

Metal complexes with an aminosubstituted tricarbollide ligand

Dmitry S. Perekalin^a, Konstantin A. Lyssenko^a, Pavel V. Petrovskii^a, Josef Holub^b,
Bohumil Štíbr^{b,*}, Alexander R. Kudinov^{a,*}

^a A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow GSP-1, Russian Federation

^b Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic (Research Centre for New Inorganic Compounds and Advanced Materials, University of Pardubice), 250 68, Řež, Czech Republic

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Abstract

The reaction of the tricarbollide salt $\text{Ti}[7\text{-}t\text{BuNH-7,8,9-C}_3\text{B}_8\text{H}_{10}]$ (TII) with $[(\text{cod})\text{Rh}(\text{THF})_x]^+$ gives the rhodium complex $[1\text{-}(\text{cod})\text{-12-}t\text{BuNH-1,2,4,12-RhC}_3\text{B}_8\text{H}_{10}]$ in almost quantitative yield. Analogous reactions of TII with $[(\text{ring})\text{M}(\text{THF})_x]^{2+}$ ($(\text{ring})\text{M} = \text{Cp}^*\text{Rh}$ and $(1,3,5\text{-C}_6\text{H}_3\text{Me}_3)\text{Ru}$) afford the corresponding metallatricarbollides $[1\text{-}(\text{ring})\text{-12-}t\text{BuNH-1,2,4,12-MC}_3\text{B}_8\text{H}_{10}]$ in ca. 50% yield. Refluxing TII with $[\text{Mn}(\text{CO})_3(\text{MeCN})_3]^+$ in THF give the tricarbollide analogue of cymantrene, $[1,1,1\text{-}(\text{CO})_3\text{-12-}t\text{BuNH-1,2,4,12-MnC}_3\text{B}_8\text{H}_{10}]$, 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.

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1. Introduction

A convenient, high-yield synthesis of the amino-substituted tricarbollide anion $[7\text{-}t\text{BuNH-7,8,9-C}_3\text{B}_8\text{H}_{10}]^-$ (**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, $[7,8\text{-C}_2\text{B}_9\text{H}_{11}]^{2-}$, 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.

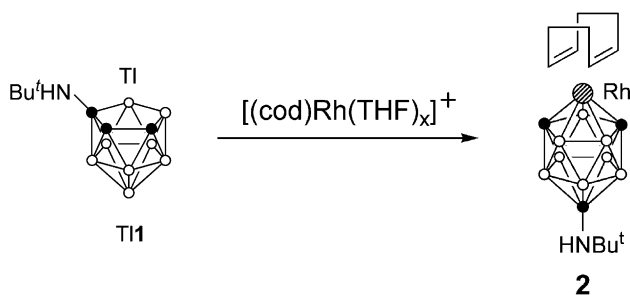
2. Results and discussion

2.1. Synthesis of metallatricarbollides

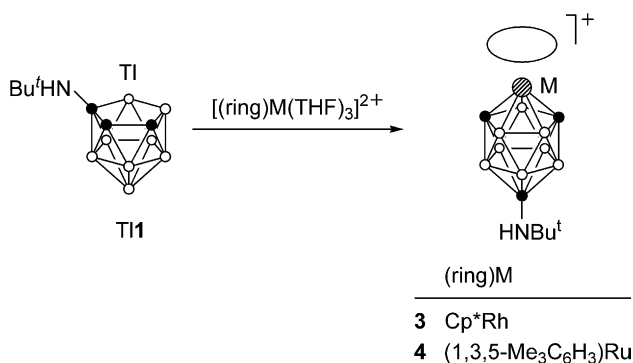
One of the methods for the preparation of the $[(\text{cod})\text{RhCp}]$ complex is the reaction between $[(\text{cod})\text{RhCl}]_2$ and CpTi [7]. We have found, however, that the analogous direct reaction of $[(\text{cod})\text{RhCl}]_2$ with the thallium salt of tricarbollide anion, $\text{Ti}[7\text{-}t\text{BuNH-7,8,9-C}_3\text{B}_8\text{H}_{10}]$ (TII), 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 $[(\text{cod})\text{RhCl}]_2$ with AgOTf in THF was used to generate $[(\text{cod})\text{Rh}(\text{THF})_x]^+$

* Corresponding authors. Tel.: +420 2 661 73109; fax (internat.): +420 2 20941502 (B. Štíbr); Fax (internat.): +7 095 1355085 (A.R. Kudinov).

E-mail addresses: stibr@iic.cas.cz (B. Štíbr), arkudinov@ineos.ac.ru (A.R. Kudinov).



Scheme 1.



Scheme 2.

[8]. Indeed, the reaction of this labile solvate complex with Tl1 gives the rhodium tricarbollide complex [1-(cod)-12-*t*BuNH-1,2,4,12-RhC₃B₈H₁₀] (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 (≥ 110 °C).

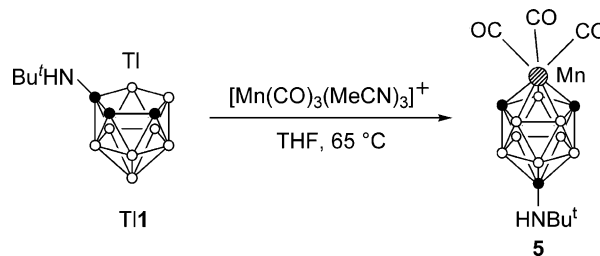
Similarly as in the case of [(cod)RhCl]₂, direct reactions of either [Cp*RhCl₂]₂ or [(1,3,5-C₆H₃Me₃)RuCl₂]₂ with Tl1 do not lead to tricarbollide complexes.¹ These reactions were, therefore, carried out using the labile THF solvates [Cp*Rh(THF)₃]²⁺ [9] and [(1,3,5-C₆H₃Me₃)Ru(THF)₃]²⁺, which were generated 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-RhC₃B₈H₁₀]⁺ (3) and [1-(C₆H₃Me₃)-12-*t*BuNH-1,2,4,12-RuC₃B₈H₁₀]⁺ (4) (yields ca. 50%), which were characterized as triflate salts.

In an analogous manner, no reactions were observed upon refluxing either [Mn(CO)₅Br] or [Re(CO)₅Br] with

¹ The chloride-bridged cations [Cp*Rh(μ-Cl)₃RhCp*]⁺ and [(C₆H₃Me₃)Ru(μ-Cl)₃Ru(C₆H₃Me₃)]⁺ are formed instead.

Tl1 in THF for 24 h. However, the reaction of the more labile [Mn(CO)₃(MeCN)₃]⁺ cation with Tl1 in refluxing THF yields the manganese complex, [1,1,1-(CO)₃-12-*t*BuNH-1,2,4,12-MnC₃B₈H₁₀] (5), which can be considered as a tricarbollide analogue of cymantrene (Scheme 3).

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



Scheme 3.

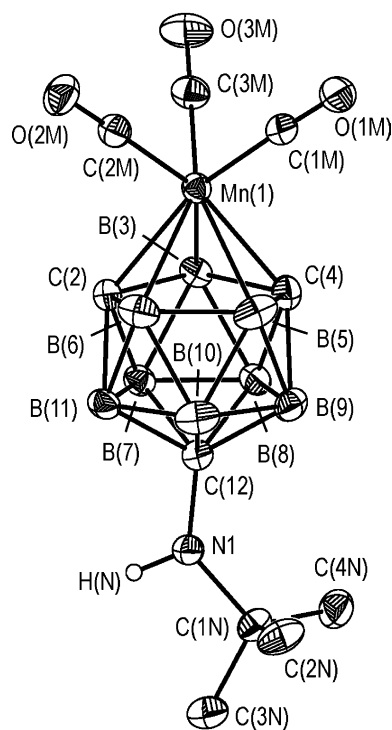


Fig. 1. Molecular structure of 5. Atoms are represented by 50% thermal ellipsoids. Selected distances (Å): Mn(1)–C(2) 2.193(2), Mn(1)–C(4) 2.187(2), Mn(1)–C(1M) 1.784(3), Mn(1)–C(2M) 1.788(3), Mn(1)–C(3M) 1.802(3), Mn(1)–B(3) 2.156(3), Mn(1)–B(5) 2.158(3), Mn(1)–B(6) 2.144(3), Δ(Mn(1)···C₂B₃-plane) 1.609, 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).

consistent with C_s symmetry of the complexes. The ^1H NMR spectra exhibit sharp *t*Bu singlets, broader singlets due to cage CH protons together with the corresponding resonances attributable to organic ligands (the NH-proton is usually not observed).

2.2. A single-crystal X-ray diffraction study of **5**

In order to confirm the cluster configuration in the metallatricarbollide complexes isolated, we investigated the structure of **5** by means of a single-crystal X-ray diffraction analysis (Fig. 1). Complex **5** displays the geometry expected for a 12-vertex $\{1,2,4,12\text{-MnC}_3\text{B}_8\}$ cluster core. The metal-to-plane distance $\Delta(\text{Mn}\cdots\text{C}_2\text{B}_3)$ (1.609 Å) is significantly shorter than that in the charge-compensated dicarbollide complex $[(\eta\text{-}9\text{-}(\text{Me}_2\text{S})\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10})\text{Mn}(\text{CO})_3]$ (**6**) (1.643 Å) [10], thus suggesting stronger bonding with the tricarbollide ligand.

The conformation of the $\text{Mn}(\text{CO})_3$ fragment with respect to the C_2B_3 plane in **5** is practically the same as in cymantrene: two of the carbonyl groups, C(1M)–O(1M) and C(2M)–O(2M), are located in *trans* positions to the cage carbon atoms C(2) and C(4), respectively, while the remaining C(3M)–O(3M) group is *trans*-oriented to the center of the B(5)–B(6) connectivity (Fig. 2). Such an orientation of the carbonyl groups in the crystal structure of **5** could explain the significant nonequiva-

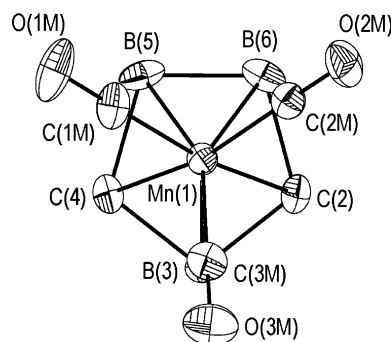


Fig. 2. Conformation of the $\text{Mn}(\text{CO})_3$ fragment with respect to the C_2B_3 plane in the molecular structure of **5**. Atoms are represented by 50% thermal ellipsoids.

lence of the Mn–CO bond lengths, although the C–O bond lengths remain almost equal. It should be noted that a different conformation of the $\text{Mn}(\text{CO})_3$ fragment is observed in **6** where the CO groups are *trans*-oriented to the boron atoms and to the center of the C–C bond.

The C_2B_3 ligand face is characterized by a flattened envelope conformation with the 0.156 Å shift of the B(3) atom up from the C(2)–B(6)–B(5)–C(4) plane. The N(1) atom in **5** is essentially tetrahedral, with the sum of bond angles C(12)–N(1)–C(1N), C(12)–N(1)–H(N) and C(1N)–N(1)–H(N) being equal to 349.2°. It should be noted that the lone pair of electrons (Lp) on

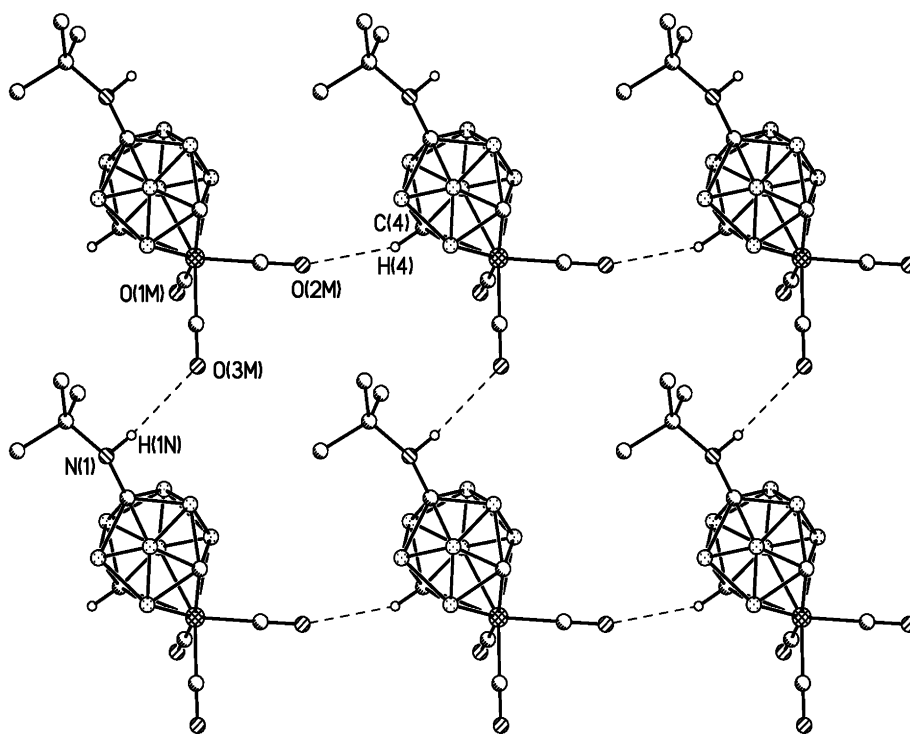


Fig. 3. The N–H \cdots OC and C–H \cdots OC bonded layers in crystal of **5**. Contact N(1)–H(1N) \cdots O(3M) $[-1+x, y, z]$: H(1N) \cdots O(3M) 2.60 Å, angle N(1)–H(1N)–O(3M) 148°, N(1) \cdots O(3M) 3.409(3) Å. Contact C(4)–H(4) \cdots O(2M) $[x, 1+y, z]$: H(4) \cdots O(2M) 2.48 Å, angle C(4)–H(4)–O(2M) 151°, C(4) \cdots O(2M) 3.465(3) Å.

the N(1) atom is located in an antiperiplanar position with respect to the B(10) atom (torsion angle Lp–N(1)–C(12)–B(10) 178°). Bearing this in mind, the elongation of the C(12)–B(10) connectivity (1.747(3) Å) in comparison to the remaining C(12)–B connectivities (1.706(3)–1.734(3) Å) could be interpreted as a consequence of possible charge transfer from the orbital containing the lone pair of electrons on the N(1) atom to a vacant antibonding orbital associated with C(12)–B(10) connectivity.

Moreover, the analysis of intermolecular interactions has revealed that the molecules in the crystal structure of **5** are assembled by weak H···OC contacts, N(1)–H(1N)···O(3M) and C(4)–H(4)···O(2M), into layers parallel to the crystallographic plane **ab** (Fig. 3).

The IR spectrum of **5** displays strong CO vibration bands at 2031, 1968 and 1950 cm⁻¹. These appear in a higher region than those for **6** (2020, 1950 and 1925 cm⁻¹) and cymantrene (2026 and 1935 cm⁻¹) [10]. These facts are in agreement with a stronger acceptor character of the tricarbollide ligand **1** in comparison with Cp⁻ and the charge-compensated [9-(SMe₂)-7,8-C₂B₉H₁₀]⁻ dicarbollide ligand. On the other hand, the frequency values observed for **5** approach those reported for the pyrrolyl complex [(C₄H₄N)Mn(CO)₃] (2032, 1974, and 1964 cm⁻¹) [11], suggesting that the donor-acceptor properties of **1** and C₄H₄N⁻ might be very similar.

3. Conclusion

We have demonstrated that neutral and cationic transition metal complexes of the amino-substituted tricarbollide ligand **1** can be synthesized using reactive metal-complex precursors. The formation of metallatricarbollides is always accompanied by polyhedral rearrangement that brings carbon atoms to the positions of maximum space separation over the cluster area. The IR data suggest that ligand **1** is a stronger acceptor than Cp⁻ and the charge-compensated dicarbollide ligand [9-(SMe₂)-7,8-C₂B₉H₁₀]⁻.

4. Experimental

All reactions were carried out under an argon atmosphere, however the subsequent isolation of products was conducted in air. The starting materials TI1 [1], [Mn(CO)₃(MeCN)₃]BF₄ [12], [(cod)RhCl]₂ [13], [Cp^{*}RhCl]₂ [14] and [(C₆H₃Me₃)RuCl]₂ [15] were prepared according to the literature procedures. The ¹H and ¹¹B NMR spectra were recorded on a Bruker AMX-400 spectrometer (¹H 400.13 MHz, ¹¹B 128.38 MHz) relative to residual protons of the solvents (¹H) or BF₃·Et₂O (external standard, ¹¹B).

4.1. [1-cod-12-*t*BuNH-1,2,4,12-RhC₃B₈H₁₀] (**2**)

A mixture of [(cod)RhCl]₂ (30 mg, 0.06 mmol) and AgOTf (31 mg, 0.12 mmol) in THF (5 ml) was stirred for 40 min and then TI[7-*t*BuNH-7,8,9-C₃B₈H₁₀] (53 mg, 0.13 mmol) was added. The resulting mixture was stirred overnight and opened to air. The yellow solution was filtered and evaporated to dryness in vacuo. The residue was dissolved in CH₂Cl₂/petroleum ether (1:2) mixture and filtered through a thin layer (3 cm) of silica gel. The filtrate was evaporated to dryness to give small yellow crystals of **2** (48 mg, 96%). ¹H NMR (CDCl₃) δ: 4.61 (s, 4H, CH of cod), 2.43 (s, 2H, CH-cage), 2.33 (d, 4H, CH₂ of cod), 2.19 (d, 4H, CH₂ of cod), 1.28 (s, 9H, *t*Bu). ¹¹B{¹H} NMR (CDCl₃) δ: -22.6 (2B), -20.8 (1B), -19.0 (1B), -13.6 (2B), -12.6 (2B). Calc. for C₁₅H₃₂B₈NRh (%): C 43.33, H 7.76, B 20.80, N 3.37. Found (%): C 43.70, H 7.74, B 20.49, N 3.28.

4.2. [1-Cp^{*}-12-*t*BuNH-1,2,4,12-RhC₃B₈H₁₀][CF₃SO₃] (**3OTf**)

A mixture of [Cp^{*}RhCl]₂ (43 mg, 0.07 mmol) and AgOTf (72 mg, 0.28 mmol) in THF (5 ml) was stirred for 1 h to generate [Cp^{*}Rh(THF)₃]²⁺. Then, TI[7-*t*BuNH-7,8,9-C₃B₈H₁₀] (57 mg, 0.14 mmol) was added and the reaction mixture was stirred overnight. The resulting yellow solution was filtered and evaporated to dryness in vacuo. The residue was dissolved in a small amount (1 ml) of CH₂Cl₂ and placed onto the top of a short silica gel column (5 cm). The pale-orange band was eluted with THF, collected, and evaporated to dryness. The resulting solid was reprecipitated from CH₂Cl₂/ether to give pure **3OTf** (51 mg, 61%) as a white powder. ¹H NMR (acetone-d₆) δ: 4.13 (br s, 1H, NH), 3.34 (s, 2H, CH-cage), 2.17 (s, 15H, Cp^{*}), 1.28 (s, 9H, *t*Bu). ¹¹B{¹H} NMR (128 MHz, CDCl₃) δ: -18.1 (2B), -13.4 (3B), -8.9 (1B), -3.0 (2B). Calc. for C₁₈H₃₅B₈F₃NO₃RhS (%): C 36.52, H 5.96, B 14.61, N 2.37. Found (%): C 36.41, H 5.88, B 14.60, N 2.34.

4.3. [1-C₆H₃Me₃-12-*t*BuNH-1,2,4,12-RuC₃B₈H₁₀]-[CF₃SO₃] (**4OTf**)

A mixture of [(C₆H₃Me₃)RuCl]₂ (38 mg, 0.07 mmol) and AgOTf (72 mg, 0.28 mmol) in THF (5 ml) was stirred for 1 h to generate [(C₆H₃Me₃)Ru(THF)_x]²⁺. Then, TI[7-*t*BuNH-7,8,9-C₃B₈H₁₀] (57 mg, 0.14 mmol) was added and the reaction mixture was stirred overnight. The resulting light-yellow solution was filtered and evaporated to dryness in vacuo. The residue was dissolved in a small amount of CH₂Cl₂ and placed onto the top of a short silica gel column (5 cm). The pale-orange band was eluted with THF, collected, and evaporated to dryness. The resulting solid was crystallized

from $\text{CH}_2\text{Cl}_2/\text{ether}$ at -10°C to give pure **4OTf** (42 mg, 52%). ^1H NMR (acetone- d_6) δ : 6.56 (3H, $\text{C}_6\text{H}_3\text{Me}_3$), 3.34 (s, 2H, CH-cage), 2.37 (s, 9H, $\text{C}_6\text{H}_3\text{Me}_3$), 1.25 (s, 9H, *t*Bu). $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3) δ : -20.4 (2B), -15.6 (3B), -10.9 (1B), -7.0 (2B). Calc. for $\text{C}_{17}\text{H}_{32}\text{B}_8\text{F}_3\text{NO}_3\text{RuS}$ (%): C 35.51, H 5.61, B 15.04. Found (%): C 35.25, H 5.49, B 15.15.

4.4. 1,1,1-(CO)₃-12-*t*BuNH-1,2,4,12-MnC₃B₈H₁₀ (**5**)

A solution of $[\text{Mn}(\text{CO})_3(\text{MeCN})_3]\text{BF}_4$ (52 mg, 0.15 mmol) and $\text{Ti}[7\text{-}i\text{BuNH-7,8,9-C}_3\text{B}_8\text{H}_{10}]$ (61 mg, 0.15 mmol) in 10 ml of THF was refluxed for 15 h and the resulting mixture was evaporated in vacuo. The residue was dissolved in $\text{CH}_2\text{Cl}_2/\text{petroleum ether}$ (1:2) mixture and eluted through a short layer of silica gel (3 cm). Slow evaporation of the clear solution gave yellow crystals of **5** (27 mg, 54% yield). ^1H NMR (CDCl_3) δ : 2.68 (s, 2H, CH-cage), 1.28 (s, 9H, *t*Bu). $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3) δ : -20.3 (2B), -16.6 (1B), -15.0 (1B), -12.2 (2B), -10.5 (2B). Calc. for $\text{C}_{10}\text{H}_{20}\text{B}_8\text{MnNO}_3$ (%): C 34.95, H 5.87, B 25.16, N 4.08. Found (%): C 34.88, H 5.73, B 24.84, N 4.02.

4.5. X-ray diffraction analysis of **5**

Suitable crystals of **5** were grown up by slow evaporation of a CH_2Cl_2 solution. At 120 K crystals of **5** ($\text{C}_{10}\text{H}_{20}\text{B}_8\text{MnNO}_3$) were monoclinic, space group $P2_1/n$, $a = 9.476(2)$, $b = 8.170(2)$, $c = 21.576(5)$ Å, $\beta = 101.466(5)^\circ$, $V = 1637.1(6)$ Å³, $Z = 4$, $M = 343.69$, $d_{\text{calc}} = 1.394$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 8.11$ m⁻¹, $F(000) = 704$. Intensities of 10,891 reflections were measured with a Smart 1000 CCD diffractometer at 120 K ($\lambda(\text{Mo K}\alpha) = 0.71072$ Å, $2\theta < 58^\circ$), and 4275 independent reflections ($R_{\text{int}} = 0.0400$) were used for further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The refinement converged to $wR_2 = 0.0994$ and $\text{GOF} = 1.097$ for all independent reflections ($R_1 = 0.0444$ was calculated against F for 29,658 observed reflections with $I > 2\sigma(I)$). All calculations were performed using SHELXTL PLUS 5.0. Crystallographic data (excluding structure factors) for the structure of **5**

have been deposited to the Cambridge Crystallographic Data Centre; No. CCDC-252553. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ UK (fax (internat.): +44 1223/336 033; E-mail: deposit@ccdc.cam.ac.uk).

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