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Preliminary communication

PREPARATION AND CRYSTAL STRUCTURE OF [μ-Ni(C_5H_5)P(C_6H_5)$_3$] [μ-C_5H_5] [ZnC_5H_5]$_2$, A NICKEL-BRIDGED CYCLOPENTADIENYLZINC DIMER

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Summary

[μ-Ni(C_5H_5)P(C_6H_5)$_3$] [μ-C_5H_5] [ZnC_5H_5]$_2$ has been obtained from the reaction of Cp_2Zn with Ni(COD)$_2$ in the presence of Ph_3P and its structure determined by X-ray crystallography. It consists of two cyclopentadienylzinc moieties bridged by the Ni atom of a $CpNiPPh_3$ group and by a Cp group. A possible mechanism for the formation of the compound is discussed.

We recently reported the formation of the nickel-zinc cluster compound $Cp_6Ni_2Zn_4$ from dicyclopentadienylzinc and di-1,5-cyclooctadienenickel [1]. In a study of the scope of this type of reaction we have treated Cp_2Zn with Ni(COD)$_2$ in the presence of triphenylphosphine and obtained a new nickel-zinc compound. When a solution of 3.2 g (12.5 mmol) of Ph_3P in 50 ml of benzene was added in the course of 2 h to a stirred suspension of 4.88 g (25.0 mmol) of Cp_2Zn and 3.43 g (12.5 mmol) of Ni(COD)$_2$ in 30 ml of benzene at room temperature, a dark-red mixture was formed. This was stirred for 16 h, then the solvent was removed in vacuo and the product was washed twice with 30 ml of pentane. Dark-red crystals of the product, I, were obtained by recrystallization from hot benzene.

The structure of I was determined by X-ray diffraction. The molecule contains two zinc atoms held together by a bridging cyclopentadienyl group and the nickel atom of a $CpNiPPh_3$ group, and each zinc atom has a terminal cyclopentadienyl group attached to it. A PLUTO drawing of the molecule is shown in Fig. 1. Selected bond distances and bond angles are given in Table 1.

Crystal data: $C_{38}H_{35}PNiZn_2$, monoclinic, space group $P2_1/a$ with a 19.54(5), b 18.28(3), c 9.22(2) Å and β 104.6(2)°, V 3186(12) Å^3, $Z = 4$. The data were collected on an ENRAF—NONIUS CAD4F diffractometer using Mo-K_α radiation; the structure was solved by standard Patterson and Fourier methods. Because of the poor quality of the data set*, only the metal atoms and the phosphorus atom were refined anisotropically. The phenyl groups, the Cp(Ni) group and the bridging Cp(Zn) group were refined as rigid hexagons and pentagons. The positional and thermal parameters of the carbon atoms of the terminal Cp(Zn) groups were all refined independently.

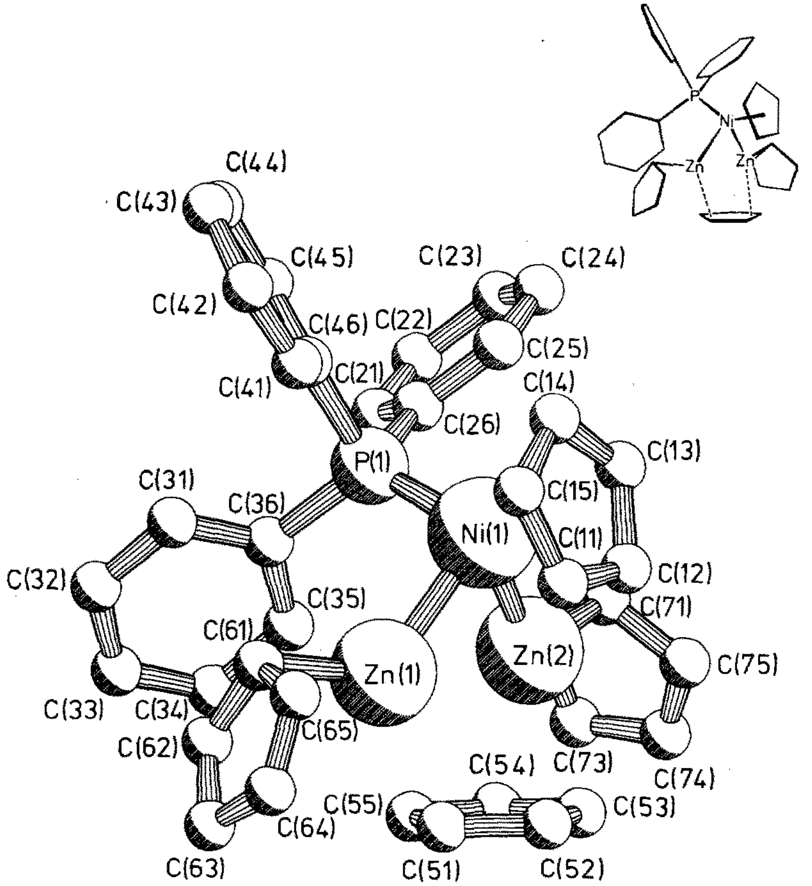

Fig. 1. PLUTO drawing of $Cp_3Zn_2Ni(Cp)PPh_3$.

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*The crystals of I were very brittle and all of the several crystals examined showed reflections which were split into four or more components in an irregular way. These splitting were attributed to the presence of internal fractures, which appear to be an inherent property of the crystals. The usual method of correcting intensities for background radiation could not be used because in numerous cases one component of a reflection appeared in the part of the scan normally used for a background estimate. Therefore, "uncontaminated" background scans were used to construct a continuous background as a function of θ, and this was used to correct the observed reflection intensities. Subsequent data reduction was carried out in the usual way. Further details of this structure determination may be obtained from one of the authors (ALS)**.

TABLE 1

SELECTED BOND DISTANCES AND BOND ANGLES IN $Cp_3Zn_2Ni(Cp)PPh_3$

Bond distances (Å)

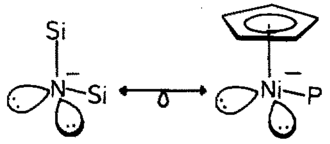
Ni(1)—Zn(1)	2.379(5)	Zn(1)—Zn(2)	2.967(5)	Zn(2)—C(54)	2.18(2)
Ni(1)—Zn(2)	2.383(5)	Zn(1)—C(51)	2.24(2)	Zn(2)—C(53)	2.44(2)
Ni(1)—P(1)	2.12(1)	Zn(1)—C(55)	2.44(2)	Zn(2)—C(71)	2.09(4)
Ni(1)—C(11)	2.11(3)	Zn(1)—C(61)	2.01(4)	Zn(2)—C(72)	2.66(4)
Ni(1)—C(12)	2.08(3)	Zn(1)—C(62)	2.61(4)	Zn(2)—C(75)	2.64(4)
Ni(1)—C(13)	2.08(2)	Zn(1)—C(65)	2.61(4)	C(71)—C(72)	1.39(6)
Ni(1)—C(14)	2.12(2)	C(61)—C(62)	1.38(6)	C(72)—C(73)	1.33(6)
Ni(1)—C(15)	2.14(3)	C(62)—C(63)	1.41(6)	C(73)—C(74)	1.40(7)
P(1)—C(26)	1.80(2)	C(63)—C(64)	1.41(6)	C(74)—C(75)	1.29(6)
P(1)—C(36)	1.83(2)	C(64)—C(65)	1.33(5)	C(75)—C(71)	1.38(6)
P(1)—C(46)	1.86(2)	C(65)—C(61)	1.37(6)		

Selected bond angles (°)

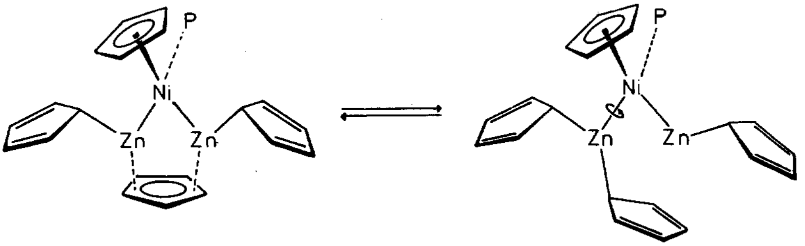
Zn(1)—Ni(1)—Zn(2)	77.1(2)	Ni(1)—Zn(1)—C(51)	122.2(6)
Zn(1)—Ni(1)—P(1)	92.8(3)	Ni(1)—Zn(1)—C(61)	124(1)
Zn(2)—Ni(1)—P(1)	95.3(3)	C(51)—Zn(1)—Z(61)	111(1)
Ni(1)—P(1)—C(26)	112.3(9)	Ni(1)—Zn(2)—C(54)	127.5(5)
Ni(1)—P(1)—C(36)	119.4(7)	Ni(1)—Zn(2)—C(71)	119(1)
Ni(1)—P(1)—C(46)	112.9(9)	C(54)—Zn(2)—C(71)	114(1)
C(26)—P(1)—C(36)	104(1)		
C(26)—P(1)—C(46)	103(1)		
C(36)—P(1)—C(46)	104(1)		

Hydrogen atoms were placed at calculated positions and assigned a thermal parameter of 0.07 Å^2. The refinement converged at R_F = 0.087, R_{wF} = 0.075.

The structure of I strongly resembles that of $[\mu\text{-}N(SiMe_3)_2][\mu\text{-}C_5H_5]\text{-}[ZnC_5H_5]_2$ (II) [2]. This analogy can be rationalized by noting that the $Ni(Cp)PPh_3$ group and the $N(SiMe_3)_2$ group are isolobal [3]. The fragment $Ni(Cp)PPh_3^-$, like the anion $N(SiMe_3)_2^-$, has two lone pairs pointing in the right directions to form a bridge between the two zinc atoms of a Cp_3Zn_2 fragment:



The NMR spectra of II at room temperature showed separate resonances due to the terminal and bridging cyclopentadienyl groups, and exchange between the two positions was observed only at elevated temperatures [2]. The NMR spectra of I at room temperature show only one resonance for the zinc-bound cyclopentadienyl groups (^{1}H: δ 6.23 (s) ppm; ^{13}C: δ 109.7 (s) ppm in C_6H_6 relative to $(CH_3)_4Si$), indicating that the activation energy for exchange is less than ca. 13 kcal/mol, compared to ca. 17 kcal/mol for II [2] (low temperature spectra of I could not be obtained because of the low solubility of this compound). The most probable mechanism for the exchange involves opening of the cyclopentadienyl bridge:



The observed difference in behaviour between I and II indicates that the cyclopentadienyl bridge is appreciably weaker in I. The reason for this is not clear at present.

The surrounding of the nickel atom in I can best be compared with that of the cobalt atom in $(C_5H_5Zn)_2Co(C_5H_5)PPh_3$ (III) [4]. Indeed, the fragments $Co(C_5H_5)PPh_3{}^{2-}$ and $Ni(C_5H_5)PPh_3{}^{-}$ are isoelectronic, and a comparison of relevant bond lengths and bond angles (Table 2) shows that the $Zn_2M(C_5H_5)P$ cores of both molecules are rather similar.

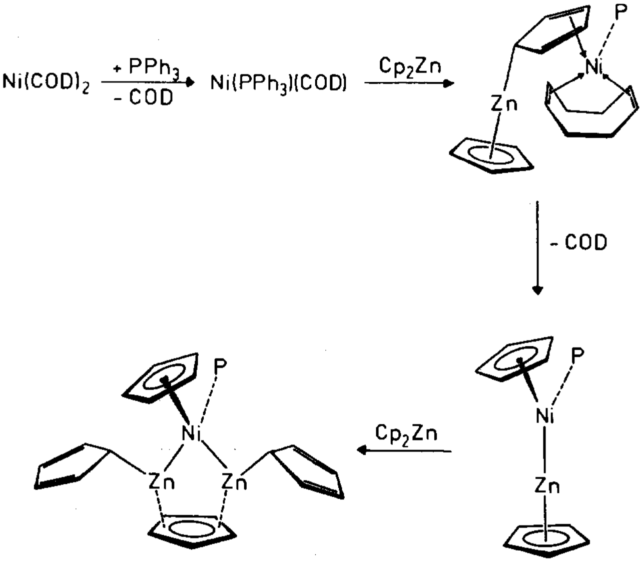
TABLE 2

GEOMETRICAL DATA FOR THE $Zn_2M(Cp)P$ FRAGMENTS OF $(CpZn)_2Co(Cp)PPh_3$ AND $Cp_3Zn_2Ni(Cp)PPh_3$

M	Bond lengths			Angles	
	M—Zn (Å)	M—P (Å)	M—Cp (Å)[a]	ZnMZn (°)	ZnMP (°)
Co	2.288, 2.289	2.12	1.69	74.9	91.4, 86.0
Ni	2.379, 2.383	2.12	1.72	77.1	92.8, 95.3

[a] Perpendicular M—Cp ring-plane distance.

SCHEME 1



The formation of I from Cp_2Zn, $Ni(COD)_2$ and PPh_3 can be rationalized in terms of the insertion of a coordinatively unsaturated nickel species into the Cp—zinc bond of Cp_2Zn, analogous to the processes proposed for the formation of III [5] and $Cp_6Ni_2Zn_4$ [1b,5]. The first step must be the displacement of a COD ligand of $Ni(COD)_2$ by a PPh_3 molecule, to give a 16-electron nickel complex. This can coordinate with Cp_2Zn, and then loss of the second COD ligand is followed by insertion into the Cp—zinc bond. The resulting nickel-zinc complex finally picks up a second molecule of Cp_2Zn to form I (Scheme 1).

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**The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.