Reaction of Bis(pentamethylcyclopentadienyl)zinc with Bis(cyclo-octa-1,5-diene)nickel: Crystal Structure of $(C_5Me_5Ni)_2C_{16}H_{24}$

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The reaction of $(C_5Me_5)_2Zn$ with bis(cyclo-octa-1,5-diene)nickel yields $(C_5Me_5Ni)_2C_{16}H_{24}$ *via* a novel zinc-induced ligand coupling.

In the course of our study on organozinc–transition metal compounds, we recently prepared the first example of a zinc–nickel cluster, $(cp)_6Ni_2Zn_4$.[1] This cluster was obtained by heating bis(cyclopentadienyl)zinc, $(cp)_2Zn$, with bis(cyclo-octa-1,5-diene)nickel, $Ni(cod)_2$, in benzene. It is probably formed by twofold insertion of unsaturated nickel intermediates into the zinc–cyclopentadienyl bond of $(cp)_2Zn$.[2] The cyclopentadienyl groups in this cluster are very closely packed and it might be expected that the use of substituted cyclopentadienylzinc compounds in the reaction with $Ni(cod)_2$ would prevent the formation of the complete cluster and give rise to more open structures. To this end, we studied the reaction of $(C_5Me_5)_2Zn$† with $Ni(cod)_2$.

When a 1 : 1 molar mixture of these compounds in benzene was heated at 60 °C for 24 h, a dark red solution containing a black precipitate was obtained. Concentration of the supernatant solution *in vacuo* to half its volume resulted in the precipitation of a ruby-red crystalline compound in >30%

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† $(C_5Me_5)_2Zn$ was prepared by the reaction of C_5Me_5Na with zinc chloride in tetrahydrofuran at room temperature; details of the preparation and properties of $(C_5Me_5)_2Zn$ will be published shortly.

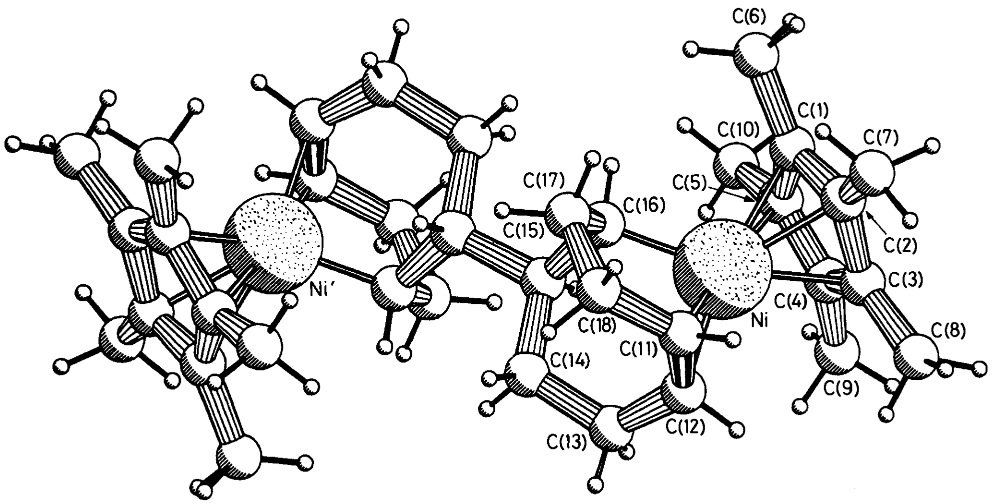
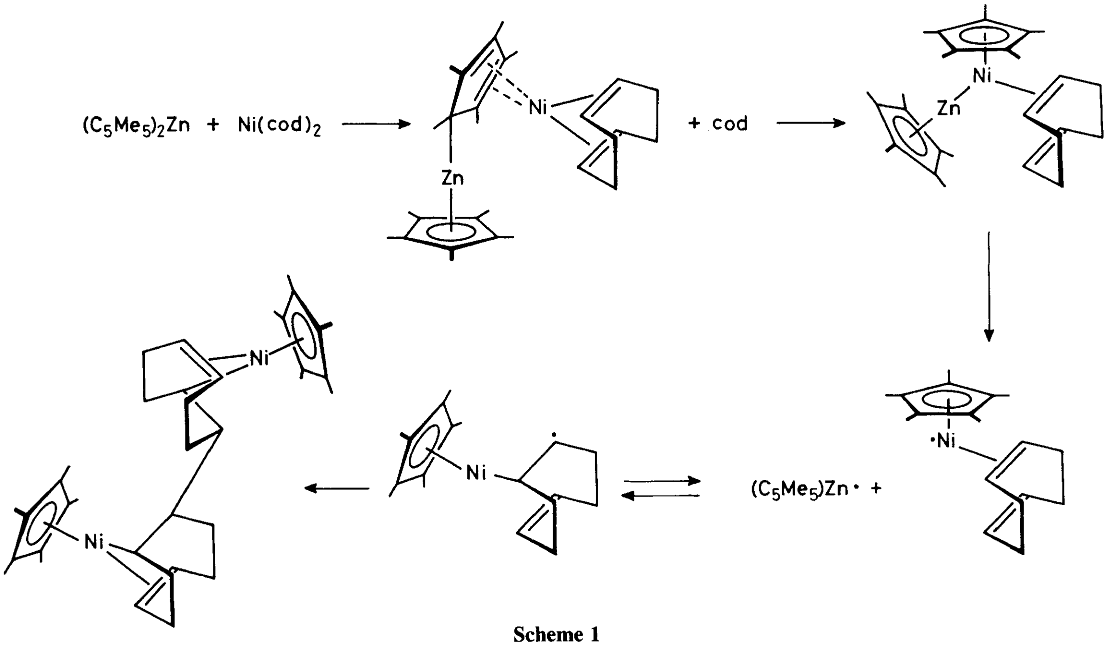


Figure 1. Drawing of the dimer located on a crystallographic inversion centre illustrating the overall geometry of $(C_5Me_5Ni)_2C_{16}H_{24}$. Relevant bond distances (Å): Ni–C(1): 2.116(5); Ni–C(2): 2.176(6); Ni–C(3): 2.141(6); Ni–C(4): 2.139(5); Ni–C(5): 2.089(5); Ni–C(11): 1.989(6); Ni–C(12): 1.982(5); Ni–C(16): 1.955(6); C(1)–C(2): 1.382(8); C(2)–C(3): 1.441(7); C(3)–C(4): 1.430(8); C(4)–C(5): 1.400(7); C(5)–C(1): 1.487(7).



Scheme 1

yield. This compound contains nickel, but is zinc-free. It is stable towards oxidation and hydrolysis and even resists aqueous HCl. Its composition and structure were established by *X*-ray analysis.‡

The compound consists of two C_5Me_5Ni fragments bonded to a 16 carbon diene formed by dimerisation of two cod molecules (Figure 1). Each nickel atom is co-ordinated to a C_5Me_5 ring in a slightly asymmetric fashion and is bonded to the cod dimer by an Ni–C σ-bond and an Ni(C=C) π-bond. The asymmetry of the C_5Me_5–nickel interaction is apparent from the variation in the distances between the nickel and the C_5Me_5 ring carbon atoms (2.089—2.176 Å) and from the differences in the carbon–carbon bond lengths within the C_5Me_5 ring. There are two short C–C bonds [C(1)–C(2) and C(4)–C(5)] and three long C–C bonds [C(3)–C(4), C(2)–C(3), and C(1)–C(5)]. The nickel is pseudo-tetrahedrally surrounded by C(16) and the centres of the bonds between C(1)–C(2), C(4)–C(5), and C(11)–C(12). Similar asymmetric bonding of nickel to a cyclopentadienyl ring was found in $(C_5H_5NiC_3H_4)_2$.[3] The asymmetry can be rationalized in terms of the tendency of d^{10} nickel to attain tetrahedral co-ordination.

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‡ *Crystal data:* $C_{36}H_{54}Ni_2$, $M = 604.25$, monoclinic, space group $A2/a$, $a = 13.210(1)$, $b = 9.457(1)$, $c = 27.081(1)$ Å, $\beta = 112.26(1)°$, $U = 3131.0(5)$ Å^3, $Z = 4$, $D_c = 1.282$ g cm^{-3}, $D_m = 1.29$ g cm^{-3}, $F(000) = 1304$ electrons, Ni-filtered Cu-K_α radiation, $\lambda = 1.5418$ Å, μ(Cu-K_α) = 14.9 cm^{-1}. The structure was solved by Patterson and Fourier methods and refined by least-squares techniques to $R = 0.059$ for 2177 reflections with $I > 2.5\,\sigma(I)$, (CAD4F, ω–2θ scan, θ <70°). Hydrogen atoms were located from a difference Fourier map. 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.

The bonding of the cod dimer to nickel is similar to that proposed for the cyclo-octenyl ligand in $C_5H_5NiC_8H_{13}$,[4] obtained from the reaction of cyclopentadiene with $Ni(cod)_2$,§ and that between a cod moiety and Pt in $[Pt\{1,4\text{-}(4\text{-}NO_2C_6H_4)_2N_4\}\{CHC(PEt_3)H(CH_2)_2CH{=}CHCH_2CH_2\}(PEt_3)]$.[5] In the latter compound, the cod moiety is coupled to PEt_3 at the same position as where in the title compound the C–C linkage between the cod fragments is found.

This unprecedented coupling between cod ligands bound to nickel may be explained by a homolytic cleavage of the zinc–nickel bond in a $C_5Me_5Zn{-}Ni(C_5Me_5)(cod)$ intermediate (Scheme 1).

The data were collected by Dr. A. J. M. Duisenberg. Part of this work (A. L. S.) was supported by The Netherlands Foundation for Chemical Research (SON) with financial aid from The Netherlands Organization for the Advancement of Pure Research (ZWO).

Received, 21st March 1985; Com. 378

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§ C_5Me_5 does not react with $Ni(cod)_2$, even upon heating at 50 °C for 17 h in benzene solution.