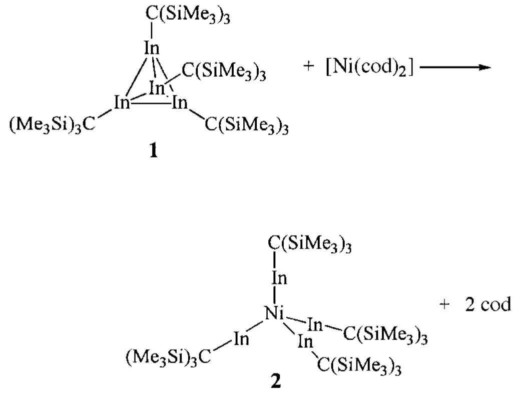
# Ni[In{C(SiMe$_3$)$_3$}$_4$]: An Organometallic Nickel–Indium Compound Analogous to [Ni(CO)$_4$]**

Werner Uhl*, Michael Pohlmann, and Rudolf Wartchow

The monomeric alkyl–element(I) compounds E–R containing the bulky alkyl substituent C(SiMe$_3$)$_3$ and the monovalent, coordinatively and electronically unsaturated elements Ga, In, and Tl have recently been identified unambiguously as degradation products of the tetrahedral clusters E$_4$[C(SiMe$_3$)$_3$]$_4$.[1–3] The molecular structure of the most stable compound, GaC(SiMe$_3$)$_3$, was determined by electron diffraction in the gas phase above 200 °C.[4] The tetrathallium compound is only weakly associated in the solid state and dissociates completely to the monomer on dissolution in benzene,[3] while the tetragallium cluster shows complete dissociation into the monomers only at high dilution in benzene.[1] The most stable of the clusters is In$_4$[C(SiMe$_3$)$_3$]$_4$ (**1**).[2] Owing to its low thermal stability the monomeric fragment could not be characterized by electron diffraction,[4] and dissociation was not observed even in highly diluted solutions in benzene.[2] However, InR was detected as a reactive intermediate by trapping reactions with benzil derivatives in boiling *n*-hexane.[5] The monomeric fragments have two empty p orbitals perpendicular to the element–carbon bond axis and an electron lone pair at the Ga, In, or Tl atoms; hence, their frontier orbitals are similar to those of carbon monoxide. Indeed, CO ligands are substituted by InR groups when transition metal carbonyl complexes are treated with the indium cluster **1**.[6] These reactions opened a new route to organometallic compounds of the transition metals with elements of Group 13 and led to novel compounds with unusual structures, for example, an Fe$_2$In$_3$ cluster.[7] Similar reactions have been reported by Schnöckel et al., who synthesized carbonyl analogous complexes with the ligand aluminum(I) pentamethylcyclopentadienide AlCp*.[8] In contrast to CO, the ER fragments almost exclusively occupy bridging positions between two metal atoms in the known derivatives. A single case of terminal coordination was recently reported by Fischer et al. in [(CO)$_4$Fe(AlCp*)],[9] for which significant π backbonding from the metal atom to the ligand was calculated. Up to now, analogues of mononuclear, binary carbonyl complexes with exclusively terminal ER groups were unknown. Such compounds would be proof of the isolobal relationship between CO and ER and would extend the class of carbonyl-analogous compounds by a remarkable new example.

For the synthesis of a nickel complex exclusively coordinated by four indanediyl ligands (InR) we did not use [Ni(CO)$_4$] but bis(cyclooctadiene)nickel [Ni(cod)$_2$], because of the facile substitution of the alkene ligands. In accordance with our experience of the chemical reactivity of **1**, solutions of the starting materials could be kept at room temperature for several days without any observable reaction. At 50 °C the reaction was complete after 2 h [Eq. (a)]. Dark red crystals of the product **2** were isolated by recrystallization from cyclopentane in 75 % yield. Compound **2** is extremely moisture-sensitive; reaction with water forms [In$_4$O(OH)$_6$R$_4$],[10] which was identified by NMR spectroscopy and could not be removed by recrystallization. Therefore, all manipulations were performed with strict exclusion of water, and all solvents were additionally dried by treatment with *n*-butyllithium and freshly distilled before use. Elemental analysis of **2** is in agreement with the formula [Ni{InC(SiMe$_3$)$_3$}$_4$], and determination of the relative molecular mass by cryoscopy in benzene gave the value expected for the undissociated molecule. The absorption of longest wavelength in the UV/Vis spectrum of **2** is at 395 nm, and the characteristic band of the In$_4$ cluster at 490 nm is no longer present.[2] The signal of the α-carbon atom in the $^{13}$C NMR spectrum of **2** is at $\delta = 61.6$: It is shifted downfield by more than 30 ppm relative to the signals of indium(III) compounds ($\delta < 30$).[11] The corresponding signals of bridging InR groups in transition metal complexes occur in the range of $\delta = 48–52$,[6] and the signal of the tetraindium compound **1** is shifted even further to low field ($\delta = 72.0$)[2] owing to the the delocalized electron system in the central In$_4$ cluster. Compound **2** has surprisingly high thermal stability and decomposes above 285 °C; however, attempts to sublime it in vacuo were unsuccessful.



(a)

Compound **2** (Figure 1) crystallizes in the cubic space group $Fd\bar{3}m$[12] with the center of the molecule on a special crystallographic position ($\bar{4}3m$), that is, the Ni atoms are coordinated in an undistorted tetrahedral manner by four InC(SiMe$_3$)$_3$ ligands (In-Ni-In 109.5°), and the Ni-In-C units with two-coordinate In atoms are exactly linear (Ni-In-C 180.0°). Hence, **2** is isostructural with [Ni(CO)$_4$] and analogous compounds with σ-donor/π-acceptor ligands such as [Ni(PF$_3$)$_4$] and [Ni(CNR)$_4$].[13] The complex Ni[SnR$_2$]$_4$ is also similar,[14] although the frontier orbitals of the SnR$_2$ groups do not correspond exactly to those of InR. The Ni–In bond lengths of **2** (231.0(1) pm) are considerably shorter than all Ni–In bond lengths reported to date, in spite of the high steric

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[*] Prof. Dr. W. Uhl, Dipl. Chem. M. Pohlmann
Fachbereich Chemie der Universität
Postfach 2503, D-26111 Oldenburg (Germany)
Fax: (+49) 441-798-3352

Dr. R. Wartchow
Institut für Anorganische Chemie der Universität Hannover
(Germany)

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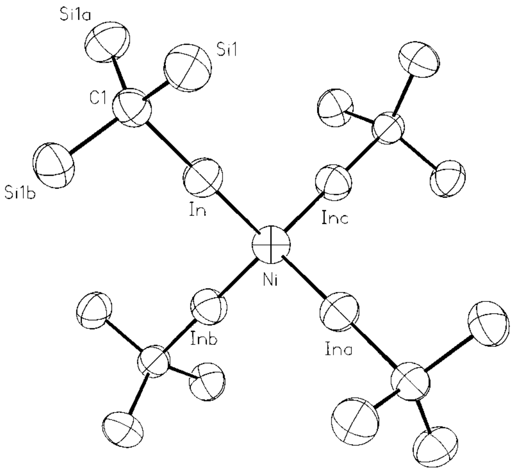

Figure 1. Molecular structure of **2**; methyl groups are omitted for clarity. Selected bond lengths [pm] and angles [°]: In–Ni 231.0(1), In–C1 219.5(13), C1–Si1 187.2(4); In-Ni-In 109.5, Ni-In-C1 180.0, In-C1-Si1 105.3(4).

stress in the molecule caused by the four bulky substituents. Organometallic coordination compounds show Ni–In distances longer than 244.6 pm (av. 269.2 pm[15–17]), and distances of 262 pm[18] are observed in some alloys. The sum of the covalent radii can be estimated to be about 260 pm. The short Ni–In bond lengths in complexes such as $[Cp(Ph_3P)Ni-InBr_2(OPPh_3)]$ (244.6 pm)[16] and $[Cp(CO)Ni-InBr_2(NC_7H_{13})]$ (246.2 pm)[17] have been explained in terms of Ni(dπ)–ligand(σ*) interactions. The intramolecular In–In distances of 377 pm in **2** lie in the range of twice the van der Waals radius of indium (380 pm) and indicate no significant bonding interaction between the In atoms. The extent of the π backbonding in **2**, indicated by the very short Ni–In bonds, is uncertain. Theoretical investigations confirm such interactions in $[Fe(CO)_4(AlCp^*)]$,[9] in which, however, the contributing orbitals on the aluminum atoms are partially occupied by the cyclopentadienyl ligands.

## *Experimental Section*

All procedures were carried out under purified argon. The solvents were dried by standard methods (toluene over Na/benzophenone, cyclopentane over $LiAlH_4$) and subsequently with solvent-free *n*-butyllithium, distilled in vacuo at room temperature, and used immediately or stored over molecular sieve. **1** (300 mg, 0.217 mmol) and $[Ni(cod)_2]$ (65 mg, 0.237 mmol) were dissolved in toluene (25 mL) and stirred at 50 °C for 2 h. The solvent was completely removed in vacuo, and the residue was recrystallized from cyclopentane at –30 °C. Yield of **2**: 240 mg (0.166 mmol, 76 %), dark red crystals. **2** crystallizes with varying amounts of cyclopentane, which can be removed by vacuum treatment of powdered samples. Decomposition (argon, sealed capillary): 285 °C. $^1H$ NMR (300 MHz, $C_6D_6$): $\delta = 0.427$ (s, $SiMe_3$). $^{13}C$ NMR (75 MHz, $C_6D_6$): $\delta = 6.50$ ($SiMe_3$), 61.6 (InC). IR (Nujol, CsBr plates): $\tilde{\nu} = 1263$ m, 1250 m ($\delta(CH_3)$); 1169 vw, 1155 vw, 1044 w, 1020 w; 864 vs, 837 vs, 774 w, 721 w ($\rho(CH_3(Si))$; 669 w ($\nu_{as}SiC$); 644 w, 613 vw ($\nu_sSiC$); 577 m; 521 vw, 465 $cm^{-1}$ vw (νInC). UV/Vis (*n*-hexane): $\lambda_{max}$ ($\lg\varepsilon$) = 250 (5.0), 280 (5.0), 395 nm (4.5). Relative molecular mass (cryoscopy in benzene): found 1475; calcd 1444.3.

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[12] Crystal structure analysis of **2**: Single crystals of **2** were obtained from cyclopentane at 0 °C and were not dried in vacuo; $C_{40}H_{108}In_4NiSi_{12} \cdot 2.7\,C_5H_{10}$, cubic, space group $Fd\bar{3}m$, $a = 2608.7(3)$ pm, $V = 17753(4)$ Å$^3$, $Z = 8$, $\rho_{calcd} = 1.204$ g cm$^{-3}$, crystal dimensions 0.5 × 0.5 × 0.3 mm, Stoe IPDS diffractometer, $Mo_{K\alpha}$ radiation, 300 K, measurement range: $4.4 < 2\theta < 47.8°$, 200 exposures, $\Delta\varphi = 1.1°$, 704 independent reflections, 332 reflections with $F > 4\sigma(F)$, $\mu = 1.419$ mm$^{-1}$, programs SHELXTL PLUS REL 4.1 and SHELXL-93, 54 parameters, $R1 = 0.037$ and $wR2$ (all data) = 0.085, max./min. residual electron density: $0.30/-0.50 \times 10^{30}$ e m$^{-3}$. Owing to the crystallographic position ($b$, $\bar{4}3m$) the $C(SiMe_3)_3$ groups are rotationally disordered, and six positions are observed for the three Si atoms with occupancy factors of 0.5. Two methyl groups lie on a mirror plane with bonds to two Si atoms, and the third methyl group occupies two positions above and below this plane. The cyclopentane molecules are strongly disordered over crystallographic symmetry elements; positions of the hydrogen atoms were not calculated. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100776. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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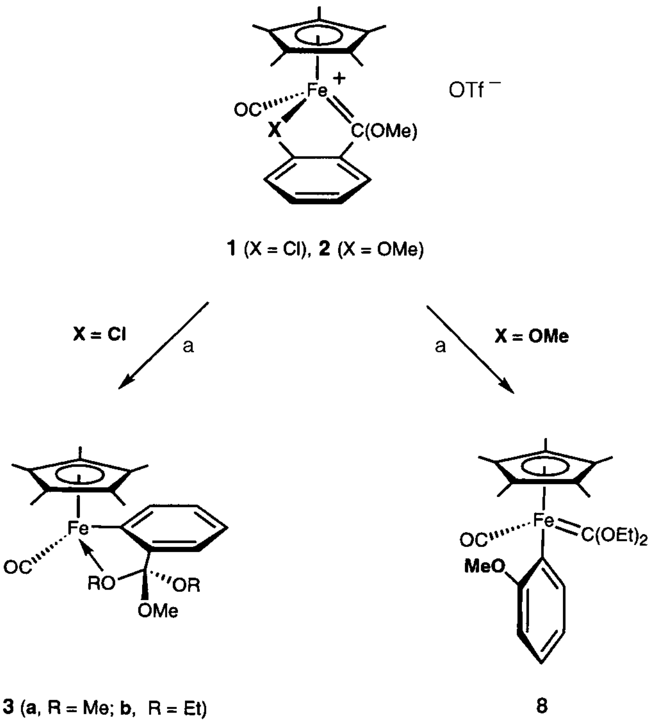
# Selective Activation of Ar–Cl and Ar–C Bonds with Iron(II) Complexes[**]

Géraldine Poignant, Sourisak Sinbandhit, Loïc Toupet, and Véronique Guerchais*

Selective bond-activation reactions mediated by transition metals are currently the focus of synthetic and mechanistic interest. These fundamental processes are particularly important in carbene and arene chemistry.[1, 2] In this context, the electrophilic arylcarbene chelate complexes **1** (X = Cl) and **2** (X = OMe) are good candidates for promoting new reactions within the coordination sphere, since the chelating group X can be activated by the Lewis acidic organo-iron fragment[3, 4] or dissociate to provide a vacant coordination site.[5, 6] Here we report on the reactivity of **1** and **2**[5] towards alkoxides. The outcome of the reaction depends on the nature of the chelate group; selective activation of Ar–Cl and Ar–C bonds was achieved.

Complex **1** reacts cleanly with alkoxides RONa to give the unexpected neutral chelate complexes **3a** (R = Me) and **3b** (R = Et), which were isolated as stable black crystals in 83–89% yield from pentane (Scheme 1). Both contain two additional alkoxy groups. The $^1$H NMR spectrum ($C_6D_6$, 25 °C) of **3a** exhibits three broad signals for the methoxy substituents, one of which corresponds to the coordinated OMe group, while the other two methoxy groups are diastereotopic. The coalescence of these signals on warming ($T_C$(300 MHz) = 42 °C) to give a singlet at $\delta = 2.90$, indicates free exchange on the NMR time scale. For **3b**, the $^1$H and $^{13}$C NMR spectra each exhibit two well-resolved pairs of signals for the methyl and methylene groups, which indicates the presence of two different ethoxy groups. Moreover, in the $^1$H NMR spectrum (25 °C) one of the methylene groups gives rise to an AB system at $\delta = 3.00$ and 2.78 ($^2J_{H,H} = 10$ Hz) when the corresponding methyl signal at $\delta = 0.98$ is selectively $^1$H-decoupled.



Scheme 1. a) RONa (3 equiv)/ROH, THF, −80 °C→room temperature. TfO = trifluoromethanesulfonate.

As expected the OMe ligand is labile, and treatment of **3a** with $PMe_3$ quantitatively yields orange crystals of **4**. In this

$[Fe(C_5Me_5)(CO)(PMe_3)\{\eta^1\text{-}C_6H_4\text{-}o\text{-}C(OMe)_3\}]$ **4**

case, the three OMe groups are magnetically equivalent in the $^1$H ($\delta = 3.29$) and $^{13}$C ($\delta = 49.9$) NMR spectra (25 °C). An X-ray structure analysis confirms the proposed structure (Figure 1).[7] The Fe$C\equiv O$ unit deviates from the expected linear geometry (Fe-C-O 171.0(3)°). The bond angles at $C_{ipso}$ of the aryl group are quite different owing to the presence of the bulky tris(methoxy)methyl substituent.

The formation of complexes **3a–b** involves cleavage of the Ar–Cl bond. This cleavage is promoted by coordination of the chlorine atom, as shown by the following experiment. Treatment of the nonchelated complex $\mathbf{5}^+OTf^-$[5] under the same conditions led to formation of the acetal complexes **6a** (R = Me) and **6b** (R = Et) by addition of $RO^-$ to the electrophilic carbene carbon atom. Although stable in the

$[Fe(C_5Me_5)(CO)_2\{\eta^1\text{-}C(OMe)C_6H_4\text{-}o\text{-}Cl\}]OTf$ $\mathbf{5}^+OTf^-$

$[Fe(C_5Me_5)(CO)_2\{\eta^1\text{-}C(OMe)(OR)C_6H_4\text{-}o\text{-}Cl\}]$ **6a,b**

solid state as a yellow powder, these species undergo thermal decomposition in solution at 0 °C. Addition of $HBF_4 \cdot OEt_2$ to a crude solution of **6a** led quantitatively to the carbene

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[*] Dr. V. Guerchais, G. Poignant
UMR 6509 CNRS-Université de Rennes 1
"Organométalliques et Catalyse: Chimie et Electrochimie Moléculaires"
Beaulieu, Université de Rennes 1
F-35042 Rennes Cedex (France)
Fax: (+33) 299-281646
E-mail: guerchai@univ-rennes1.fr

Dr. S. Sinbandhit
Centre Régional de Mesures Physiques de l'Ouest (C.R.M.P.O.)
Beaulieu, Université de Rennes 1
F-35042 Rennes Cedex (France)

Dr. L. Toupet
UMR 6626 Groupe Matière Condensée et Matériaux
Beaulieu, Université de Rennes 1
F-35042 Rennes Cedex (France)

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