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Synthesis of tetrahydridoplatinum complex bound in enlarged tetraphosphamacrocycle and its reaction with CO_2

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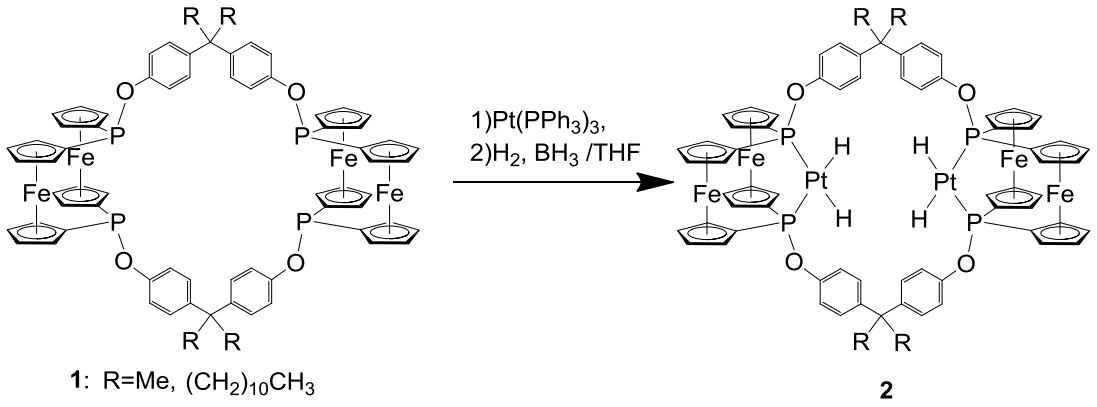
The two metal centers incorporated in a large phospamacrocycle **1** can be expected to afford a unique reaction site where the two metal centers cooperatively activate small molecules.[1] Herein, we report syntheses of tetrahydridodiplatinum complexes which would potentially be multi-reduction reagents for CO_2.

The tetrahydridodiplatinum complex **2** was prepared by two steps. First, the macrocycle **1** was allowed to react with 2eq $Pt(PPh_3)_3$ to form $\{Pt(PPh_3)\}_2$@macrocycle **1**, then the complex dissolved in THF was treated with H_2 at low temperature in the presence of BH_3 which abstracted PPh_3 from the platinum centers. The ^{31}P NMR spectrum of the reaction mixture showed the formation of the tetrahydridodiplatinum complex **2** in a good yield.

A reaction of **2** with carbondioxide was carried out using $^{13}CO_2$ under a H_2 atmosphere in THF. The ^{13}C NMR spectrum of the reaction mixture showed a quartet signal at 51.3 ppm, which could be assigned to a methoxy group. However, this methoxy product was found to be formed from the unprecedented direct reaction between BH_3-THF and CO_2, which was confirmed by a separate reaction. Although, we could not succeed in the metal-catalyzed CO_2 reduction, we found simple and effective method for the reduction of CO_2 to the methoxy group.



1: R=Me, $(CH_2)_{10}CH_3$ **2**

(1) Mizuta, T.; Inami, Y.; Kubo, K.; Miyoshi, K. *Inorg. Chem.* **2009**, *48*, 7534.