Reactivity of the Heavier Group-13 Monochlorides $[\{CH(SiMe_3)_2\}_2AlCl]$, InCl, TlCl, and of the Elements Ga and Hg Towards the Unsupported Ni–Ni Bond of $[\{(\eta^5\text{-}Cp)Ni(PEt_3)\}_2]$ – A Straightforward Synthetic Approach to the Synthesis of Mixed Main-Group/Transition-Metal Clusters Containing Unsupported Metal–Metal Bonds☆

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The dinuclear compound $[\{(\eta^5\text{-}Cp)Ni(PEt_3)\}_2]$ (**1**) containing an unbridged Ni–Ni bond reacts with the heavier group 13 monochlorides $[\{CH(SiMe_3)_2\}_2Al^{III}Cl]$, In^ICl, and Tl^ICl by scission of the metal–metal bond. In the case of InCl and TlCl the chloro-bridged dimers $[\{(\eta^5\text{-}Cp)Ni(PEt_3)_2ECl\}_2]$ (E = In **2**, Tl **5**) were formed. The Tl compound **5** is unstable and decomposes via disproportionation and formation of the halogen-free Tl^{III} compound $[\{(\eta^5\text{-}Cp)Ni(PEt_3)\}_3Tl]$ (**6**). **2** can be dehalogenated with activated magnesium to yield the halogen-free In^{III} compound $[\{(\eta^5\text{-}Cp)Ni(PEt_3)\}_3In]$ (**4**). The Ga analogue of **4** and **6** $[\{(\eta^5\text{-}Cp)Ni(PEt_3)\}_3Ga]$ (**7**) is accessible by a conproportionation of **1** with Ga metal in refluxing THF. In contrast to InCl and TlCl the aluminium(III) monochloride $[\{CH(SiMe_3)_2\}_2AlCl]$ reacts with **1** by a ligand redistribution reaction and formation of the salt $[(\eta^5\text{-}Cp)Ni(PEt_3)_2]^+$-$[\{CH(SiMe_3)_2\}_2AlCl_2]^-$ (**8**). Elemental Hg or Mg amalgam show the same activity as elemental Ga towards **1** and insert into the Ni–Ni bond by forming the linear Hg-bridged complex $[\{(\eta^5\text{-}Cp)Ni(PEt_3)\}_2Hg]$ (**9**). The molecular structures of **2**, **4**, **8**, and **9** were determined by X-ray crystallography. The In atom in **4** has a distorted trigonal-planar configuration with the central In atom being surrounded by three $[(\eta^5\text{-}Cp)Ni(PEt_3)]$ fragments. **4** represents the first Ni–In cluster containing exclusively unsupported In–Ni bonds, as well as the first carbonyl-free Ni–In cluster. On the basis of spectroscopic data the same structure is assigned to the Ga and Tl analogues of **4**. The Ni–Hg–Ni arrangement in **9** is exactly linear, as determined by X-ray crystallography.

Introduction

The chemistry of main-group/transition-metal compounds has attracted great interest and has triggered a large amount of research activity in this field over the last decade[1]. Recently, a growing interest in the synthesis of mixed transition-metal/main-group element complexes which are suitable for the deposition of mixed metal/main-group element films has emerged[2]. Compounds containing aluminium, gallium, or indium directly bonded to a transition-metal are currently of interest as potential single-source precursors for the deposition of binary intermetallic phases[3]. This interest stems from the fact that such phases are useful as Schottky barriers and Ohmic contacts for group 13/15 semiconductors[4]. In this paper we present a new synthetic route to compounds containing element combinations which are relevant for such material applications.

Unbridged transition-metal bonds, M–M, exhibit a high reactivity towards insertion and addition reactions of metal–ligand fragments, especially when the M–M bond is polarized, as observed for early-late bimetallic bonds[5] or transition-metal/main-group element bonds[16]. For complexes containing homometallic M–M bonds as in dimers L_xM-ML_y (where $L_x = L_y$), no electronic polarization effects are available to enhance the reactivity and subsequently cleave the particular M–M bond. Drastic reaction conditions are therefore often necessary to enhance the reactivity of these M–M bonds towards insertion or addition reactions. One way to activate such M–M bonds is to sterically overcrowd the ligand L periphery at each $L_{x=y}M$ fragment. This may result in a substantial weakening of the M–M bonding, an increased reactivity, and consequently, a homolytic scission of the particular M–M bond in such complexes.

To this end we have concentrated our activity on the dimeric $[\{(\eta^5\text{-}Cp)Ni(PEt_3)\}_2]$ (**1**), containing an unbridged Ni–Ni bond[7]. Although the length of the M–M bond in **1** is in the usual range for a Ni–Ni single bond and shows no significant elongation, **1** displays an unusually high reactivity with respect to scission of its unbridged Ni–Ni bond.

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[++] X-ray crystallography.

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This may in fact be a result of the sterically crowded environment around both Ni atoms of **1**, as revealed by X-ray crystallography and by ^{1}H-NMR spectroscopy in solution. Rotation of the PEt_3 ligand around the Ni−Ni bond vector is restricted even in solution due to steric hindrance[7].

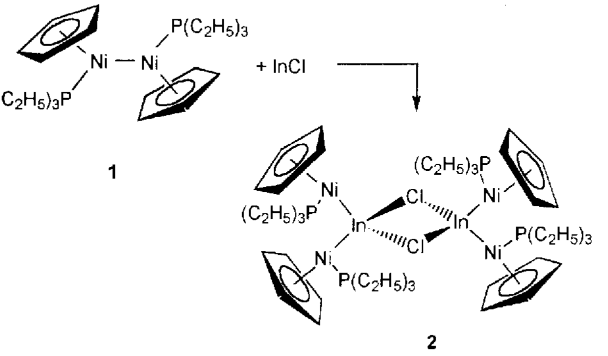
We have found previously that $SnCl_2$ inserts into the Ni−Ni bond of **1** yielding $[\{(\eta^5\text{-Cp})Ni(PEt_3)\}_2SnCl_2]$[7]. Subsequent dehalogenation leads to the stannio(IV) monochloride complex $[\{(\eta^5\text{-Cp})Ni(PEt_3)\}_3SnCl]$[7]. Herein we describe our studies of insertion reactions of **1** with group 13 monochlorides $[\{(Me_3Si)_2CH\}_2AlCl]$, InCl, and TlCl and with elemental Ga and Hg leading to clusters containing unsupported bonds between Ni and these group 13 metals. These reactions represent a new synthetic approach to the synthesis of this type of compounds.

Results and Discussion

Reaction of $[\{\eta^5\text{-Cp})Ni(PEt_3)\}_2]$ (1) with Indium(I) Chloride

1 reacts readily with InCl at room temperature to form a dark orange coloured chloro-bridged In/Ni complex $[\{(\eta^5\text{-Cp})Ni(PEt_3)\}_2InCl]_2$ (**2**) (eq. 1).

Equation 1



2 is stable in solution (toluene or THF) at room temperature or at elevated temperatures; it is slightly soluble in ether and insoluble in pentane. According to an X-ray crystal structure investigation, **2** is dimeric in the solid state (Figure 1)[8].

The two chlorine atoms bridge two individual $[\{(\eta^5\text{-Cp})Ni(PEt_3)\}_2In]$ fragments. The In atoms show a strongly distorted tetrahedral geometry with bond angles Ni1−In−Ni2 136.0(1)°, Ni1,2−In−Cl 106°, Cl−In−Cl 80.2(1)°. The intramolecular In−In distances are nonbonding (4.14 Å). The Ni−In distances [2.495(1) and 2.503(1) Å] are significantly different but are within the range observed for other complexes with Ni−In and In−X (Cl, Br, I) bonding e.g. $[\{(\eta^5\text{-Cp})(CO)_2Fe\}_2\text{-}InCl]_2$[9], $[(C_6H_5)_3(\eta^5\text{-Cp})Ni\text{-}InBr\text{-}\{O{=}P(C_6H_5)_3\}]$[10], and $[(\eta^5\text{-}C_5H_4)(CH_2)_2NMe_2]\text{-}(CH_3)_3\text{-}Ni\text{-}InI_2$[11a]. The two In−Cl distances in **2** are only slightly different [2.678(2) and 2.735(2) Å].

Homometallic M−M bonding in the heavier group-13 organometallics has only recently been established unequivocally[12,13]. However, until now no organometallic derivatives $L_nM'M\text{-}MM'L_n$ with direct M−M bonding between heavier group-13 metals have been known[14]. In an attempt to dehalogenate **2** with activated Mg[15] to obtain a halogen-free cluster containing unsupported Ni−In bonds we obtained the tris(organonickel)-substituted cluster **4**.

Equation 2

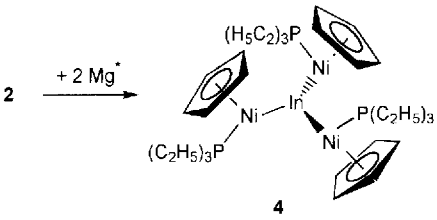
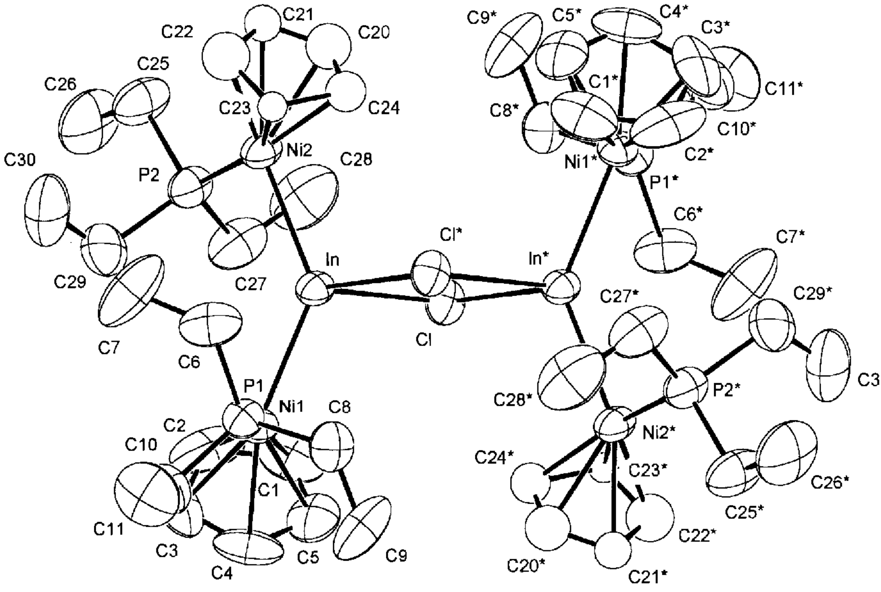


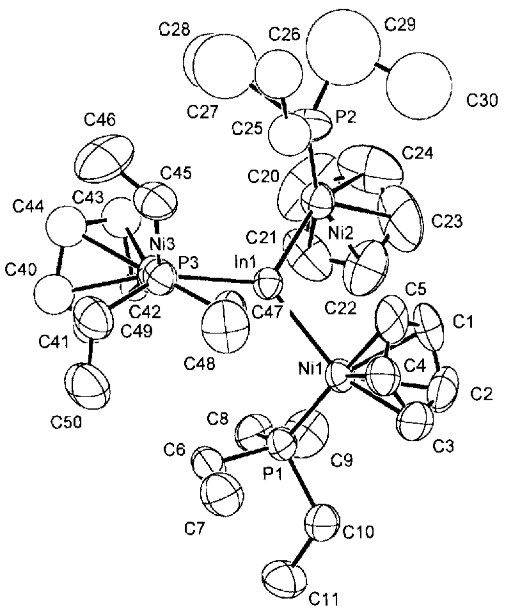
Figure 1. Molecular structure of **2** in the solid state as determined by X-ray crystallography[a]



[a] Selected bond length [Å] and angles [°]: In−Ni1 2.495(1), In-Ni2 2.503(1), In−Cl 2.678(2), In−Cl* 2.735(2), Ni−P1 2.117(2), Ni−P2 2.100(2); Cl−In−Cl* 80.2(1), Cl−In−Ni1 106.4(1), Cl*−In−Ni(1) 107.3(1), P2−Ni2−In 94.4(1), P1−Ni1−In 94.4(1), Cl*−In−Ni2 107.1(1), Cl−In−Ni2 105.6(1), Ni2−In−Ni1 136.0(1), In*−Cl−In 99.9(1).

Its main structural feature is an In atom with trigonal-planar coordination and bond angles Ni1–In–Ni2 113.5(1)°, Ni1–In–Ni3 126.3(1)°, and Ni2–In–Ni3 119.8(1)° as determined by X-ray crystallography (Figure 2).

Figure 2. Molecular structure of **4** in the solid state as determined by X-ray crystallography[a]



[a] Selected bond length [Å] and angles [°]: Ni1–In 2.526(1), Ni2–In1 2.536(1), Ni3–In 2.538(1), Ni1–P1 2.110(2), Ni2–P2 2.080(2), Ni3–P3 2.123(2); Ni(2)–In–Ni(1) 113.5(1), Ni3–In–Ni1 126.3(1), Ni3–In–Ni2 119.9(1), P1–Ni1–In 94.2(1), P2–Ni2–In 95.1(1), P3–Ni3–In1 99.3(1).

In comparison to **4** a nearly ideal trigonal-planar structure with Co–In–Co average bond angles of 119.8° is found for the isostructural cluster $[In\{Co(CO)_4\}_3]$[16] as well as for the mixed organometallic Ru/In cluster $[\{(\eta^5\text{-Cp})Ru(CO)_2\}_3In]$ (Ru–In–Ru 119.9°)[17]. **4** is a member of the group of transition-metal complexes containing group-13 elements and displaying trigonal-planar stereochemistry of the heteroatom of which only metal carbonyl derivatives such as $[E\{Co(CO)_4\}_3]$ (E = Ga, In, Tl)[18–20], $[E\{Mn(CO)_5\}_3]$ (E = Ga, In, Tl)[21–23], $[M_2(CO)_8\text{-}\mu\text{-}\{EM(CO)_5\}_2]$ (E = Ga, In; M = Mn, Re)[24–26], $[E\{(\eta^5\text{-Cp})M(CO)_3\}_3]$ (E = Ga, Tl; M = Mo, W)[27–29], $[\{(\eta^5\text{-Cp})Ru(CO)_2\}_3In]$[18], $[NEt_4]_2[(In_2Br_4\text{-}\mu\text{-}\{Fe(CO)_4\}_2]$[30], $[Ga\{(\eta^5\text{-Cp})Fe(CO)_2\}_3]$[31] are known to date. **4** represents the first carbonyl-free Ni–In cluster containing unsupported Ni–In bonds and is stable in solution and in the solid state.

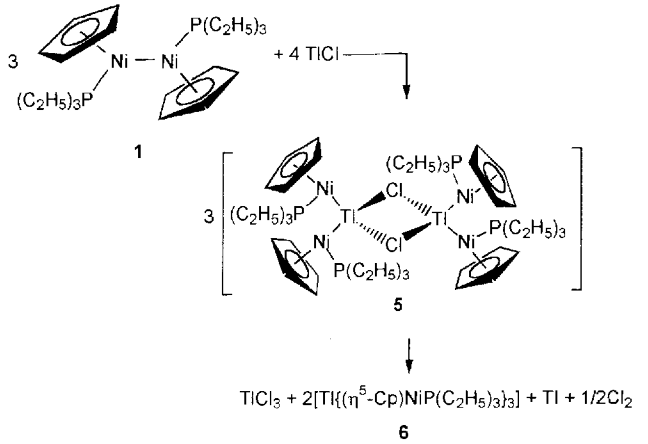
The average Ni–In bond length in **4** is 2.533 Å and deserves discussion. A calculated Ni–In single bond distance based on the covalent radii of indium {1.414 Å from the structure of $[In_2\{CH(SiMe_3)_2\}_4]$[12c] which contains three-coordinated In} and nickel {1.203 Å from $[\{(\eta^5\text{-Cp})Ni(PEt_3)\}_2]$ **1**[7]} is 2.617 Å. However, the Ni–In bond length in **4** is apparently elongated when compared to the carbonyl-free complexes $[(C_6H_5)_3(\eta^5\text{-Cp})Ni\text{–}InBr\{O{=}P(C_6H_5)_3\}]$[10] and $[(\eta^5\text{-}C_5H_4)(CH_2)_2NMe_2](CH_3)_3NI\text{–}InI_2$[11] containing unsupported Ni–In bonds. In general, short σ bonds between transition-metal–ligand fragments and In and Ga fragments occur (i) when the group-13 metal atom has a low coordination number and additional electronegative ligands and (ii) the transition metal bears no strongly π-accepting ligands[9–11]. Although these conditions are fulfilled for **4** (e.g. threefold coordination) its Ni–In bond is significantly elongated when compared to the complexes mentioned above. We assigned this fact to the sterically encumbered environment around the Ni atom of **4**. The bonding might best be explained by an ionic formulation $[In]^{3+} + 3\ (\eta^5\text{-Cp})Ni[P(C_2H_5)_3]^{-}$[31].

Reaction of $[\{(\eta^5\text{-Cp})Ni(PEt_3)\}_2]$ (1) with Thallium(I) Chloride

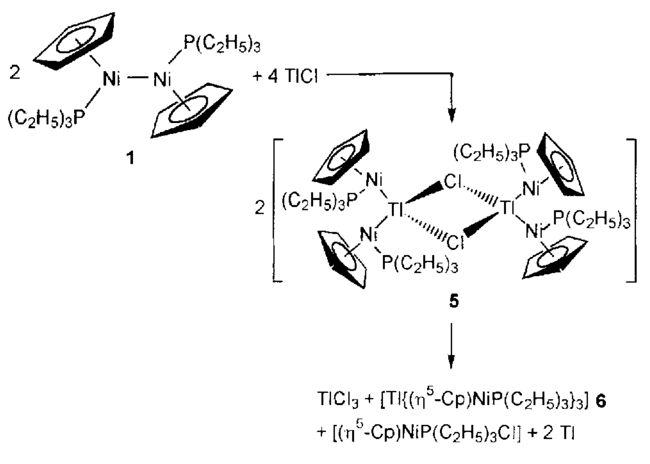
Reports of transition-metal complexes containing trigonal-planar coordinated Tl are scarce[32]. We therefore studied a similar reaction to that given in eq. 1, the reaction of TlCl with **1** in THF solution at room temperature (eq. 3).

After stirring the reaction mixture overnight, we observed, in contrast to the reaction of **1** with InCl, a metallic mirror (presumably elemental Tl) which indicates either a disproportionation reaction of **5** formed in situ (eq. 3), or a redox reaction of **5** with unreacted **1** followed by disproportionation and subsequent formation of **6** (eq. 4). However, we could not detect any $[(\eta^5\text{-Cp})Ni(PEt_3)Cl]$ in the reaction mixture. Experimental support for a disproportionation

Equation 3



Equation 4

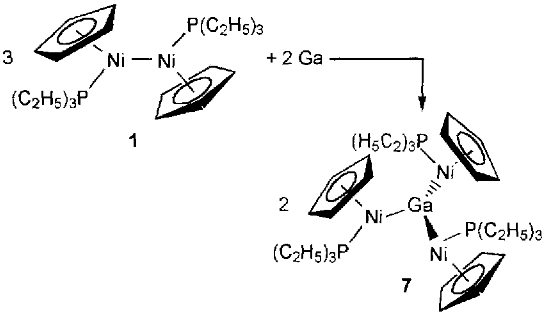


pathway comes from the observation of Walther and co-workers who found that Tl–M bonds in R_2Tl-ML_n complexes (ML_n = [(η^5-Cp)M(CO)$_2$L]; M = Mo, W; L = CO, PPh_3) are unstable towards disproportionation[33]. From the spectroscopic data we deduce for **6** a structure similar to that found for **4**. The ^{1}H-, ^{13}C{^{1}H}-, and ^{31}P{^{1}H}-NMR spectra of **6** show significant $^3J_{HTl}$, $^2J_{CTl}$, and $^2J_{PTl}$ coupling (see Experimental Section).

Reaction of [{(η^5-Cp)Ni(PEt$_3$)}$_2$] (1) with Elemental Gallium

Extending our studies to the group-13 element Ga, we started from Ga metal instead of GaCl and reacted elemental Ga with **1** in order to synthesize the Ga analogues of **4** and **6**. Refluxing a nearly threefold stoichiometric excess of Ga with **1** in THF for two days afforded a brown reaction mixture from which, after purification by column chromatography, purple crystals of [{(η^5-Cp)Ni(PEt$_3$)}$_3$Ga] **7** could be isolated by a conproportionation reaction (eq. 5).

Equation 5



As expected, the NMR spectra (^{1}H, ^{13}C, ^{31}P) of the Ga analogue **7** resemble the spectra of the In compound **4** closely (see Experimental Section). On this basis, as well as on the chemical composition of **7** determined by elemental analysis, we assign the same structure to **7** as to **4**.

Reaction of [{(η^5-Cp)Ni(PEt$_3$)}$_2$] (1) with [{(Me$_3$Si)$_2$CH}$_2$AlCl]

As a further extension to our studies with the monochlorides InCl and TlCl we turned our attention to the element Al. However, the monochloride AlCl is a metastable molecule, stable only below −195°C and accessible by a high-temperature synthesis[13e,34]. No reaction under straightforward conventional experimental conditions similar to those given above is therefore possible between AlCl and **1**. We have thus restricted our studies of Al to the monochloride [{(Me$_3$Si)$_2$CH}$_2$AlCl][12a,35] which contains Al^{III}, and its reaction with the Ni–Ni bonded dimer **1**. A greenish brown solution of **1** in ether reacted immediately with ClAl^{III}R$_2$ [R = CH(SiMe$_3$)$_2$] resulting in a colour change to deep brown (eq. 6).

Subsequent workup of the reaction mixture and crystallization afforded brown crystals of **8** in 40% yield. The reaction of **1** and ClAlR$_2$ [R = CH(SiMe$_3$)$_2$] proceeded with scission of the Ni–Ni bond, but in contrast to the reaction of InCl and TlCl no formation of Ni–E bonds; instead a salt-like structure as revealed from an X-ray structure determination, was formed (Figure 3). Aside from this product we could not detect any other complex in the reaction mixture e.g. the possible dialan reduction product [{(SiMe$_3$)$_2$CH}$_2$Al]$_2$[12a].

Equation 6

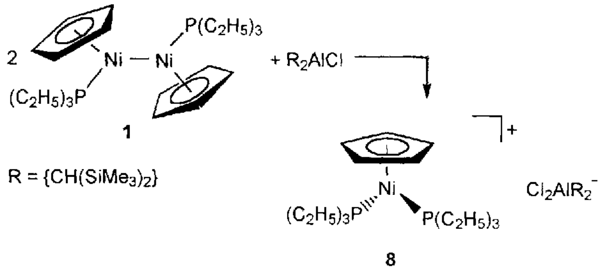
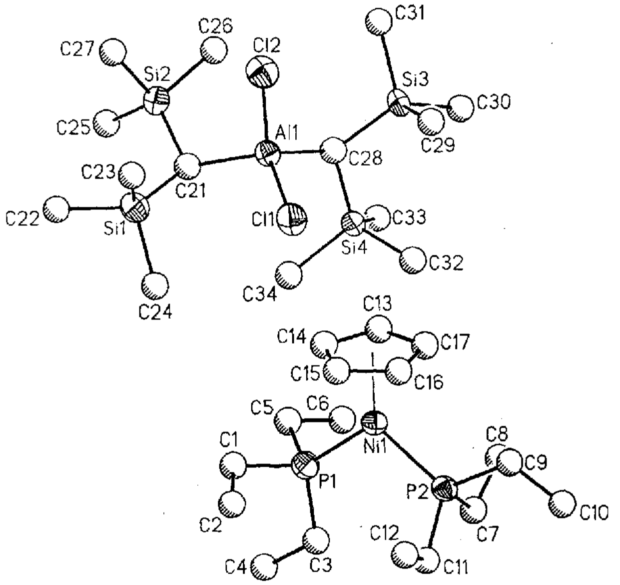


Figure 3. Molecular structure of **8** in the solid state as determined by X-ray crystalllography[a]



[a] Selected bond length [Å] and angles [°]: Ni–P 2.170(4), Al–Cl1 2.196(4), Al–Cl2 2.198(4), Al–C21 1.983(13), Al–C28 1.986(12); P1–Ni–P2 104.8(1), Cl1–Al–Cl2 101.9(1), Cl2–Al1–C21 106.3, Cl2–Al1–C28.

The cationic organonickel fragment of **8** has a 18-VE configuration and a half-sandwich structure. The two Ni–P bond lengths are equal within experimental error [2.170(4) Å] and are in accord with the Co–P bond distances in the isostructural, paramagnetic 17-VE C$_5$Me$_5$Co analogue (2.246 Å)[36]. The closed shell 8e$^-$ anion of **8** (Cl$_2$AlR$_2$)$^-$ [R = CH(SiMe$_3$)$_2$] exhibits a strongly distorted tetrahedral geometry around its Al centre. The closely related ionic complex [(η^5-Cp)Ni{P(C$_6$H$_5$)$_3$}$_2$][InBr$_4$] has recently been prepared by Fischer[10] but was not structurally characterized.

We have also studied thermal and photochemical reactions of **1** with Uhl's dialan [{(SiMe$_3$)$_2$CH}$_2$Al]$_2$[12a] containing an unbridged Al–Al bond, in order to synthesize clusters with direct Ni–Al bonds. To the best of our knowledge compounds of this type have only been described in three cases[37]. However, to our surprise, either under thermal (THF, 60°C) or photolytic conditions (5 hours, UV irradiation, 240 nm) the dialan showed no reactivity towards **1**. Following UV-irradiation of a solution of **1** and the dialan $[\{(SiMe_3)_2CH\}_2Al]_2$ for five hours in pentane the dialan could be recovered in 90% yield whereas **1** was completely decomposed. This decomposition process is possibly initiated by a scission of the Ni−Ni bond followed by further decomposition processes of the photolytically generated 17-VE $[(Cp)Ni(PEt_3)]^{\bullet}$ radical fragments. If one recalls that $[\{(SiMe_3)_2CH\}_2Al]_2$ is described as photolytically labile generating $[\{(SiMe_3)_2CH\}_2Al]^{\bullet}$ and $[\{(SiMe_3)_2CH\}_2\text{-}Al\text{-}Al\{(SiMe_3)_2CH^{\bullet}\}_2]$ radicals upon UV irradiation[13d] its inertness towards **1** is most surprising.

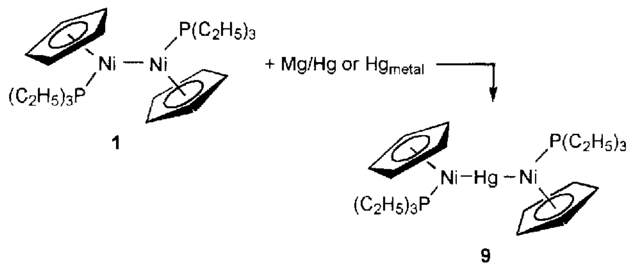
Reaction of $[\{(\eta^5\text{-}Cp)Ni(PEt_3)\}_2]$ (1) with Elemental Hg

In an attempt to extend our studies towards insertion reactions of group 2 metal atoms into the Ni−Ni bond of **1** we include the elemental magnesium in our investigations. Since amalgamation is a well-known technique in organometallic synthesis for activating electropositive metals we reacted Mg/Hg alloy with **1** according to the method of Vickers who observed insertion of Mg atoms into the Ni−Ni bond of the dimer $[\{(\eta^5\text{-}Cp)Ni(CO)_2\}_2]$ by reaction with Mg/Hg alloy[38]. Surprisingly, the more noble Hg rather than Mg inserted into the Ni−Ni bond of **1** resulting in the formation of the trinuclear complex $[\{(\eta^5\text{-}Cp)Ni(PEt_3)\}_2Hg]$ **9** (eq. 7). No insertion of Mg was observed in this reaction. We found that **9** could also be formed by a direct reaction of Hg metal and **1**.

The solid-state molecular structure of **9** as determined by X-ray structure investigation is depicted in Figure 4.

The Hg atom occupies a centre of inversion resulting in a linear Ni−Hg−Ni* arrangement which is also found for the Ni/Hg/Ge cluster $[\mu\text{-}Hg_5\text{-}\{(Ph_3Ge)_2Ni(\eta^5\text{-}Cp)\}_2]$[39]. The observed Ni−Hg single bond length in **9** is 2.468(1) Å and is in the range of other Ni−Hg[39] and Ni−Cd[40] distances showing a linear Ni−Hg(Cd)−Ni arrangement. The Hg−Ni−P bond angle [88.5(1) Å] and the short P−Hg distance [3.203(1) Å] (sum of van der Waals radii P−Hg: 3.18 Å) may account for a P−Hg interaction in **9** in the solid state. However, in solution, as judged from the ^{31}P-NMR spectrum, the $^2J_{^{31}P-^{199}Hg}$ coupling constant (699 Hz) clearly does not confirm this, since for $^2J_{^{31}P-^{199}Hg}$ interactions values from 4300 up to 5700 Hz are observed[41].

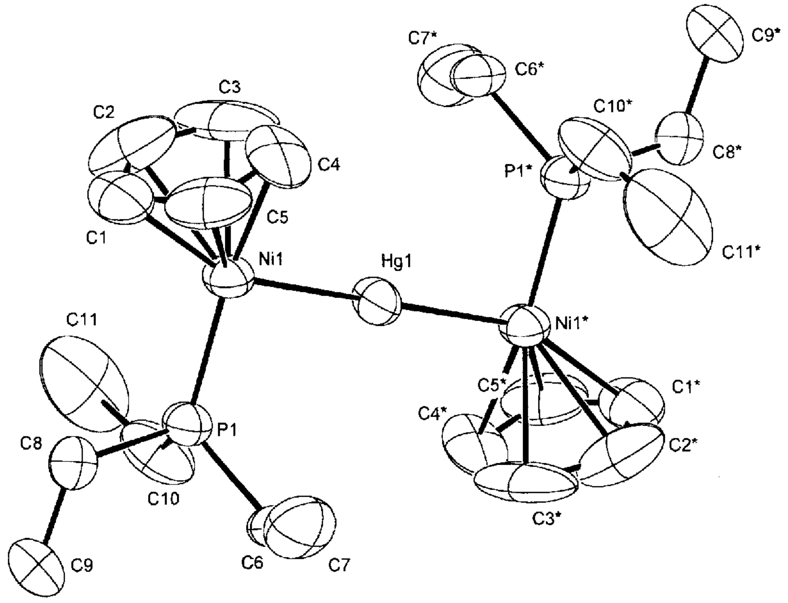
Equation 7



Conclusion

In examining the reactivity of the dimer **1** towards main group monochlorides we have found that the heavier group 13 monochlorides InCl and TlCl react in different ways with the Ni−Ni bond of **1**. While InCl forms the chloro-bridged dimer **2**, as a stable compound, the appropriate Tl dimer, which may eventually be formed as an unstable intermediate in this reaction, decomposes by a disproportionation route to form the halogen-free tris-organonickel complex **6** directly. In contrast to this observation the corresponding In analogue **4** is, however, accessible via a dehalogenation reaction with activated magnesium metal. The Ga derivative **7** can be prepared by reacting **1** with

Figure 4. Molecular structure of **9** in the solid state as determined by X-ray crystallography[a]



[a] Selected bond length [Å] and angles [°]: Hg−Ni 2.468(1), Ni−P 2.108(2), Hg−P 3.203(2); P−Hg−Ni 41.1(1), P*−Hg−Ni 138.9(1), Ni−Hg−Ni 180.0(1), Hg−Ni−P 88.5.

Table 1. Crystal data and structure refinement for **2**, **4**, **8**, and **9**

	2	**4**	**8**	**9**
empirical formula	$C_{44}H_{80}Cl_2In_2P_4Ni_4$	$C_{33}H_{60}InNi_3P_3$	$C_{31}H_{73}AlCl_2NiP_2Si_4$	$C_{22}H_{40}HgNi_2P_2$
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Nicolet R3mV	Enraf-Nonius CAD4
λ, Å	0.71069	1.54178	0.71069	0.71069
space group	$P\bar{1}$ (no.2)	C2/c (no.15)	$P\bar{1}$ (no.2)	$P\bar{1}$ (no.2)
crystal size, mm	0.37 x 0.37 x 0.37	0.08 x 0.31 x 0.25	0.33 x 0.27 x 0.17	0.15 x 0.24 x 0.41
a, Å	9.500(1)	21.780(1)	11.600(2)	7.621(1)
b, Å	11.979(1)	8.693(1)	14.354(3)	8.451(1)
c, Å	12.905(1)	40.600(2)	14.939(3)	11.407(1)
α, °	107.877(5)	90	90.82(3)	79.98(1)
β, °	100.135(5)	93.20(1)	108.32(3)	86.14(1)
γ, °	95.369(4)	90	103.48(3)	66.55(1)
V, $Å^3$	1358.7(2)	7674.7(6)	2286.0(8)	663.7(2)
d_{calc}, Mg · m^{-3}	1.55	1.46	1.13	1.71
Z	1	8	2	1
μ, cm^{-1}	24.31	78.36	7.5	73.05
Θ_{max}, °	27.45	37.5	20.0	32.0
scan method	ω scan	ω scan	ω scan	ω scan
index ranges	$-13 \le h \le 13, -16 \le k \le 16, 0 \le l \le 17$	$-28 \le h \le 28, 0 \le k \le 11, 0 \le l \le 51$	$0 \le h \le 5, -12 \le k \le 11, -12 \le l \le 12$	$-12 \le h \le 12, -13 \le k \le 13, 0 \le l \le 18$
refl. Collected	6480	16447	2200	4815
independent refl.	6197	7734	1983	4815
obs. refl.($I>2\sigma(I)$)	5639	6384	1742	3752
parameters	208	586	213	124
abs. Correction	psi-scan	psi-scan	-	psi-scan
min., max.	0.965, 0.999	0.524, 1.000	-	0.824, 0.998
Structure solution	heavy atom	heavy atom	direct	heavy atom
refinement	Full matrix least-squares on $F^{[a]}$	Full matrix least-squares on $F^{2[b]}$	Full matrix least-squares on $F^{[c]}$	Full matrix least-squares on $F^{[a]}$
R	0.041	0.065	0.051	0.048
R_w	0.049	0.172	0.071	0.045
Residual Electron Density	1.02	1.80	0.36	1.92
Goodness of fit	8.99	1.32	2.28	4.46

All H-atom positions were calculated and refined in fixed positions: [a] $w = 1/\sigma^2(F_o)$. – [b] $w = 1/[\sigma^2(F) + (0.100P)^2 + 0.000P]$, where $P = (F_o^2 + 2F_c^2)/3$. – [c] $w^{-1} = [\sigma^2(F_o) + 0.0005 \cdot F_o^2]$.

elemental Ga. The monochloride $ClAlR_2$ [R = $CH(SiMe_3)_2$] does not react with **1** to form a Ni–Al cluster similar to **4**, **6**, and **7**. Instead scission of the Ni–Ni bond of **1** followed by an PEt_3 ligand transfer reaction and formation of the salt **8** is observed. A three atom Ni–Hg–Ni bridge is found in **9** which is accessible either by an insertion reaction into the Ni–Ni bond of **1** by elemental Hg or by using Hg/Mg alloy as the metal source.

In summary, the versatility of the Ni–Ni bonded dimer **1** to serve as a unique educt for the formation of carbonyl-free transition-metal/main-group clusters with unsupported metal–metal bonds has been proven.

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Experimental Section

General: All reactions were carried out under an argon or nitrogen atmosphere, solvents were dried over Na/K alloy, CaH_2 or $NaAlEt_4$ and were freshly distilled prior to use. Aluminium oxide was dried heating for 5 days to 180°C under vacuum. **1**[7], $[\{CH(SiMe_3)_2\}_2Al]_2$[12a] and $[\{CH(SiMe_3)_2\}_2AlCl]$[35] were prepared as published. Other chemicals were commercially available and were used without further purification. – NMR spectra were recorded on Bruker AC 200, AM 200, AM 300, or WH 400 FT spectrometers. ^1H- and ^{13}C-NMR chemical shifts were referred to the remaining proton signals of the deuterated solvents and referenced to TMS. ^{31}P-NMR chemical shifts are referred to the external standard H_3PO_4. – IR spectra were recorded on a Nicolet 7199-FTIR spectrometer as KBr mulls. – The mass spectra were routinely performed on a Finnigan MAT 311A/DF by electron impact at 70 eV unless noted otherwise. – Elemental analyses were performed by Mikroanalytisches Laboratorium Dornis & Kolbe, Mülheim an der Ruhr or by the microanalytical laboratory of the University of Essen.

Synthesis of $[\{(\eta^5\text{-}Cp)Ni(PEt_3)\}_2InCl]_2$ (**2**): To a solution of 463 mg (0.96 mmol) of **1** in toluene 139 mg (0.93 mmol) of InCl was added at –20°C. The mixture was warmed to room temperature and stirred for 16 h whilst the colour changed to orange. The solvent was evaporated and the residue exhaustively extracted with ether. The extract was concentrated in vacuo and crystallized at 0°C. **2** was formed as dark crystals. Yield: 298 mg (50%). – ^1H NMR (300 K, $[D_8]$THF, 200.1 MHz): δ = 5.12 (5H, s, Cp-H), 1.60 (6H, q, $J_{HH} = J_{HP} = 7.7$ Hz, CH_2), 1.06 (9H, dt, $J_{HP} = 15.4$ Hz, CH_3). – ^{13}C NMR (300 K; $[D_8]$THF, 50.3 MHz): δ = 87.5 ($J_{CP} = 27$ Hz, C-Cp), 21.1 ($J_{CP} = 27$ Hz, CH_2), 8.5 (CH_3). – ^{31}P NMR (300 K, $[D_8]$THF, 81.0 MHz): δ = 29.2. – $C_{44}H_{80}Cl_2In_2Ni_4P_4$ (1268.32): calcd. C 41.67, H 6.36, Cl 5.59, In 18.11, Ni 18.51, P 9.77; found C 42.16, H 6.54, Cl 5.64, In 17.84, Ni 18.29, P 9.77%.

Synthesis of $[\{(\eta^5\text{-}Cp)Ni(PEt_3)\}_3In]$ (**4**): A solution of **2** in toluene was prepared from 407 mg (0.84 mmol) of **1** and 123 mg (0.82 mmol) of InCl as described above. After stirring overnight the solvent was evaporated and the residue dissolved in THF. The solution was transferred to 19 mg (0.78 mmol) of activated magnesium. The colour of the mixture changed within 4 h from orange to purple. The solution was evaporated to dryness and the residue was extracted with pentane. The extract was concentrated in vacuo and crystallized at 0°C. **4** was isolated as dark needles. Yield: 259 mg (55%). – ^1H NMR (300 K, $[D_8]$THF, 200.1 MHz): δ = 5.02 (5H, s, Cp-H), 1.55 (6H, quintet, $J_{HH} = J_{HP} = 7.5$ Hz, CH_2), 1.09 (9H, dt, $J_{HP} = 15.0$ Hz, CH_3). – ^{13}C NMR (300 K, $[D_8]$THF, 50.3 MHz): δ = 87.3 ($J_{CP} = 2$ Hz, C-Cp), 21.6 ($J_{CP} = 25$ Hz, CH_2), 8.4 (CH_3). – ^{31}P NMR (300 K, $[D_8]$THF, 81.0 MHz): δ = 22.1. – $C_{33}H_{60}InNi_3P_3$ (840.66): calcd. C 47.15, H 7.19, In 13.66, Ni 20.94, P 11.05; found C 46.90, H 7.27, In 13.56, Ni 20.79, P 10.95%.

Synthesis of $[\{(\eta^5\text{-}Cp)Ni(PEt_3)\}_3Tl]$ (**6**): To a solution of 532 mg (1.10 mmol) of **1** in ether was added 264 mg (1.10 mmol) of TlCl. The mixture was stirred for 16 h, while the colour changed to dark brown. In addition, a metallic glimmering solid was formed, which was removed by filtration and discarded. The resulting solution was concentrated in vacuo and crystallized at 0°C. **6** was obtained in the form of large metallic glimmering crystals. Yield: 180 mg (26%). – ^1H NMR (300 K, $[D_8]$THF, 200.1 MHz): δ = 4.84 (5H, d, $J_{HTl} = 12$ Hz, Cp-H), 1.50 (6H, q, $J_{HH} = J_{HP} = 7.5$ Hz, CH_2), 1.14 (9H, dt, $J_{HP} = 15.0$ Hz, CH_3). – ^{13}C NMR

(300 K, [D$_8$]THF, 50.3 MHz): δ = 87.4 (J_{CTl} = 21 Hz, C-Cp), 19.5 (J_{CP} = 26 Hz, J_{CTl} = 85 Hz, CH$_2$), 8.2 (J_{CTl} = 10 Hz, CH$_3$). – ^{31}P NMR (300 K, [D$_8$]THF, 81.0 MHz): δ = 11.7 (J_{PTl} = 530 Hz). – $C_{33}H_{60}Ni_3P_3Tl$ (930.22): calcd. C 42.61, H 6.50, Ni 18.93, P 9.99, Tl 21.97; found C 42.86, H 6.68, Ni 18.51, P 9.91, Tl 22.16%.

Synthesis of [{(η^5-Cp)Ni(PEt$_3$)}$_3$Ga] (**7**): To a solution of 410 mg (0.85 mmol) of **1** in THF was added 200 mg (2.87 mmol) of metallic gallium and the mixture refluxed for 48 h. The colour changed to red brown. The solution was removed from the excess gallium, aluminium oxide added, and the solvent evaporated. The resulting residue was placed on a column filled with aluminium oxide and separated by chromatography with ether. The purple zone was eluted and evaporated to dryness and the residue recrystallized from pentane. **7** was obtained as dark crystals. Yield: 93 mg (14%). – ^{1}H NMR (300 K, C$_6$D$_6$, 200.1 MHz): δ = 5.14 (5H, s, H-Cp), 1.27 (6H, q, J_{HH} = J_{HP} = 7.6 Hz, CH$_2$), 0.78 (9H, dt, J_{HP} = 15.3 Hz, CH$_3$). – ^{13}C NMR (300 K, C$_6$D$_6$, 50.3 MHz): δ = 89.6 (C-Cp), 21.4 (J_{CP} = 26 Hz, CH$_2$), 9.0 (CH$_3$). – ^{31}P NMR (300 K, C$_6$D$_6$, 81.0 MHz): δ = 21.3. – $C_{33}H_{60}GaNi_3P_3$ (795.62): calcd. Ni 22.14, P 11.68; found Ni 21.88, P 11.67%.

[(η^5-Cp)Ni(PEt$_3$)$_2$]$^+$[{(SiMe$_3$)$_2$CH}$_2$AlCl$_2$]$^-$ (**8**): 220 mg (0.454 mmol) of **1** and 100 mg (0.26 mmol) of [{CH(SiMe$_3$)$_2$}$_2$AlCl] were dissolved in 30 ml of ether and stirred for 20 hours at 20°C. During this time a brown microcrystalline residue was formed and the colour of the reaction mixture changed from green brown to dark brown. After evaporation of the solvent the solid residue was dissolved in a mixture of THF/pentane (3:1), filtered, and cooled to −30°C. 140 mg of **8** (0.181 mmol, 40%) as dark brown crystals were isolated. A second crop of crystals were obtained from the mother liquor by prolonged cooling to −30°C. – ^{1}H NMR (300 K, [D$_8$]THF, 300.1 MHz): δ = 5.60 (s, 5H, Cp), 1.73 (m, 6H, CH$_2$–), 1.16 (q, 9H, J_{H-P} 15 Hz, CH$_3$), 0.1 (s, 36H, SiMe$_3$), −1.22 (s, 2H, –CH$_2$–). – ^{13}C{^{1}H} NMR (300 K, [D$_8$]THF, 75.1 MHz): δ = −32.4 (–CH$_2$), 4.7 (SiMe$_3$), 7.9 (CH$_3$), 18.60 (J_{PC} 27 Hz, –CH$_2$–), 94.5 (Cp). – ^{31}P{^{1}H} NMR (300 K, [D$_8$]THF): δ = 30.38. – ESI pos. (CH$_3$CN) cation: 358.98 (90) [{CpNiPEt$_3$}$_2$], 281.93 (100); ESI neg. (CH$_3$CN) anion: 415.05 (100) [{(SiMe$_3$)$_2$CH}$_2$AlCl$_2$]. – $C_{31}H_{72}AlCl_2NiP_2Si_4$ [775.78] calcd. C 47.94, H 9.66; found C 47.99, H 9.35%.

Synthesis of [{(η^5-Cp)Ni(PEt$_3$)}$_2$Hg] (**9**): To a solution of 556 mg (1.15 mmol) of **1** in THF was added 3 ml (20.3 mmol) of Hg and the mixture was refluxed for 24 h. The colour changed to orange. The solution was removed from the excess mercury and the solvent evaporated. The residue was extracted with pentane, the extract concentrated in vacuo and crystallized at −30°C. **9** was obtained as long orange needles. Yield: 504 mg (64%). – ^{1}H NMR (300 K, C$_6$D$_6$, 400.1 MHz): δ = 5.16 (5H, H-Cp), 1.12 (6H, q, J_{HH} = J_{PH} = 7.6 Hz, CH$_2$), 0.96 (9H, dt, J_{PH} = 15.3 Hz, CH$_3$). – ^{13}C{^{1}H} NMR (300 K, C$_6$D$_6$, 50.3 MHz): δ = 85.4 (C-Cp), 21.4 (J_{PC} = 27 Hz, CH$_2$), 8.4 (CH$_3$). – ^{31}P NMR (300 K, C$_6$D$_6$, 81.0 MHz): δ = 29.8 (J_{PHg} = 699 Hz). – MS (70 eV), *m/z* (%): 684 (3) [M$^-$], 364 (3) [M$^+$ – CpNi(PEt$_3$)], 241 (80) [CpNi(PEt$_3$)H$^+$]. – $C_{22}H_{40}HgNi_2P_2$ (684.52): calcd. C 38.60, H 5.89, Hg 29.30, Ni 17.15, P 9.05; found C 38.39, H 6.02, Hg 29.35, Ni 17.19, P 8.94%.

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