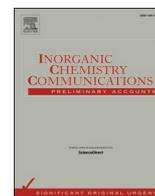




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Short communication

Manganacarborane based on 5,6-dicarba-*nido*-decaborane with triphenylphosphine at boron atomElena V. Balagurova^{a,*}, Ivan A. Godovikov^a, Elena G. Kononova^a, Fedor M. Dolgushin^{a,b}, Mikhail I. Shevchenko^c, Igor T. Chizhevsky^{a,1}^a A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28, Vavilov Str., Moscow 119991, Russian Federation^b Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences, 31 Leninsky prosp., 119991 Moscow, Russian Federation^c Higher Chemical College of the Russian Academy of Sciences, D.I. Mendeleev University of Chemical Technology of Russia, 9, Miusskaya Square, Moscow 125047, Russian Federation

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ABSTRACT

In the reaction of the ionic complex of manganese based on 5,6-dicarba-*nido*-decaborane [1,1,1-(CO)₃-*isonido*-1,2,4-MnC₂B₈H₁₀]⁻ tmdaH[±] (1) (tmdaH⁺ - protonated form of *N,N,N',N'*-tetramethyl-1,8-diaminonaphthalene) with triphenylphosphine (PPh₃) in the presence of boron trifluoride etherate (BF₃·Et₂O) in benzene, the neutral complex 1,1,1-(CO)₃-7-PPh₃-*isonido*-1,2,4-MnC₂B₈H₉ (2) was isolated as one of the main products. The position of the PPh₃ substituent in the carborane ligand was established by ¹H, ¹¹B, ³¹P, ¹³C, [¹¹B-¹¹B]-COSY, ¹H{¹¹B} NMR spectroscopy methods and confirmed by X-ray diffraction analysis.

Since the appearance of the first organometallic compounds of carboranes (the carborane complexes of such transition metals as cobalt, rhodium, ruthenium, iron) they have been intensively studied, that cannot be said about manganese derivatives. The research in the chemistry of manganese carborane derivatives has been left out for some reason [1].

However, the carborane complexes of manganese can be rather promising. Thus, the derivatives of tricarbonylcarborane complex {[3,3,3-(CO)₃-3,1,2-MnC₂B₉H₁₁]⁻} are analogues of the derivatives of cymantrene {C₅H₅Mn(CO)₃} known to be used in various fields, for example, in immunology [2], as additives in diesel fuel [3], as catalysts [4–6], etc. In this regard, carborane complexes of manganese as an element that can form compounds in various oxidation states may be of undoubted interest from the point of view of the general development of the chemistry of this class of compounds, namely, the structure, the nature of bonding and properties, as well as searching for new fields of application.

Another issue of interest is the targeted introduction of a charge-compensating substituent at boron atoms of the carborane ligand of metallacarborane based on 5,6-dicarba-*nido*-decaborane which is completely unexplored to our knowledge. Judging by literature there are two main ways of introducing substituent at boron atoms of

metallacarboranes. The first approach consists in the direct introduction of a substituent into the metallacarborane, while the second one is the synthesis of metallacarborane from the substituted carborane ligand. Using these methods, it is possible to prepare compounds containing substituents at different position in the carborane cage.

For example, the reaction of the modified anion [9-SMe₂-7,8-C₂B₉H₁₀]⁻ with the {Mn(CO)₃} fragment gives the complex 3,3,3-(CO)₃-4-SMe₂-3,1,2-MnC₂B₉H₁₀ with SMe₂ group at the α -position with respect to the carbon atoms of the five-membered surface of the carborane ligand η^5 -coordinated with the metal atom [7], while the complex [3,3,3-(CO)₃-8-SMe₂-3,1,2-MnC₂B₉H₁₀] with the same substituent in the β -position, was synthesized by the reaction of the complex [3,3,3-(CO)₃-*closo*-3,1,2-MnC₂B₉H₁₁]⁻ with SMe₂ in the presence of H₂SO₄ [8].

Examples of the formation of substituted metal complexes in the reactions of unsubstituted starting carboranes with metal complexes without introducing any additional components (initiators) into the reaction medium are known as well. Thus, the product of the reaction of carborane *nido*-7,8-C₂B₉H₁₃ with [MnMe(CO)₅] in THF is the complex [Mn(CO)₃{ η^5 -7,8-C₂B₉H₁₀-10-O(CH₂)₄}] with the ligand O(CH₂)₄ at the β -position with respect to the carbon atoms of the pentagonal surface of the carborane ligand [9]. In the series of metallacarboranes based on 5,6-*nido*-C₂B₈H₁₂ carborane, such reactions have been described for

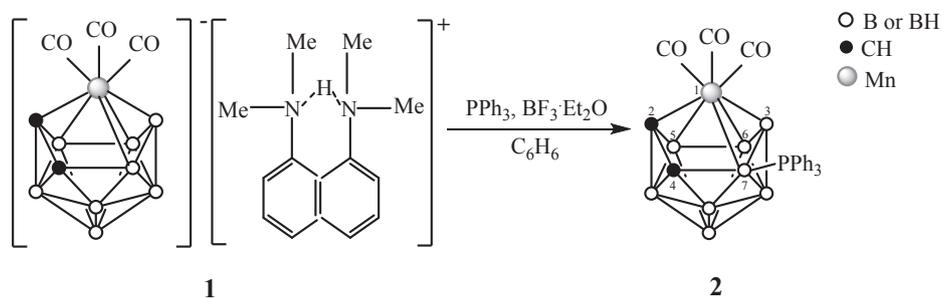
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Scheme 1. The reaction of complex(1) with triphenylphosphine.

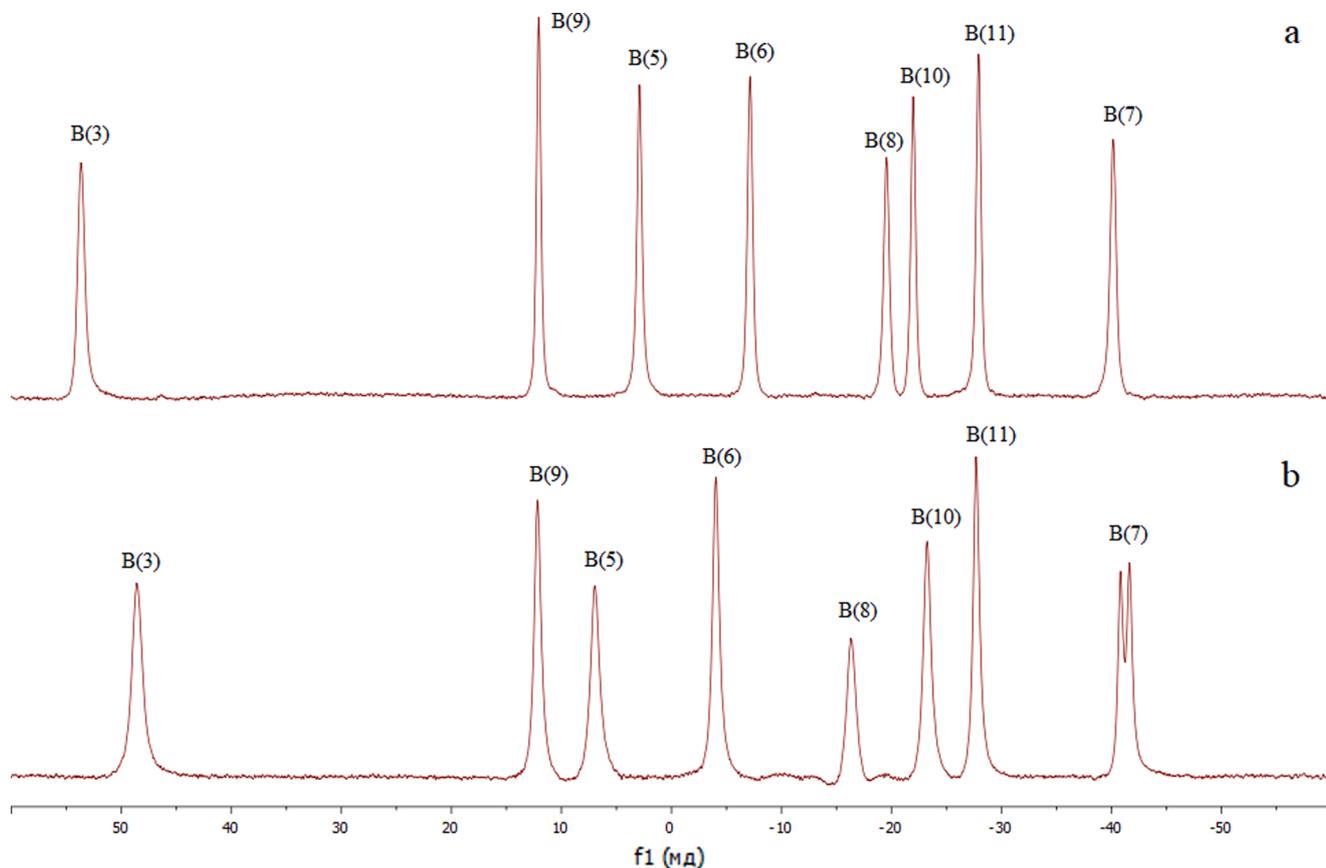


Fig. 1. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra (CH_2Cl_2): a) complex 1; b) complex 2.

ruthenium and osmium complexes. Ruthenacarborane 1,1-(PPh_3) $_2$ -1-H-3- PPh_3 -1,2,4-Ru $\text{C}_2\text{B}_8\text{H}_9$ is formed by the reaction of the salt $[\text{C}_2\text{B}_8\text{H}_{11}]^-\text{tmdaH}^+$ and $\text{RuClH}(\text{PPh}_3)_3$ in benzene [10]. The reaction of $[\text{C}_2\text{B}_8\text{H}_{11}]^-\text{Na}^+$ and the complex $(\text{PPh}_3)_3\text{OsCl}_2$ in THF gives osmacarborane 1,1-(PPh_3) $_2$ -1-H-3-O(CH_2) $_4$ -1,2,4-Os $\text{C}_2\text{B}_8\text{H}_9$ [11]. These reactions lead to ruthena- and osmacarboranes substituted at the boron atom with a low intracluster coordination number.

We tried to introduce a substituent into the previously synthesized manganacarborane $[1,1,1-(\text{CO})_3\text{-isonido-1,2,4-MnC}_2\text{B}_8\text{H}_{10}]^-\text{tmdaH}^+$ (1) [12]. In the reaction of complex (1) with triphenylphosphine in the presence of $\text{BF}_3\cdot\text{Et}_2\text{O}$ (the reagents are taken in an equimolar ratio) (S1) while refluxing in benzene for 1 h, the neutral complex $[1,1,1-(\text{CO})_3\text{-7-PPh}_3\text{-isonido-1,2,4-MnC}_2\text{B}_8\text{H}_9]$ (2) was isolated as a main product (Scheme 1). After column chromatography (eluent benzene, the first orange band) and crystallization from benzene:hexane system, complex 2 in the form of orange crystals was isolated with a yield up to 20%.

The structure of complex 2 was established by ^1H , $^{11}\text{B}/^{11}\text{B}\{^1\text{H}\}$, ^{31}P , ^{13}C , $[\text{B}\{^1\text{H}\}-\text{B}]\text{-COSY}$ and $^1\text{H}\{^{11}\text{B}\}$ NMR spectroscopy, IR spectroscopy

[13] and confirmed by X-ray diffraction analysis.

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The IR spectrum of the complex exhibits intense absorption bands at 2025, 1961, and 1933 cm^{-1} which are attributed to three CO-groups. The ^1H (CD_2Cl_2) NMR spectrum of complex 2 lacks signals at δ 19.0 ppm (1H^+) and δ 3.25 ppm (12H, CH_3) corresponding to the cation tmdaH^+ in the starting complex 1, in the δ range 7.70–7.45 ppm a multiplet with an intensity of 15H corresponds to the number of hydrogen atoms of PPh_3 , two signals δ 4.09 and 2.66 ppm each of 1H intensity belong to the hydrogen atoms at the carbon atoms of carborane ligand. The presence of phosphorus in the complex is confirmed by a broadened quadruplet at δ 8.73–6.83 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum characteristic of the phosphorus atom bound to the boron atom of the carborane cage [10]. In the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum, eight signals, one of which is located at δ 48.6 ppm demonstrate the preservation of the *isonido*-structure of the metallacarborane fragment $\{\text{Mn-C}_2\text{B}_8\}$, which,

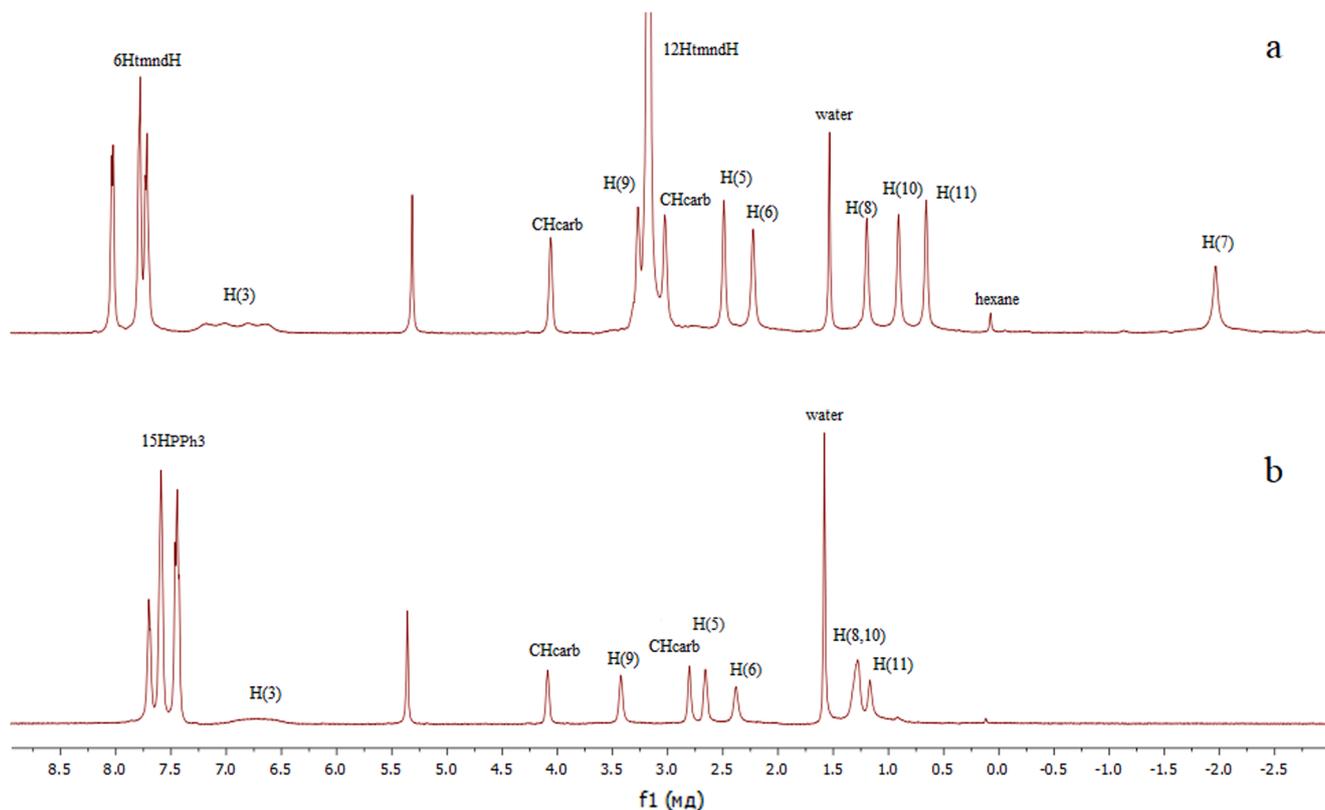


Fig. 2. $^1\text{H}\{^{11}\text{B}\}$ NMR spectra (CH_2Cl_2): a) complex 1 (signal from tmndH^+ δ 19.0 ppm not shown); b) complex 2.

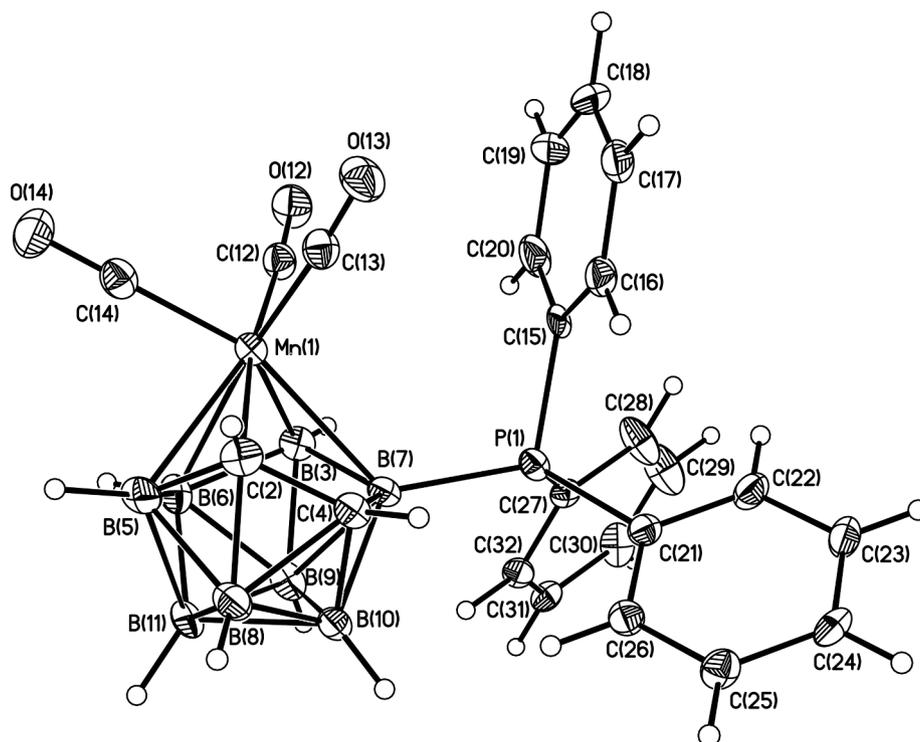


Fig. 3. Molecular structure of complex 2 (thermal ellipsoids drawn at the 50% probability level). Selected bond lengths (\AA) in 2: Mn(1)-C(12) 1.806(3), Mn(1)-C(13) 1.817(3), Mn(1)-C(14) 1.810(2), Mn(1)-C(2) 2.078(4), Mn(1)-B(3) 2.081(5), Mn(1)...C(4) 2.581(4), Mn(1)-B(5) 2.278(5), Mn(1)-B(6) 2.310(5), Mn(1)-B(7) 2.416(3), B(7)-P(1) 1.945(3), C(2)-C(4) 1.482(6).

Table 1

Crystal data, data collection and structure refinement parameters for complex 2.

Identification code	2
CCDC No	2,061,433
Empirical formula	C ₂₃ H ₂₄ B ₈ MnO ₃ P
Molecular weight	520.81
Crystal size (mm)	0.36 × 0.14 × 0.02
Temperature (K)	100(2)
Crystal system	monoclinic
Space group	P2 ₁ /c
a (Å)	10.7333(5)
b (Å)	13.4052(6)
c (Å)	17.0553(8)
β (deg)	97.5134(15)
V (Å ³)	2432.88(19)
Z	4
D _{calcd} (g cm ⁻³)	1.422
linear absorption μ (cm ⁻¹)	6.35
T _{min} /T _{max}	0.848/0.987
2θ _{max} (deg)	58
Reflections collected	71,148
Independent reflections (R _{int})	6484 (0.0498)
Observed reflections (I > 2σ(I))	4494
Number of parameters	335
R ₁ (on F for I > 2σ(I)) ^a	0.0566
wR ₂ (on F ² for all data) ^b	0.1130
GOOF	1.101
Largest diff. peak/hole (e Å ⁻³)	0.475/-0.506

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2 \}^{1/2}.$$

according to the literature data [14], is characterized by the presence of a downfield signal belonging to a boron atom with a low intracuster coordination number. Doublet at δ = 41.2 ppm indicates the presence of other than hydrogen substituent at this boron atom (Fig. 1).

To determine the position of this boron atom in the carborane ligand, the [¹¹B–¹¹B]-COSY correlation spectrum of complex 2 was obtained (see S2). As a result, it was found that the replacement of the hydrogen atom by the PPh₃ moiety occurs at the boron atom in position B(7) of metallacarborane fragment {Mn–C₂B₈}. According to the structure of complex 1 [12], the B(7) atom belongs to the open tetrahedral plane C (2)–C (4)–B (7)–Mn (1), which is characteristic of the *isonido*-structure complexes [14] and is the most distant from metal atom in comparison with other boron atoms of the hexagonal face of the carborane ligand.

The ¹H{¹¹B} spectrum with broadband suppression for boron atoms confirmed the absence of a hydrogen atom at the boron atom in the position B(7) (Fig. 2). Previously, the substitution on the carborane cage at this position was observed in one of the ligands of the *commo*-complex of rhodium formed in the reaction of 5,6-*nido*-C₂B₈H₁₂ carborane with μ-chloride rhodium dimers in the MeOH:C₆H₆ solvent system [14a].

The structure of complex 2, established on the basis of multinuclear spectroscopy data, was confirmed by X-ray diffraction analysis (Fig. 3, Table 1) [15]. The structure of metallacarborane moiety in 2 closely matches the same fragment in anionic complex 1.

Thus, for the first time, a reaction was carried out with the targeted introduction of the PPh₃ substituent at the boron atom of the manganese anionic complex based on 5,6-*nido*-C₂B₈H₁₂ carborane. Based on NMR and X-ray data the structure of one of the isolated products was established as 11-vertex neutral cluster, in which the ligand environment of manganese (+I) consists of three CO groups and a single-charged carborane ligand. PPh₃ molecule is localized at the boron atom in the position B(7) of the metallacarborane fragment {Mn–C₂B₈}, in which the hexagonal surface of *nido*-carborane is η⁵-coordinated with the manganese atom due to the elongation of Mn(1)–C(4) bond [14].

Declaration of Competing Interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.inoche.2021.108557>.

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- (CD₂Cl₂, 20 °C, J = J(B,H) Hz) [H{B}], δ: 48.6 (d, B, J = 3) [6.86-6.57]; 2.2 (d, B, J = 4) [3.43]; 7.0 (d, B, J = 2) [2.80]; -4.0 (d, B, J = 34) [2.38]; -6.4 (d, B, J = 37) [1.58]; -23.2 (d, B, J = 43) [1.27]; -27.7 (d, B, J = 4) [1.6]; -4.2 (d, B, J(B,P)=29 Hz). 3P{H} NMR (CD₂Cl₂, 20 °C, J = J(P,B) Hz), δ 7.78 (q, P, J = 25). 3C NMR (CD₂Cl₂, -20 °C): δ 29.6, 26.82 (CO), 35.75, 32.95, 29.39, 22.6 (Ph), 44.7, 35.74 (CH-carb). IR (KBr, cm⁻¹): 2025, 96, 933 ν (CO). Anal. Calc. For: C₂₃H₂₄B₈O₃PMn: C, 53.04; H, 4.6; B, 6.60; P 5.96. Found: C, 52.80; H, 4.79; B, 6.67; P 5.93.
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