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Preliminary communication

Convenient synthesis of pentamethylcyclopentadienyl-tantalum-diene complexes via the reaction of Cp^*TaCl_4 with methylated-allyl anions *

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Abstract

Treatment of Cp^*TaCl_4 (**1**) with two equivalents of a 2-butenyl Grignard reagent in THF afforded the tantalum-1,3-butadiene complex $Cp^*TaCl_2(C_4H_6)$ (**2a**). Similarly, the reaction of **1** with methylated-allyl anions gave the corresponding diene complexes Cp^*TaCl_2(diene) (**2b**: diene = isoprene, **2c**: 2,3-dimethyl-1,3-butadiene, **2d**: 1,3-pentadiene).

Diene complexes of tantalum have been prepared by the reduction of tantalum complexes, such as $TaCl_2$[bis(dimethylphosphino)ethane]$_2$, in the presence of dienes [1], or by treatment of the dinuclear complex of Ta^{III}, $[Cp^*TaBr_2]_2$, with butadiene [2]. Recently, we have reported that Cp^*TaCl_2(diene) complexes could be prepared by the reaction of Cp^*TaCl_4 and diene-magnesium compounds [3]. Although the above methods have some limitations they are useful. The first method sometimes caused polymerization or dimerization of diene and so the application of this method has been restricted to stable dienes in reducing conditions. As there is no free diene present, the latter reaction proceeded under rather moderate and mild conditions. However, so far only four diene-magnesium compounds are known [4]. We report here the synthesis of diene complexes of tantalum *via* the hydrogen-transfer reaction of the labile bis(methylated-allyl) species of pentamethylcyclopentadienyltantalum(V).

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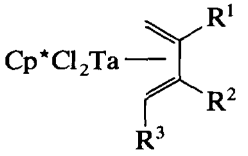
In a typical reaction, to a solution of $Cp^{\star}TaCl_4$ (**1**) (1.36 g, 2.97 mmol) in THF (20 mL), cooled at 0°C, was added dropwise a solution of 2 equivalents of the prenyl Grignard reagent (6.00 mmol) in ether (12 mL). This solution was allowed to warm to room temperature and the solvent was removed under reduced pressure. Recrystallization from a mixture of hexane and toluene then afforded $Cp^{\star}TaCl_2$(isoprene) (**2b**) (0.97 g, 72% yield), which was characterized by comparison of its spectral data with those previously reported [3]. Treatment of **1** and 2 equivalents of the 2-butenyl Grignard reagent in THF afforded the 1,3-butadiene complex **2a** (17% yield) as violet crystals after extraction with a hexane–toluene mixture and after recrystallization from hexane. The structure of **2a** was also characterized by comparison of its spectral data with those previously reported [3].



(**2a**: $R^1 = R^2 = R^3 = H$;
2b: $R^1 = CH_3$, $R^2 = R^3 = H$;
2c: $R^1 = R^2 = CH_3$, $R^3 = H$;
2d: $R^1 = R^2 = H$, $R^3 = CH_3$)

Our established strategy can be applied to the preparation of diene complexes **2c** and **2d**. Treatment of $Cp^{\star}TaCl_4$ with two equivalents of allyl Grignard reagents, derived from 2,3-dimethyl-1,3-butadiene and 1,3-pentadiene, with PropylMgCl in ether [5] afforded **2c** [3] and **2d** (new compound) [6*] in 45 and 20% yields, respectively.

The formation of these complexes may be rationalized by a bis(allyl) intermediate, which undergoes hydrogen transfer to give allyl-hydride-diene species, and subsequent reductive elimination of allyl and hydride afforded the diene complexes **2**. Recently it was reported that thermal decomposition of a methylated-allyl ligand bonded to group 4 transition metal or actinide complexes caused intramolecular hydrogen transfer from a methyl group of the allyl ligand, yielding diene complexes such as $Cp^{\star}M$(diene)(allyl) [7–9], $Cp^{\star}Zr$(diene)(CH_2PPh_2) [10], and $Cp^{\star}_2Th$(butadiene) [11].

Such hydrogen transfer (from a hydrocarbon ligand bound to tantalum) reactions have been noted as a characteristic feature of organotantalum complexes. Schrock-type carbene complexes have been synthesized by the α-hydrogen abstraction followed by elimination of R–H [12]. Several examples of hydrogen abstraction from one or two methyl groups of the pentamethylcyclopentadienyl ligand giving hydride complexes have also been reported [13]. Thus, the methyl hydrogen on the allyl-tantalum intermediate can be easily abstracted, resulting in the formation of diene complexes. Lower yield of the butadiene complexes, compared with those of the isoprene and 2,3-dimethylbutadiene complexes, may be ascribed to the lower number of methyl groups on the allyl moiety.

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* Reference number with asterisk indicates a note in the list of references.

Hereby we conclude that we established a new convenient route to an extensive series of tantalum-diene complexes, which may be fruitful starting material for a variety of organotantalum complexes and catalysts.

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