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The metal atom route to stable binary nickel stannylene complexes: synthesis of $[Ni(SnR_2)_4]$ [R = $CH(SiMe_3)_2$ or C_6HBu^t-2-Me_3-3,4,5] †

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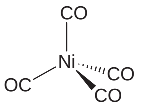
The reaction of toluene solvated zerovalent nickel atoms with Lappert's and Weidenbruch's stannylenes $:Sn\{CH(SiMe_3)_2\}_2$ and $:Sn(C_6HBu^t\text{-}2\text{-}Me_3\text{-}3,4,5)_2$ at −78 °C gave the first homoleptic nickel(hydrocarbyl)stannylene complexes of composition $[Ni(SnR_2)_4]$ as stable, red to purple crystals in 58 and 33% yield. The parent stannylenes represent ligand systems capable of stabilizing small transition metal centers like Ni^0 without the necessity of any further stabilizing coligands.

Introduction

Organometallic chemistry offers a number of homoleptic, yet reactive sources of Ni^0. The individual ligand environments in these compounds stabilize the low valent central nickel atom to such an extent that these compounds are moderately stable but in turn also highly reactive. The stability of **1**–**4** is mainly dependent on the π-electron accepting strength of the ligands, which is of course extraordinarily high for CO but decreases rapidly in the case of the alkenic ligands cod, *trans*,*trans*,*trans*-cyclododeca-1,5,9-triene (cdt) and ethylene.



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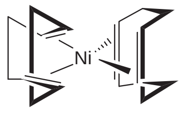

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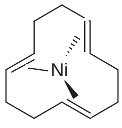

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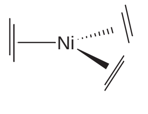

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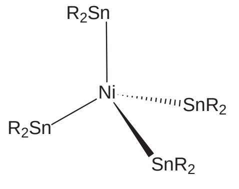
Main group metal ligands ER_2 are extremly rare in stabilizing zerovalent transition metal atoms in homoleptic complexes, binary $[Ni\{Sn(NBu^t)_2SiMe_2\}_4]$ **5** being the lone example so far, in which four stannylenes $:Sn(NBu^t)_2SiMe_2$ **6**[2] stabilize a zerovalent nickel(0) center.[1] However, its synthesis parallels the one devized a few years earlier by Lappert and co-workers[3] for the synthesis of the first homoleptic stannylene complexes (M = Pt **7a** or Pd **7b**) containing the amidostannylene $:Sn\{N(SiMe_3)_2\}_2$ ligand which allows complexation of zerovalent platinum(0) or palladium(0) centers.



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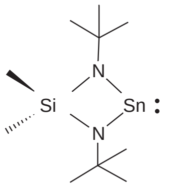
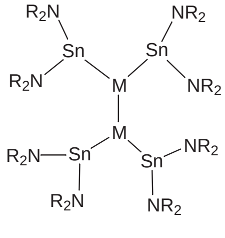
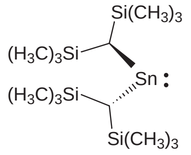


R = **6**



R = $Si(CH_3)_3$, M = Pt **7a**, Pd **7b**



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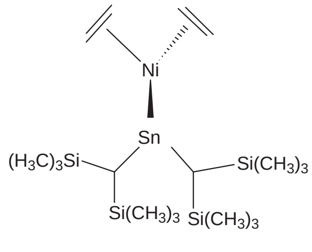

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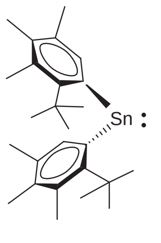

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The first organostannylene to be observed directly was Lappert's $:Sn\{CH(SiMe_3)_2\}_2$ **8**[4]. Up to now research in this field has been very active and a remarkable number of new congeners of **8** has been synthesized.[5] Interestingly, no example of a homoleptic metal complex of these ligands is known. This fact triggered our interest in the quest for stable, isolable homoleptic complexes of **8** as well as for Weidenbruch's bis(2-*tert*-butyl-3,4,5-trimethylphenyl) stannylene **9**.[6]

Attempts to react $[Ni(C_2H_4)_3]$, the most reactive source of zerovalent Ni conventionally available, with **8** did not result in complete substitution of all ethylene ligands and subsequent formation of a homoleptic binary nickel(0) stannylene complex. Instead only one ethylene was substituted, forming the bis(ethylene)mono(stannylene)nickel(0) complex **10**.[8] This finding may indicate that either the π-accepting ability of **7** is not strong

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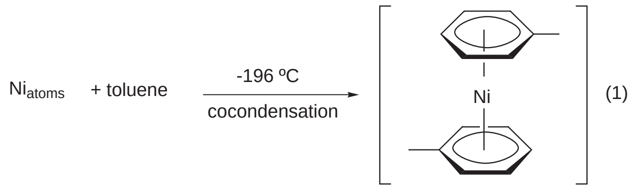
† Dedicated to Prof. R. Sustmann on the occasion of his 60th birthday.

enough or that the tris(ethylene) complex **4** is not labile enough to allow complete displacement of all three ethylenes.

Results and discussion

Based on these findings and failures in $Sn^{II}R_2/Ni^0$ chemistry to synthesize homoleptic $[Ni(SnR_2)_4]$ complexes, we turned our attention to the metal vapor approach[9] in order to learn whether homoleptic stable stannylene analogues of nickel tetracarbonyl similar to **5** are accessible *via* this unconventional metal atom based synthesis technique. The cocondensation technique has recently allowed the synthesis of homoleptic carbene complexes as shown by the work of Cloke and coworkers[10] (Pd or Pt). Herein we used a related metal atom based approach, the low temperature metal atom solution technique.[9]

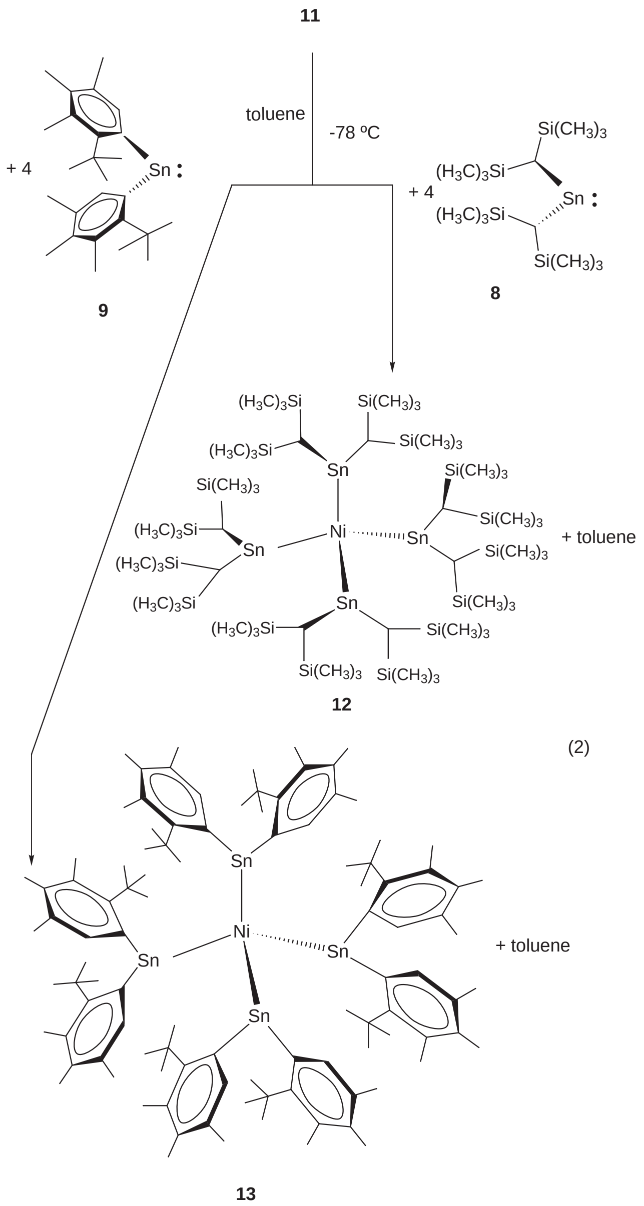
Highly reactive bis(toluene)nickel **11** serves as a source for zerovalent nickel. It is prepared by cocondensing nickel atoms together with toluene gas at −198 °C [eqn. (1)].[11] Compound **11** decomposes already autocatalytically between −50 and −40 °C with liberation of toluene and decomposition into finely divided nickel metal particles which are surface covered by traces of hydrocarbons. This material is known to be reactive in a number of catalytic transformations.[12] However, careful preparation and isolation techniques allow one to store and handle arene solutions of **11** by standard Schlenk techniques, thus making them valuable highly reactive sources of Ni^0 in a "bottled" form for stoichiometric organometallic reactions. The term "solvated metal atoms" has been coined for such solutions.[13] These solutions are even more reactive towards complete arene ligand displacement than the well known tris(ethylene)nickel(0) which can be prepared from **11** *via* ligand exchange.[14] Reactions in which toluene ligands remain in stable products derived from **11** are rare,[15] compared to those in which both toluene ligands are displaced. This vindicates **11** as the ultimate candidate for the synthesis of yet unknown homoleptic nickel complexes of stannylenes **8** and **9**.



11

stable up to -50 °C
in toluene

The addition of a toluene solution of compound **11** to a suspension of **8** or **9**, in toluene at −100 °C, according to eqn. (2) leads to formation of red to purple solutions when warming to −78 °C indicating instantaneous reaction. Both reactions are extraordinarily fast even at that low temperature. The unusual red to purple colour of crystalline **12** and **13** in the solid state as well as in solution points to a strong intraligand π conjugation, especially when bearing in mind that complexes of the nominal composition NiL_4 having ligands without significant intraligand π conjugation like PR_3 are usually colourless or only light yellow.[16] The high acceptor nature of the stannylene $[Sn\{CH(SiMe_3)_2\}_2]$ is known from Lappert's pioneering work on transition metal complexes of these ligands.[17] We have recently shown that this remarkable π-electron accepting strength of subvalent **8** and **9** can be used to stabilize unusual Sn^{II}/Fe^0 and Sn^{II}/Co^I organobimetallics, the latter being an element combination for which no other examples had been described. In solution this high electron accepting strength is manifested in strongly shielded ^{119}Sn NMR signals compared to those of the 'free' ligand **9**[18] and in the solid state in short Fe–Sn and Co-Sn bonds.[18,19]



On the basis of the unequivocal total elemental analysis on compounds **12** and **13** both have the homoleptic composition $[Ni(SnR_2)_4]$. Proton and ^{13}C NMR spectra are in accord with their formulation as homoleptic binary stannylene complexes [eqn. (2)]. Thus, there is only one set of ^1H NMR signals for the $CH(SiMe_3)_2$ and 2-*tert*-butyl-3,4,5-trimethylphenyl ligands, respectively. The presence of two **12**, or eleven **13** signals in the ^{13}C NMR spectra is in accord with the assumption of equivalent $:SnR_2$ stannylene fragments in **12** and **13**. No additional signals for free stannylenes are observed in either of the cases, ruling out a dissociation type equilibrium in solution as observed for four-co-ordinated nickel(0) complexes like $[Ni(PEt_3)_4]$ [eqn. (3)].[20] Concentrated solutions, of **12** or of **13**,

$$[Ni(PEt_3)_4] \rightleftharpoons Ni(PEt_3)_3 + PEt_3 \qquad (3)$$

do not change their intense bright red to purple colour upon cooling to −78 °C, which if so would be indicative for a reversible $[Ni(SnR_2)_3]/[Ni(SnR_2)_4]$ equilibrium. Such a color change is observed for solutions of $[Ni(PEt_3)_4]$ which indeed show a rapid dissociative–associative exchange process. Thus **12** and **13** may retain their $[Ni(SnR_2)_4]$ stoichiometry in the solid as well as in solution. Unfortunately both complexes did not form crystals of sufficient quality for X-ray analysis.

Conclusion

Stannylenes **12** and **13** represent ligand systems capable of stabilizing small transition metal centers like Ni^0 without the necessity of any further stabilizing coligands. This is shown here for the first time for "non-base-stabilized" di(hydrocarbyl)-stannylenes. Considerable π-back-bonding ability of the ligands is a prerequisite to enhance the stability of these compounds and such an ability of **8** and **9** can indeed be deduced from the colour and spectral data of **12** and **13**. Our findings should allow further exploitation of **8** and **9** as well as other stannylenes as versatile bonding partners to low valent transition metal centers. It can be expected that even more homoleptic metal complexes of stannylenes are stable and accessible in a straightforward manner by employing the synthetically useful metal vapor approach, especially when using the solvated metal atom technique, which is known for a variety of transition metal atoms in combination with a number of different solvents.[21]

Experimental

General information

Metal atom reactions were conducted in laboratory built all glass static metal vapor reactors based on the design of Klabunde and co-workers.[21,22] Nickel metal (chunks) was 99% pure. Metal evaporation was from resistively heated alumina crucibles (Mathis, Co., California, USA). In metal vapor reactions an amount of *ca.* 20–30% is lost due to deposition of metal vapor outside of the reaction zone of the nickel atom–toluene cocondensate. Except for the metal vapor synthesis, all manipulations were carried out under an atmosphere of dry nitrogen gas with standard Schlenk techniques. Compounds **8** and **9** were prepared according to published procedures.[4,6] Microanalyses were performed by the microanalytical laboratory of the Chemistry Department of the University/GH-Essen. All solvents were dried appropriately and stored under nitrogen. The NMR spectra were recorded on a Bruker AC 300 spectrometer (300 MHz for ^{1}H, 75 MHz for ^{13}C) and referenced against the remaining protons of the deuteriated solvent used. The samples were prepared by vacuum transfer of predried, degassed solvents onto the appropriate amount of solid sample, followed by flame sealing of the NMR tube. The MS spectra were recorded on a MAT 8200 instrument using standard conditions (EI, 70 eV) and the fractional sublimation technique.

Synthesis of $[Ni(SnR_2)_4]$ [R = $CH(SiMe_3)_2$ 12 or C_6HBu^t-2-Me_3-3,4,5 13]

Compound **8** (0.9 g, 2.05 mmol) or **9** (2 g, 4.3 mmol) was dissolved in 20 ml toluene and placed on the bottom of a static metal vapor reactor. This solution was degassed by three freeze–thaw–pump cycles and subsequently cooled to −196 °C. After 2 g (34 mmol, or 0.7 g, 12 mmol) of Ni atoms had been cocondensed with 100 ml of toluene the reactor was warmed to −100 °C whereupon the toluene–nickel matrix melted. Slow warming to −78 °C gave purple to red solutions which were filtered over a pad of alumina at that temperature to remove unchanged nickel metal, warmed to room temperature and pumped to dryness. Crystallization of the crude residues from diethyl ether (**12**, −30 °C) or pentane (**13**, −78 °C) during several days afforded **12** (0.54 g, 0.30 mmol, 58%) and **13** (0.71 g, 0.37 mmol, 33%) as microcrystalline, deep red solids. Compound for **12**: MS (EI, 70 eV) *m*/*z* 1807(1), M^+; 1203(15), $[M^+ - SnR_2 - CH_3 - 2SiMe_3]$; and 1059(100%), $[M^+ - 2SnR_2 + (CH_3)_3Si_2H]$; ^{1}H NMR (300 MHz, C_6D_6, 27 °C, $SiMe_4$) δ 0.17 [s, 144 H, $Si(CH_3)_3$] and 1.31 (s, 8 H, CH); ^{13}C NMR (75 MHz, C_6D_6, 27 °C, $SiMe_4$) δ 3.7 [$Si(CH_3)_3$] and 22.4 (CH); ^{119}Sn(C_6D_6, 27 and −30 °C) no signal detected (Found: C, 37.30; H, 8.67; Ni, 3.23. Calc. for $C_{56}H_{152}NiSi_{16}Sn_4$: C, 37.18; H, 8.49; Ni, 3.25%). Compound **13**: MS (EI, 70 eV) decomp; ^{1}H NMR (300 MHz, C_6D_6, 27 °C, $SiMe_4$) δ 7.30 (s, 8 H, =CH), 2.78, 2.11, 1.92 (all s, 72 H, CH_3) and 1.46 [s, 72 H, $C(CH_3)_3$]; ^{13}C NMR (300 MHz, C_6D_6, 27 °C, $SiMe_4$) δ 153.0, 140.9, 138.7, 135.6, 133.5 (C_{tert} aryl), 126.4 (CH aryl), 37.8 [$C(CH_3)_3$], 33.8 [$C(CH_3)_3$]; 25.3, 21.4 and 15.7 (CH_3 aryl); ^{119}Sn(C_6D_6, 27 and −30 °C) no signal detected (Found: C, 64.37; H, 7.67; Ni, 2.94. Calc. for $C_{104}H_{152}NiSn_4$: C, 64.52; H, 7.93; Ni, 3.03%).

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