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Preliminary communication

NEW SYNTHETIC PATHWAYS IN DICYCLOPENTADIENYLTANTALUM CHEMISTRY

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Summary

The dihalides [Ta(η-C_5H_5)$_2X_2$] (X = Cl, Br) are prepared in 80% yield by treatment of TaX_5 with Sn(C_5H_5)-n-Bu_3. The trihydride [Ta(η-C_5H_5)$_2H_3$] is formed in 42% yield from [Ta(η-C_5H_5)$_2Cl_2$] and [$NaAlH_2(OCH_2CH_2OCH_3)_2$]. The trihydride with butyllithium gives a tantalum-lithio derivative which reacts with benzyl chloride giving [Ta(η-C_5H_5)$_2$(CH_2Ph)Cl].

Trialkyl(cyclopentadienyl)tin compounds have been found to provide convenient synthetic routes to the new monocyclopentadienyl halides of niobium and tantalum [M(η-C_5H_5)X_4] (M = Nb, Ta; X = Cl, Br) [1, 2]. Also, an improved route to dicyclopentadienyltantalum dichloride has been recently described by treating a toluene suspension of [Ta(η-C_5H_5)Cl_4] with [$AlEtCl_2$]$_2$ [3].

Here we report that trialkyl(cyclopentadienyl)tin compounds can provide direct access to dicyclopentadienyltantalum complexes in very high yields. When dichloromethane suspensions of the tantalum pentahalides: TaX_5 (X = Cl, Br) are treated with 3 equivalents of Sn(C_5H_5)-n-Bu_3 at room temperature deep green solutions are obtained. Addition of toluene and concentration of these solutions give green crystals of [Ta(η-C_5H_5)$_2X_2$] (I, X = Cl, yield 87%; II, X = Br, yield 84%). The yield of compound I is considerably higher than in the original method [4] and quantities of I as high as 35 g may be conveniently prepared in a single experiment.

Treatment of a suspension of [Ta(η-C_5H_5)X_2] in toluene with [$NaAlH_2(OCH_2CH_2OCH_3)_2$] gave in 42% yield the trihydride [Ta(η-C_5H_5)$_2H_3$] (III). In a typical experiment 7.2 g of [Ta(η-C_5H_5)$_2Cl_2$] suspended in 500 cm^3 of dry toluene at 0°C were treated dropwise by a benzene solution containing 12.2 g of [$NaAlH_2(OCH_2CH_2OCH_3)_2$]. The reaction mixture was then hydrolysed. Sublimation of the reddish solid obtained, at 105°C under 10^{-3} mmHg gave 2.5 g of white crystals of III. This reaction represents a reliable and reproducible method of synthesising the elusive [Ta(η-C_5H_5)$_2H_3$] [5].

Treatment of the trihydride III with butadiene in toluene at 80°C for 6 h gives green crystals of the previously described [4] (1-methylallyl) dicyclopentadienyltantalum (IV) in 56% yield.

When toluene solutions of III are treated with 1 equivalent or an excess of n-butyllithium, an orange solution is formed which deposits orange-yellow needles (V) after a few minutes. The crystals of V are extremely reactive towards oxygen and moisture. Hydrolysis of V reforms III quantitatively. Compound V is insoluble or decomposed in most organic solvents. The infrared spectrum of V shows a band characteristic of cyclopentadienyl groups and a broad band at 1590 cm^{-1} which can be assigned to ν(Ta—H). We assume V is a tantalum-lithio derivative analogous in type to the compound $[W(\eta\text{-}C_5H_5)_2HLi]_4$ [6].

The presence of at least one tantalum—lithium bond in V can be deduced on the basis of the reaction of V with benzyl chloride. Treatment of a toluene suspension of V at –80°C with an excess of benzyl chloride gives black crystals of the new compound $[Ta(\eta\text{-}C_5H_5)_2(CH_2Ph)Cl]$ (VI) in 66% yield. Compound VI has been characterized by elemental analysis (Found C, 47.95; H, 4.1; Cl, 7.95. $C_{17}H_{17}ClTa$ calcd.: C, 47.65; H, 3.9; Cl, 8.1%], infrared and the ESR spectrum ($\langle g \rangle$ 1.965, A_{iso} 115 G).

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