

The Structure of a Nickel–1,3-Diene Complex†

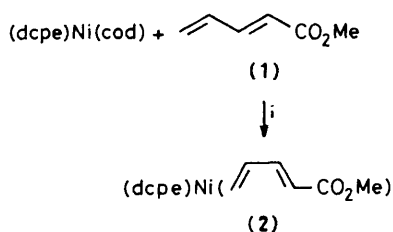
H. Michael Büch, Paul Binger,* Richard Goddard, and Carl Krüger*

Max-Planck-Institut für Kohlenforschung, Lembeckstr. 5, D-4330 Mülheim-Ruhr, Federal Republic of Germany

When $(dcpe)Ni(cod)$ [$dcpe = (C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$, $cod = \text{cyclo-octa-1,5-diene}$] reacts with penta-2,4-dienoic acid methyl ester (**1**) at 0 °C, the cod ligand is displaced by the substituted diene to give a new nickel-1,3-diene complex; a crystal structure determination of this compound reveals unexpected structural features that might be important in understanding the nickel(0) catalysed reactions of (**1**).

† Part of the doctoral thesis of H. M. Büch, Universität Kaiserslautern, 1982.

Since penta-2,4-dienoic acid methyl ester (**1**) can be smoothly cyclodimerised or codimerized in the presence of nickel(0)

Scheme 1. i, Et₂O, 0 °C, -cod.

catalysts,^{1,2} it appeared that it might be interesting to study the stoichiometric reactions of (1) with various nickel(0) complexes. We report here the preparation and structure of (dcpe)Ni(CH₂=CH=CH-CO₂Me) (2) [dcpe = (C₆H₁₁)₂-PCH₂CH₂P(C₆H₁₁)₂]. To our knowledge this is the first X-ray analysis of a complex containing a substituted 1,3-diene η⁴-coordinated to a nickel atom.

(dcpe)Ni(cod) (cod = cyclo-octa-1,5-diene) reacts at 0 °C with (1) with liberation of cod to give (2) as a red crystalline compound in 82% yield (Scheme 1).[†] Neither the i.r. spectrum of (2) (KBr disc) (ν_{CO} 1650 cm⁻¹) nor the n.m.r. spectra gave conclusive information about the structure. The ³¹P{¹H}

[†] Compound (2): C₃₂H₅₆NiO₂P₂, m.p. 130–131 °C; ¹H n.m.r. (80 MHz, C₆D₆CD₃, 22 °C): δ 5.87 (m, 1H, ³J 7 Hz), 4.97 (m, ³J 8 and 13.5 Hz), 3.57 (s, 3H), 3.50 (m, 1H, ³J 11.5 Hz), 3.27 (m, 1H), 3.06 (m, 1H), and 2.0–1.0 (br., 48H). Satisfactory microanalyses were obtained.

n.m.r. spectrum (32 MHz) recorded between -100 and 0 °C showed an AB-pattern (δ_A = 80.5, δ_B = 56.5 p.p.m., J_{AB} 32.0 Hz) while at +90 °C a sharp singlet (δ 65.5 p.p.m.) was observed, suggesting that at higher temperatures a dissociative 'arm-off'-process,³ occurs. The ¹H and ¹³C n.m.r. spectra recorded at room temperature were in accordance with an η⁴-bonding of the diene (highest complexation shifts for the inner protons⁴). At lower temperatures, however, it became clear that an additional dynamic process occurs. Unfortunately this process could not be frozen out and at -80 °C only broad unresolved signals were observed. In order to get unambiguous proof of the structure of (2) a three-dimensional X-ray analysis was undertaken.

Crystal data: C₃₂H₅₆NiO₂P₂, M = 593.42, monoclinic, space group C2/c, a = 23.180(4), b = 13.059(2), c = 24.089(2) Å; β = 114.423(8)°, U = 6639 Å³, D_c = 1.187 g cm⁻³, Z = 8, μ(Mo-Kα) = 7.05 cm⁻¹; of the 7484 reflections measured, 3220 were unobserved (2σ). Data were corrected for the effects of Lorentz and polarisation but not for those of absorption. H atoms were located from a difference Fourier map, but their positions were not refined; R = 0.042, R_w = 0.044.§

The results of the X-ray analysis⁵ are summarised in Figure 1 (arbitrary numbering scheme), which includes important bond

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

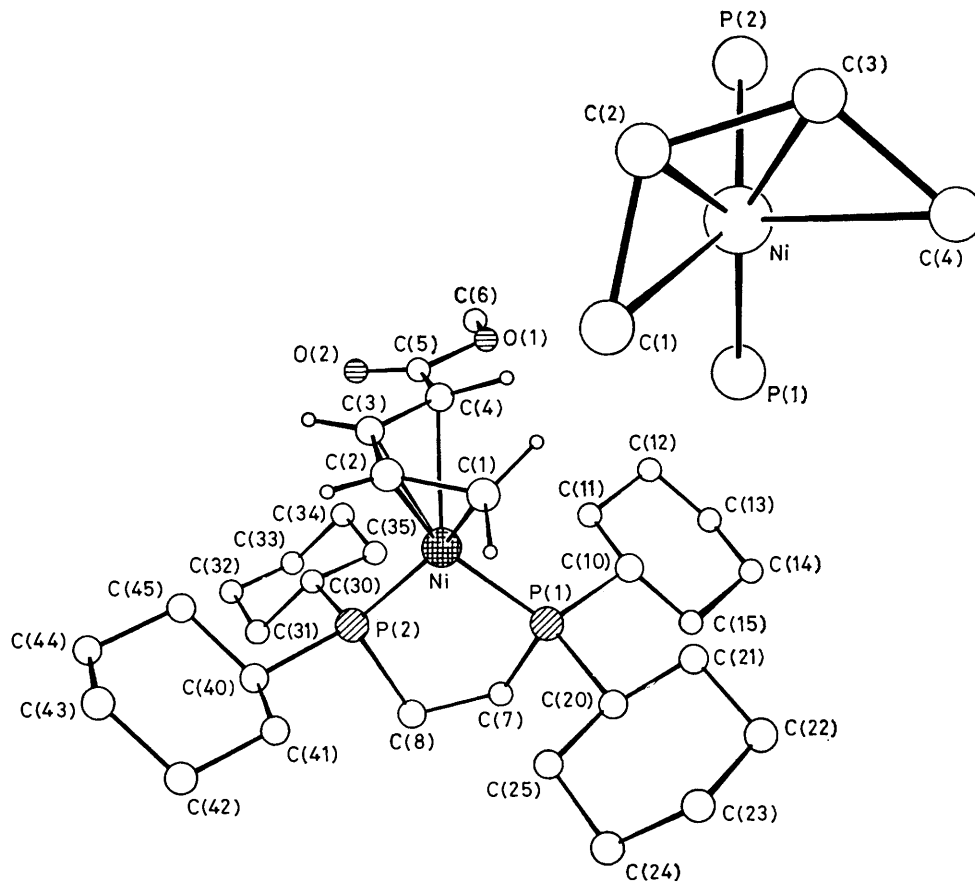


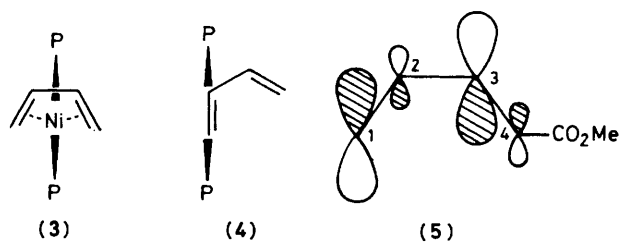
Figure 1. Molecular structure of (dcpe)Ni(CH₂=CH=CH=CH-CO₂Me) (2). Some relevant bond distances are Ni-C(1) 2.106(4), Ni-C(2) 2.018(4), Ni-C(3) 2.075(3), Ni-C(4) 2.360(4), C(1)-C(2) 1.405(6), C(2)-C(3) 1.427(6), C(3)-C(4) 1.413(6), C(4)-C(5) 1.445(6), C(5)-O(2) 1.215(6), C(5)-O(1) 1.371(6), O(1)-C(6) 1.424(6), Ni-P(1) 2.146(1), P(1)-C(10) 1.857(4), P(1)-C(20) 1.865(4), P(1)-C(7) 1.871(4), Ni-P(2) 2.178(1), P(2)-C(30) 1.861(4), P(2)-C(40) 1.864(4), P(2)-C(8) 1.865(3), C(8)-C(7) 1.517(5) Å.

lengths and a view of the inner co-ordination sphere of (2). No unusually short intermolecular distances were observed.

To a first approximation the nickel atom adopts a tetrahedral geometry if one assumes that P(1), P(2), and the mid-points of the two C=C double bonds occupy vertices of a regular polyhedron. The Ni-P(1) bond length [2.146(1) Å] is considerably shorter than the Ni-P(2) bond [2.178(1) Å]. The diene unit C(1)–(4) is essentially planar. Nevertheless it is neither internally symmetric [angle \angle C(1)–C(2)–C(3) = 119.1°, \angle C(2)–C(3)–C(4) = 122.1°] nor is it symmetrically bonded to the nickel atom. The most striking feature of the molecule is the unusually long Ni–C(4) bond length [2.360(4) Å]. The other three bonding Ni–C distances lie within the expected range (2.018–2.106 Å). In comparable iron complexes such an unsymmetrical bonding of the diene unit has not yet been observed.⁸ All these complexes show equidistant bonding Fe–C distances and the terminal substituents lie above the plane defined by the four diene carbon atoms away from the metal. In contrast, the carboxy methyl group in (2) lies *ca.* 0.2 Å below the diene plane towards the nickel atom. The C=O bond length [C(5)–O(2) = 1.215 Å] lies within the expected range, so a zwitterionic structure with Ni bearing the positive and O(2) the negative charge can probably be ruled out.

The tendency for the substituted butadiene to co-ordinate to the nickel atom in the way it does may be a reflection of the propensity of nickel to form 16e complexes with poor acceptor ligands.⁷ Thus the bonding of the substituted diene to the metal can be formulated as being part-way between an η^4 (3) and an η^2 (4) situation;⁸ thus it should be borne in mind that the influence of the carboxy methyl group might be an important factor in determining the final orientation of the diene.⁹ The ester group will not only have the effect of reducing the energy of the LUMO of the butadiene and hence increasing its acceptor properties, but will also modify it as shown in (5). The carbon atoms 1 and 3 are thus in a position to interact with a filled metal d-orbital and enhance the backbonding.

It is interesting to note that the end of the diene where the



nickel atom in (2) is most strongly bonded is also the part where oxidative C–C coupling occurs when (1) reacts with R_3P-Ni^0 complexes.¹

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