

Journal of Organometallic Chemistry, 186 (1980) 237–240
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SYNTHESIS OF MONOCYCLOPENTADIENYLTRICARBONYL-NIOBIUM (AND -TANTALUM) DICHLORIDES

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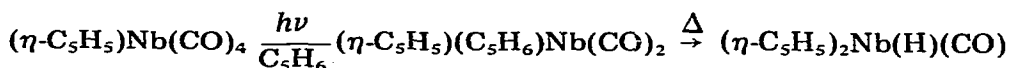
(Received July 16th, 1979)

Summary

The syntheses and properties of the new carbonyl complexes of niobium and tantalum, $(\text{cp})\text{Nb}(\text{CO})_3\text{Cl}_2$ and $(\text{cp})\text{Ta}(\text{CO})_3\text{Cl}_2$, are described.

Introduction

Since the preparation in 1964 of $(\text{cp})\text{M}(\text{CO})_4$ ($\text{M} = \text{Nb}$ or Ta) [1,2], there have been few publications dealing with new carbonyl derivatives of niobium and tantalum. The first [3,4] deal with the preparation of $(\text{cp})_2\text{Nb}(\text{H})\text{CO}$, which involves the preliminary formation of $(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_6)\text{Nb}(\text{CO})_2$, followed by thermal decomposition of the latter viz.



More recently [5], a report on the preparation of $(\text{cp})_2\text{Nb}(\text{CO})\text{Cl}$ has appeared.

The present report stems from an attempt to seek a more efficient route to the preparation of $(\text{cp})\text{M}(\text{CO})_4$ ($\text{M} = \text{Nb}$ or Ta) than that originally given [1]; this latter involves the initial preparation of the appropriate hexacarbonylmetallate(–I) (which requires high temperatures and high pressures, beyond the capabilities of many autoclaves), followed by treatment with an equimolar mixture of mercury(II) chloride and sodium cyclopentadienide in dimethoxyethane. The route adopted here, which is similar to that used by Demerseman et al. for the synthesis of $(\text{cp})_2\text{Ti}(\text{CO})_2$ [6], involves the treatment of the recently reported complexes $(\text{cp})\text{NbCl}_4$ or $(\text{cp})\text{TaCl}_4$ [7,8] with aluminium and a small amount of mercury(II) chloride in tetrahydrofuran under carbon monoxide. The availability of the starting materials as well as the simplicity of

the experimental part make this an attractive route to the syntheses of carbonyl derivatives. However, in each case the reaction stopped before all the chlorine had been eliminated, affording instead new carbonyl derivatives of each metal. We now report on their isolation and on their properties.

Experimental

All experiments were carried out using an inert atmosphere or in vacuo. The products were stored in Schlenk tubes. Tetrahydrofuran was distilled from sodium diphenylketyl and n-heptane from lithium aluminium hydride.

Reaction of monocyclopentadienylniobium tetrachloride with carbon monoxide

Monocyclopentadienylniobium tetrachloride (4.40 g, 14 mmol), aluminium powder (0.53 g, 20 mmol), a small amount of mercury(II) chloride and 100 cm³ of tetrahydrofuran were introduced into a reaction flask. After being evacuated at -196°C the flask was filled with carbon monoxide and stirred for two days at room temperature; the carbon monoxide used was replenished periodically. The orange-red solid, together with the excess of aluminium was filtered from the mother liquor. The aluminium was separated by extraction with tetrahydrofuran. n-Heptane (10 cm³) was slowly added with stirring to the remaining orange solution and the tetrahydrofuran was evaporated under a slow stream of nitrogen. The orange-red product crystallized very quickly and was isolated by filtration, washed with n-heptane, and dried under vacuum, m.p. (dec.) 150°C, yield 65%. Found: C, 30.6; H, 1.77; Cl, 22.9; Nb, 29.4%. C₈H₅Cl₂NbO₃ calcd.: C, 30.70; H, 1.61; Cl, 22.69; Nb, 29.68%.

Reaction of monocyclopentadienyltantalum tetrachloride with carbon monoxide

Monocyclopentadienyltantalum tetrachloride (5.34 g, 14 mmol) aluminium powder (0.50 g, 18 mmol) a small amount of mercury(II) chloride (0.01 g) and 150 cm³ of tetrahydrofuran were introduced into a reaction flask. After being evacuated at -196°C the flask was filled with carbon monoxide and stirred for two days at room temperature as indicated above. The orange-red solution was chromatographed through a silica column, which was washed with 40 cm³ of tetrahydrofuran. The volume of the solvent was reduced to ~20 cm³ under reduced pressure, and 10 cm³ of n-heptane added slowly. Evaporation of the tetrahydrofuran under a slow stream of nitrogen resulted in the crystallization of the orange-red product, (cp)Ta(CO)₃Cl₂, m.p. (impure sample, dec.) 125°C, yield <10%.

Results and discussion

The orange-red products isolated by the procedures outlined above appear to be formed according to the following reaction scheme:

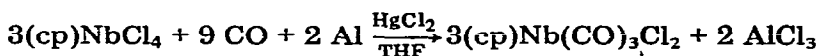


TABLE 1

CHEMICAL AND SPECTROSCOPIC PROPERTIES OF THE CARBONYL DERIVATIVES OF NIOBIUM AND TANTALUM

Complex	Colour	M.p. ($^{\circ}$ C)	$\nu(\text{CO})$ (cm^{-1}) ^a	τ (ppm) ^b
(cp)Nb(CO) ₃ Cl ₂	orange-red	dec. 150	2044, 1956	4.51
(cp)Ta(CO) ₃ Cl ₂	orange-red	dec. 125	2030, 1935	4.66

^a Tetrahydrofuran solution. ^b C₅H₅ resonance, acetonitrile solution.

The addition of the small amount of mercury(II) chloride to the reaction mixture activates the aluminium and helps to initiate the reaction, which is thereby complete in two rather than seven days.

The niobium complex is characterised by its analytical data, its CO stretching frequencies as determined from the infrared spectrum, and its ¹H NMR spectrum (Table 1).

Considerable difficulty was experienced in attempting to isolate the tantalum complex. Whereas (cp)Nb(CO)₃Cl₂ precipitates out of the reaction mixture, from which it is readily filtered off and extracted with tetrahydrofuran in order to effect separation from unreacted aluminium, (cp)Ta(CO)₃Cl₂ is more soluble in the reaction mixture, and remains therein together with the aluminium(III) chloride by-product. Chromatography did not prove to be effective in separating (cp)Ta(CO)₃Cl₂ from AlCl₃, and recrystallisation presented several problems since the complex is not very stable in solution.

In consequence, the tantalum complex could only be characterised by its infrared and NMR spectra (Table 1), but these resemble so closely those determined for the fully characterised niobium analogue that no doubt exists as to its formation. Moreover, the complex cannot be (cp)Ta(CO)₄ because many of its properties, viz. thermal instability, involatility and insolubility in solvents such as cyclohexane, differ widely from those reported for (cp)Ta(CO)₄ [2].

The infrared-active carbonyl stretching frequencies of the two new complexes are, on an average, above those reported for (cp)M(CO)₄ (M = Nb, $\nu(\text{CO})$ 2000, 1901 cm^{-1} ; M = Ta, $\nu(\text{CO})$ 2020, 1900 cm^{-1}) [2] and even more above that reported for Ta(CO)₆⁻; (1850 cm^{-1}) [9], as expected on account of the progressive lowering in the oxidation state of the metal atom from III to I to -I. Moreover, they are also above those reported for the similarly trivalent niobium complexes (cp)₂Nb(CO)Cl (1902 cm^{-1}) [5] and (cp)₂Nb(H)CO (1900 cm^{-1}) [3] since for these monocarbonyls any metal carbonyl back-bonding must take place into a single M-C bond rather than into three such bonds.

The ease of preparations of the new complexes described renders it probable that they will be useful starting materials for a variety of reactions, in particular substitution reactions.

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