

Redetermination of the Structure of Ethylenebis(triphenylphosphine)nickel(0)

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Abstract. $[\text{Ni}(\text{C}_2\text{H}_4)(\text{C}_{18}\text{H}_{15}\text{P})_2]$, $\text{C}_{38}\text{H}_{34}\text{NiP}_2$, triclinic, $P\bar{1}$, $a = 10.449(3)$, $b = 17.534(2)$, $c = 10.078(5)$ Å, $\alpha = 102.88(2)$, $\beta = 117.66(3)$, $\gamma = 90.23(2)^\circ$, $V = 1582$ Å³, $Z = 2$, $D_c = 1.2832$ Mg m⁻³. Final $R = 0.044$ for 6200 observed reflections. The double bond in the π -bonded ethylene is lengthened to 1.391(5) Å. The four protons are situated in a plane 0.17(1) Å from the C atoms.

Introduction. The structure was first determined by Dreissig & Dietrich (1968) and independently by Cheng, Cook, Koo, Nyburg & Shiomi (1971; for preliminary report see Cook, Koo, Nyburg & Shiomi, 1967). Both studies were based, however, on film data. The redetermination was necessary to obtain more detailed information about the bonding of the ethylene within the complex. 41 664 reflections were measured as step-scan profiles on a Nonius CAD-4 diffractometer with β -filtered Mo $K\alpha$ radiation. The data comprise twice the whole reciprocal sphere up to $\sin \theta/\lambda = 0.7121$ Å⁻¹. After evaluation of the integrated intensities from the profiles, and corrections for Lorentz and polarization factors, equivalent structure factors were averaged to a unique set of 9948 reflections, 3748 of which [with $I < 1.5\sigma(I)$] were ignored in the large-block least-squares refinement. $\sum w||F_o| - |F_c||^2$ was minimized with the following weighting scheme: $w = 0$ if $|F_c| < 0.7|F_o|$, else $w = XY$, where $X = 1$ if $\sin \theta > 0.4$, else $X = \sin \theta/0.4$, and $Y = 1$ if $|F_o| < 20$, else $Y = 20/|F_o|$. A final comparison of the average $w||F_o| - |F_c||^2$ as a function of F_o and $\sin \theta$ revealed no systematic trends. The H atoms were refined with isotropic, all other atoms with anisotropic, vibration parameters. R converged to 0.044 for the observed reflexions. A difference map was featureless with the highest peak of 0.5 e Å⁻³ about 1 Å from Ni and another peak of 0.4 e Å⁻³ 0.9 Å from P(1). The computing was carried out mainly with the XRAY system (1976). The atomic

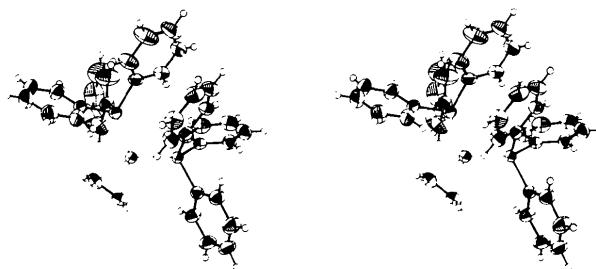


Fig. 1. ORTEP (Johnson, 1976) stereoscopic view of the molecule (50% probability ellipsoids are shown for all atoms except H, which are represented by spheres of diameter 0.2 Å).

coordinates are compiled in Table 1.† They have been transformed with respect to our 1968 paper to define the asymmetric unit by one coherent molecule. A survey of the molecule and the thermal vibrations is given in Fig. 1. The phenyl rings are planar (r.m.s.d. 0.006 Å) within the limits of error.

Discussion. The central part of the complex (Fig. 2) was found to be even more planar (r.m.s.d. 0.05 Å) than in our 1968 study. Therefore our conclusions

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35787 (50 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

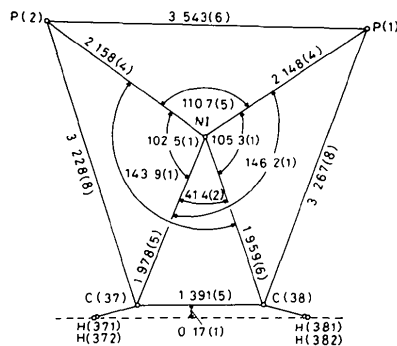


Fig. 2. Interatomic distances (Å) and angles ($^\circ$) of the atoms bonded to Ni.

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Table 1. Atomic coordinates and isotropic thermal parameters (\AA^2) with e.s.d.'s in parentheses

For non-hydrogen atoms $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

	x	y	z	U_{eq}/U
Ni(1)	.60035(4)	.77216(2)	-.01210(4)	.0398
F(1)	.76283(6)	.86334(3)	.03083(6)	.0332
P(2)	.58406(8)	.67103(4)	-.18881(8)	.0418
C(1)	.9522(3)	.8475(1)	.1144(3)	.0352
C(2)	1.0681(3)	.8959(2)	.1477(3)	.0435
C(3)	1.2090(3)	.8758(2)	.2085(4)	.0568
C(4)	1.2359(4)	.8032(3)	.2388(4)	.064
C(5)	1.1234(4)	.7515(2)	.2124(4)	.065
C(6)	.9810(3)	.7701(2)	.1491(3)	.0505
C(7)	.7854(3)	.9610(1)	.1591(3)	.0361
C(8)	.8080(3)	.9634(2)	.3077(3)	.0471
C(9)	.8312(4)	1.0350(2)	.4131(3)	.0540
C(10)	.8304(4)	1.1042(2)	.3716(4)	.0571
C(11)	.8076(5)	1.1031(2)	.2257(5)	.066
C(12)	.7854(4)	1.0318(2)	.1193(4)	.0538
C(13)	.7213(3)	.8871(1)	-.1517(3)	.0354
C(14)	.8154(3)	.8851(2)	-.2136(3)	.0441
C(15)	.7678(4)	.8982(2)	-.3596(3)	.0596
C(16)	.6287(4)	.9144(2)	-.4422(3)	.0574
C(17)	.5338(4)	.9171(2)	-.3816(4)	.0552
C(18)	.5795(3)	.9030(2)	-.2376(3)	.0494
C(19)	.6604(4)	.6758(2)	-.3194(3)	.0525
C(20)	.8105(4)	.6876(2)	-.2595(4)	.064
C(21)	.8718(5)	.6950(2)	-.3535(6)	.087
C(22)	.7834(6)	.6919(3)	-.5070(6)	.100
C(23)	.6370(6)	.6809(3)	-.5669(5)	.103
C(24)	.5747(5)	.6726(3)	-.4734(4)	.079
C(25)	.6609(4)	.5862(2)	-.1155(4)	.0513
C(26)	.7137(8)	.5289(3)	-.1889(6)	.111
C(27)	.769(1)	.4664(4)	-.1278(9)	.143
C(28)	.7710(7)	.4577(3)	.0033(8)	.106
C(29)	.7189(6)	.5127(4)	.0759(6)	.103
C(30)	.6654(5)	.5776(3)	.0197(5)	.077
C(31)	.3943(3)	.6318(2)	-.3296(3)	.0445
C(32)	.2976(4)	.6861(2)	-.3795(4)	.0550
C(33)	.1528(4)	.6617(3)	-.4867(5)	.067
C(34)	.1026(4)	.5825(3)	-.5416(5)	.071
C(35)	.1945(5)	.5286(2)	-.4930(5)	.071
C(36)	.3407(4)	.5523(2)	-.3872(4)	.0566
C(37)	.4380(4)	.7439(2)	.0244(4)	.066
C(38)	.5151(4)	.8167(2)	.1206(4)	.070
H(2)	1.051(4)	.946(2)	.132(4)	.052(9)
H(3)	1.287(4)	.913(2)	.231(5)	.07(1)
H(4)	1.333(5)	.790(3)	.288(5)	.08(1)
H(5)	1.133(5)	.702(3)	.229(5)	.08(1)
H(6)	.901(4)	.734(2)	.126(4)	.056(9)
H(8)	.812(4)	.912(2)	.333(4)	.053(9)
H(9)	.848(5)	1.038(3)	.517(5)	.08(1)
H(10)	.840(5)	1.153(3)	.443(5)	.08(1)
H(11)	.804(6)	1.147(3)	.191(6)	.11(2)
H(12)	.774(4)	1.033(2)	.023(4)	.06(1)
H(14)	.908(3)	.871(2)	-.158(4)	.042(7)
H(15)	.831(5)	.894(2)	-.398(5)	.07(1)
H(16)	.601(5)	.923(3)	-.539(5)	.08(1)
H(17)	.434(5)	.929(2)	-.439(5)	.07(1)
H(18)	.517(4)	.906(2)	-.196(5)	.07(1)
H(20)	.869(4)	.689(2)	-.157(4)	.06(1)
H(21)	.970(5)	.702(3)	-.304(6)	.09(1)
H(22)	.828(6)	.697(3)	-.569(7)	.11(2)
H(23)	.572(6)	.680(3)	-.672(7)	.11(2)
H(24)	.476(5)	.664(3)	-.517(6)	.09(1)
H(26)	.715(7)	.533(4)	-.283(7)	.12(2)
H(27)	.794(8)	.426(5)	-.190(9)	.16(3)
H(28)	.814(7)	.414(4)	.042(8)	.13(2)
H(29)	.720(5)	.516(3)	.158(5)	.09(1)
H(30)	.627(5)	.617(3)	.068(6)	.09(1)
H(32)	.332(4)	.741(2)	-.342(4)	.06(1)
H(33)	.088(5)	.699(3)	-.523(6)	.09(1)
H(34)	.002(5)	.567(3)	-.619(6)	.09(1)
H(35)	.176(5)	.478(3)	-.520(6)	.09(1)
H(36)	.403(4)	.516(2)	-.360(4)	.048(8)
H(372)	.448(4)	.697(2)	.057(5)	.07(1)
H(371)	.351(4)	.741(2)	-.068(5)	.07(1)
H(381)	.578(4)	.818(2)	.220(5)	.07(1)
H(382)	.479(5)	.867(3)	.095(5)	.08(1)

about the hybridization state dsp^2 of the Ni atom remain valid. They agree also with the geometry of the ethylene group which could now be elucidated. C(37)–C(38) is 0.04 Å shorter than the 1.43 (1) Å reported by Cheng, Cook, Koo, Nyburg & Shiomi (1971). The four C–H bonds are all slightly bent away from the Ni atom (Figs. 1, 2), so that a plane fitted to the H positions (r.m.s.d. 0.006 Å) is 0.15 (1) Å below the C–C bond. This distance has to be corrected for the systematic shifts of the H positions towards the C atoms caused by the use of the non-bonded-atom model in the refinement. The short average C–H length of 0.94 (2) Å should therefore be lengthened to 1.07 Å, the value found for ethylene (Sutton, 1958). Thus the plane through the actual proton positions is 0.17 (1) Å from the C–C bond. The C–C bond makes angles of 15.5 and 18.5° with the planes of the methylene groups H(371)–C(37)–H(372) and H(381)–C(38)–H(382) respectively. The H–C–H angles are 113 (3) and 118 (4)°.

In disagreement with Cheng, Cook, Koo, Nyburg & Shiomi (1971), the deviation from planarity of the central part of the molecule (Fig. 2) cannot be described simply by a twist of the two planes C(37)–Ni–C(38) and P(1)–Ni–P(2) around the approximate twofold axis, since both C atoms are on the same side of the latter plane. The deviations are probably due to the intramolecular contacts P(1)–C(38) [3.267 (8)], P(2)–C(37) [3.228 (8)], H(30)–H(372) [2.32 (7)], and H(30)–C(37) [2.95 (7) Å]. The closest distances of phenyl groups to the methylene group C(38)–H(381)–H(382) are longer: H(8)–C(38) 3.03 (7) and H(8)–H(381) 3.03 (7) Å.

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