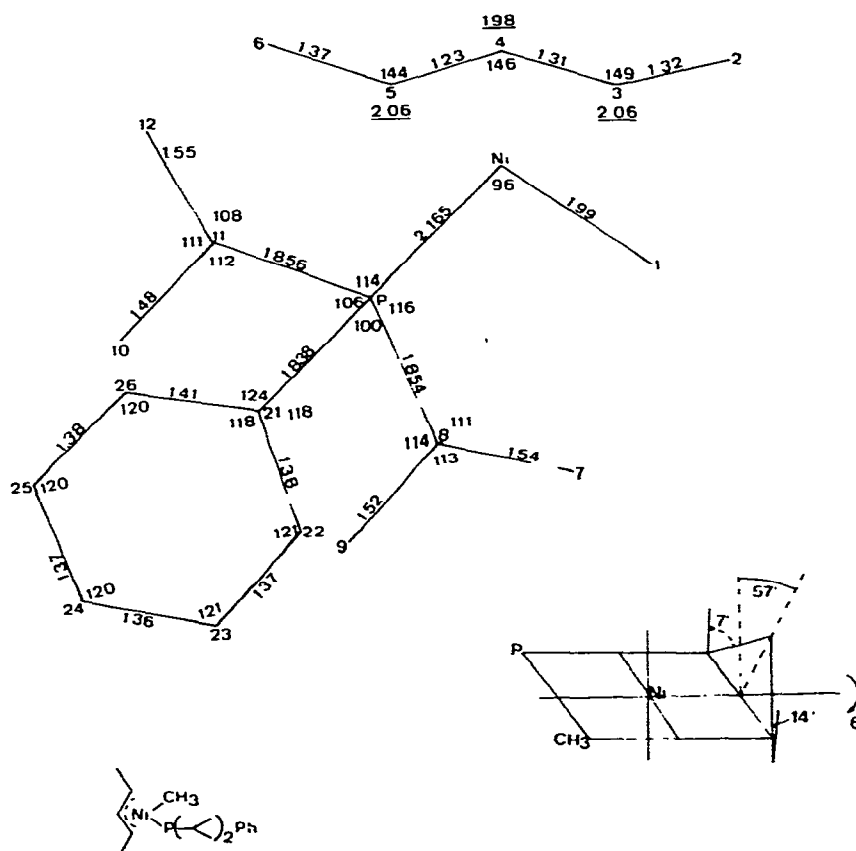

Fig. 1. Interatomic distances and angles in complex I, (π-pentenyl)(diisopropylphenylphosphine)methyl nickel(II).
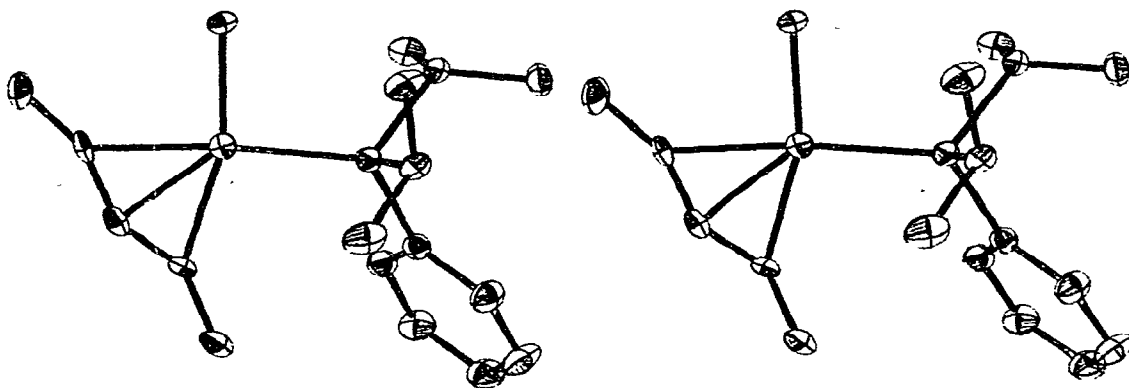
Fig. 2. Stereoscopic drawing of complex I.

those found in the free phosphine [11]. The Ni—P bond distance is 2.165 (3) Å, which is only slightly shorter (0.01 Å) than that found in complex II and is in the range (2.159 to 2.175 Å) found in complexes where the nickel is in a similar bonding environment. Two types of P—C bond distances [1.855 (5) av. and 1.838 (8) Å] are observed and are consistent with the difference between sp^3 and sp^2 carbon covalent radii respectively. In the isopropyl groups the carbon—carbon bond lengths average 1.52 Å with r.m.s; deviation of 0.03 Å. These C—C bond distances are equal within expected internal deviations, and are in accordance with $C(sp^3)$—$C(sp^3)$ bond distances generally obtained in X-ray investigations. The six C—C distances in the phenyl ring average 1.38 Å with a r.m.s. deviation of 0.02 Å. This is in good agreement with the accepted value for benzene of 1.397 Å. Because of the approximate quantitative agreement between the formally calculated e.s.d.'s and the r.m.s. deviations, the estimated errors for this part of the molecule are not seriously underestimated.

The Ni—C(σ) distance is 1.99 Å with an estimated error of 0.01 Å. A comparison given in the discussion of complex II indicates this error also may not be grossly underestimated.

Even though the Ni—C(π) bond distances to the allyl fragment [2.06 (1) Å av. terminal and 1.98 (1) Å central] are similar to those frequently found in π-allyl—nickel complexes [12], the internal geometry of the pentenyl part of the molecule clearly suffers from systematic errors. In the absence of decomposition shortening of the C—C bonds and corresponding opening of the C—C—C angles could be attributed to thermal motion as described in $(C_3H_5)_4Mo_2$ [13], but a rigid body analysis of the thermal parameters in the present study indicated this simple explanation to be unrealistic. Chemical evidence [4] for the probable decomposition points towards the following reaction:
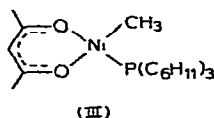

However, any further attempts to establish a more satisfactory model would require a carefully monitored data set in at least three directions, and the difficult task of obtaining a formulation that would account for the decomposition. At

present these obstacles are sufficient to prevent any further attempts to obtain better data for this compound.

Coordination geometry about the nickel is an important feature of the molecule. Assuming the pentenyl group to occupy two coordination sites and the phosphorus and methyl (C1) atoms to occupy the remaining two, the nickel has approximate square-planar coordination. Deviations from ideal square-planar coordination are best described with respect to the P, Ni, C1(methyl) plane. The out-of-plane distances for C3, C4 and C5 are —0.13, +0.19 and +0.11 Å respectively. Alternatively a clear, but less precise description of this distortion can be given by an in-plane-twist angle* of 5.5° of the pentenyl group away from the phosphorus atom. Although the magnitude of this distortion is subject to large uncertainties because of the systematic errors exhibited in the pentenyl group, the results are in accordance with the observed NMR spectrum [5].

An equally valid description would be to consider out-of-plane deviations of the methyl group. Methyl group distortions have been observed in complex III, where the pentenyl group has been replaced by an acetylacetonate group

$$\begin{array}{c} \diagdown \\ \diagup \end{array} \hspace{-0.5em} \begin{array}{l} =O \\ \\ =O \end{array} \hspace{-0.5em} \diagdown Ni \diagdown \hspace{-0.3em} \begin{array}{l} CH_3 \\ \\ P(C_6H_{11})_3 \end{array}$$

(III)

and the phosphine ligand is slightly different [14]. However, bonding of the Ni to the allyl fragments is not as rigorously defined as to acetylacetonate groups because of the following: (1) the allyl unit bonds as a group and therefore has no well defined bonding sites; (2) the non-bonding orbitals of the allyl system (a_2), which have less overlap than the bonding orbitals [$b_1(I)$] [15], control the orientation of the allyl group and are more effected by the influences of asymmetrical metal orbitals, i.e. trans effects. Thus, the above descriptions of the coordination appear appropriate.

The tilt of the allyl plane away from the coordination plane is characteristic of metal—allyl square-planar complexes. The magnitude of the tilt has been subjected to theoretical considerations [15]. In complex I the tilt direction of the allyl group is away from the coordination plane and is consistent with that predicted. The observed magnitude of this tilt, (146°) however, is suspect and attributed to decomposition effects. Further comments on the tilt will be made in discussing complex II.

Complex II

Interatomic distances and angles are given in Fig. 3, which also shows the numbering scheme for the molecule. In Fig. 4 the stereoscopic drawing illustrates the absolute configuration (R)** of the complex. In addition this three-dimen-

---

* The in-plane-twist angle is defined by the angle which the vector C5→C3 makes with the P, Ni, C1 plane, assuming positions which corresponds to the average values for the C3—C4 and C4—C5 bond lengths; otherwise this angle is 5.7°.

** Schenkluhn [5] has defined a nomenclature for square-planar complexes according to a pseudo-tetrahedral model. In complex II the central carbon (C4) of the allyl is assumed to occupy one position, where as the phosphorus ligand and methyl group occupy two other positions of the tetrahedron. The remaining position is vacant so that the R sequence is: phosphine ligand > allyl > methyl > (0).
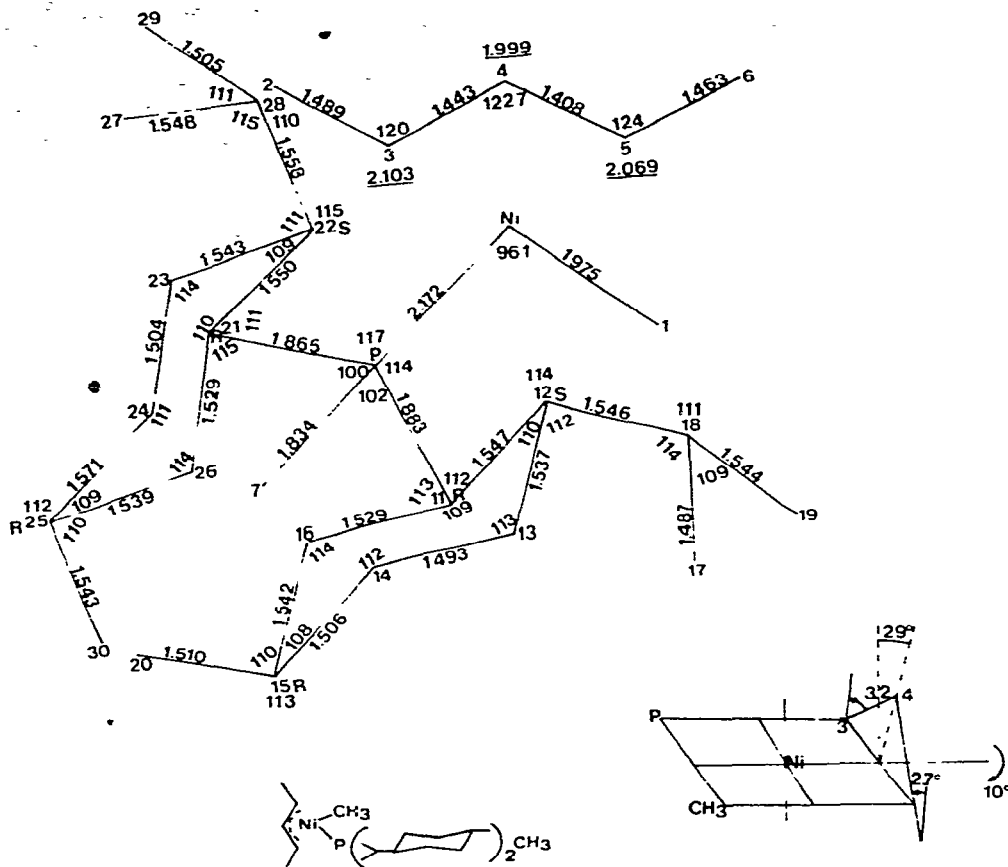
Fig. 3. Interatomic distances and angles in complex II, (π-pentenyl)(dimenthenylmethylphosphine)methyl-nickel(II).

sional drawing allows the viewer to see the conformation of the phosphine li-gand with respect to the nickel system and shows one of its isopropyl groups (C28) oriented such that its central hydrogen (H28) is directed towards an octa-hedral site of the nickel. Intramolecular non-bonded Ni - - - C distances less than 4 Å are given in Table 6. Interestingly the Ni . . . C28 distance (3.26 Å) is shorter than the Ni second-nearest neighbour distances about the phosphine (3.43 Å av.) ligand. This is possibly significant. Although the exact geometrical forms of the "active nickel catalysts" are not known, this preferential orientation of one of the menthyl groups plays a significant role in the directional characteristics of this ligand during the activity of this specific catalyst system.

TABLE 6

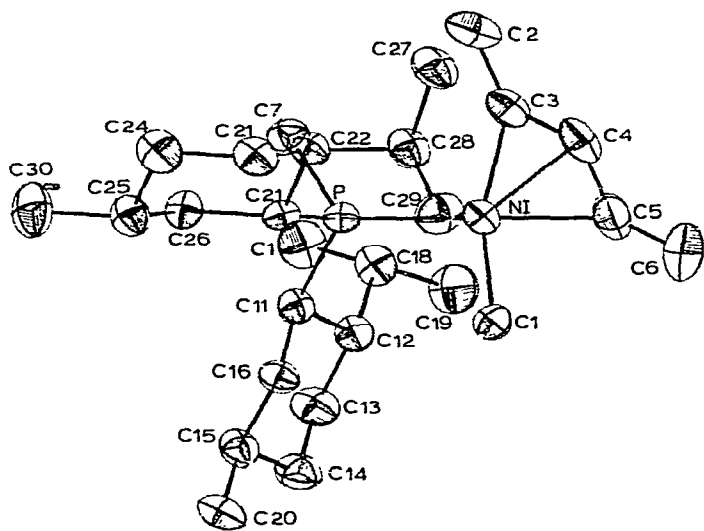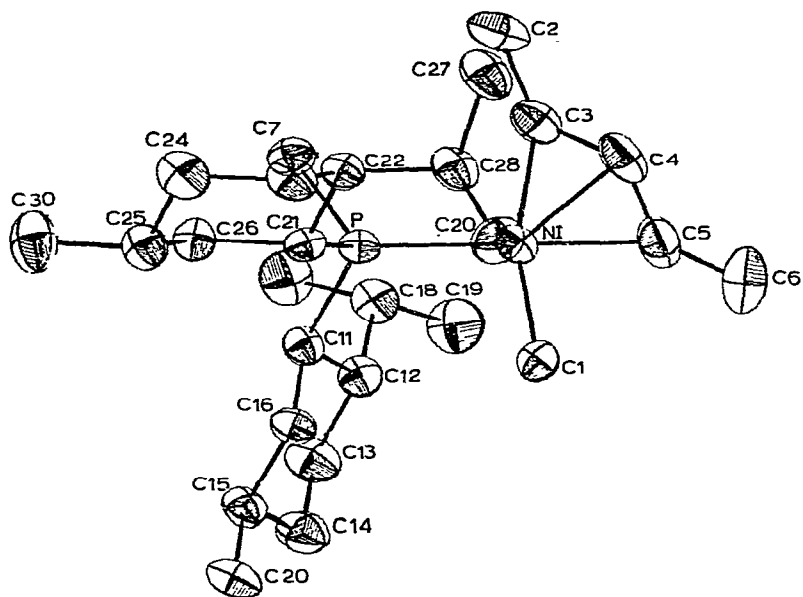| Ni . . . C2 | 3.24 Å | Ni . . . C18 | 3.69 Å |
Ni . . . C6	3.19	Ni . . . C21	3.44
Ni . . . C7	3.44	Ni . . . C22	3.81
Ni . . . C11	3.40	Ni . . . C28	3.26
Ni . . . C12	3.54	Ni . . . C29	3.79

Fig. 4. Stereoscopic drawing of complex II.

Differences in P—C11 and P—C21 distances, 1.883 (3) and 1.865 (4) Å are attributed simply to conformational requirements of each methyl ring and are considered different because of steric strain. The shorter P—C7 distance 1.834 Å is believed to result from second-order hybridization effects [16, 17], where the P—C bond s character is increased on replacement of a CH_3 group for a $CH(CH_2)_2$ group, and is consistent with observation [17, 18]. Angles about the phosphorus atom are of two types: C—P—C (102° av.) and Ni—P—C (116° av.), so that the general geometry of the phosphine ligand, just as in complex I, appears unchanged upon coordination.

Qualitative trends in Ni—C(σ) bond distances appear to be developing, but must be carefully interpreted with respect to the environment about the nickel atom as well as to the substituents on the carbon atom sigma-bonded to the nickel. For example in complexes I and II the Ni—C(σ) bond lengths [1.99 (1) and 1.975 (4) Å respectively], could have been predicted to be longer than that in III [1.94 (1) Å], because the oxygen atoms in acetylacetone are poorer acceptors than the carbon atoms in allyl groups. Similarly the corresponding Ni—P bond lengths should reflect the same effect. They are in agreement with the expected trend [2.165 (3) and 2.172 (1) Å in I and II respectively and 2.159 (2) Å in III]. Extension of these interpretations appear to be easily applied, the *trans* influence series is used as the basis for predictions.

, Other aspects of Ni—C(σ) bonds, including a different oxidation state of nickel [19] and other hybridizations of the carbon atom [20], conform to these trends, according to bond lengths. Ambiguous interpretations in Ni—C(σ) bond lengths have arisen when substituents on the sigma-bonded carbon are other than carbon and hydrogen, but may be attributed to less than accurate results in the structure of (π-C_5H_5)NiPPh$_3$(CF$_3$) [21]. Even though the agreement in this quoted structure between the Ni—C(σ) distances for the two independent molecules in the asymmetric unit is very good [1.95 (2) and 1.95 (3) Å], the large difference between the respective 'equivalent' Ni—P distances [2.148 (8) and 2.172 (9) Å] suggests even larger standard deviations for the Ni—C distances. Until further studies of substituted alkyls are completed, Ni—CX$_3$ bond lengths are expected to be shorter than comparable Ni—CH$_3$ lengths when X is more electronegative than hydrogen [16, 17].

The interatomic distances of the pentenyl group, which are illustrated in Fig. 3, show the ligand to be unsymmetrical. The Ni—C(π) distances are 2.103 (4), 1.999 (4) and 2.069 (4) Å, also displaying asymmetry in bonding towards the nickel. The direction of this asymmetry is consistent with the greater *trans* directing ability of the CH$_3$ group and may explain the differences in C—C bond lengths in the pentenyl group. There are two modes currently considered operative in *trans* effects: *(1)* a σ component and to a lesser extent *(2)* a π component [22]. Apparently the carbon atom (C5) of the π-bond C4—C5 *trans* to the phosphorus receives less back-donation than C3, thus C5 has shorter bond lengths. Additional supporting, albeit slight evidence for this effect is provided by the difference in conformational or dihedral angles of the terminal methyl groups with the allyl plane (C3, C4 and C5). Carbon atoms C2 and C6 are twisted out the allyl plane towards the nickel atom by 3.2 and 2.7° respectively, supporting the assumption of an increased p-character in the hybrid orbitals of C3 with respect to C5. This fact, together with the observed bond lengths, points towards a tendency to a σ—π-formulism for the allyl linkage.

Coordination about the nickel atoms in complex II is quite similar to the distorted square-planar arrangement described for complex I. Deviations from ideal square-planar coordination, relative to the plane P, Ni, C1(methyl), are given by the out-of-plane distances for C3, C4 and C5 (+0.069, —0.296 and +0.505 Å, respectively). The in-plane-twist angle, defined in the discussion of complex I, is $10.0°$ ($10.3°$ assuming a symmetric allyl group) and is in the same direction as in complex I.

Tilting of allyl groups away from the Ni atom coordination plane is a characteristic geometrical feature of allyl fragments in square-planar complexes. The magnitude of this tilt in II is $118.8°$, which is defined as the angle between the allyl plane (C3, C4 and C5) and the plane of Ni, P and C1. Although this value is larger than the predicted value of $106°$ [15], the uncertainty in the definition of the basal plane could account for this difference. A favorable comparison with other Ni—allyl structures is not convenient because of the lack of well defined coordination planes or from restrictive definitions of these planes. Brauer has suggested that the angle, defined by the vector: metal to the center-of-mass of the allyl and the allyl plane, would avoid these problems and would be sufficient for most descriptions [23]. The corresponding angles for complexes I and II are 148 and $117°$ respectively and are sufficient to describe relative orientations of allyl groups in any metal—π-allyl system.

References

1 B. Bogdanovic, B. Henc, H.-G. Karmann, H.-G. Nüssel, D. Walter and G. Wilke, Ind. Eng. Chem., 62 (1970) 34; B. Bogdanovic, B. Henc, B. Meister, H. Pauling and G. Wilke, Angew. Chem., 84 (1972) 1070; B. Bogdanovic, Angew. Chem., 85 (1973) 1013.
2 P. Heimbach, P.W. Jolly and G. Wilke, Advan. Organometal. Chem., 8 (1970) 29.
3 B.L. Barnett, B. Büssemeier, P. Heimbach, P.W. Jolly, C. Krüger, I. Tkatchenko and G. Wilke, Tetrahedron Lett., (1972) 1457.
4 H. Bönnemann, H. Schenkluhn and G. Wilke, to be published.
5 H. Schenkluhn, Dissertat., Univ. of Bochum, 1971.
6 C. Krüger, Angew. Chem., 84 (1972) 412; Angew. Chem., Int. Ed. Engl., 11 (1972) 387.
7 R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
8 D.T. Cromer and J.T. Waber, Acta Crystallogr., 18 (1965) 104.
9 D.T. Cromer and D. Liberman, J. Chem. Phys., 53 (1970) 1891.
10 W.C. Hamilton, Acta Crystallogr., 18 (1965) 502.
11 J.J. Daly, Perspectives in Structural Chemistry, Vol. III, Wiley, New York, 1970, pp. 172—173.
12 M.R. Churchill and R. Mason, Advan. Organometal. Chem., 5 (1967) 100.
13 F.A. Cotton and J.R. Pipal, J. Amer. Chem. Soc., 93 (1971) 5441.
14 B.L. Barnett and C. Krüger, J. Organometal. Chem., 42 (1972) 169.
15 S.F.A. Kettle and R. Mason, J. Organometal. Chem., 5 (1966) 573.
16 A.D. Walsh, Trans. Faraday Soc., 43 (1947) 60.
17 H.A. Bent, J. Chem. Phys., 33 (1960) 1259.
18 W.A. Bernett, J. Org. Chem., 34 (1969) 1772.
19 B.L. Barnett and C. Krüger, J. Cryst. Mol. Struct., 2 (1972) 271.
20 M.R. Churchill, Perspectives in Structural Chemistry, Vol. III, Wiley, New York, 1970 pp. 147—150.
21 M.R. Churchill and T.A. O'Brien, J. Chem. Soc. A, (1970) 161.
22 S.F.A. Kettle, Coordination Compounds, Thomas Nelson and Sons, London, 1969, pp. 189—190.
23 D.J. Brauer, private communication.