

THE MOLECULAR AND CRYSTAL STRUCTURE OF BIS(ETHYLENE)(TRICYCLOHEXYLPHOSPHINE)NICKEL

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SUMMARY

The molecular and crystal structure of bis(π -ethylene)(tricyclohexylphosphine)nickel has been determined by direct methods and refined anisotropically to a final R value of 6.48%. The nickel atom shows slightly distorted trigonal symmetry with planar arrangement of the ligands. Relatively short contacts exist between the two olefin molecules as well as between the olefins and the phosphorus. Both ethylenes have the same C-C distance (1.41 Å) and distances from the nickel atom (1.987–2.042 Å) the nickel-phosphorus bond is 2.196 Å, the phosphorus having a slightly distorted tetrahedral geometry. All cyclohexyl rings are in the chair form and bonded equatorially to the phosphorus. Some short intermolecular contacts of the olefins across a center of symmetry are discussed.

INTRODUCTION

The synthesis of the hitherto unknown bis(π -monoolefin)nickel-complexes has been described recently by Jolly, Tkatchenko and Wilke¹. These compounds serve as models in the investigation of the mechanism of the oligomerisation of olefins on transition metal catalysts. From the structural point of view they are of particular interest because of the recent speculations about the bonding arrangement between olefins and transition metals^{2,3}. Two general types of olefin-transition metal complexes are known: first the Zeise-salt type, in which the olefin- π -skeleton is arranged perpendicular to the ligand-transition metal plane, and second, an arrangement in which the olefin skeleton is within this plane. Some deviations from exact planarity have been recorded³, for the latter arrangement, one example of which is found in monoethylenebis(triphenylphosphine)nickel, the structure of which has been determined independently by two groups^{4,5} and for which two different angles of tilt are reported. It seems that considerably more information on these systems is needed before detailed conclusions on the bonding can be drawn. We therefore undertook an X-ray investigation of bis(π -ethylene)(tricyclohexylphosphine)nickel.

EXPERIMENTAL

Bis(ethylene)(tricyclohexylphosphine)nickel (I) (grown from anhydrous ether/

pentane with strict exclusion of oxygen and moisture) forms plate-shaped crystals along {001}. Preliminary photographic examination (Weissenberg- and Precession method) showed the crystals to be of monoclinic symmetry, the space group being $P2_1/n$ (non-standard setting of $P2_1/c$). Cell constants were derived from a least squares refinement of 2θ -values of 47 general reflections, determined on a diffractometer. They are given, together with other information on the unit cell, in Table 1.

TABLE 1

$a = 18.468 \pm 0.002 \text{ \AA}$, $b = 17.290 \pm 0.001 \text{ \AA}$, $c = 9.615 \pm 0.001 \text{ \AA}$, $\beta = 99.70 \pm 0.7^\circ$.
$Z = 4$, $d(\text{calcd.}) = 1.198 \text{ g/ml}$.
$h0l$ for $h + l = 2n$, $0k0$ for $k = 2n$, $P2_1/n$ (No. 14)

Three dimensional intensity data were collected on a crystal of the dimensions $0.81 \times 0.54 \times 0.2 \text{ mm}$, mounted along {001} on a computer-operated Siemens-Hoppe diffractometer by our standard procedure (5-step 2θ -scan)⁶ to a limit of 2θ 40° ($\text{Mo-K}\alpha$). Out of 2008 reflections measured, 1776 were considered to be sufficient above background [$I_0 > 2\sigma \cdot (I_0)$] to be treated as observed. Standard deviations were based on counting statistics. Data reduction ($I_0 \rightarrow F_0$) was carried out as described previously⁶. As a φ -scan at χ 90° had shown no abnormal curving, no absorption correction was applied to the data (μ 9.58 cm^{-1}). The structure was solved by direct methods. Positional parameters of the heavy atoms were taken from an E -map, computed with 370 signed normalised structure factors, using the method of Dewar⁷ as adapted to our computer system*. Starting symbolic phases, interactions and starting E 's are given in Table 2.

TABLE 2

h	k	l	Interactions	E	Symb. sign	Sign
5	2	4	77	3.089	A	+
-6	7	2	69	2.249	B	-
-2	6	1	74	3.185	C	-
0	1	5	56	2.241	D	-
-7	4	1	69	2.586	E	+

The heavy atom arrangement as found was in accordance with a three-dimensional Patterson synthesis. All other lighter atoms were found in three successive Fourier syntheses. Five cycles of isotropic least squares refinement, using unit weights for all reflections, lowered the R -factor to 15%; five additional cycles of anisotropic refinement resulted in R 12.7%. At this stage a difference Fourier map was computed to locate hydrogen atoms.

For some positions in the cyclohexyl rings, hydrogen atoms were not evident from this map, in which case calculated positions were used. Thus, 39 hydrogen atoms were included in the atoms list and the anisotropic refinement, using statistical

* All computations were done on a PDP-10 time-sharing computer with adapted commonly available programs.

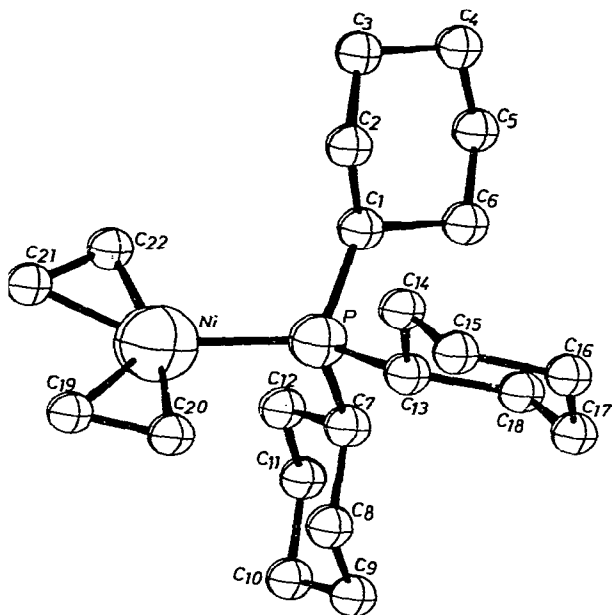


Fig. 1.

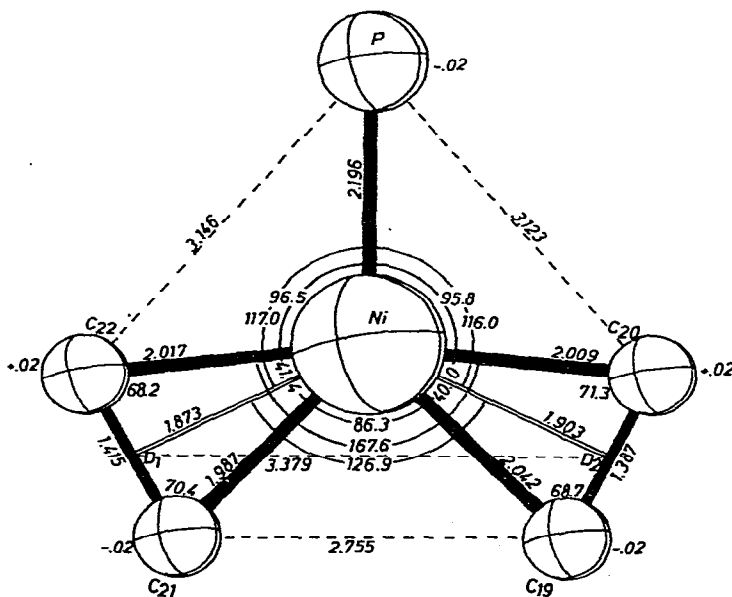


Fig. 2. A view of the metal-ligand arrangement.

TABLE 3

FINAL ATOMIC COORDINATES AND THEIR STANDARD DEVIATIONS ($\times 10^4$)

Atom	X	ΣX	Y	ΣY	Z	ΣZ
NI 1	916	0	1144	0	944	1
P 1	2562	2	1262	1	1424	2
C 1	3039	6	2134	5	613	9
C 2	2641	7	2895	5	1125	9
C 3	2829	9	3568	5	191	12
C 4	3937	10	3643	6	127	10
C 5	4382	8	2892	6	-309	11
C 6	4179	7	2208	5	635	10
C 7	3224	6	454	4	668	9
C 8	3039	7	-327	5	1320	10
C 9	3568	7	-982	5	700	10
C 10	3259	7	-1035	6	-874	10
C 11	3407	7	-258	6	-1586	10
C 12	2889	7	410	5	-912	8
C 13	3112	6	1222	5	3292	8
C 14	2724	6	1861	5	4187	9
C 15	2975	7	1689	5	5746	9
C 16	4111	7	1589	5	6247	9
C 17	4521	6	991	6	5332	10
C 18	4267	6	1151	5	3776	9
C 19	-165	7	632	5	1887	11
C 20	779	6	567	5	2715	9
C 21	-197	7	1432	5	-598	10
C 22	725	7	1720	6	-905	10
H 1	3080	0	2230	0	-350	0
H 2A	2907	0	3018	0	2047	0
H 2B	1913	0	2844	0	1272	0
H 3A	2585	0	3432	0	-771	0
H 3B	2518	0	4032	0	541	0
H 4A	4178	0	3769	0	1087	0
H 4B	4130	0	4061	0	-523	0
H 5A	5116	0	2951	0	-471	0
H 5B	4145	0	2759	0	-1280	0
H 6A	4499	0	1728	0	258	0
H 6B	4406	0	2347	0	1616	0
H 7	4180	0	490	0	950	0
H 8A	3196	0	-304	0	2334	0
H 8B	2336	0	-446	0	1307	0
H 9A	4290	0	-859	0	726	0
H 9B	3427	0	-1458	0	1183	0
H 10A	3624	0	-1446	0	-1392	0
H 10B	2514	0	-1151	0	-888	0
H 11A	4131	0	-138	0	-1618	0
H 11B	3225	0	-287	0	-2628	0
H 12A	3027	0	902	0	-1417	0
H 12B	2145	0	297	0	-931	0
H 13	2980	0	790	0	3790	0
H 14A	3042	0	2335	0	3899	0
H 14B	1996	0	1887	0	4062	0
H 15A	4628	0	772	0	3118	0
H 15B	4615	0	1665	0	3462	0

TABLE 3 (contd.)

Atom	X	ΣX	Y	ΣY	Z	ΣZ
H 16A	5250	0	956	0	5456	0
H 16B	4243	0	494	0	5605	0
H 17A	4498	0	2085	0	6079	0
H 17B	4155	0	1412	0	7268	0
H 18A	2607	0	2069	0	6382	0
H 18B	2576	0	1203	0	6052	0
H 19A	10	0	300	0	1320	0
H 19B	-260	0	1170	0	2110	0
H 20A	1110	0	10	0	2370	0
H 20B	1410	0	740	0	3430	0
H 21A	-440	0	1750	0	20	0
H 21B	-70	0	880	0	-1300	0
H 22A	1130	0	1270	0	-1600	0
H 22B	1230	0	2180	0	-240	0

TABLE 4

FINAL THERMAL PARAMETERS ($\times 10^3$)

Atom	$U_{1,1}$	$U_{2,2}$	$U_{3,3}$	$U_{1,2}$	$U_{1,3}$	$U_{2,3}$
Ni 1	34	44	60	5	0	-7
P 1	38	35	38	2	5	3
C 1	49	28	64	-0	20	4
C 2	73	47	46	3	17	5
C 3	124	34	90	7	41	0
C 4	155	45	57	-17	45	3
C 5	111	58	91	-16	64	-0
C 6	57	52	83	-6	29	7
C 7	42	30	42	10	2	2
C 8	63	38	70	4	20	5
C 9	73	44	61	6	17	-0
C 10	62	53	71	8	17	-22
C 11	74	55	62	7	24	-11
C 12	74	54	19	5	10	9
C 13	49	43	39	3	16	3
C 14	64	49	46	0	19	-14
C 15	71	69	38	15	14	-1
C 16	81	70	50	-3	11	-3
C 17	49	88	46	7	-7	2
C 18	36	70	55	3	6	-2
C 19	64	65	113	0	46	-24
C 20	32	101	44	-21	6	-24
C 21	72	62	77	31	-13	-22
C 22	56	75	75	-4	-32	-23

weights [$w 1.0/\sigma^2(|F_0|)$] was continued for 6 more cycles. Atomic scattering factors used were those of Cromer and Waber⁸ for non-hydrogen atoms, and those of Stewart, Davidson and Simpson⁹ for hydrogens. In the final cycles, the real part of the anomalous dispersion for Ni and P was corrected for with the values given by Cromer^{8,*}.

* A structure factor list may be obtained from the authors (C.K.) on request.

TABLE 5

BOND DISTANCES (Å) AND THEIR STANDARD DEVIATIONS

Ni-C19	2.042	(0.010)	C7-C8	1.526	(0.012)
Ni-C20	2.009	(0.009)	C8-C9	1.513	(0.013)
Ni-C21	1.987	(0.010)	C9-C10	1.504	(0.014)
Ni-C22	2.017	(0.010)	C10-C11	1.536	(0.013)
Ni-P	2.196	(0.002)	C11-C12	1.548	(0.013)
P-C1	1.861	(0.009)	C12-C7	1.512	(0.012)
P-C7	1.870	(0.008)	C13-C14	1.545	(0.011)
P-C13	1.826	(0.008)	C14-C15	1.510	(0.012)
C1-C2	1.534	(0.012)	C15-C16	1.535	(0.014)
C2-C3	1.518	(0.013)	C16-C17	1.520	(0.013)
C3-C4	1.510	(0.018)	C17-C18	1.503	(0.012)
C4-C5	1.519	(0.015)	C18-C13	1.551	(0.011)
C5-C6	1.544	(0.014)	C19-C20	1.387	(0.013)
C6-C1	1.537	(0.012)	C21-C22	1.415	(0.014)

TABLE 6

BOND ANGLES (°) AND THEIR STANDARD DEVIATIONS

C22-Ni-C20	167.6	(0.4)	P-C7-C12	110.3	(0.6)
Ni-C22-C21	68.2	(0.5)	P-C7-C8	112.4	(0.6)
C22-C21-Ni	70.4	(0.6)	P-C13-C18	121.3	(0.5)
C21-Ni-C22	41.4	(0.4)	P-C13-C14	113.7	(0.5)
C21-Ni-C19	86.3	(0.4)	C1-C2-C3	111.5	(0.8)
Ni-C19-C20	68.7	(0.5)	C2-C3-C4	110.8	(0.8)
C19-C20-Ni	71.3	(0.5)	C3-C4-C5	112.1	(0.8)
C19-Ni-C20	40.0	(0.4)	C4-C5-C6	112.1	(0.8)
C22-Ni-C19	127.6	(0.4)	C5-C6-C1	109.4	(0.7)
C21-Ni-C20	126.3	(0.4)	C6-C1-C2	109.1	(0.7)
C21-Ni-P	137.9	(0.3)	C7-C8-C9	112.4	(0.7)
C19-Ni-P	135.8	(0.3)	C8-C9-C10	111.9	(0.8)
C20-Ni-P	95.8	(0.3)	C9-C10-C11	111.2	(0.8)
C22-Ni-P	96.5	(0.3)	C10-C11-C12	111.4	(0.7)
Ni-P-C1	113.3	(0.3)	C11-C12-C7	112.3	(0.7)
Ni-P-C7	112.3	(0.3)	C12-C7-C8	109.1	(0.7)
Ni-P-C13	115.6	(0.3)	C13-C14-C15	111.9	(0.7)
C1-P-C13	109.3	(0.4)	C14-C15-C16	112.2	(0.7)
C1-P-C7	102.8	(0.4)	C15-C16-C17	109.6	(0.7)
C7-P-C13	102.3	(0.4)	C16-C17-C18	114.0	(0.8)
P-C1-C6	118.5	(0.6)	C17-C18-C13	111.2	(0.6)
P-C1-C2	113.3	(0.6)	C18-C13-C14	107.8	(0.6)

The final atomic parameters are given in Tables 3 and 4. The final R -value for 1776 reflection settled at 0.064 (including unobserved: 0.073) the estimated standard deviations given were calculated from the inverse matrices of the final least-squares cycle. The structure of (I) with its numbering scheme is illustrated in Fig. 1.

Intramolecular distances and angles are given in Tables 5 and 6. Estimated standard deviations for those values were derived from the corresponding values of the positional parameters given in Table 3.

found recently in other examples of tricyclohexylphosphine–nickel-systems¹¹. This distance is exactly the same as that in bis(triphenylphosphine)(ethylene)nickel, indicating an equivalence in the bond order of the two different phosphines to the nickel. The difference in behaviour of the NiL₂-systems¹⁰, where L₂ indicates chemically different phosphines with unequal steric requirements and electronic influences, thus does not show up in different Ni–P-bond lengths. The phosphorus atom of the phosphine groups shows slightly distorted tetrahedral geometry; the angles involving nickel are slightly larger than those which involve carbon and phosphorus. Because of this arrangement, the rings are slightly bent away from the central metal atom. All cyclohexyl rings are in the chair conformation and bonded equatorially to the phosphorus. The average C–C bond length is 1.513 Å and compares well to our previous

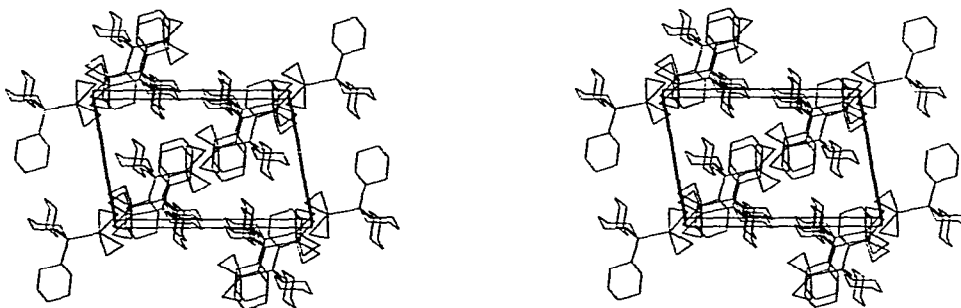


Fig. 4. Stereoscopic view of a unit cell content, viewed along *b*. The *a*-axis is horizontal.

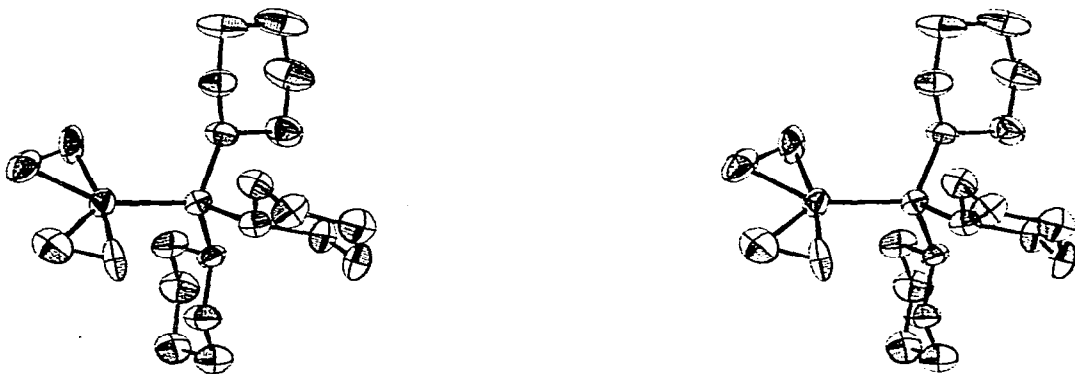


Fig. 5. Stereoscopic view of the molecule, oriented as in Fig. 1, showing the 50% probability thermal ellipsoids.

findings. There are some short intermolecular contacts which deserve attention. Figure 3 shows the arrangement of the central part of the molecules across a center of symmetry. A relatively short contact between the bonded ethylene species exists (3.838 to 4.644 Å) while the nickel atoms are 4.850 Å apart. Other short intermolecular contacts are found between C(17)–C(17) (3.755 Å) across the center of symmetry and C(4)–C(19) (3.74 Å) along the glide plane. These short contacts are evident from the packing diagram (Fig. 4).

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REFERENCES

- 1 P. W. JOLLY, I. TKATCHENKO AND G. WILKE, *Angew. Chem.*, 83 (1971) 328.
- 2 P. HEIMBACH AND R. TRAUNMÜLLER, *Justus Liebigs Ann. Chem.*, 727 (1969) 208.
- 3 J. K. STALICK AND J. A. IBERS, *J. Amer. Chem. Soc.*, 92 (1970) 5333.
- 4 W. DREISSIG AND H. DIETRICH, *Acta Crystallogr., Sect. B*, 24 (1968) 108.
- 5 C. D. COOK, C. HOE, S. C. NYBURG AND M. T. SHIOMI, *Chem. Commun.*, (1967) 426.
- 6 C. KRÜGER, *J. Organometal. Chem.*, 22 (1970) 697.
- 7 R. B. K. DEWAR, *Dissertation*, University of Chicago, 1968.
- 8 D. T. CROMER AND J. T. WABER, *Acta Crystallogr.*, 18 (1965) 104; D. T. CROMER AND D. LIEBERMAN, *J. Chem. Phys.*, 53 (1970) 1891.
- 9 R. F. STEWART, E. R. DAVIDSON AND W. T. SIMPSON, *J. Chem. Phys.*, 42 (1965) 3175.
- 11 P. W. JOLLY, K. JONAS, C. KRÜGER AND Y.-H. TSAY, *J. Organometal. Chem.*, 33 (1971) 109.
- 12 B. L. BARNETT, C. KRÜGER AND Y.-H. TSAY, to be published.

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