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Metal complexes with an aminosubstituted tricarbollide ligand

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Abstract

The reaction of the tricarbollide salt Tl[7-*t*BuNH-7,8,9-$C_3B_8H_{10}$] (Tl**1**) with $[(cod)Rh(THF)_x]^+$ gives the rhodium complex [1-(cod)-12-*t*BuNH-1,2,4,12-$RhC_3B_8H_{10}$] in almost quantitative yield. Analogous reactions of Tl**1** with $[(ring)M(THF)_x]^{2+}$ ((ring)M = Cp*Rh and (1,3,5-$C_6H_3Me_3$)Ru) afford the corresponding metallatricarbollides [1-(ring)-12-*t*BuNH-1,2,4,12-$MC_3B_8H_{10}$] in ca. 50% yield. Refluxing Tl**1** with $[Mn(CO)_3(MeCN)_3]^+$ in THF give the tricarbollide analogue of cymantrene, [1,1,1-$(CO)_3$-12-*t*BuNH-1,2,4,12-$MnC_3B_8H_{10}$], the structure of which was determined by single-crystal X-ray diffraction analysis. In all cases, the formation of the metallatricarbollide complexes is accompanied by polyhedral rearrangement leading to the maximum separation of the cage carbon atoms.

Keywords: Boron; Metallacarboranes; Tricarbollide; Polyhedral rearrangement; X-ray diffraction

1. Introduction

A convenient, high-yield synthesis of the aminosubstituted tricarbollide anion [7-*t*BuNH-7,8,9-$C_3B_8H_{10}]^-$ (**1**), reported in 1999 [1], allowed for the development of its metal-complexation chemistry. Anion **1** is supposed to be a much closer analogue of Cp^- than the well-known dicarbollide dianion, $[7,8\text{-}C_2B_9H_{11}]^{2-}$, due to its monoanionic character. A characteristic feature of the iron [2–4], cobalt [5] and ruthenium [6] tricarbollide sandwich complexes prepared earlier is that their formation is accompanied by extensive polyhedral rearrangement. Herein, we report the synthesis of analogous ruthenium, rhodium, and manganese tricarbollide complexes along with a single-crystal X-ray diffraction analysis of one of them.

2. Results and discussion

2.1. Synthesis of metallatricarbollides

One of the methods for the preparation of the [(cod)RhCp] complex is the reaction between $[(cod)RhCl]_2$ and CpTl [7]. We have found, however, that the analogous direct reaction of $[(cod)RhCl]_2$ with the thallium salt of tricarbollide anion, Tl[7-*t*BuNH-7,8,9-$C_3B_8H_{10}$] (Tl**1**), gives no isolable metallacarborane species, presumably due to the low reactivity of the starting rhodium compound. In order to activate the rhodium precursor, the reaction of $[(cod)RhCl]_2$ with AgOTf in THF was used to generate $[(cod)Rh(THF)_x]^+$

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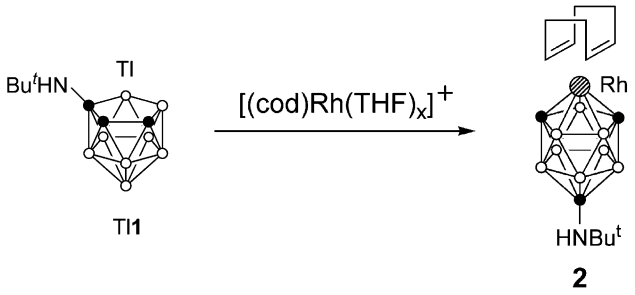
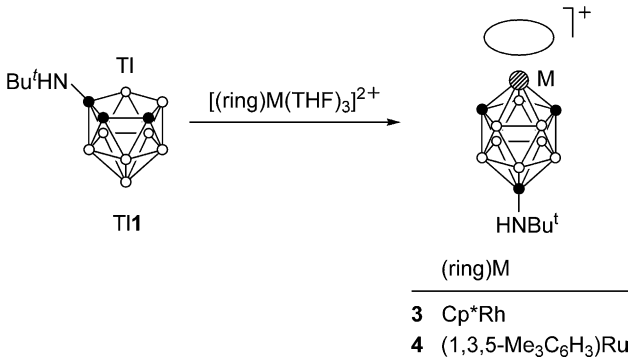


Scheme 1.



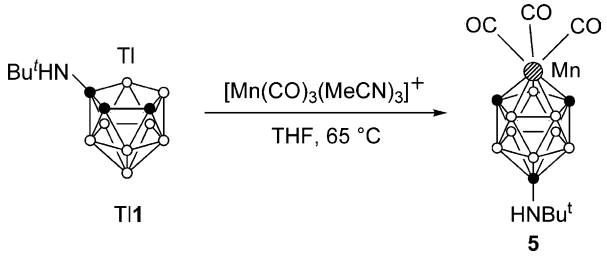
Scheme 2.

[8]. Indeed, the reaction of this labile solvate complex with Tl**1** gives the rhodium tricarbollide complex [1-(cod)-12-*t*BuNH-1,2,4,12-RhC$_3$B$_8$H$_{10}$] (**2**) in almost quantitative yield (Scheme 1). It should be noted that, even at room temperature, the formation of **2** is accompanied by polyhedral rearrangement leading to the maximum separation of the cage carbon atoms. The same rearrangement pattern has been observed previously for all other metal complexes of anion **1**, but at considerably higher temperatures ($\geqslant$110 °C).

Similarly as in the case of [(cod)RhCl]$_2$, direct reactions of either [Cp*RhCl$_2$]$_2$ or [(1,3,5-C$_6$H$_3$Me$_3$)RuCl$_2$]$_2$ with Tl**1** do not lead to tricarbollide complexes.[1] These reactions were, therefore, carried out using the labile THF solvates [Cp*Rh(THF)$_3$]$^{2+}$ [9] and [(1,3,5-C$_6$H$_3$Me$_3$)Ru(THF)$_3$]$^{2+}$, which were generated via reactions of the corresponding chlorides with AgOTf in THF (Scheme 2). The reactions with anion **1** led subsequently to the isolation of the cationic complexes of constitution [1-Cp*-12-*t*BuNH-1,2,4,12-RhC$_3$B$_8$H$_{10}$]$^+$ (**3**) and [1-(C$_6$H$_3$Me$_3$)-12-*t*BuNH-1,2,4,12-RuC$_3$B$_8$H$_{10}$]$^+$ (**4**) (yields ca. 50%), which were characterized as triflate salts.

In an analogous manner, no reactions were observed upon refluxing either [Mn(CO)$_5$Br] or [Re(CO)$_5$Br] with Tl**1** in THF for 24 h. However, the reaction of the more labile [Mn(CO)$_3$(MeCN)$_3$]$^+$ cation with Tl**1** in refluxing THF yields the manganese complex, [1,1,1-(CO)$_3$-12-*t*BuNH-1,2,4,12-MnC$_3$B$_8$H$_{10}$] (**5**), which can be considered as a tricarbollide analogue of cymantrene (Scheme 3).

All the compounds obtained were characterized by ^{1}H and ^{11}B NMR spectroscopy, and elemental analysis. The ^{11}B{^{1}H} NMR spectra display typically five 2:2:1:1:2 singlets (with incidental overlaps), which is



Scheme 3.

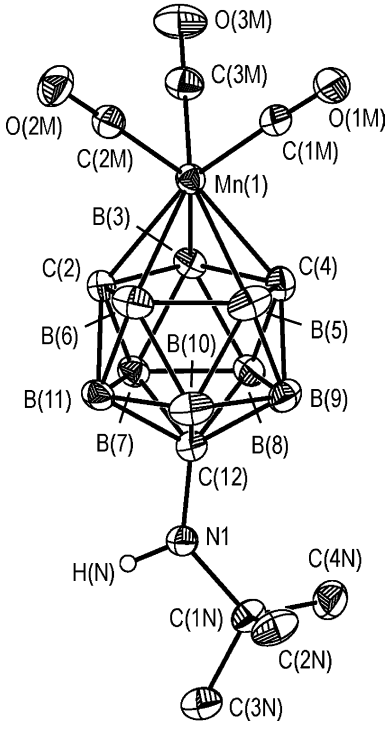


Fig. 1. Molecular structure of **5**. Atoms are represented by 50% thermal ellipsoids. Selected distances (Å): Mn(1)–C(2) 2.193(2), Mn(1)–C(4) 2.187(2), Mn(1)–C(1M) 1.784(3), Mn(1)–C(2M) 1.788(3), Mn(1)–C(3M) 1.802(3), Mn(1)–B(3) 2.156(3), Mn(1)–B(5) 2.158(3), Mn(1)–B(6) 2.144(3), Δ(Mn(1)···C$_2$B$_3$-plane) 1.609, C(1M)–O(1M) 1.146(3), C(2M)–O(2M) 1.143(3), C(3M)–O(3M) 1.144(3), C(2)–B(3) 1.692(4), C(2)–B(6) 1.698(4), C(4)–B(3) 1.692(3), C(4)–B(5) 1.711(4), B(5)–B(6) 1.753(5), C(12)–B(7) 1.719(4), C(12)–B(8) 1.735(4), C(12)–B(9) 1.696(4), C(12)–B(10) 1.747(4), C(12)–B(11) 1.706(4), C(12)–N(1) 1.424(3).

[1] The chloride-bridged cations [Cp*Rh(μ-Cl)$_3$RhCp*]$^+$ and [(C$_6$H$_3$Me$_3$)Ru(μ-Cl)$_3$Ru(C$_6$H$_3$Me$_3$)]$^+$ are formed instead.