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Mixed-ligand di-μ-chloro-bridged rhodium dimers as key intermediates in the synthesis of acyclic (π-allyl)-*closo*-rhodacarboranes

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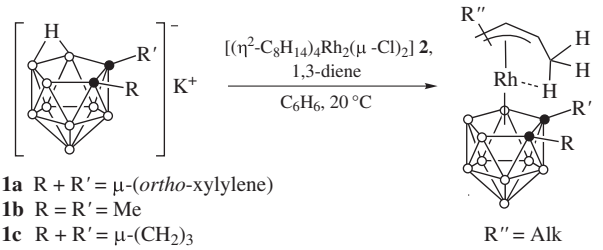
The mixed-ligand di-μ-chloro-bridged rhodium dimers $[(\eta^2\text{-}C_8H_{14})(\eta^4\text{-}2\text{-methylbuta-1,3-diene})Rh(\mu\text{-}Cl)]_2$ and $[(\eta^2\text{-}C_8H_{14})(\eta^4\text{-}2,3\text{-dimethylbuta-1,3-diene})Rh(\mu\text{-}Cl)]_2$ were synthesized and characterized. These compounds are key precursors in the preparative synthesis of the acyclic (π-allyl)-*closo*-rhodacarborane complexes [3-{π-(R″-allyl)}-1-R-2-R′-*closo*-3,1,2-$RhC_2B_9H_9$], which were obtained earlier *via* the one-pot metallation of the K^+ salts of the [7-R-8-R′-*nido*-7,8-$C_2B_9H_{10}]^-$ anions with $[(\eta^2\text{-}C_8H_{14})_4Rh_2(\mu\text{-}Cl)_2]$ in the presence of substituted buta-1,3-diene ligands.

Previously, we reported a convenient synthesis of new acyclic (π-allyl)rhodacarboranes of the general formula [3-{π-(R″-allyl)}-1-R-2-R′-*closo*-3,1,2-$RhC_2B_9H_9$] (where R″ is an aliphatic substituent).[1] These (π-allyl)-*closo*-rhodacarboranes were prepared by room-temperature one-pot reactions between the K^+ salts of [7-R-8-R′-*nido*-7,8-$C_2B_9H_{10}]^-$ anions **1a–c** and di-μ-chloro-bridged reagent $[(\eta^2\text{-}C_8H_{14})_4Rh_2(\mu\text{-}Cl)_2]$ **2** in the presence of an excess of aliphatic 1,3-dienes, as exemplified by Scheme 1. The molecular structures of these π-allyl complexes were determined by X-ray diffraction analysis, which revealed the presence of a rare Me···Rh agostic bond in these molecules,[1] in accord with their high stability in both a solid state and solution.



1a R + R′ = μ-(*ortho*-xylylene)
1b R = R′ = Me
1c R + R′ = μ-$(CH_2)_3$

R″ = Alk

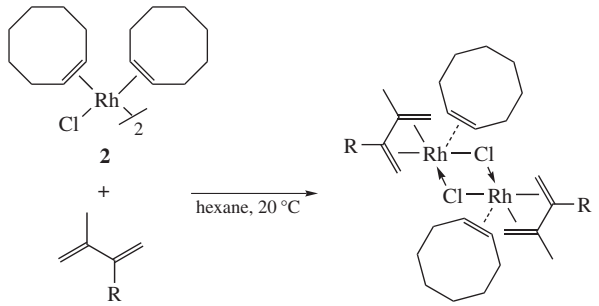
Scheme 1

Apart from this particular synthetic motif, efforts have been made toward establishing a plausible mechanism by which these reactions may proceed so as to have efficient access to other π-allyl rhodium carborane complexes which can be used as unmodified catalyst precursors for the selective hydroformylation of alkenes.[1] As a result, we were encouraged to find possible organometallic intermediate complexes which could be easily formed from starting di-μ-chloro-bridged reagent **2** and acyclic 1,3-dienes and, at the same time, would be active metallation species in reactions with [*nido*-7,8-R′,R″-7,8-$C_2B_9H_{12}]^-$ monoanions giving rise to the desired acyclic (π-allyl)-*closo*-rhodacarboranes in good yields.

Evidently, this three-component one-pot method used for the synthesis of the above (π-allyl)-*closo*-rhodacarboranes[1] is conceptually based on two-step reactions which apparently involve the displacement of cyclooctene ligands in **2** by a given 1,3-diene at the first step. It is well known that in the case of alkene–rhodium dimers, such as $[(C_2H_4)_2Rh(\mu\text{-}Cl)]_2$, only one of two possible diene–rhodium complexes, either $[(\eta^4\text{-diene})_2RhCl]$ or $[(\eta^4\text{-diene})RhCl]_2$, can be isolated in the reaction with 2-methylbuta-1,3-diene (isoprene) **3** and 2,3-dimethylbuta-1,3-diene **4** regardless of the ratio between reactants.[2] At the same time, according to published data,[3] if complex **2** was used as a starting material in the displacement reaction with acyclic 1,3-dienes **3** or **4**, the formation of electron-deficient mononuclear Rh^I species $[(\eta^4\text{-1,3-diene})(\eta^2\text{-cyclooctene})RhCl]$ might be expected. We surmised that the latter mixed-ligand complexes could exist in a dimeric di-μ-chloro-bridged form which is stable in both a solid state and solution.

Indeed, the reaction of **2** with either **3** or **4** reported here definitely evidences the dimeric mixed-ligand structure of the products formed, $[(\eta^2\text{-}C_8H_{14})(\eta^4\text{-2-methylbuta-1,3-diene})RhCl]_2$ **5** and $[(\eta^2\text{-}C_8H_{14})(\eta^4\text{-2,3-dimethylbuta-1,3-diene})RhCl]_2$ **6**, respectively (Scheme 2).† Complex **6** was purified by dissolving in *n*-hexane and cooling at –78 °C; then, the resulting crystalline material was recrystallized from CH_2Cl_2 at –20 °C to give single crystals suitable for a low-temperature X-ray diffraction study.

The molecular structure of **6** is shown in Figure 1.‡ In a crystal, the molecule of **6** occupies a special position at an inversion



3 R = H
4 R = Me

5 R = H
6 R = Me

Scheme 2

† *Synthesis of the dimeric complexes* $[(\eta^2\text{-}C_8H_{14})(\eta^4\text{-diene})RhCl]_2$ **5**, **6** (*general procedure*). To a slurry of complex **2** in 6 ml of *n*-hexane (distilled before use under argon) 1,3-diene **3** or **4** (a threefold molar excess) was added dropwise with stirring. The resulting mixture was stirred for 1 h at ambient temperature and then kept overnight at –78 °C. Crystalline solids that formed were collected by filtration and dried *in vacuo* affording **5** or **6**, respectively. Complex **6** can be recrystallized from CH_2Cl_2 at –20 °C to give single crystals suitable for X-ray diffraction.

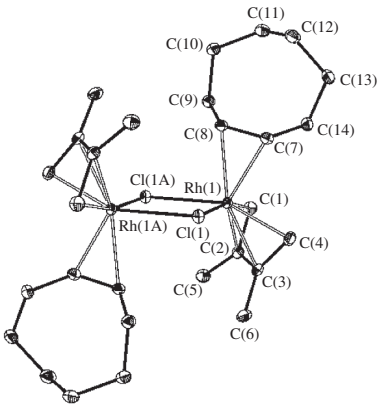
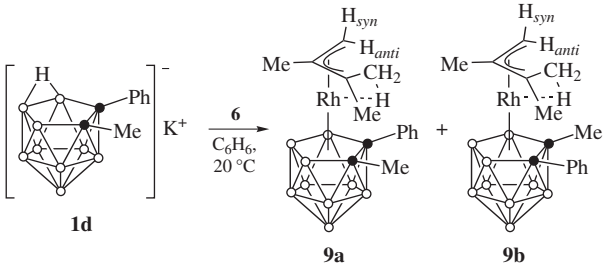


Figure 1 ORTEP representation of the molecular structure of complex **6** with thermal ellipsoids drawn at a 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and bond angles (°): Rh(1)–Cl(1) 2.5001(3), Rh(1)–Cl(1A) 2.5098(3), Rh(1)–C(7) 2.250(1), Rh(1)–C(8) 2.260(1), Rh(1)–C(1) 2.063(1), Rh(1)–C(2) 2.159(1), Rh(1)–C(3) 2.164(1), Rh(1)–C(4) 2.085(1), C(1)–C(2) 1.447(2), C(2)–C(3) 1.417(2), C(3)–C(4) 1.445(2), C(7)–C(8) 1.381(2), C(8)–C(9) 1.510(2), C(7)–C(14) 1.504(2), Rh(1)···Rh(1A) 3.6392(2); Cl(1)–Rh(1)–Cl(1A) 86.83(1), Rh(1)–Cl(1)–Rh(1A) 93.17(1).

centre, thus having a centrosymmetric structure. Two crystallographically equivalent $[(\eta^2\text{-}C_8H_{14})(\eta^4\text{-}C_6H_{10})RhCl]$ fragments in **6** are linked together by two symmetrical μ-chloro bridges [Rh–Cl, 2.5001(3) and 2.5098(3) Å], while the butadiene and cyclooctene ligands are in *trans* position to each other. Each rhodium atom in **6** is bound to one 2,3-dimethylbuta-1,3-diene ligand, which acts as an η^4-coordinating ligand, and one weakly coordinated cyclooctene ligand. Of particular interest is the coordination geometry of the rhodium atoms, as determined in structure **6**. Assuming that each μ-chloro ligand occupies only one coordination site and the Rh–Rh bond in **6** is excluded [Rh···Rh, 3.6392(2) Å], the rhodium atoms in this complex have a coordination number of five. The Rh–(μ-Cl_2)–Rh four-membered ring is planar with the Rh(μ-$Cl)_2$ angle of 86.83(1)°. Although the cyclooctene ligand in **6** is located rather far from the rhodium centre, it still remains coordinated to each of the rhodium atoms. Note that the Rh–C(12M) and Rh–C(34M) bond lengths in the 2,3-(dimethyl)butadiene ligand and the Rh–C(78M) bond length in the cyclooctene ligand [C(12M), C(34M) and C(78M) are the midpoints of the double bonds in these ligands] are significantly different being 1.984(1), 1.998(1) and 2.147(1) Å, respectively. To the best of our knowledge, the only precedent of crystallographically characterized dimeric di-μ-chloro-bridged five-coordinate Rh^I complexes with a comparable molecular architecture is $[(\eta^2,\kappa^1\text{-}C_{10}H_8NBoc)(CO)RhCl]_2$ (where $C_{10}H_8NBoc$ is *N*-Boc-azabenzonorbornadiene).[4]

Mixed-ligand complexes **5** and **6** are key intermediates in the formation of agostic *closo*-(π-allyl)rhodacarboranes species of these series. It was found that both **5** and **6** react with **1b** in C_6H_6 at room temperature to give acyclic (π-allyl)-*closo*-rhodacarboranes: [3-{(1-3-η^3)-C_5H_9}-1,2-Me_2-*closo*-3,1,2-$RhC_2B_9H_9$] **7a**,**b** (two isomers) and [3-{(1-3-η^3)-C_6H_{11}}-1,2-Me_2-*closo*-3,1,2-$RhC_2B_9H_9$] **8**, respectively, in high yields. The structures of complexes **7a**,**b** and **8** were deduced by a comparison of their ^{1}H NMR spectra with those of authentic samples which have been prepared earlier *via* the one-pot method[1] outlined in Scheme 1. In addition, the reaction of **6** with **1d** (R = Me, R′ = Ph) was found to afford the new π-allyl derivative [3-{(1-3-η^3)-C_6H_{11}}-1-Me-2-Ph-*closo*-3,1,2-$RhC_2B_9H_9$] isolated in 56% yield (total content) as an inseparable mixture of two diastereomers **9a**,**b** (Scheme 3). These isomeric complexes were characterized by elemental analysis and multinuclear NMR spectroscopy, although the precise stereochemistry of **9a**,**b** cannot be assigned based on these data only.§



Scheme 3

For **5**: yellow microcrystals, 51% yield. ^{1}H NMR (400.13 MHz, CD_2Cl_2) δ: 5.50 (m, 4H, 1,2-CH, COE), 4.97 [br.t, 2H, H(3), J_t 7.3 Hz], 2.39 [br.s, 2H, $H(1)_{syn}$], 2.35 [d, 2H, $H(4)_{syn}$, J_{vic} 5.4 Hz], 2.16 (br.s, 8H, 3,8-CH_2, COE), 2.06 (s, 6H, Me), 1.54 (br.s, 16H, 4,5,6,7-CH_2, COE), 0.48 [br.s, 2H, $H(1)_{anti}$], 0.43 [d, 2H, $H(4)_{anti}$, J_{vic} 9.0 Hz]. $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2) δ: 122.0 (1,2-CH, COE), 101.4 [C(2)], 85.6 [C(3)], 39.5 [C(1)], 36.9 [C(4)], 30.5, 27.1 (4,5,6,7-CH_2, COE), 27.0 (3,8-CH_2, COE), 22.0 (Me). Found (%): C, 48.91; H, 6.88; Cl, 11.33. Calc. for $C_{26}H_{44}Cl_2Rh_2$ (%): C, 49.31; H, 7.00; Cl, 11.20.

For **6**: yellow microcrystals, 65% yield. ^{1}H NMR (400.13 MHz, CD_2Cl_2) δ: 5.52 (m, 4H, 1,2-CH, COE), 2.21 [br.s, 4H, $H(1,4)_{syn}$], 2.15 (br.s, 8H, 3,8-CH_2, COE), 1.97 [s, 12H, 2,3-Me], 1.54 (br.s, 16H, 4,5,6,7-CH_2, COE), 0.24 [br.s, 4H, $H(1,4)_{anti}$]. $^{13}C\{^1H\}$ NMR (150.93 MHz, CD_2Cl_2) δ: 121.2 (1,2-CH, COE), 96.1 [C(2,3)], 37.5 [C(1,4)], 30.5, 27.1 (4,5,6,7-CH_2, COE), 27.0 (3,8-CH_2, COE), 18.8 (2,3-Me). Found (%): C, 49.35; H, 6.85; Cl, 11.56. Calc. for $C_{28}H_{48}Cl_2Rh_2$ (%): C, 50.83; H, 7.26; Cl, 10.74.

‡ *Crystal data for* **6**: $C_{28}H_{48}Cl_2Rh_2$, *M* = 661.38, orthorhombic, space group *Pbca*, *a* = 10.5900(4), *b* = 14.2438(5) and *c* = 18.1388(6) Å, *V* = = 2736.1(2) Å^3, d_{calc} = 1.606 g cm^{-3}, *Z* = 4, MoKα radiation (λ = 0.71073 Å), μ = 1.416 mm^{-1}, *T* = 100(2) K, $2\theta_{max}$ = 60°, R_1 = 0.0169 for 3702 reflections with $I > 2\sigma(I)$, and wR_2 = 0.0395 for all 3965 unique reflections (R_{int} = 0.0296). The SHELXTL program package[5] was used for the calculations.

CCDC 921336 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2013.

§ *Diastereomeric complexes* [3-{(1-3-η^3)-C_6H_{11}}-1-Me-2-Ph-*closo*-3,1,2-$RhC_2B_9H_9$] **9a**,**b**. To a solution of **6** (65 mg, 0.1 mmol) in 4 ml of degassed benzene, K salt **1d**[7] (66 mg, 0.25 mmol) was added in one portion as a solid. After 2 h of vigorous stirring, the resulting red solution was treated by column chromatography on silica gel, eluting a colored fraction with a mixture of CH_2Cl_2–hexane (1:2). After the removal of the solvent *in vacuo* and recrystallization of the residue from a mixture of CH_2Cl_2–hexane, 43 mg (53%) of isomeric complexes **9a**,**b** were obtained as a light red amorphous solid.

For **9a**,**b**: IR (KBr, ν/cm^{-1}): 2548 (ν_{BH}). ^{1}H NMR (600.22 MHz, CD_2Cl_2; **9a**:**9b** = 1:2.3*) δ: 7.84* (dd, 2H, Ph, J_1 7.7 Hz, J_2 1.9 Hz), 7.51 (d, 2H, Ph, *J* 7.4 Hz), 7.36–7.26 (m, 6H, Ph, Ph*), 4.25* [d, 1H, $H(3')_{syn}$, J_{gem} 1.8 Hz], 3.98 [d, 1H, $H(3')_{syn}$, J_{gem} 2.2 Hz], 2.86 (s, 3H, Me_{carb}), 2.63 [br.s, 1H, $H(3')_{anti}$], 2.55* [br.s, 1H, $H(3')_{anti}$], 2.39* (s, 3H, Me_{carb}), 2.16* (s, 3H, Me_{syn}), 2.00 (s, 3H, Me_{syn}), 1.70* (d, 3H, 2′-Me, *J* 2.2 Hz), 1.67 (d, 3H, 2′-Me, *J* 2.0 Hz), 0.00* [s, 3H, Me_{anti}(agost.)], –0.33 [s, 3H, Me_{anti}(agost.)]. $^{13}C\{^1H\}$ NMR (150.93 MHz, CD_2Cl_2, $J_{^{13}C,^{103}Rh}$) δ: 147.0, 144.1, 129.8, 129.5, 129.2, 128.9, 128.4, 127.4 (C_{Ar}, C^*_{Ar}), 117.9 [d, C(2′), *J* 5.4 Hz], 117.9* [d, C(2′), *J* 5.5 Hz], 116.1, 111.4 (C_{carb}), 109.9*, 104.3* (C_{carb}), 97.9* [d, C(1′), *J* 5.8 Hz], 96.9 [d, C(1′), *J* 5.9 Hz], 61.2 [d, C(3'), *J* 8.9 Hz], 60.3* [d, C(3′), *J* 9.3 Hz], 36.7 (Me_{carb}), 32.6* (Me_{carb}), 21.5* (Me_{syn}), 20.4* (2′-Me, 2′-Me*), 20.2 [Me^*_{anti}(agost.), Me_{syn}], 20.1 [Me_{anti}(agost.)]. ^{11}B NMR (193 MHz, CD_2Cl_2, $J_{^{11}B,^1H}$) δ: 20.1 (d, *J* 147 Hz), 14.5 (d, *J* 125 Hz), 13.7 (d, *J* 147 Hz), 10.0 (d, *J* 144 Hz), 4.1 (d, *J* 140 Hz), 3.3 (d, *J* 166 Hz), 2.4 (d, *J* 171 Hz), –1.3 (d, *J* 166 Hz), –2.2 (d, *J* 175 Hz), –3.1 (d, *J* 160 Hz), –3.9 (d, *J* 152 Hz), –4.7 (d, *J* 160 Hz), –5.6 (d, *J* 196 Hz), –6.5 (d, *J* 140 Hz), –18.7 (d, *J* 152 Hz), –20.0 (d, *J* 153 Hz). Found (%): C, 43.71; H, 7.20; B, 22.83. Calc. for $C_{15}H_{28}B_9Rh$ (%): C, 44.09; H, 6.91; B, 23.81.

Nido-dicarbaundecaborate salts are known to display the acidic character of the *endo*-hydrogen atom which is located over the pentagonal C_2B_3-open face. Taking this into account, we propose two alternative reaction sequences leading to the formation of the (π-allyl)-*closo*-rhodacarborane complexes. The first involves the initial attack of the *endo*-hydrogen either on the metal centre of above intermediate complexes **5** or **6** followed by the addition of metal hydride to one of the double bonds of the acyclic η^4-diene ligand or directly to a double bond of the diene ligand giving rise to an unsymmetrical η^3-allyllic unit. According to this, the dianionic $\{nido\text{-}7\text{-}R\text{-}8\text{-}R'\text{-}C_2B_9\}^{2-}$ species generated *in situ* after the elimination of the *endo*-hydrogen atom and potassium chloride can undergo relatively fast metallation through an open face of the cage ligand with (π-allyl)rhodium species ultimately forming the agostic (π-allyl)-*closo*-rhodacarborane products.

Alternatively, these reactions can proceed through the initial formation of *exo-nido* species, namely, either [*exo*-{Rh(η^4-diene)-(η^2-C_8H_{14})}-*nido*-7-R-8-R′-$C_2B_9H_{10}$] or [*exo*-{Rh(η^4-diene)}-*nido*-7-R-8-R′-$C_2B_9H_{10}$], which then undergoes intramolecular attack by acidic *nido*-carborane *endo*-hydrogen on the metal centre and subsequent *exo-nido-to-closo* rearrangement of the diene–hydride intermediate. Hydride transfer from the metal atom to the acyclic η^4-diene ligand, similar to the above pathway, would finally result in the desired (π-allyl)rhodium-carborane complexes.

Both of the pathways are consistent with our earlier observation that, in [3-{(1-3-η^3)-$C_8H_8D_5$}-1,2-(4′-$MeC_6H_4)_2$-*pseudocloso*-3,1,2-$RhC_2B_9H_9$], the species closely related to **7**–**9**, mostly the *endo*-deuteration of the (1-3-η^3)-cyclooctenyl ligand at the C(4)–C(8) carbon atoms had occurred during its preparation from [Cs][10-*endo*-D-7,8-(4′-$MeC_6H_4)_2$-*nido*-7,8-$C_2B_9H_9$].[6] Further experiments to establish the mechanism of formation of the acyclic (π-allyl)-*closo*-rhodacarboranes are currently underway in our laboratory.

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