

Short communication

Photochemistry of metallaborane: A novel method for functionalized carborane synthesis

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ABSTRACT

The photointeractions of a stable 10-vertex manganadecaborane [*nido*-6-Mn(CO)₃B₉H₁₃][NMe₄] (**1**) and various unsaturated molecules were studied. The investigated unsaturated molecules include nitriles (1,5-dicyanopentane, acetonitrile, methyl cyanofornate), ketones (4-heptanone, 1-indanone, ethyl pyruvate), aldehyde (benzaldehyde), imines (N-benzylidenemethylamine), alkene (methyl acrylate), isocyanates (phenyl isocyanate) and various alkynes. The manganadecaborane was found to photoreact with both terminal and internal alkynes to afford the carborane with general formula [7-R-8-R'-7,8-*nido*-C₂B₉H₁₀][NMe₄] (**2**) in good yield. This not only represents a novel method for generating the substituted *nido*-C₂B₉ complex but also implies photochemical approach can be an alternative methodology for metallaborane and metallacarborane chemistry.

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Metallaborane and metallacarborane cluster chemistry are fascinating fields of study [1–6]. The synthesis, reactivities and applications of them continue attracting attentions recently [7–17]. Most of the reported studies employed thermal based methodologies. Given these challenges in the field such as synthesis of boron hydride clusters with more than twelve vertices [18–23], alternative synthetic methodology such as photochemical approach can be investigated.

The photochemistry has been reported for several small vertex metallaboranes [24–27]. The photochemical properties of metallaborane and metallacarborane have also been reported [28–30]. Our group investigated the thermal and photochemical pathways for a stable 10-vertex manganadecaborane species [*nido*-6-Mn(CO)₃B₉H₁₃][NMe₄] (**1**) [31]. We discovered that under UV photochemical irradiation, the complex **1** was converted into either the [*hypercloso*-Mn(CO)₃B₉H₉][NMe₄] by the loss of two equivalents of dihydrogen (H₂) from the cage or to a mixture of two polyhedral borane anions [*arachno*-B₉H₁₄][NMe₄] and [*nido*-B₉H₁₂][NMe₄], depending upon the solvent employed [31].

We report herein the further investigating on the photochemical properties of the complex **1**. It was found that the UV photochemical irradiation reaction of complex **1** can be influenced by a series

of unsaturated species such as Nitrile and Alkenes. In addition, carborane derivative products were isolated when there were alkyne species presented (Fig. 1). This photochemical cluster expansion can be applied to areas such as synthesis of heteroatom metallaborane [32].

The synthesis [33] and UV absorption study [31] of complex **1** were previously reported. Importantly, none of the unsaturated species examined herein was found to undergo any observable reactions with complex **1** under dark or thermal conditions.

The interaction of complex **1** with unsaturated molecules nitriles (1,5-dicyanopentane, acetonitrile, methyl cyanofornate), ketones (4-heptanone, 1-indanone, ethyl pyruvate), aldehyde (benzaldehyde), imines (N-benzylidenemethylamine), alkene (methyl acrylate) and isocyanates (phenyl isocyanate) were investigated under UV irradiation conditions. We found that under photoirradiation in dry dichloromethane, complex **1** did not react with these molecules to form new species but only the previous known demetallation products **4a** ([*arachno*-B₉H₁₄][NMe₄]) and **4b** ([*nido*-B₉H₁₂][NMe₄]) were observed (Fig. 2 and Table 1) [31]. However, different ratio for the two products can be observed according to different unsaturated reactant (Table 1). This not only suggests that photo interactions between complex **1** and the unsaturated species but also suggests that the unsaturated molecule can be used to fine-tune the photo-reactivity of complex **1** and demonstrate the flexibility of the reactivity.

The photo-irradiation of complex **1** at the presence of alkynes were found to form a variety of photo-insertion products. The course

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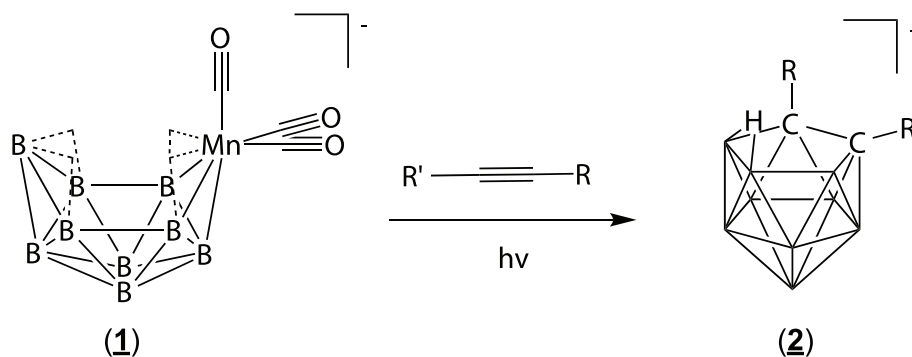


Fig. 1. Photoinsertion reactions between alkynes and complex **1**.

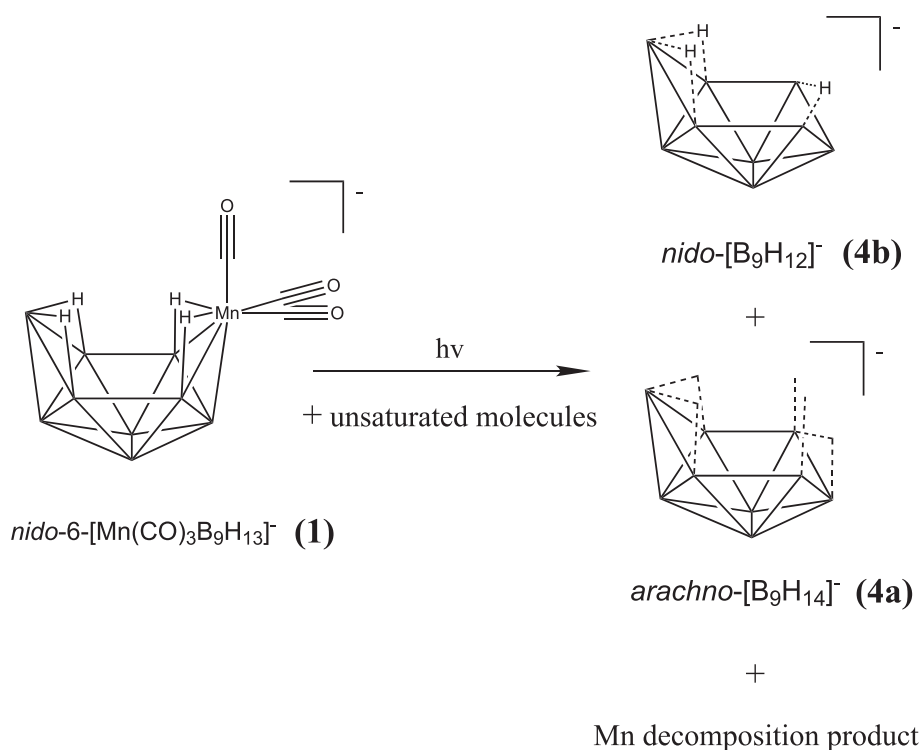


Fig. 2. Photointeraction of complex **1** with unsaturated molecules.

of the photoreaction of **1** with an excess (10-fold) of 1-hexyne was monitored by ^{11}B NMR spectroscopy. Fig. 3 shows the ^{11}B NMR spectra for this reaction ranging in time from 0 to 170 min of

Table 1
Photointeractions of unsaturated molecules with complex **1**.

Entry	Types	Reactants	Products ratio ^a
1		Complex 1 alone	1:10
2	Nitriles	1,5-Dicyanopentane	1:9
3	Nitriles	Acetonitrile	1:9
4	Nitriles	Methyl cyanofornate	1:5
5	Ketone	4-Heptanone	0:0 ^b
6	Ketone	1-Indanone	0:0
7	Ketone	Ethyl pyruvate	0:0
8	Aldehyde	Benzaldehyde	0:0
9	Imine	N-benzylidenemethylamine	All 4a
10	Alkene	Methyl acrylate	1:9
11	Isocyanates	Phenyl isocyanate	9:1
12	Isocyanates	<i>n</i> -Butyl isocyanate	3:1

^a Products ratio were **4b** ($[\text{B}_9\text{H}_{12}]^-$) to **4a** ($[\text{B}_9\text{H}_{14}]^-$).

^b No signals or very small amount for either **4b** or **4a**.

irradiation. Six new signals were detected from the photoreaction of complex **1** (one peak overlaps with the starting complex **1**). It can be observed that these new peaks increased in intensity as the peaks of the starting manganadecaborane decreased in intensity, ultimately with the complete disappearance of the starting signals after about 170 min of irradiation.

The single product **2a** from the photoreaction was separated and characterized using ^1H and ^{11}B NMR spectroscopy, IR spectroscopy, and EI-MS. A 2-D ^{11}B - ^{11}B COSY NMR spectrum of the reaction solution is given in Fig. 4. The crosspeaks observed in the 2D experiment included crosspeaks from the resonance at -11.06 ppm with those at -17.19 and -33.32 ppm, a crosspeak from the resonance at -13.01 ppm with that at -37.19 ppm, crosspeaks from the resonance at -17.19 ppm with those at -21.44 , -33.32 and -37.19 ppm, and a crosspeak between the resonances at -21.44 and -37.19 ppm. The presence of these crosspeaks provided connectivity between all of the new boron signals indicating the formation of a single product compound.

In addition to 1-hexyne, a number of other alkynes were also found to yield similar products from this type of photoinsertion

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