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Insertion of organoindium carbenoids into rhodium halide bonds: revisiting a classic type of transition metal–group 13 metal bond formation

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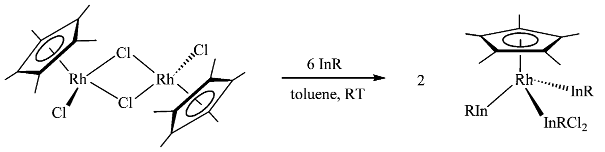
Insertion of the carbenoid group 13 metal species InCp* (Cp* = pentamethylcyclopentadienyl) and $InC(SiMe_3)_3$ into the Rh–Cl bonds of $[\{RhCp^*Cl_2\}_2]$ yields the new complexes $[Cp^*Rh(InCp^*)_3(Cl)_2]$ 1 and $[Cp^*Rh(\mu^2\text{-}Cl)_2(InC(SiMe_3)_3)_3]$ 2, respectively, exhibiting novel cage-like intermetallic complexes with In–Cl–In bridges.

The formation of stable bonds between transition metals and group 13 metals has been an area of research for more than half a century. Among the numerous methods of forming these metal–metal bonds developed since then, the insertion of low valent group 13 halides into transition metal halides has proven to be one of the most smooth and fascinating, yet mysterious routes.[1] Hsieh reported in a series of papers in the early seventies of the last century on the insertion of Indium(I) halides into metal–metal and metal–halogen bonds of mainly carbonyl containing transition metal complexes. The insertion of InX (X = Cl, Br) into M–X (M = Co, Fe, Rh) was found to take place readily yielding pure microcrystalline compounds in all cases.[2] At that time however many of the required molecular transition metal halide complexes were not readily available, and also the molecular structures of the products could not be fully identified. Due to the relative insolubility of the products the structural conclusions could only be based on elemental analyses and IR spectroscopy.

The stability and accessibility of group 13 alkyls, *i.e.* $In(I)C(SiMe_3)_3$[3] or In(I)Cp*,[4] allows us to revisit this concept of transition metal-group 13 metal bond formation and some unanswered questions concerning the molecular structures of the products as well as the driving forces leading to the insertion can be re-addressed. The introduction of alkyl groups at the indium in the place of the halides leads to a drastic enhancement of the solubility of the carbenoid ligands as well as the products, but also provides a valuable tool to "tune" the electronic as well as steric properties of the Indium(I) species. Furthermore, a detailed study of this insertion process seems to be especially interesting and useful in the light of our recent research in the field of homoleptic transition metal–group 13 metal complexes and cluster compounds. By treating $[Pd(II)(tmeda)X_2]$ (X = Cl, CH_3) with InCp*, we were successful in isolating the linear trinuclear Pd(0) cluster $[Pd_3(\mu^2\text{-}InCp^*)_4(InCp^*)_4]$.[5] The Pd d^{10} metal center in this complex is not significantly basic, thus the acidic $[InCp^*(CH_3)_2]$ or $[InCp^*Cl_2]$ moieties formed in the course of the reaction are cleaved leaving the product $[Pd_3(InCp^*)_8]$. By choosing more basic transition metal centers we expected to be successful in isolating some "intermediates" of the insertion reaction, as the In(III) species formed should show relatively strong interactions with the transition metal center of the product. Thus, we considered Rh(I)Cp* as the transition metal fragment of choice for these studies, providing both a basic metal center in $RhCp^*(L)_2$ complexes as well as good accessibility *via* reduction from the Rh(III) halide compounds $[\{RhCp^*X_2\}_2]$.[6]

Reaction of $[\{RhCp^*Cl_2\}_2]$ with six equivalents of $InC(SiMe_3)_3$ in toluene at room temperature leads to a deep red solution. On removal of the solvent, red microcrystals of $[RhCp^*\{InC(SiMe_3)_3\}_3Cl_2]$ (**1**) could be isolated.† Analogously, reaction of $[\{RhCp^*Cl_2\}_2]$ with six equivalents of InCp* and subsequent cooling to 0 °C yields red single crystals of $[RhCp^*(InCp^*)_3Cl_2]$ (**2**).‡ Both reactions are depicted in Scheme 1.



Scheme 1 R = $C(SiMe_3)_3$ (**1**), R = Cp* (**2**)

1 and **2** are stable at room temperature under inert gas atmosphere and dissolve well in aprotic organic solvents such as benzene or toluene. The ^1H NMR spectrum of **1** in C_6D_6 shows two singlets at 1.90 and 0.51 ppm, representing the Cp* and $C(SiMe_3)_3$ groups, respectively, with an integral ratio of about 15 : 81. Compound **2** similarly gives rise to two resonances at 2.18 and 1.77 ppm with an integral ratio of about 15 : 45, assignable to the Cp* ligands of Rh and In, respectively. The ^{13}C NMR spectra bear no unusual features.

The NMR data of both compounds are not consistent with a simple acid–base adduct of a $RhCp^*(InR)_2$ fragment and $In(III)RCl_2$. Instead, in both complexes the three InR ligands are equivalent on the NMR time scale. Obviously a fast exchange of the chlorides between all In atoms is taking place, resulting in three equivalent InR ligands. At −80 °C in toluene-d^8 the spectra of both compounds remain unchanged. It is noteworthy that a similar fluxional process was observed in the acid–base adduct of GaCp* and $GaCp^*X_2$ (X = Cl, Br), showing coalescence of the Cp* rings even at −80 °C in toluene-d^8. However, the crystal structure of this compound clearly showed the presence of two different Ga centers, one assignable to an oxidation state of + III (η^1-Cp*, two chlorines), the other one of +I (η^5-Cp*). The nature of the related fluxional process exchanging the halogens as well as the hapticity of the Cp* moieties was reported to be rather complex and has yet to be fully reported.[7] DFT calculations on the systems $R_3E–ER$ and their isomers $R_2E–ER_2$ revealed, that the difference in energy between these two forms is strongly dependent on both, the R groups as well as the group 13 metal E. The adducts $Cl_3B–GaH$ and $Cl_3B–InH$ for example exhibit bridging chlorines in the energetic minimum.[8] However, to the best of our knowledge, there is so far no experimental evidence for these kinds of "intermediates" for this chlorine exchange process.

The molecular structure of **1** (Fig. 1) reveals the two chlorine atoms occupying bridging positions. One indium atom (In(1)) is found in a special position being coordinated by two chlorines. However, the distance of the chlorines to the tetracoordinated indium is longer than to the tricoordinated indium centers, reflecting the fluxionality of the chlorines in solution. The Rh–In distances are all very similar, lying between 2.6244(6) Å and 2.5617(7) Å.

Analogous to complex **1**, the molecular structure of **2** (Fig. 2) exhibits a distorted tetrahedral $RhIn_3$ geometry. In contrast to complex **1**, however, only one of the chloride atoms is found in a bridging position, Cl(2) is terminally coordinated to In(3) which results in a slightly shorter In–Cl bond length. The strong

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difference in hapticity of the Cp* rings is a rather striking feature of complex **2**. The Cp* ring on In(3) is clearly σ bonded. The C–C bond lengths of the C_5 ring alternate, with C=C double bonds of 1.36 Å and C–C single bond distances of 1.47 Å. In contrast, the Cp* on In(1) is clearly η^5-bonded, with the In(1)–C bond lengths ranging from 2.382(9) to 2.587 (19) Å. The bridging chloride atom Cl(1) has some ground state trans-effect on the coordination of the Cp* at In(2) which exhibits a "non-classical" hapticity best described as an η^3 or η^2 bonding mode. The In–C bond lengths of 2.332(9) (In(2)–C(22)) and 2.404(9) Å (In(2)–C(21)) are in the range of bonding interactions, while the other In–C distances are distinctly longer. This unusual hapticity of the Cp* ring has no evident influence on the C–C bond lengths of the C_5 ring with distances between 1.395(12) and 1.440(13) Å. The only noteworthy structural analogy is $[Cp^*(CO)_2Fe(GaCp^*Cl)]$ obtained on reduction of $[Cp^*(CO)_2FeCl]$ with GaCp*, where an η^2 bonding mode is observed for the Cp* bound to the GaCl-moiety in the product.[9]

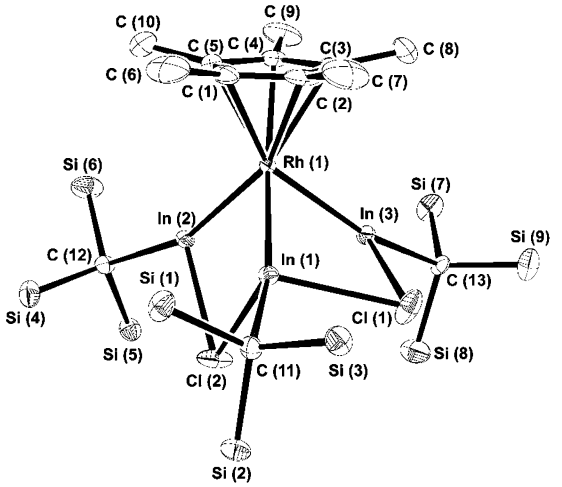

Fig. 1 Molecular structure of **1**. Selected bond lengths (Å) and angles (°) (All methyl groups of the $SiMe_3$ moieties have been omitted for clarity): Rh(1)–In(1) 2.6244(6), Rh(1)–In(2) 2.5617(7), Rh(1)–In(3) 2.5618(6), In(1)–Cl(1) 2.7182(17), In(1)–Cl(2) 2.7006(16), In(2)–Cl(2) 2.6215(15), In(3)–Cl(1) 2.6302(16), In(1)–C(11) 2.257(5), In(2)–C(12) 2.241(5), In(3)–C(13) 2.218(5), Cl(1)–In(1)–In(3)–In(2) 156.9(7), Cl(2)–In(1)–In(2)–In(3) 98.8(5), C(1)–C(2)–C(3)–C(8) 166.9(6).

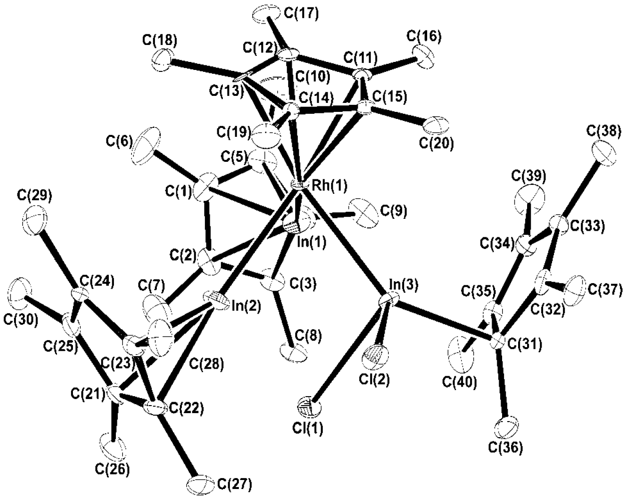

Fig. 2 Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Rh(1)–In(1) 2.522(3), Rh(1)–In(2) 2.537(3), Rh(1)–In(3) 2.572(4), In(2)–Cl(1) 2.923(4), In(3)–Cl(1) 2.664(4), In(3)–Cl(2) 2.500(3), In(1)–C(η^5–Cp*) 2.382(9)–2.587(10), In(2)–C(21), 2.404(9), In(2)–C(22) 2.332(9), In(2)–C(23) 2.596(9), In(2)–C(24) 2.778(10), In(2)–C(25) 2.660(10), In(3)–C(31) 2.209(9), C(31)–C(32) 1.463(12), C(32)–C(33) 1.356(12), In(2)–In(3)–Cl(1) 59.42(7), In(3)–In(2)–Cl(1) 51.67(9).

In summary, we have isolated and characterized the products of the insertion of InR into the the Rh–Cl bonds of $[\{RhCp^*Cl_2\}_2]$. The new compounds show interesting cage-like structures with In–Cl–In bridges. Both complexes are fluxional in solution. This fluxional process is reflected in their solid state structures, which can be regarded as trapped "intermediates" of a chlorine exchange between In(I) and In(III) centers, giving new evidence for the actual complexity of this classical insertion reaction.

Notes and references

† *Spectroscopic data* for **1**: δ_H(298 K, 250.1 MHz, C_6D_6) 1.90 [s, 15H, CH_3], 0.51 [s, 81H, $SiMe_3$]; δ_C(298 K, 62.9 MHz, C_6D_6] 94.4 [d, (^1J (Rh–C) = 4.3 Hz), ring atoms, Cp*Rh], 39.6 [d, (^2J (Rh–C) = 5.5 Hz), In–C], 13.4 [CH_3, Cp*Rh], 7.6 [$SiMe_3$]. Elemental Anal. Calc. for $C_{40}H_{96}Cl_2In_3RhSi_9$, C, 35.63; H, 7.18. Found: C, 36.25; H, 7.44.

Spectroscopic data for **2**: δ_H(298 K, 250.1 MHz, C_6D_6) 2.18 [s, 45H, CH_3], 1.77 [d, (^3J(Rh–H) = 0.57 Hz), 15H, CH_3]; δ_C(298 K, 62.9 MHz, C_6D_6] 118.1 [ring atoms, Cp*In], 96.7 [d, (^1J(Rh–C) = 5.1 Hz), ring atoms, Cp*Rh], 13.9 [CH_3, Cp*Rh], 11.7 [CH_3, Cp*In]. Elemental Anal. Calc. for $C_{40}H_{60}Cl_2In_3Rh$, C, 45.36; H, 5.71. Found: C, 45.56; H, 5.46.

‡ *Crystallographic data* for **1** (red, 0.30 × 0.15 × 0.15 mm): $C_{40}H_{96}Cl_2In_3RhSi_9$, M = 1348.2, monoclinic, a = 14.509(3), b = 18.830(4), c = 22.633(4) Å, β = 92.882(4)°, U = 6176(2) Å^3, T = 213(2) K, space group $P2_1/n$, Z = 4, μ(Mo-Kα, λ = 0.71073 Å) = 1.6555 mm^{-1}, 34096 reflections measured, 10683 unique (R_{int} = 0.0438) which were used in all calculations. The final $wR(F^2)$ was 0.1039 (all data); measurements: Bruker-axs-SMART-diffractometer; programs used: SHELXS-86 and SHELXL-97. CCDC 204637. See http://www.rsc.org/suppdata/cc/b3/b301928d/ for crystallographic files in .cif format.

Crystallographic data for **2** (red, 0.35 × 0.20 × 0.20 mm) $C_{40}H_{60}Cl_2In_3Rh$ M = 1059.2, orthorhombic, a = 10.732(19), b = 21.72(4), c = 35.49(5) Å, U = 8272(24) Å^3, T = 213(2) K, space group $Pbca$, Z = 8, μ(Mo-Kα, λ = 0.71073 Å) = 2.1999 mm^{-1}, 21255 reflections measured, 7199 unique (R_{int} = 0.0764) which were used in all calculations. The final $wR(F^2)$ was 0.1392 (all data); measurements: Bruker-axs-SMART-diffractometer; programs used: SHELXS-86 and SHELXL-97. CCDC 204638. See http://www.rsc.org/suppdata/cc/b3/b301928d/ for crystallographic files in .cif format.

1 R. A. Fischer and J. Weiß, *Angew. Chem.*, 1999, **111**, 3002; R. A. Fischer and J. Weiß, *Angew. Chem. Int. Ed.*, 1999, **38**, 2830.
2 (*a*) A. T. T. Hsieh and M. J. Mays, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 223; (*b*) A. T. T. Hsieh, *Inorg. Chim. Acta*, 1975, **14**, 87; (*c*) A. T. T. Hsieh and M. J. Mays, *J. Organomet. Chem.*, 1972, **37**, 9; (*d*) A. T. T. Hsieh and M. J. Mays, *J. Chem. Soc., Chem. Commun.*, 1971, 1234.
3 (*a*) R. D. Schluter, A. H. Cowley, D. A. Atwood, R. A. Jones and J. L. Atwood, *J. Coord. Chem.*, 1993, **30**, 25; (*b*) W. Uhl, R. Graupner, M. Layh and U. Schütz, *J. Organomet. Chem.*, 1995, **493**, C1.
4 O. T. Beachley, Jr., R. Blom, M. R. Churchill, K. Faegri, Jr., J. C. Fettinger, J. C. Pazik and L. Victoriano, *Organometallics*, 1989, **8**, 346.
5 T. Steinke, C. Gemel, M. Winter and R. A. Fischer, *Angew. Chem.*, 2002, **114**, 4955; T. Steinke, C. Gemel, M. Winter and R. A. Fischer, *Angew. Chem. Int. Ed.*, 2002, **41**, 4761.
6 J. W. Kang, K. Moseley and P. M. Maitlis, *J. Am. Chem. Soc.*, 1969, **91**, 5970.
7 P. Jutzi, B. Neumann, G. Reumann, L. O. Schebaum and H.-G. Stammler, *Organometallics*, 2001, **20**, 2854.
8 A. Y. Timoshkin and G. Frenking, *J. Am. Chem. Soc.*, 2002, **124**, 7240.
9 P. Jutzi, B. Neumann, L. O. Schebaum, A. Stammler and H.-G. Stammler, *Organometallics*, 2000, **19**, 1445.