

SYNTHESIS AND REACTIVITY TOWARDS Ni(COD)₂ OF SUBSTITUTED
DICYCLOPENTADIENYLZINC COMPOUNDS;
CRYSTAL STRUCTURES OF ZINC-NICKEL CLUSTERS

Zn₄Ni₂(η⁵-C₅H₄*t*-Bu)₄(η¹-C₅H₄*t*-Bu)₂
AND Zn₄Ni₂(η⁵-C₅H₄SiMe₃)₂(η³-C₅H₄SiMe₃)₂(η¹-C₅H₄SiMe₃)₂

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RÉSUMÉ. — De nouveaux complexes cyclopentadiényles substitués du zinc Zn(C₅H₄R)₂ (R = Me, *t*-Bu, SiMe₃) ont été synthétisés. Leur réaction avec Ni(COD)₂ conduit aux clusters Zn₄Ni₂(C₅H₄R)₆ avec des rendements qui diminuent fortement lorsqu'on augmente l'encombrement stérique du groupe R. Les clusters sont formés par deux insertions successives du nickel dans la liaison Zn-Cp suivies d'une dimérisation de deux espèces radicalaires. Les structures moléculaires de Zn₄Ni₂(C₅H₄R)₆, pour R = *t*-Bu et SiMe₃, ont été déterminées et comparées à celle de Zn₄Ni₂Cp₆. Ces structures sont inhabituelles du fait de la présence de différents modes de coordination (η⁵, η³ et η¹) des ligands cyclopentadiényles pour des métaux des groupes principaux. Zn₄Ni₂(C₅H₄*t*-Bu)₆ cristallise dans le système monoclinique, groupe P2₁/c. Paramètres de maille *a* = 12,00 (1) Å, *b* = 17,43 (1) Å, *c* = 13,44 (2) Å, β = 112,81 (5)°, *Z* = 2, *R* final 0,077. Zn₄Ni₂(C₅H₄SiMe₃)₆ cristallise dans le même système monoclinique, groupe P2₁/c. Paramètres de maille *a* = 12,45 (5) Å, *b* = 18,539 (5) Å, *c* = 13,504 (5) Å, β = 112,21 (5)°, *Z* = 2, *R* final 0,090.

ABSTRACT. — The new substituted cyclopentadienylzinc compounds Zn(C₅H₄R)₂ (R = Me, *t*-Bu, SiMe₃) were synthesized. Their reaction with Ni(COD)₂ afforded cluster compounds Zn₄Ni₂(C₅H₄R)₆ whose yields drop dramatically with increasing bulk of the group R. These clusters are formed *via* two consecutive insertions of a Ni centre into a Zn-Cp bond followed by a dimerization of two radical species. The crystal structures of Zn₄Ni₂(C₅H₄R)₆ (R = *t*-Bu and SiMe₃) were determined and they are compared with those of the parent compound Zn₄Ni₂Cp₆. These structures are unprecedented in showing examples of η⁵, η³ and η¹ coordination of the cyclopentadienyl groups to a main group metal. Crystals of Zn₄Ni₂(C₅H₄*t*-Bu)₆ are monoclinic, space group P2₁/c, with *a* = 12.00 (1) Å, *b* = 17.43 (1) Å, *c* = 13.44 (2) Å, β = 112.81 (5)°, *Z* = 2. The structure was refined to *R* = 0.077. Crystals of Zn₄Ni₂(C₅H₄SiMe₃)₆ are monoclinic, space group P2₁/c, with *a* = 12.455 (5) Å, *b* = 18.539 (5) Å, *c* = 13.504 (5) Å, β = 112.21 (5)°, *Z* = 2. The structure was refined to *R* = 0.090.

Introduction

Our current studies of catalytic activities of mixed organo-metallic compounds are primarily concerned with cyclopentadienyl compounds containing transition and main group metals. The preparation and crystal structure determination of the cluster compound Zn₄Ni₂Cp₆ (Cp = cyclopentadienyl) was reported recently¹. Some preliminary experiments were

carried out to determine the catalytic effects of this cluster in oligo- or polymerisation reactions of heteroatom-substituted alkenes and alkynes. One might expect catalytic activity for this cluster compound since substrates can be doubly activated: once at the heteroatomic site by zinc and once at the unsaturated site by nickel. No special catalytic activity was observed, however, and the slight activity observed in a few cases was probably due to active nickel species formed by decomposition of the cluster.

As can be seen from a space-filling model (Fig. 1) of the cluster, the Cp-rings are "locked" together and completely shield the metal octahedron.

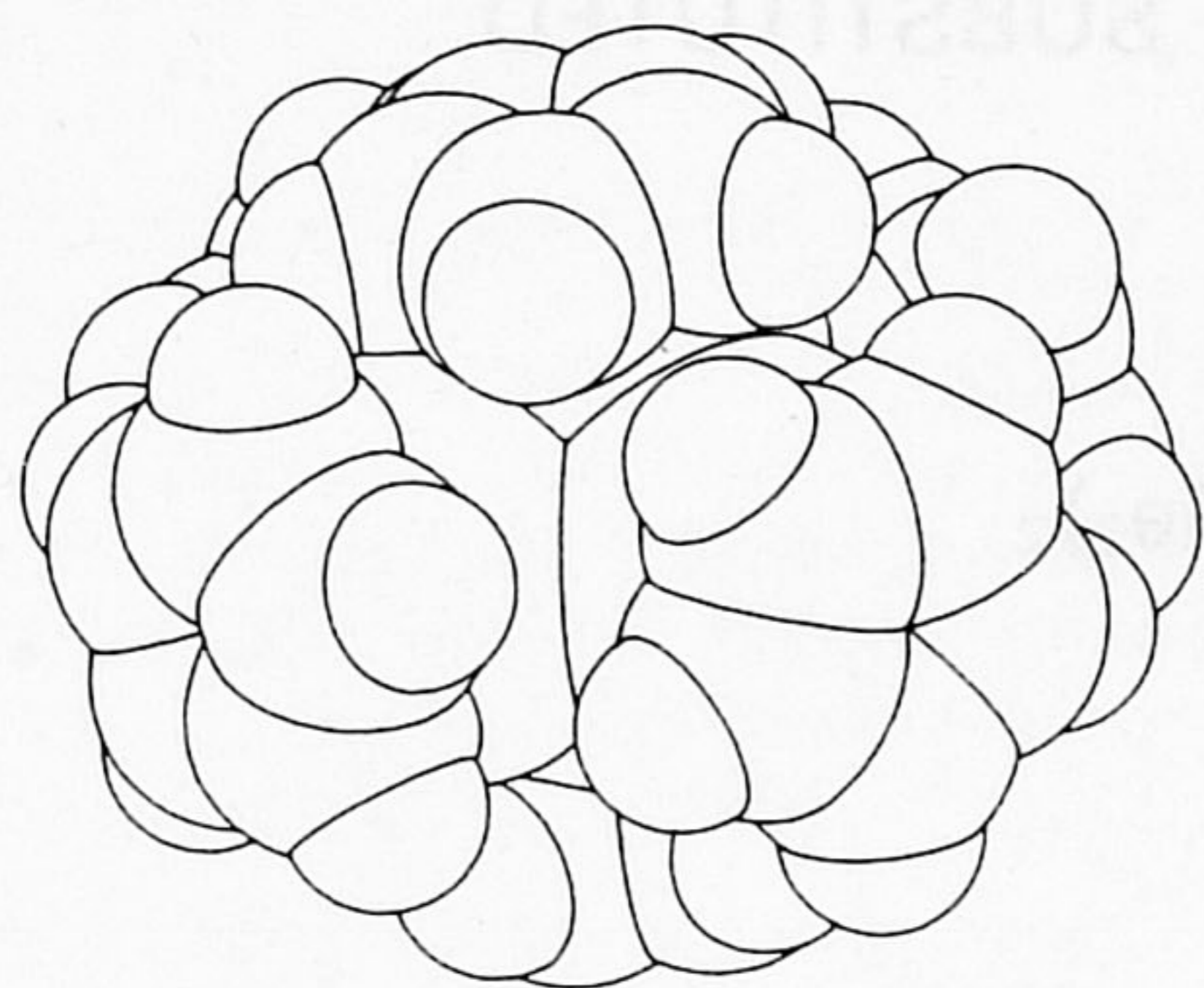


Figure 1. — Space filling model of the cluster compound $Zn_4Ni_2Cp_6$.

Since the lack of catalytic activity could result from the very compact structure of the cluster, we have investigated the influence of substituents in the cyclopentadienyl rings on the course of the cluster formation reaction. The presence of one or more substituents might well prevent the final formation of a cluster like $Zn_4Ni_2Cp_6$ — which is thought to arise from the dimerization of two Zn_2NiCp_3 radical species (Fig. 4) — and result in more open, reactive species. To this end we have prepared some substituted cyclopentadienylzinc starting compounds *i. e.* $Zn(C_5H_4Me)_2$, $Zn(C_5H_4t-Bu)_2$ and $Zn(C_5H_4SiMe_3)_2$ and reacted them with $Ni(COD)_2$ (COD = 1,5-cyclooctadiene). The synthesis of $Zn(C_5Me_5)_2$ and its reaction with $Ni(COD)_2$ to form the interesting product $[(NiC_5Me_5)_2C_{16}H_{24}]$ was reported earlier².

Results

SYNTHESES AND REACTIONS OF SUBSTITUTED DICYCLOPENTADIENYLZINC COMPOUNDS

Bis(methylcyclopentadienyl)zinc is easily prepared by treating methylcyclopentadienyl-sodium with a half equivalent of dry zinc dichloride in diethyl ether.

Bis(*tert*-butylcyclopentadienyl)zinc and bis(trimethylsilylcyclopentadienyl)zinc are prepared similarly by reacting the potassium salts of the corresponding substituted cyclopentadienes in tetrahydrofuran (THF) with a half equivalent of zinc dichloride. These new zinc compounds are white, air and moisture sensitive, solids which were principally characterized by ^{13}C - and 1H -NMR (Table I).

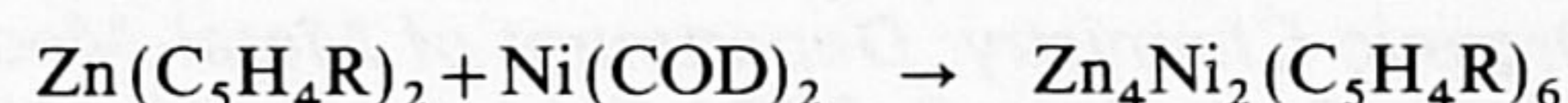
The reactions of these three di(substituted-cyclopentadienyl)zinc compounds with $Ni(COD)_2$ in benzene afforded the new green cluster compounds $[Zn_4Ni_2(C_5H_4R)_6]$, in

Table I. — $^1H^a$ - and $^{13}C^b$ -NMR data of $(C_5H_4R)_2Zn^c$.

	R	δ -Cp-Zn		δ -R
1H	I, H	5.86(s)		—
	II, Me	5.44(t, 2H)	5.29(t, 2H)	3.13(s, 3H)
	III, <i>t</i> -Bu	5.78(t, 2H)	5.00(t, 2H)	1.22(s, 9H)
	IV, SiMe ₃	6.31(s, 2H)	5.56(s, 2H)	0.15(s, 9H)
^{13}C	I, H	107.45		—
	II, Me	129.48	106.29 101.07	14.50
	III, <i>t</i> -Bu	145.29	108.85 95.10	32.04 ^d
	IV, SiMe ₃	121 ^e	116.22 104.76	-0.06

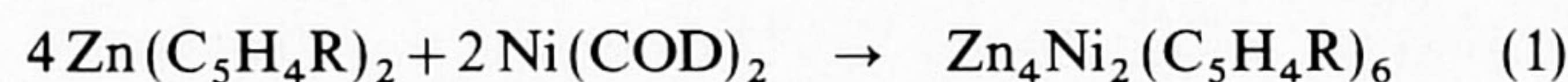
^a 200 MHz, ^b 50.2 MHz, ^c In THF-d₈, 20°C, relative to TMS. s : singlet, t : triplet, ^d the quaternary carbon atom was not observed. ^e broad.

Table II. — Yield of zinc-nickel cluster compounds in the reaction:



R	Temperature (°C)	Reaction time (h)	Yield (%)
I, H	75	2	67
II, Me	75	4	30
III, <i>t</i> -Bu	80	16	11
IV, SiMe ₃	80	16	12

yields which are very dependent on the group R (Table II, Equation 1):



I : R = H, II : R = Me, III : R = *t*-Bu, IV : R = SiMe₃.

These thermally stable clusters share the same metal/ligand stoichiometry as $Zn_4Ni_2Cp_6$, obtained from the reaction of $ZnCp_2$ with $Ni(COD)_2$. All these mixed metal clusters are air and moisture sensitive green solids. The products were characterized by ^{13}C and 1H NMR spectroscopy and the relevant NMR data are gathered in Table III.

In the product forming reactions, significant amounts of other products are formed. When R was H, up to 17% of nickelocene and traces of metallic zinc were found. Similarly when R was Me, about 10% of $Ni(C_5H_4Me)_2$ was recovered and the balance of the metals was recovered as metallic zinc and nickel. However, from the reactions where R was *t*-Bu or SiMe₃, only traces of the corresponding nickelocenes were found and the remaining metal was recovered in elemental form.

These reactions affording cluster compounds should be compared with the reaction of bis(pentamethylcyclopentadienyl)zinc with $Ni(COD)_2$ which resulted in a totally different product *i. e.* the organonickel compounds $[(NiC_5Me_5)_2C_{16}H_{24}]$, in which two NiC_5Me_5 moieties are bridged by a

Table III. — $^1H^a$ and $^{13}C^b$ NMR data of $(C_5H_4R)_6Zn_4Ni_2^c$.

	R	δ -Cp-Zn	δ -Cp-Ni	δ -R (Cp-Zn)	δ -R (Cp-Ni)
1H	I, H	6.23(s, 20H)	4.64(s, 10H)	—	—
	II, Me	6.31(m, 8H), 6.19(m, 8H)	4.79(s, 8H)	2.52(s, 12H)	2.02(s, 6H)
	III, <i>t</i> -Bu	6.63(m, 8H), 6.50(m, 8H)	5.00(m, 4H), 4.80(m, 4H)	1.65(s, 36H)	1.35(s, 18H)
	IV, SiMe ₃	6.43(m, 8H), 6.35(m, 8H)	5.05(m, 4H), 4.88(m, 4H)	0.45(s, 36H)	0.30(s, 18H)
^{13}C	I, H	106.9	88.5	—	—
	II, Me	110.6, 102.9 ^d	89.4, 84.0 ^d	16.3	15.5
	III, <i>t</i> -Bu	112.9, 102.2 ^d	84.4, 80.4 ^d	32.9	32.9
	IV, SiMe ₃	109.2, 107.4 ^d	87.7, 86.7 ^d	1.8	1.8

^a 200 MHz. ^b 50.2 MHz. ^c in C_6D_6 , 20°C, relative to TMS. s : singlet, m : multiplet. ^d The quaternary carbon atoms were not detected.

dimer of COD. The preparation and crystal structure of this latter species have been reported³.

To establish the effect of substituents in the cyclopentadienyl rings upon the structure and bonding of the cluster compounds, suitable crystals of $Zn_4Ni_2(C_5H_4 t-Bu)_6$ and $Zn_4Ni_2(C_5H_4SiMe_3)_6$ were grown from pentane and X-ray diffraction studies were carried out.

CRYSTAL STRUCTURES OF $Zn_4Ni_2(\eta^5-C_5H_4 t-Bu)_4(\eta^1-C_5H_4 t-Bu)_2$ (III) AND $Zn_4Ni_2(\eta^5-C_5H_4SiMe_3)_2(\eta^1-C_5H_4SiMe_3)_2$ (IV)

Crystals of (III) and (IV) are isomorphous and the monoclinic unit cell in both cases contains two hexanuclear molecules with no short intermolecular contacts. The molecular structures of the clusters differ principally only in the bonding of the peripheral cyclopentadienyl groups to the octahedral Zn_4Ni_2 metal core. Bond distances are presented in Tables IV and V.

Table IV. — Bond distances (Å) for $Zn_4Ni_2(C_5H_4 t-Bu)_6$.

Zn(2)–Zn(3)	2.811(5)	C(14)–C(15)	1.41(5)
Zn(2)–Zn(3')	2.917(5)	C(16)–C(17)	1.50(3)
Zn(2)–Ni(1)	2.392(5)	C(16)–C(18)	1.57(3)
Zn(2)–Ni(1')	2.435(5)	C(16)–C(19)	1.57(3)
Zn(2)–C(21)	2.39(2)	C(21)–C(22)	1.38(4)
Zn(2)–C(22)	2.46(3)	C(21)–C(25)	1.34(4)
Zn(2)–C(23)	2.40(4)	C(21)–C(26)	1.48(4)
Zn(2)–C(24)	2.28(2)	C(22)–C(23)	1.42(4)
Zn(2)–C(25)	2.27(3)	C(23)–C(24)	1.39(5)
Zn(3)–Ni(1)	2.375(5)	C(24)–C(25)	1.42(4)
Zn(3)–Ni(1')	2.399(5)	C(26)–C(27)	1.46(4)
Zn(3)–C(33)	2.08(2)	C(26)–C(28)	1.57(3)
Ni(1)–Ni(1')	2.575(5)	C(26)–C(29)	1.48(5)
Ni(1)–C(11)	2.07(3)	C(31)–C(32)	1.39(4)
Ni(1)–C(12)	2.08(3)	C(31)–C(35)	1.42(4)
Ni(1)–C(13)	2.10(2)	C(31)–C(36)	1.40(4)
Ni(1)–C(14)	2.08(3)	C(32)–C(33)	1.40(5)
Ni(1)–C(15)	2.09(3)	C(33)–C(34)	1.42(5)
C(11)–C(12)	1.36(4)	C(34)–C(35)	1.41(4)
C(11)–C(15)	1.32(4)	C(36)–C(37)	1.49(4)
C(11)–C(16)	1.49(3)	C(36)–C(38)	1.52(3)
C(12)–C(13)	1.38(4)	C(36)–C(39)	1.50(4)
C(13)–C(14)	1.34(4)	–	–

Symmetry code: $' = 2 - x, -y, 2 - z$.

Description of the molecular structures

I. The metal core. — In both the *t*-Bu- (III) and the SiMe₃-cluster (IV) the metal core is an octahedron with the two nickel atoms occupying apical sites above and below a square of zinc atoms. The Ni–Ni and Ni–Zn edge distances are around 2.4 and 2.6 Å, respectively.

When these structures are compared with that of the parent $Zn_4Ni_2Cp_6$, it appears that substitution in the cyclopentadienyl rings has little effect on the geometry of the metal core itself. The largest bondlength differences for comparable bonds within the cores of the three clusters are only about 0.05 Å.

The largest differences in comparable bond angles (Ni–Zn–Ni, Zn–Ni–Zn) are less than 4°.

II. Cyclopentadienyl groups bonded to nickel. — The bonding of the cyclopentadienyl rings to nickel in the three clusters is very similar — always η^5 - and the effect of different substi-

Table V. — Bond distances (Å) for $Zn_4Ni_2(C_5H_4SiMe_3)_6$.

Zn(2)–Zn(3)	2.818(4)	Si(2)–C(28)	1.88(2)
Zn(2)–Zn(3')	2.976(3)	Si(2)–C(29)	1.75(4)
Zn(2)–Ni(1)	2.428(3)	Si(3)–C(31)	1.81(2)
Zn(2)–Ni(1')	2.433(4)	Si(3)–C(37)	1.85(2)
Zn(2)–C(21)	2.14(2)	Si(3)–C(38)	1.77(3)
Zn(2)–C(22)	2.38(2)	Si(3)–C(39)	1.86(2)
Zn(2)–C(25)	2.45(2)	C(11)–C(12)	1.41(3)
Zn(3)–Ni(1)	2.389(3)	C(11)–C(15)	1.34(3)
Zn(3)–Ni(1')	2.425(3)	C(12)–C(13)	1.46(3)
Zn(3)–C(33)	2.06(2)	C(13)–C(14)	1.35(3)
Ni(1)–Ni(1')	2.569(4)	C(14)–C(15)	1.54(3)
Ni(1)–C(11)	2.08(3)	C(21)–C(22)	1.38(4)
Ni(1)–C(12)	2.11(1)	C(21)–C(25)	1.49(4)
Ni(1)–C(13)	2.09(2)	C(22)–C(23)	1.35(5)
Ni(1)–C(14)	2.13(2)	C(23)–C(24)	1.29(6)
Ni(1)–C(15)	2.09(3)	C(24)–C(25)	1.39(3)
Si(1)–C(11)	1.91(2)	C(31)–C(32)	1.32(4)
Si(1)–C(17)	1.89(2)	C(31)–C(35)	1.42(3)
Si(1)–C(18)	1.87(2)	C(32)–C(33)	1.38(3)
Si(1)–C(19)	1.91(3)	C(33)–C(34)	1.51(4)
Si(2)–C(21)	1.83(2)	C(34)–C(35)	1.30(4)
Si(2)–C(27)	1.83(3)		

Symmetry code: $' = 2 - x, -y, 2 - z$.

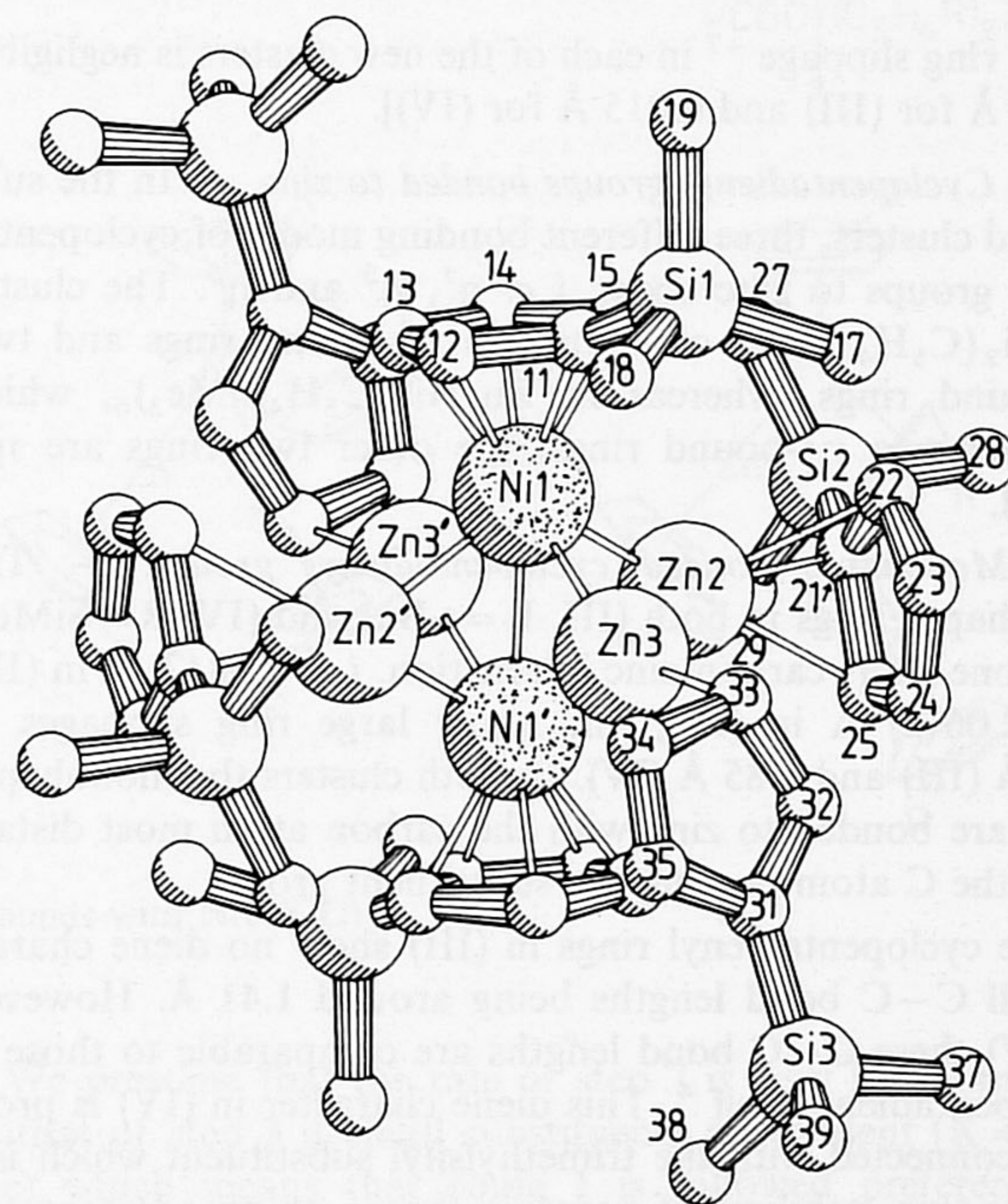


Figure 2. — Crystal structure of $Zn_4Ni_2(\eta^5-C_5H_4 t-Bu)_4(\eta^1-C_5H_4 t-Bu)_2$.

tuents on the structural parameters is small. There is a trend towards somewhat stronger and more symmetric bonding upon introduction of a bulky substituent in the cyclopentadienyl rings.

In (I), (R=H), the mean carbon-nickel distance for the pentahapto bound cyclopentadienyl ring is 2.12 Å, with individual distances ranging from 2.06(4) to 2.18(4) Å. In (III), (R=*t*-Bu), the mean carbon-nickel distance has decreased to 2.08 Å and bondlength differences are within the e. s. d. (0.03 Å). For (IV), (R=SiMe₃) the situation is intermediate; the mean carbon-nickel distance is 2.10 Å and bondlength differences are again within the e. s. d. (0.03 Å). In the latter compound the C–C distances in the Cp-ring suggest some diene character.

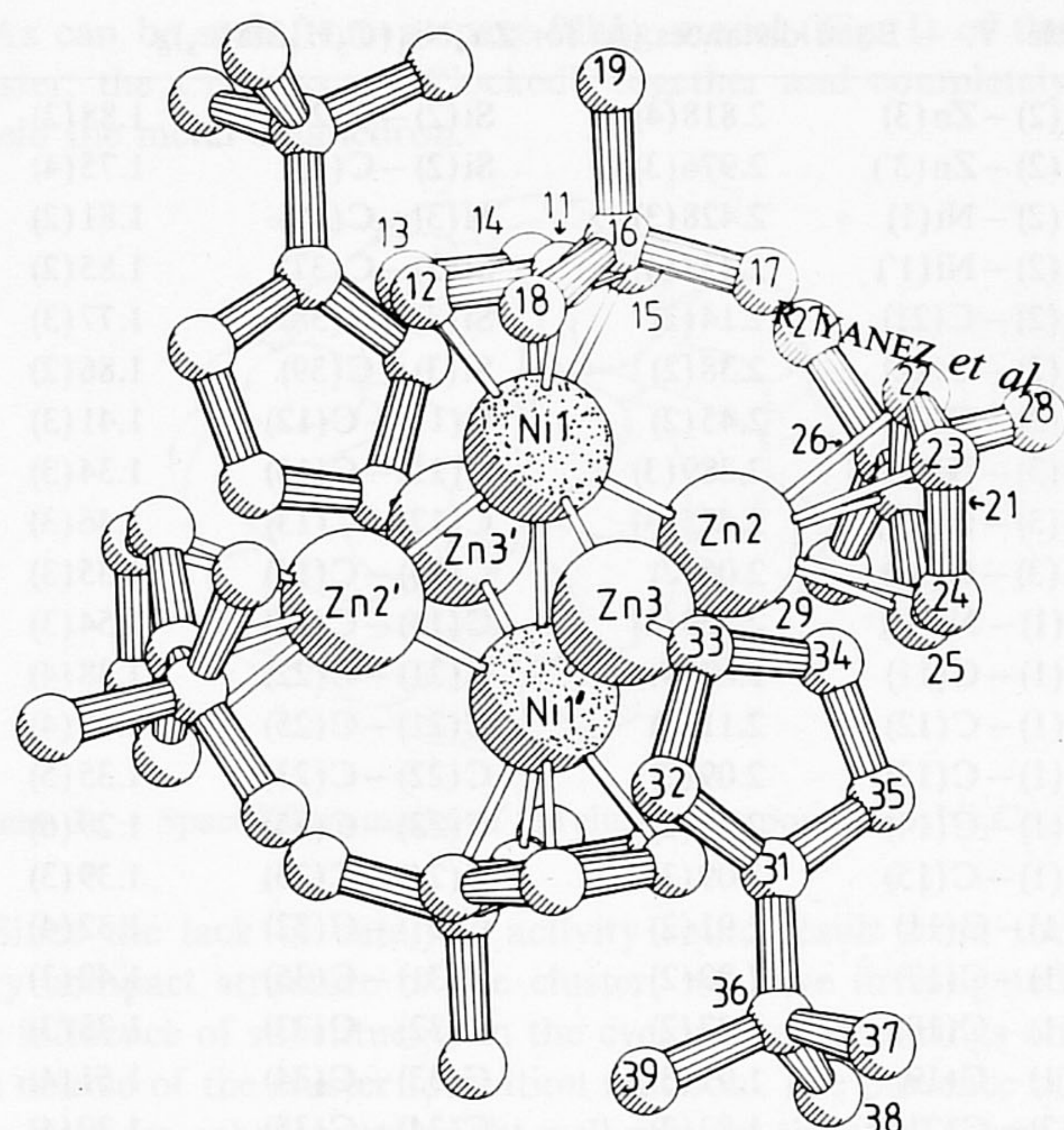


Figure 3. — Crystal structure of $Zn_4Ni_2(\eta^5-C_5H_4SiMe_3)_2(\eta^3-C_5H_4SiMe_3)_2(\eta^1-C_5H_4SiMe_3)_2$.

The ring slippage¹⁷ in each of the new clusters is negligible [0.009 Å for (III) and 0.015 Å for (IV)].

III. Cyclopentadienyl groups bonded to zinc. — In the substituted clusters, three different bonding modes of cyclopentadienyl groups to zinc occur, *i.e.* η^1 , η^3 and η^5 . The cluster $Zn_4Ni_2(C_5H_4t-Bu)_6$ contains two η^1 -bound rings and two η^5 -bound rings, whereas in $Zn_4Ni_2(C_5H_4SiMe_3)_6$, which also has two η^1 -bound rings, the other two rings are η^3 -bound.

(i) **Monohapto bonded cyclopentadienyl groups.** — The monohapto rings in both (III, $R=t-Bu$) and (IV, $R=SiMe_3$) have one short carbon-zinc interaction, *i.e.* 2.08(2) Å in (III) and 2.06(2) Å in (IV), and show large ring slippages of 1.88 Å (III) and 1.85 Å (IV). In both clusters the monohapto rings are bonded to zinc with the carbon atom most distant from the C atom bearing the substituent group.

The cyclopentadienyl rings in (III) show no diene character, all C—C bond lengths being around 1.41 Å. However, in (IV) these C—C bond lengths are comparable to those in cyclopentadiene itself⁴. This diene character in (IV) is probably connected with the trimethylsilyl substituent which is a well-known stabilizer of negative charge on an adjacent carbon atom⁵ and which may limit the delocalization of negative charge over the ring. Since the zinc atom will interact more strongly with the carbon atom bearing the largest negative charge it is to be expected to find the zinc atom bonded to the trimethylsilyl substituted carbon atom as was found for the monohapto ring in gaseous $Zn(C_5H_4SiMe_3)_2$ ². This is not the case in (IV) and we attribute this to steric factors. Molecular models show that there is insufficient space between the ligands to accommodate either the ring itself or the $SiMe_3$ group if the cyclopentadienyl ring were bonded *via* C(31).

There is a large (70(1)°) angle between the zinc-carbon bond and the ring plane of this cyclopentadienyl group in both (III) and (IV). For a purely covalent Zn—C bond an angle of 54° would be expected and therefore the amount of covalent character in the ring-zinc interaction is relatively small.

(ii) **Trihapto bonded cyclopentadienyl groups.** — The trihapto bonded cyclopentadienyl rings in (IV), ($R=SiMe_3$) are bonded to zinc *via* the carbon atom bearing the $SiMe_3$ group and the two adjacent carbon atoms. There are one short (2.14(2) Å) and two long [2.38(2) and 2.45(2) Å] zinc-carbon interactions. The shortest Zn—C distance is with the carbon atom adjacent to silicon, as would be expected. The other two zinc-carbon distances are clearly non bonding [2.71(2) and 2.77(2) Å]. The C—C ring bond distances (Table IV) indicate some diene character. The ring slippage is 0.72 Å, well in accord with trihapto bonding and there is no evidence for a covalent bonding interaction. The angle between the carbon-silicon bond and the plane of the cyclopentadienyl ring is small, *i.e.* 15(1)°, indicative of a predominantly sp^2 hybridisation of C(21). In the case of a covalent zinc-cyclopentadienyl interaction C(21) would be more sp^3 hybridized and the latter bond angle would show a value closer to 54°.

(iii) **Pentahapto bonded cyclopentadienyl groups.** — The pentahapto rings in (III), ($R=t-Bu$) are quite similar to those in the parent cluster $Zn_4Ni_2Cp_6$ and show the same mean carbon-zinc distance of 2.36 Å. The pentahapto character is also evident in the small ring slippage of 0.20 Å and the equivalence of the C—C bond lengths [all *ca.* 1.38(4) Å].

To our knowledge, these clusters are the first examples of cyclopentadienyl main-group metal derivatives in which the cyclopentadienyl groups are η^1 , η^3 , and η^5 bound. The apparent ease with which these cyclopentadienyl groups are able to change their hapticity is in accord with appreciable ionic character of the zinc-ring interaction. Another indication for the ionic character of this interaction is the absence of ring puckering in the trihapto bonded case. The covalently, η^3 bonded cyclopentadienyl ring in $Cp_2W(CO)_2$ shows a puckering of 20°⁶. In the two known crystal structures containing an η^3 -bonded indenyl group puckering also occurs, *i.e.* 28.5° in $(\eta^3-C_9H_7)Ir(PR_3)_3$ ⁷ and 26° in $(\eta^3-C_9H_7)(\eta^5-C_9H_7)W(CO)_2$ ⁸.

Discussion

The reactions of various substituted cyclopentadienyl zinc compounds with $Ni(COD)_2$ give rise to some spectacular hexanuclear bimetallic clusters and bimetallic homonuclear compounds and provide further support for the mechanisms proposed earlier for the formation of $Zn_4Ni_2Cp_6$ ¹ and $(NiC_5Me_5)_2C_{16}H_{24}$ ².

The main trend in the reactions of substituted cyclopentadienylzinc compounds with $Ni(COD)_2$ is a steep decline in cluster yield with increasing substituent bulk. In the most extreme case, *i.e.* $Zn(C_5Me_5)_2$, no cluster is formed at all and a zinc-free dinickel compound is obtained instead. In all reactions, the balance of the zinc and nickel present in the starting materials is recovered as zinc and nickel metal and traces of nickelocenes are found as byproducts. These observations can be explained by assuming a reaction mechanism that somewhere along the line branches into two competing routes. The actual product distribution will be determined by the relative rates of the reactions involved in the branches (see Fig. 4).

Reaction route I leads to zinc-nickel clusters *via* displacement of a nickel bonded COD ligand by a cyclopentadienyl group of $Zn(C_5H_4R)_2$ (step 1), followed by an insertion of Ni into the Zn—C₅H₄R bond (step 2). Loss of the remaining COD molecule and coordination of a second molecule of

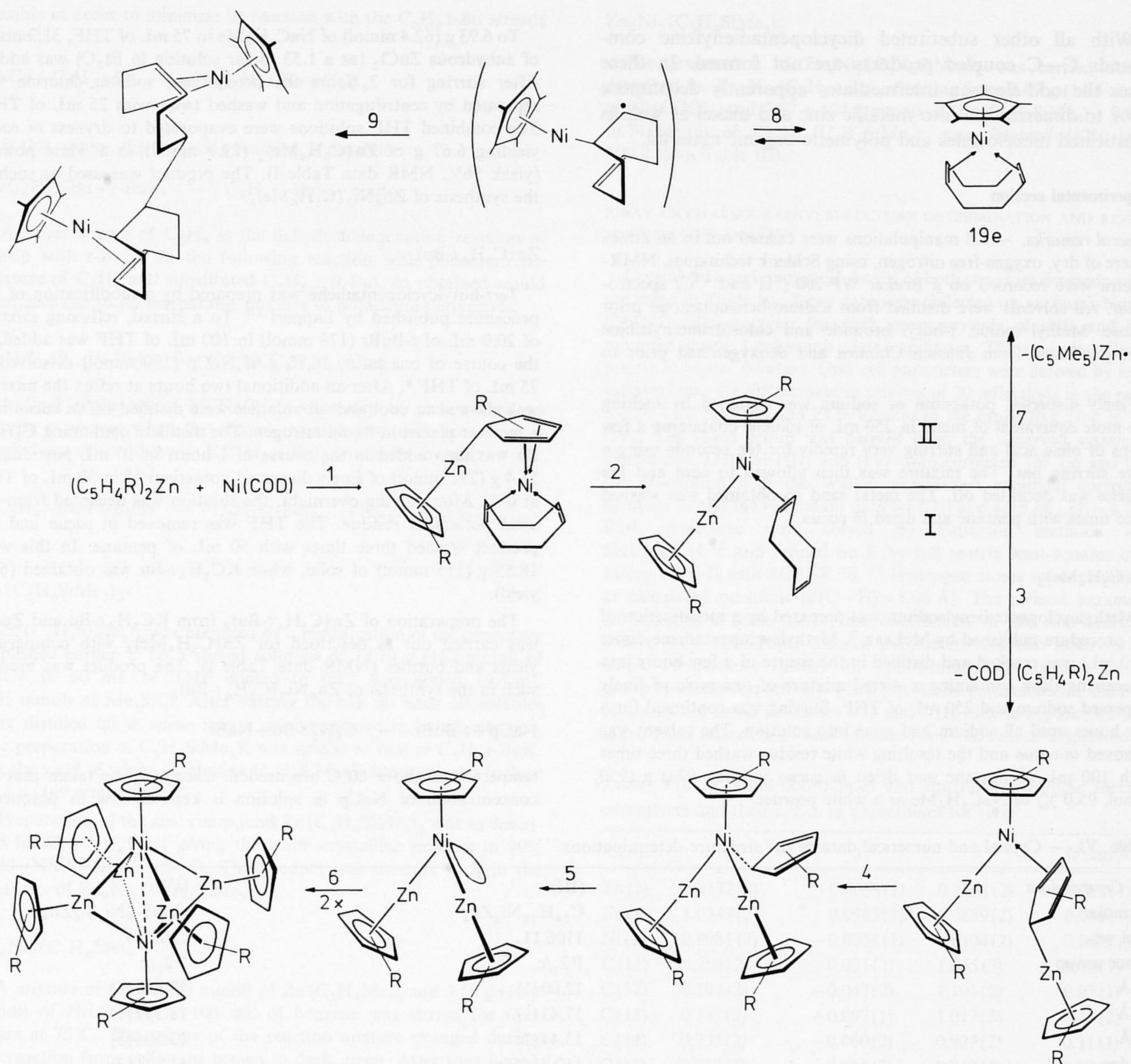


Figure 4. — General scheme for the reaction of dicyclopentadienylzinc compounds with $\text{Ni}(\text{COD})_2$.

$\text{Zn}(\text{C}_5\text{H}_4\text{R})_2$ (step 3), followed by another insertion of Ni into the $\text{Zn}-\text{C}_5\text{H}_4\text{R}$ bond (step 4) and subsequent homolytic cleavage of a $\text{Ni}-\text{C}_5\text{H}_4\text{R}$ bond (step 5) leads to odd-electron heterotrimeric $\text{Zn}_2\text{Ni}(\text{C}_5\text{H}_4\text{R})_3$ species. These species dimerize in the final stage to give $\text{Zn}_4\text{Ni}_2(\text{C}_5\text{H}_4\text{R})_6$ (step 6).

In reaction route II the first two reaction steps are the same as in route I. The following reaction step is, however, not the cleavage of the $\text{Ni}-\text{COD}$ bond (step 3) but instead a homolytic cleavage of the $\text{Zn}-\text{Ni}$ bond (step 7). This provides a 19-e $\text{Ni}(\text{C}_5\text{H}_4\text{R})\text{COD}$ species (or a coordinatively unsaturated 17-e species in the case of a monodentate-bonded COD ligand) which, if sufficiently long-lived, may dimerize to give a C-C coupled product *via* intermediate carbon-centered radicals (step 8). The latter product is accompanied by a quantitative yield of metallic zinc which must result from complete decomposition of an intermediate $\text{Zn}-\text{C}_5\text{Me}_5$ radical.

The main factors that in our opinion govern the relative rates of the steps 3 and 7 (see Fig. 4) and thus the course of the overall reaction, are steric.

We presume that the rate of step 7 is very low compared to that of step 3 if small substituents are present ($\text{R}=\text{H}$ or Me) which means that route I is followed preferentially. When, however, more bulky substituents are present ($\text{R}=\text{t-Bu}$ or SiMe_3) the rate of step 3 is decreased. At the same time, step 7 will, if anything, be promoted by steric interference. The effect will be an increasing preference for route II with increasing size of R. In the extreme case, *i.e.* with $\text{Zn}(\text{C}_5\text{Me}_5)_2$, route I is totally blocked.

Route II will, however, only produce the C-C coupled product if the odd-electron species formed in step 7 survives long enough to dimerize. Apparently, this is the case only in the reaction with $\text{Zn}(\text{C}_5\text{Me}_5)_2$ which gives $(\text{NiC}_5\text{Me}_5)_2\text{C}_{16}\text{H}_{24}$ in relatively good ($\sim 40\%$) yield. The relative stability of the $\text{C}_5\text{Me}_5\text{NiCOD}$ intermediate can be understood in terms of the electron-releasing properties of the C_5Me_5 ligand. In this 19-electron species, the C_5Me_5 ligand acts as a strong electron donor to the nickel and stabilizes the nickel-COD bond by increasing the backdonation from nickel into the two olefinic π^* orbitals.

With all other substituted dicyclopentadienylzinc compounds C–C coupled products are not formed. In these cases the odd-electron intermediates apparently decompose prior to dimerization into metallic zinc and nickel as well as substituted nickelocenes and polymeric organic material.

Experimental section

General remarks. – All manipulations were carried out in an atmosphere of dry, oxygen-free nitrogen, using Schlenk techniques. NMR-spectra were recorded on a Bruker WP-200 (^1H and ^{13}C) spectrometer. All solvents were distilled from sodium/benzophenone prior to use. Methyl iodide, *t*-butyl bromide and chlorotrimethylsilane were purchased from Janssen Chimica and deoxygenated prior to use.

Finely dispersed potassium or sodium was obtained by melting one mole equivalent of metal in 250 mL of toluene containing a few drops of oleic acid and stirring very rapidly for ten seconds using a large stirring bar. The mixture was then allowed to cool and the toluene was decanted off. The metal sand so obtained was washed three times with pentane and dried *in vacuo*.

Zn(C₅H₄Me)₂

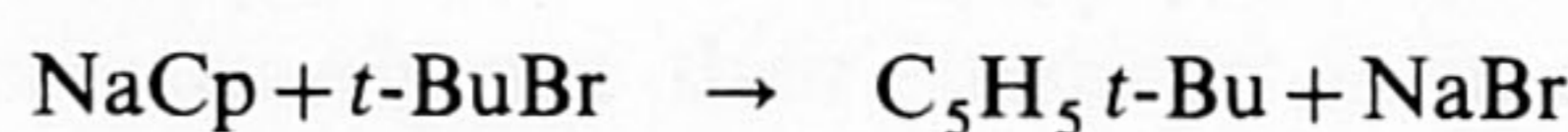
Methylcyclopentadienylsodium was prepared by a modification of the procedure published by McLean⁹. Methylcyclopentadiene-dimer (110 mL) was cracked and distilled in the course of a few hours into a receiving flask containing a stirred mixture of one mole of finely dispersed sodium and 250 mL of THF. Stirring was continued for a few hours until all sodium had gone into solution. The solvent was removed *in vacuo* and the resulting white residue washed three times with 100 mL of pentane and dried *in vacuo* yielding 97.0 g (950 mmol, 95.0%) of NaC₅H₄Me as a white powder.

To 6.93 g (62.4 mmol) of NaC₅H₄Me in 75 mL of THF, 31.2 mmol of anhydrous ZnCl₂ (as a 1.53 molar solution in Et₂O) was added. After stirring for 2 hours the precipitated sodium chloride was separated by centrifugation and washed twice with 25 mL of THF. The combined THF solutions were evaporated to dryness *in vacuo* yielding 6.67 g of Zn(C₅H₄Me)₂ (29.9 mmol) as a white powder (yield: 96%, NMR data Table I). The product was used as such in the synthesis of Zn₄Ni₂(C₅H₄Me)₆.

Zn(C₅H₄*t*-Bu)₂

Tert-butylcyclopentadiene was prepared by a modification of the procedure published by Lappert¹⁰: To a stirred, refluxing mixture of 20.0 mL of *t*-BuBr (178 mmol) in 100 mL of THF was added, in the course of one hour, 16.73 g of NaCp (190 mmol) dissolved in 75 mL of THF*. After an additional two hours at reflux the mixture was allowed to cool and all volatiles were distilled off *in vacuo* into a receiver placed in liquid nitrogen. The distillate containing C₅H₅*t*-Bu was then added in the course of 1 hour, in 10 mL portions, to 11.4 g (291 mmol) of finely dispersed potassium¹⁸ in 50 mL of THF at 0°C. After stirring overnight, the solution was decanted from the solid potassium residue. The THF was removed *in vacuo* and the product washed three times with 50 mL of pentane. In this way, 18.55 g (115 mmol) of solid, white KC₅H₄*t*-Bu was obtained (65% yield).

The preparation of Zn(C₅H₄*t*-Bu)₂ from KC₅H₄*t*-Bu and ZnCl₂ was carried out as described for Zn(C₅H₄Me)₂ with comparable yields and purities (NMR data Table I). The product was used as such in the synthesis of Zn₄Ni₂(C₅H₄*t*-Bu)₆.



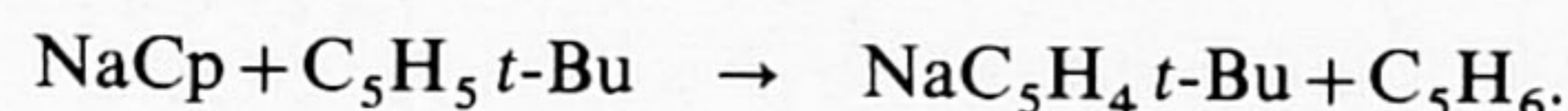
temperatures above 60°C are needed. Care must be taken that the concentration of NaCp in solution is kept as low as practically

Table VI. – Crystal and numerical data of the structure determinations.

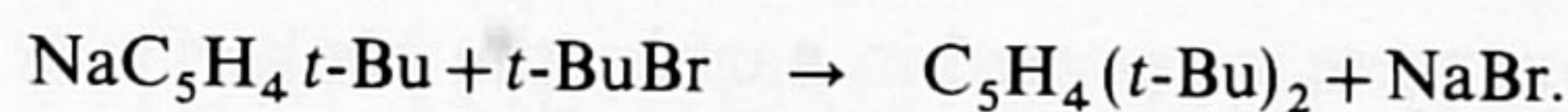
(a) Crystal data	(III)	(IV)
formula	C ₅₄ H ₇₈ Ni ₂ Zn ₄	C ₄₈ H ₇₈ Ni ₂ Si ₆ Zn ₄
mol wt.	1106.11	1202.56
space group	P2 ₁ /c	P2 ₁ /c
<i>a</i> , Å	12.00(1)	12.455(4)
<i>b</i> , Å	17.43(1)	18.539(5)
<i>c</i> , Å	13.44(2)	13.504(5)
β, deg	112.81(5)	112.21(3)
<i>V</i> , Å ³	2591(5)	2887(2)
<i>Z</i>	2	2
<i>D_x</i> , g·cm ⁻³	1.418	1.383
F(000), electrons	1156	1252
μ, cm ⁻¹	26.2 (MoKα)	40.0 (CuKα)
crystal size, mm	0.18 × 0.25 × 0.28	0.15 × 0.38 × 0.48
(b) Data collection (295 K)		
Radiation, Å	MoKα (Zr), 0.71073	CuKα (Ni), 1.5418
θ _{min} , θ _{max} (°)	0.1, 20	2.4, 50
Scan type	ω	ω/2θ
ω/2θ-scan (°)	1.30 + 0.35 tan θ	Δω = 0.80 + 0.15 tan θ
hor. and vert. apert., mm	3, 5	3, 5
data set, <i>h</i> , <i>k</i> , <i>l</i>	–11 : 11; –16 : 0; –12 : 12	0 : 12; –18 : 0; –13 : 12
reference reflections	1–1–1; –1–1 1	200; 020; 004
total data, unique data	5055, 2427	3093, 2961
observed data (<i>I</i> > 2.5 σ(<i>I</i>))	1397	2080
Total Xray Exposure time (h)	132	57
(c) Refinement		
No. of refined parameters	300	300
weighting scheme, w ⁻¹	σ ² (F)	σ ² (F)
<i>R</i> , <i>R_w</i>	0.077, 0.032	0.090, 0.091
(Δ/σ) av	0.1	0.06
min., max. res. dens. (e/Å ³)	1.08, –0.74	1.20, –0.84

*Due to the sluggish reaction of NaCp with *t*-BuBr.

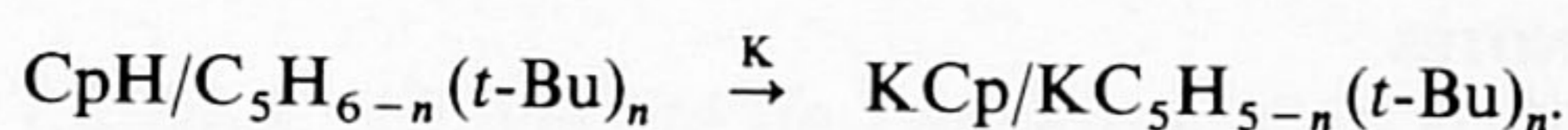
feasible in order to minimize its reaction with the C_5H_5 -*t*-Bu already formed:



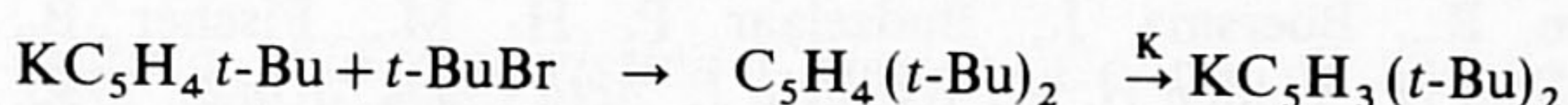
If this occurs, the following reaction is possible:



Another source of C_5H_6 is the dehydrohalogenation reaction of NaCp with *t*-BuBr. In the following reaction with potassium the mixture of C_5H_6 and substituted $C_5H_{6-n}(t-Bu)_n$ so obtained would then give rise to an inseparable mixture of potassium-derivatives:



A final slight excess of NaCp is necessary to ensure that no *t*-BuBr is present when the second reaction step with potassium is carried out since otherwise $KC_5H_3(t-Bu)_2$ would be formed:



$Zn(C_5H_4SiMe_3)_2$

$Zn(C_5H_4SiMe_3)_2$ was prepared by a modification of the procedure published earlier². To a stirred solution of 14.79 g (167 mmol) of NaCp in 60 mL of THF cooled to 0°C, was added 19.7 mL (155 mmol) of Me_3SiCl . After stirring for half an hour all volatiles were distilled off *in vacuo* into a receiver placed in liquid nitrogen. The preparation of $C_5H_4SiMe_3K$ was similar to that of $C_5H_4-t-BuK$, but the yield of white, crystalline $C_5H_4SiMe_3K$ however, was higher: 26.3 g (149 mmol, 96%).

Preparation of the zinc compound $Zn(C_5H_4SiMe_3)_2$ was as described for $Zn(C_5H_4Me)_2$ giving the white crystalline product in 90% yield (NMR data Table I). The product was used as such in the synthesis of $Zn_4Ni_2(C_5H_4SiMe_3)_6$.

$Zn_4Ni_2(C_5H_4Me)_6$

A mixture of 6.1 g (27.3 mmol) of $Zn(C_5H_4Me)_2$ and 3.58 g (13.0 mmol) of $Ni(COD)_2$ in 100 mL of benzene was stirred for four hours at 75°C. The colour of the reaction mixture changed during the reaction from yellow to brown to dark green. After four hours, the reaction mixture was centrifuged to separate the solution from the deposited zinc and nickel metal. The residue was washed twice with 40 mL of benzene and the combined benzene solutions evaporated to dryness *in vacuo*. The residue was washed twice with 30 mL of pentane to remove $Ni(C_5H_4Me)_2$ and twice with 30 mL of a 3 : 1 diethyl ether/THF mixture to remove unreacted $Zn(C_5H_4Me)_2$. Drying *in vacuo* yielded 1.88 g (2.21 mmol) of dark-green crystalline $Zn_4Ni_2(C_5H_4Me)_6$ (34% yield, NMR data Table III, element. anal. calc. : C 50.7, H 5.0, Ni 13.8, Zn 30.6; found: C 50.84, H 5.30, Ni 13.0, Zn 28.9).

$Zn_4Ni_2(C_5H_4-t-Bu)_6$

A stirred mixture of 4.20 g (15.3 mmol) of $Ni(COD)_2$ and 7.69 g (24.9 mmol) of $Zn(C_5H_4-t-Bu)_2$ in 100 mL benzene was heated to reflux. After four hours the yellow reaction mixture started to slowly turn green. Heating was continued for ca. 4 hours until no more $Ni(COD)_2$ could be detected by ¹H NMR. The reaction mixture was then cooled and centrifuged to remove the deposited zinc and nickel metal, which were washed twice with 50 mL of benzene. The combined benzene fractions were dried *in vacuo* yielding a viscous green oil. Addition of 70 mL of pentane to this oil afforded dark green crystals at -40°C. The pentane solution was decanted and stored at -40°C for 48 hours, yielding another crop of green crystals, giving a total yield of 0.76 g (0.68 mmole, 11%) of $Zn_4Ni_2(C_5H_4-t-Bu)_6$ (NMR data table III).

$Zn_4Ni_2(C_5H_4SiMe_3)_6$

The preparation of $Zn_4Ni_2(C_5H_4SiMe_3)_6$ was carried out as described for $Zn_4Ni_2(C_5H_4-t-Bu)_6$. Starting from 3.69 g (14.4 mmol) of $Ni(COD)_2$ and 7.97 g (24.6 mmol) of $Zn(C_5H_4SiMe_3)_2$, 0.89 g (0.74 mmol) of $Zn_4Ni_2(C_5H_4SiMe_3)_6$ was obtained (12% yield, NMR data Table III).

X-RAY CRYSTALLOGRAPHY: STRUCTURE DETERMINATION AND REFINEMENT OF (III) AND (IV)

Crystal data and numerical details of both structure determinations are listed in Table VI. X-ray data were collected on an Enraf-Nonius CAD4F diffractometer for dark green crystals of (III) and (IV) mounted inside Lindemann glass capillaries. The crystals reflected poorly at higher θ -values. Unit cell parameters were derived by least-squares from the diffractometer settings of 20 reflections in the range $8 < 2\theta < 24^\circ$ for (III) and 23 reflections in the range $20 < 2\theta < 36^\circ$ for (IV). The space group was derived from the observed systematic extinctions. Data of (III) and (IV) were corrected for Lp and (IV) for absorption with the Walker and Stuart empirical correction method¹¹, and the redundant data set (III) averaged ($R_{av}(I) = 8.7\%$). Both structures were solved by Patterson methods with SHELXS 84¹² and refined on F by full matrix least-squares on a Micro VAX-II with SHELX 76.¹³ Hydrogen atoms were introduced at calculated positions [$d(C-H) = 1.08 \text{ \AA}$]. The refined parameter set included a scale factor, the coordinates of the non-hydrogen atoms, their anisotropic thermal parameters and two separate isotropic temperature factors for cyclopentadienyl-ring and methyl group H-atoms respectively. Final positional parameters for the non-H atoms are listed in Tables VII and VIII. Scattering factors were taken from reference 14 and corrected for anomalous dispersion¹⁵.

Table VII. — Final coordinates and equivalent isotropic thermal parameters and their e. s. d. in parentheses for (III)

Atom	x	y	z	U(eq) Å ²
Zn(2)	0.9172(2)	0.0668(1)	0.8668(2)	0.083(1)
Zn(3)	1.0349(2)	0.0965(1)	1.0889(2)	0.076(1)
Ni(1)	0.8981(2)	-0.0058(1)	1.0104(2)	0.062(1)
C(11)	0.756(2)	0.021(1)	1.055(3)	0.09(1)
C(12)	0.804(2)	-0.047(2)	1.101(2)	0.07(1)
C(13)	0.787(2)	-0.097(1)	1.017(3)	0.11(2)
C(14)	0.735(2)	-0.060(2)	0.923(2)	0.11(1)
C(15)	0.712(2)	0.015(2)	0.949(2)	0.09(1)
C(16)	0.728(2)	0.081(1)	1.121(2)	0.08(1)
C(17)	0.725(2)	0.161(1)	1.079(1)	0.09(1)
C(18)	0.819(2)	0.085(1)	1.242(1)	0.10(1)
C(19)	0.602(1)	0.070(1)	1.129(2)	0.11(1)
C(21)	0.806(2)	0.103(1)	0.683(2)	0.09(1)
C(22)	0.728(3)	0.119(2)	0.733(2)	0.14(2)
C(23)	0.792(3)	0.178(2)	0.805(2)	0.10(1)
C(24)	0.907(3)	0.190(1)	0.807(2)	0.08(1)
C(25)	0.912(2)	0.140(2)	0.725(2)	0.09(1)
C(26)	0.753(2)	0.049(2)	0.592(2)	0.12(1)
C(27)	0.666(2)	-0.009(2)	0.594(2)	0.25(2)
C(28)	0.691(2)	0.100(1)	0.489(1)	0.17(1)
C(29)	0.856(3)	0.017(2)	0.571(2)	0.21(2)
C(31)	1.252(2)	0.253(1)	1.181(2)	0.09(2)
C(32)	1.203(3)	0.204(2)	1.235(2)	0.11(1)
C(33)	1.078(3)	0.192(1)	1.189(3)	0.10(2)
C(34)	1.044(2)	0.242(2)	1.099(3)	0.13(2)
C(35)	1.147(3)	0.277(1)	1.093(2)	0.11(1)
C(36)	1.370(2)	0.280(2)	1.206(2)	0.10(1)
C(37)	1.383(2)	0.362(1)	1.241(2)	0.15(1)
C(38)	1.403(2)	0.272(1)	1.108(2)	0.12(1)
C(39)	1.465(2)	0.236(1)	1.294(2)	0.16(2)

$$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

Table VIII. — Final coordinates and equivalent isotropic thermal parameters and their e. s. d. in parentheses for (IV)

Atom	x	y	z	U(eq) Å ²
Zn(2)	0.9051(2)	0.0696(1)	0.8795(2)	0.074(1)
Zn(3)	1.0284(2)	0.0855(1)	1.1013(2)	0.068(1)
Ni(1)	0.9082(2)	-0.0150(1)	1.0178(2)	0.072(1)
Si(1)	0.7384(5)	0.0699(3)	1.1642(5)	0.069(3)
Si(2)	0.7157(8)	0.0827(4)	0.6203(6)	0.113(4)
Si(3)	1.3379(5)	0.2846(3)	1.2084(5)	0.073(3)
C(11)	0.781(2)	0.0014(9)	1.080(2)	0.045(6)
C(12)	0.838(1)	-0.064(1)	1.121(1)	0.047(6)
C(13)	0.820(2)	-0.109(1)	1.027(2)	0.08(1)
C(14)	0.753(2)	-0.074(1)	0.937(2)	0.064(8)
C(15)	0.730(2)	0.001(1)	0.973(2)	0.07(1)
C(17)	0.716(2)	0.1632(9)	1.103(2)	0.08(1)
C(18)	0.851(2)	0.073(1)	1.303(1)	0.10(1)
C(19)	0.598(2)	0.040(1)	1.178(2)	0.10(1)
C(21)	0.796(2)	0.131(1)	0.745(2)	0.07(1)
C(22)	0.754(2)	0.157(1)	0.819(2)	0.08(1)
C(23)	0.830(4)	0.207(2)	0.879(3)	0.13(2)
C(24)	0.917(3)	0.217(1)	0.851(2)	0.10(1)
C(25)	0.905(2)	0.172(1)	0.765(2)	0.10(1)
C(27)	0.623(3)	0.017(1)	0.651(2)	0.19(2)
C(28)	0.628(2)	0.151(1)	0.519(2)	0.16(1)
C(29)	0.817(3)	0.047(2)	0.572(2)	0.18(2)
C(31)	1.220(2)	0.229(1)	1.213(2)	0.060(8)
C(32)	1.108(2)	0.229(1)	1.155(2)	0.07(1)
C(33)	1.052(2)	0.178(1)	1.192(2)	0.09(1)
C(34)	1.142(3)	0.147(1)	1.292(2)	0.10(1)
C(35)	1.237(2)	0.179(1)	1.297(2)	0.08(1)
C(37)	1.274(2)	0.357(1)	1.109(2)	0.16(2)
C(38)	1.440(2)	0.236(1)	1.173(3)	0.15(2)
C(39)	1.419(2)	0.326(1)	1.341(2)	0.10(1)

$$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

The calculation of geometrical data and the preparation of illustrations were done with the programs PLATON and PLUTON of the EUCLID-package¹⁶.

Supplementary Material

Atomic coordinates for structures III and IV have been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from Dr. Olga Kennard, University Chemical Laboratory, Lensfield Road, Cambridge CB21EW, U.K.

Structure factors and Thermal parameters for III and IV have been deposited with the British Library Document Supply Centre, at Boston Spa, Wetherby, West Yorkshire, U.K.

as supplementary publication No. = SUP 90161 and is available on request from the Document Supply Centre.

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- ¹⁸ The ring slippage is defined as the distance between the ring centroid and the perpendicular projection of the metal atom on the least-squares ring plane.
- ¹⁹ Potassium was necessary since sodium does not react with C₅H₅ *t*-Bu at room temperature. Higher temperatures could not be used because the dimerisation of the cyclopentadiene then becomes competitive.