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# Synthesis and Ligand Substitution of Tri-metallic Triply Bridging Borylene Complexes

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## Abstract:

To build upon our earlier results of heterometallic metallaboranes employing metal carbonyls, we performed the reaction of *nido*-[(Cp\*Rh)<sub>2</sub>B<sub>3</sub>H<sub>7</sub>] (**1**) (*nido*-**1**) with [M(CO)<sub>5</sub>·THF] (M = Mo or W) that yielded the trimetallic metallaborane clusters [(Cp\*Rh)<sub>2</sub>M(CO)<sub>3</sub>(μ-CO)(μ<sub>3</sub>-BH)(B<sub>2</sub>H<sub>4</sub>)] (**3**: M = Mo; **4**: M = W) having a capped borylene fragment and trimetallic triply bridging borylene complexes [(Cp\*Rh)<sub>2</sub>(μ<sub>3</sub>-BH)(μ-CO)M(CO)<sub>5</sub>] (**5**: M = Mo; **6**: M = W). The chemistry of trimetallic triply bridging borylene complexes (**5** and **6**) were explored with Lewis bases such as *tert*-butyl isocyanide and bisphosphine ligands. Photolysis of **5** and **6** with *tert*-butyl isocyanide yielded [(Cp\*Rh)<sub>2</sub>(μ<sub>3</sub>-BH)(μ-CO)M(CO)<sub>4</sub>(CN-*t*Bu)] (**7**: M = Mo; **8**: M = W) and with phosphines, PPh<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub> (n = 1, 2) they resulted in the formation of [(Cp\*Rh)<sub>2</sub>(μ<sub>3</sub>-BH)(μ-CO)M(CO)<sub>4</sub>((PPh<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>)] (**9**: n = 1, M = Mo; **10**: n = 1, M = W; **11**: n = 2, M = Mo; **12**: n = 2, M = W). All the new compounds have been characterized in solution by mass spectrometry and NMR spectroscopic techniques. The structural aspects were unambiguously established by X-ray crystallographic analysis of **3-4** and **7-10**.

## 1. Introduction

During the past two decades a library of metallaborane compounds with diverse geometries have been developed.[1-2] Typically there are two major approaches for the cluster build up reaction in metallaborane chemistry. For example i) metathesis reaction using monoborane reagents,[3-4] and

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