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Heterodinuclear group 6 metallocarboranes: synthesis and characterization of $[\text{closo-3,3,3-(CO)}_3\text{-3-SnPh}_3\text{-3,1,2-MC}_2\text{B}_9\text{H}_{11}]^-$ (M = Cr, Mo, W)

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Abstract

Heterodinuclear group 6 metallocarborane anions $[\text{closo-3,3,3-(CO)}_3\text{-3-SnPh}_3\text{-3,1,2-MC}_2\text{B}_9\text{H}_{11}]^-$ (M = Cr, 2; Mo, 3; W, 4) were prepared from the equimolar reaction systems of $\text{Ti}_2\text{C}_2\text{B}_9\text{H}_{11}/\text{M}(\text{CO})_3(\text{MeCN})_3/\text{SnPh}_3\text{Cl}/(\text{PPN})\text{Cl}$ in MeCN as the $[\text{PPN}]^+$ ($\text{PPN}^+ = \text{bis}(\text{triphenylphosphoranylidene ammonium cation})$) salts and were characterized by various means including multinuclear NMR and single-crystal X-ray diffraction. Crystals of $[\text{PPN}]\cdot\mathbf{4}$ are monoclinic, $C2/c$, with $a = 45.777(4)$, $b = 11.669(1)$, $c = 26.826(3)$ Å, $\beta = 125.134(2)^\circ$, $V = 11718$ Å³ and $Z = 8$. Convergence was achieved with $R(R_w) = 6.7(8.0)\%$ for 5487 ($I > 3\sigma(I)$) observed reflections. The *nido* anion $\text{C}_2\text{B}_9\text{H}_{11}^{2-}$ interacts with W via the C_2B_3 pentagonal plane and forms the *closo* WC_2B_9 geometry. The W–Sn distance of 2.825(1) Å and the observation of $^1J(^{119}\text{Sn}-^{183}\text{W}) = 262$ Hz in ^{119}Sn NMR spectrum of **4** establish the presence of a W–Sn bonding interaction. The structural integrities of **2**, **3** and **4** are similar and each compound remains intact in solution.

Despite the increasing utilization of the $[\text{nido-7,8-C}_2\text{B}_9\text{H}_{11}]^{2-}$ (**1**) ligand [1] in the chemistry of polynuclear transition metal [2,3] and main group element [4] metallocarboranes, examples of heteropolynuclear metallocarborane systems with bonding interactions between the transition metal and the main group element are very limited. Heterotetranuclear raft systems of $[\text{M}_2\text{Cu}_2(\mu\text{-CO})_4(\text{CO})_2(\mu\text{-H})_2(\text{C}_2\text{B}_9\text{H}_{10})_2]^{2-}$ (M = Mo, W) [2d] belong to this class of metallocarboranes. In an attempt to expand the class of heteropolynuclear complexes of **1**, several types of new metallocarboranes have been synthesized in our group. Reported herein are brief accounts of the synthesis and characterization of $[\text{closo-3,3,3-(CO)}_3\text{-3-SnPh}_3\text{-3,1,2-MC}_2\text{B}_9\text{H}_{11}]^-$ (M = Cr, **2**; Mo, **3**; W, **4**).

An equimolar slurry of $\text{Ti}_2 \cdot \mathbf{1}$ [5] and $\text{PPN}^+ \text{Cl}^-$ ($\text{PPN}^+ = \text{bis}(\text{triphenylphosphor- anylidene}) \text{ ammonium cation}$) in CH_3CN was allowed to react anaerobically with $[\text{M}(\text{CO})_3(\text{CH}_3\text{CN})_3]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) at room temperature, generating an orange red slurry. To this reaction mixture was added a solution of Ph_3SnCl in MeCN and stirring for a period of 12 h was followed by filtration. Treatment of the concentrated filtrate with Et_2O yielded crystalline solids. Recrystallization from $\text{DMF-Et}_2\text{O}$ afforded the analytically * pure PPN salt of **2** (greenish yellow), **3** (yellow) or **4** (pale yellow) in moderate yield.

Spectroscopic data ** for all three complexes are similar and reveal the common presence of terminal CO groups, ligated ligand **1**, and the tin moiety. The fine structure in the $\nu(\text{BH})$ region and the nature of the $\nu(\text{CO})$ are indicative of the ligation of **1** to metal and the breakdown of local C_3 symmetry, respectively. These structural implications are consistent with the result of the X-ray analysis *** on $[\text{PPN}] \cdot \mathbf{4}$.

The crystal structure consists of discrete anions **4** and PPN^+ cations. The molecular structure of **4** is shown in Fig. 1. The pentagonal C_2B_3 plane of the *nido* anion **1** interacts with W and forms the *closo* WC_2B_9 cage geometry. Three terminal carbonyl groups and a triphenyl tin moiety are situated around the tungsten atom such that two of three OC-W-CO angles are very acute (76.2 and 78.3°). The interatomic W-Sn distance of $2.825(1) \text{ \AA}$ is similar to those observed in $[(\text{W}(\text{CO})_3(\text{C}_5\text{H}_5))_2\text{SnPh}_2]$ ($2.81 \text{ \AA}$) [6], $[(\mu\text{-Cl})(\text{MeSnCl}_2)\text{W}(\text{CO})_3(\text{MeSCH}_2\text{CH}_2\text{SMe})]$ ($2.759(3) \text{ \AA}$) [7], $[(\text{Ph}_3\text{Sn})_2(\text{Ph}_2\text{Sn})_2\text{O}^i\text{Pr})\text{W}(\text{CO})_3]^-$ ($2.760\text{--}2.811 \text{ \AA}$) [8], $[\text{W}(\text{PhCCPh})_3\text{SnPh}_3]^-$ ($2.807(1) \text{ \AA}$) [9] and $[\text{W}(\text{C}(\text{H})(\text{C}_6\text{H}_4\text{Me-4})(\text{SnPh}_3)(\text{CO})_2(\text{C}_5\text{H}_5))]$ ($2.837(1) \text{ \AA}$) [10], and is indicative of the bonding interaction between formal W^0 and Sn^{IV} . It is rather surprising to note that examples of $\text{W}^0\text{--Sn}^{\text{IV}}$ bonding distances which have been characterized by X-ray crystallography are very rare although many compounds with bonding interactions between a transition metal and tin have been reported [11–13]. The structure of the cation is not unusual and adopts a bent PNP geometry ($143.0(8)^\circ$) with an average P–N distance of $1.568(12) \text{ \AA}$.

The structural integrities of **2**, **3** and **4** are similar and each compound remains intact in solution as observed by NMR spectra. The ^{119}Sn -NMR spectrum of **4** in

* Satisfactory microanalyses on C and H were obtained for all three compounds.

** **2**: IR (KBr, cm^{-1}): 2546, 2526, 2510 [$\nu(\text{BH})$]; 1960, 1890, 1865 [$\nu(\text{CO})$]. $^{11}\text{B}\{^1\text{H}\}$ NMR (CD_3CN , ppm, upfield of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ was taken as negative): $-3.8, -4.5, -9.1, -12.9, -19.3, -22.5$. ^{119}Sn NMR (ppm, referenced to Me_4Sn): 54.0 ($\text{DMSO-}d_6$), 53.2 (CD_3CN).

3: IR, 2551, 2536, 2513 [$\nu(\text{BH})$]; 1975, 1898, 1875 [$\nu(\text{CO})$]. $^{11}\text{B}\{^1\text{H}\}$ NMR: $-5.0, -7.3, -8.6, -14.5, -19.0, -21.5$. ^{119}Sn NMR: 43.6 (DMSO), 44.3 (CD_3CN). **4**: IR, 2554, 2529, 2517 [$\nu(\text{BH})$]; 1970, 1889, 1865 [$\nu(\text{CO})$]. $^{11}\text{B}\{^1\text{H}\}$ NMR: $-6.2, -8.3, -15.1, -18.8, -21.6$. ^{119}Sn NMR: -23.1 (DMSO) ($^1J(\text{Sn-W}) = 262 \text{ Hz}$).

*** Crystal data for $[\text{PPN}] \cdot \mathbf{4}$: $\text{C}_{59}\text{H}_{56}\text{B}_9\text{NO}_3\text{P}_2\text{SnW}$, $M = 1288.89$, monoclinic, $\text{C}2/c$, $a = 45.777(4)$, $b = 11.669(1)$, $c = 26.826(3) \text{ \AA}$, $\beta = 125.134(2)^\circ$, $V = 11718 \text{ \AA}^3$, $Z = 8$, $D_c = 1.46 \text{ g cm}^{-3}$. Intensity data were collected on a Huber diffractometer constructed by Professor C.E. Strouse of UCLA with Mo-K_α radiation in the $\theta\text{--}2\theta$ mode to a maximum $2\theta = 50^\circ$. Intensities of three check reflections decayed 11% during the course of the experiment (201.2 h). Of the 10198 unique reflections measured, 5487 ($I > 3\sigma(I)$) were considered observed and were used in the subsequent structure analysis. The structure was solved by use of heavy atom methods and refined by a full-matrix least-squares refinement (ORFLS). The final R (R_w) values are 0.067 (0.080).

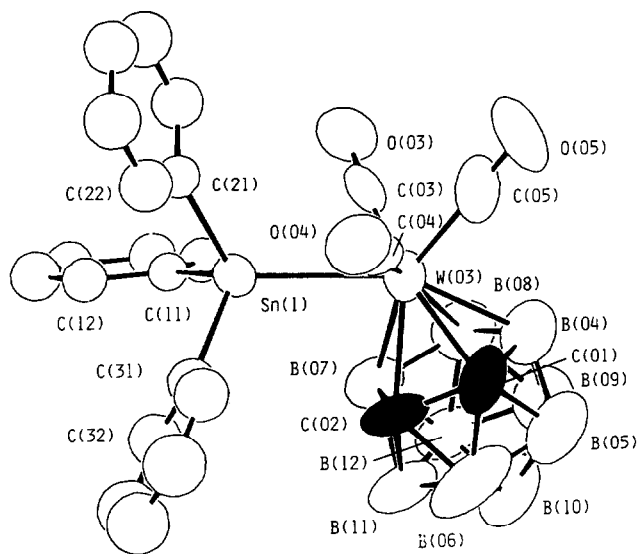


Fig. 1. A view of the molecular structure of $[closo-3,3,3-(CO)_3-3-SnPh_3-3,1,2-WC_2B_9H_{11}]^-$ (**4**) showing the atom labeling scheme adopted. Selected bond lengths (Å) and angles (deg): W(03)–Sn(1), 2.825(1); W(03)–C(01), 2.304(19); W(03)–C(02), 2.355(16); W(03)–B(04), 2.383(23); W(03)–B(07), 2.385(19); W(03)–B(08), 2.416(18); average W(03)–C(carbonyl), 1.957(15); average C–O(carbonyl), 1.174(10); average W–C–O(carbonyl), 175.2(7); C(03)–W(03)–C(04), 105.8(6); C(03)–W(03)–C(05), 78.3(6); C(04)–W(03)–C(05), 76.2(6); C(03)–W(03)–Sn(1), 70.9(4); C(04)–W(03)–Sn(1), 71.1(5); Sn(1)–W(03)–C₂B₉ centroid, 116.4; average W(03)–Sn(1)–C(phenyl), 114.5(33); average C(phenyl)–Sn(1)–C(phenyl), 103.5(24).

DMSO, displayed in Fig. 2 along with those of **2** and **3**, exhibits a ca 1 : 12 : 1 triplet due to coupling with ^{183}W ($I = 1/2$, 14.28%) thus establishing the presence of a W–Sn bonding interaction. The extent of the coupling between tin and tungsten in **4**, $^1J(^{119}Sn-^{183}W) = 262$ Hz, is larger than that (150 Hz) observed in $[Me_3SnW(CO)_3(\eta^5-C_5H_5)]$ [14]. The trend in ^{119}Sn chemical shifts of **2**, **3** and **4** is unusual in that the chemical shifts are similar for M = Cr and Mo but different from W. Another unusual trend was previously observed for the Mössbauer quadrupole splittings [15] and ^{119}Sn chemical shifts [16] of a series of $[Me_3SnM(CO)_3(\eta^5-C_5H_5)]$ (M = Cr, Mo, W) and was explained in terms of $d\pi-d\pi$ overlap between tin and the group 6 metal.

The reaction scheme adopted in this work, which is known to proceed via the formation of a heterodinuclear monoanionic metallacarborane with a Tl–group 6 metal bond [2d], has been extended to a wide range of main group element halides, but the isolation of tractable crystalline products has eluded us. With the late transition metal halides, the reaction scheme affords new heterotrinnuclear metallacarboranes which are the subject of current investigation along with the reactivity of $[M(CO)_3(SnPh_3)(C_2B_9H_{11})]^-$ and the further use of **1** in the synthesis of heteropolynuclear metallacarboranes.

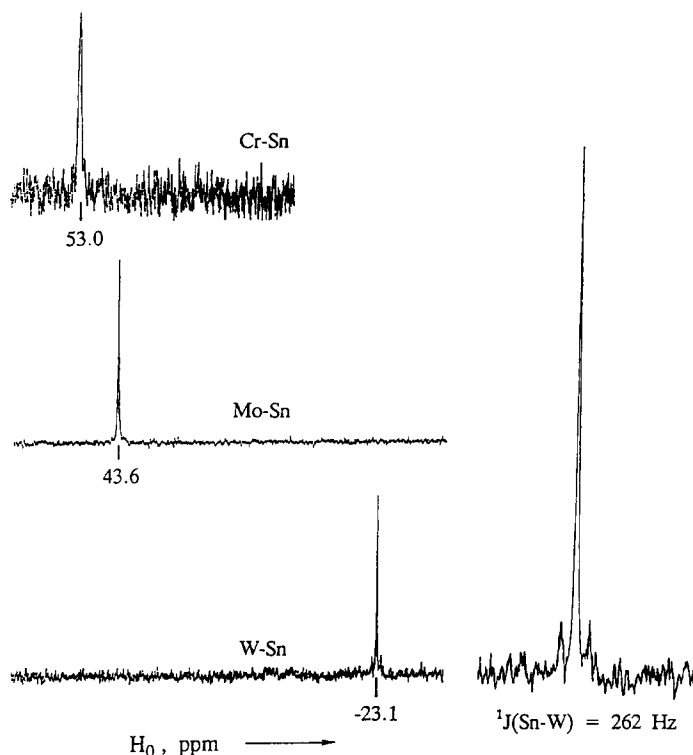


Fig. 2. ^{119}Sn NMR spectra of $(\text{PPN})[\text{closo-3,3,3-(CO)}_3\text{-3-SnPh}_3\text{-3,1,2-MC}_2\text{B}_9\text{H}_{11}]$ ($\text{M} = \text{Cr, Mo, W}$) in DMSO.

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