SYNTHESIS AND PROPERTIES OF DICYCLOPENTADIENYLTANTALUM(III) CARBONYL COMPOUNDS

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Summary

Reaction of $Cp_2Ta(H)L$ (L = C_3H_6, C_4H_8, C_5H_{10} and C_5H_8) with CO under mild conditions gives alkyltantalum carbonyl complexes $Cp_2Ta(CO)R$ (R = C_3H_7, C_4H_9, C_5H_{11} and C_5H_9, respectively). Depending upon the position of the olefin relative to the hydride ligand in the hydride-olefin complex, $Cp_2Ta(CO)H$ is also formed during the carbonylation reaction. Reduction of Cp_2Ta-Cl_2 by potassium or t-BuMgCl under one atmosphere of CO affords the very stable compound $Cp_2Ta(CO)Cl$ in moderate yields. Reaction of $Cp_2Ta(CO)Cl$ with RLi or RMgX does not give the $Cp_2Ta(CO)R$ complex.

Introduction

Transition metal carbonyl complexes, particularly of Group VIII transition metals, play important roles in industrial processes such as hydroformylation. In recent years much attention has been paid to the dicyclopentadienylcarbonyl derivatives of early transition metals, but the chemistry of niobium and in particular tantalum carbonyl complexes is relatively unexplored. The synthesis of $Cp_2Nb(CO)Cl$, by reduction of Cp_2NbCl_2 under carbon monoxide [1—3] opened up a new route to other interesting dicyclopentadienylniobium compounds [2]. The only dicyclopentadienylcarbonyl derivative of tantalum previously reported is $Cp_2Ta(CO)H$ [4], prepared from Cp_2TaH_3 and CO. The hydride-olefin complexes $Cp_2Ta(H)L$, described in a previous paper [5], turn out to be useful starting materials for other tantalum hydride species, e.g. $Cp_2-Ta(H)PEt_3$ and Cp_2TaH_3. In this paper we describe the preparation of the remarkably stable alkyl carbonyl complexes $Cp_2Ta(CO)R$ from the hydride olefin complexes $Cp_2Ta(H)L$. In addition, a convenient synthesis for the chlorocarbonyl complex $Cp_2Ta(CO)Cl$ is given.

Results and discussion

Reaction of $Cp_2Ta(H)L$ (L = C_3H_6, C_4H_8, C_5H_{10} and C_5H_8) with CO in toluene and subsequent extraction with and crystallization from pentane gives blue-green crystalline products $Cp_2Ta(CO)R$ (R = C_3H_7, C_4H_9, C_5H_{11} and C_5H_9, respectively) in good yields (Table 1). The complexes $Cp_2Ta(CO)R$ are air-sensitive and readily soluble in common organic solvents.

Elemental analyses (Table 1), chemical and physical properties are in agreement with the formula $Cp_2Ta(CO)R$.

The alkyl carbonyl complexes are monomeric (by cryoscopy in benzene) and diamagnetic. The IR spectra all are very similar, showing the characteristic η^5-C_5H_5 bands in the usual ranges, whereas ν(CO) is found between 1880—1895 cm^{-1}. The low value of this strong absorption is also observed for other bent bis-cyclopentadienyl derivatives of transition metals with a d^2—d^4 configuration [6]; it indicates considerable back-donation into the CO π-system. The PMR spectra show a sharp singlet at about δ 4.44 ppm due to the cyclopentadienyl protons, and a multiplet at δ 2.3—0.3 due to the alkyl group. The integration ratio is in accord with the assignment to Cp and alkyl protons respectively.

The alkyl signals are very complex (Fig. 1) and an interpretation is not attempted here. However, for $Cp_2Ta(CO)R$ (R = C_3H_7, C_4H_9 and C_5H_{11}) the highest field resonance at δ 0.5 ppm (2H) can be assigned to the α-hydrogens of the alkyl group by analogy with the assignment of the methyl protons of the comparable system $Cp_2Nb(CO)CH_3$ at δ —0.38 ppm. A detailed structure assignment of $Cp_2Ta(CO)C_3H_7$ and in particular the bonding mode of the alkyl group, can be made using ^{13}C NMR spectroscopy. The alkyl part of the proton-undecoupled ^{13}C NMR spectrum shows, as expected for a n-C_3H_7-group, two triplets at δ 1.75 ppm (J 120 Hz) and δ 33.61 ppm (J 119 Hz) and a quartet at δ 22.97 ppm (J 126 Hz). In accord with the assignment of the alkyl carbons in $Cp_2Nb(C_2H_5)C_2H_4$ [7], the upfield triplet resonance is assigned to the carbon atom directly bonded to the metal. The resonances of the cyclopentadienyl carbons consist of a doublet (J 179 Hz) at δ 88.90 ppm. Although both n-propyl and isopropyl products may be expected in the CO reaction of $Cp_2Ta(H)C_3H_6$,

TABLE 1

ANALYTICAL DATA OF THE COMPOUNDS $Cp_2Ta(CO)X$

Compound	Yield (%)	Analysis (found (calcd.) (%))		
		C	H	Ta
$Cp_2Ta(CO)C_3H_7$	54	44.07 (43.99)	4.58 (4.48)	47.44 (47.34)
$Cp_2Ta(CO)C_4H_9$	64	45.40 (45.47)	4.92 (4.83)	45.85 (45.66)
$Cp_2Ta(CO)C_5H_{11}$	53	46.68 (46.84)	5.23 (5.14)	43.90 (44.10)
$Cp_2Ta(CO)C_5H_9$	37	47.05 (47.07)	4.90 (4.69)	44.43 (44.32)
$Cp_2Ta(CO)Cl$	40	35.14 (35.28)	2.81 (2.69)	48.43 (48.32)
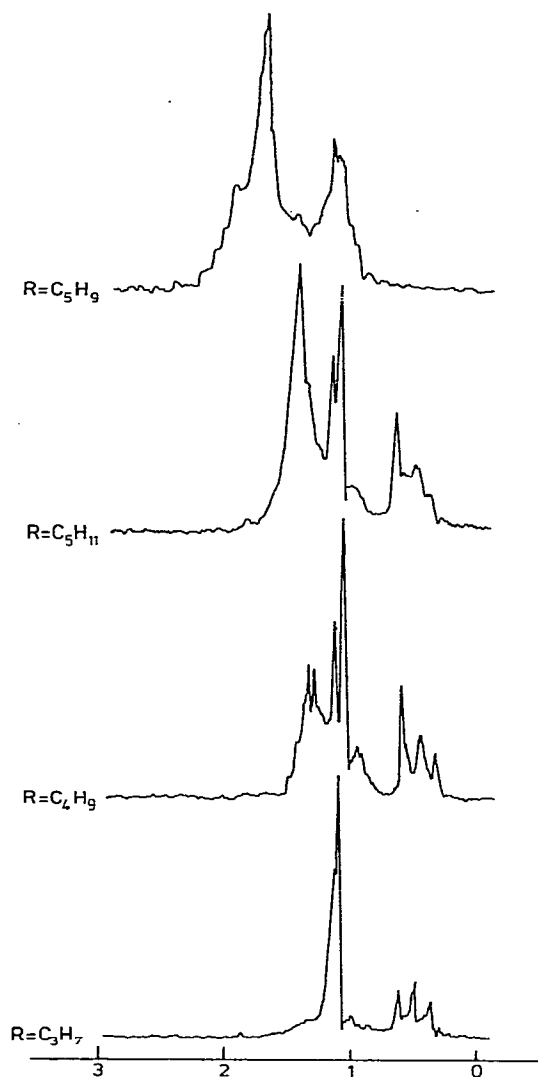
Fig. 1. PMR spectra of the $Cp_2Ta(CO)R$ complexes (alkyl region).

the exclusive formation of $Cp_2Ta(CO)$-n-C_3H_7 indicates that the carbonylation is a highly stereospecific reaction. Also, the reactions of the complexes with L = 1-butene and 1-pentene yield the n-alkyls as the sole products. The same was found in the reaction of $[Cp_2W(H)C_3H_6]^+$ with PPh_3, in which only the n-propyl product $[Cp_2W(PPh_3)$-n-$C_3H_7]^+$ is formed [8].

The decomposition temperatures and melting points of the alkylcarbonyl complexes (Table 2) show the remarkable stability of these compounds. Although, in general, alkyl compounds of the early transition metals have only marginal thermal stability, our alkylcarbonyltantalum complexes belong to the most stable alkyl-transition metal compounds in which the alkyl group is not of a special nature (space filling or lacking in β-hydrogen atoms) [9]. The explana-

TABLE 2

DTA DATA OF THE $Cp_2Ta(H)L$ AND $Cp_2Ta(CO)R$ COMPLEXES (°C)

Compound	M.p. (°C)	Decomposition temperature (°C)	Compound	M.p. (°C)	Decomposition temperature (°C)
$Cp_2Ta(H)C_3H_6$	109	125	$Cp_2Ta(CO)C_3H_7$	97	176
$Cp_2Ta(H)C_4H_8$ (a)	90	110	$Cp_2Ta(CO)C_4H_9$	71	172
$Cp_2Ta(H)C_5H_{10}$	42	112	$Cp_2Ta(CO)C_5H_{11}$	81	186
$Cp_2Ta(H)C_5H_8$	98	102	$Cp_2Ta(CO)C_5H_9$	110	154
$Cp_2Ta(H)C_4H_8$ (b)	88	113	$Cp_2Ta(CO)H$	157	219

tion of this stability may be found in the extraordinarily strong bonding of the CO ligand (as indicated by the IR spectra).

The high thermal stability is one aspect of the rather low reactivity of the complexes. Another is found in the attempted reactions with excess of CO in attempts to insert the CO ligand into the metal— alkyl bond) and with H_2. Prolonged heating (30 h at 100°C) in toluene under CO or H_2 gave no reaction at all. This is in keeping with the reported lack of reactivity of $Cp_2Ta(CO)CH_3$ towards CO [9].

The reactivity towards electrophilic reagents is higher, and $Cp_2Ta(CO)C_3H_7$ reacts at 0°C with HCl in ether with formation of propane and $Cp_2Ta(CO)Cl$.

The formation of the alkylcarbonyl complexes from the corresponding hydride-olefin compounds probably involves a concerted mechanism, in which, on entering the coordination sphere of the metal, the CO ligand weakens the Ta—H bond, permitting insertion of the olefin into this bond. Similar mechanisms have been suggested for the carbonylation of $Cp_2Nb(H)C_2R_2$ to give the alkenylcarbonyl complexes $Cp_2Nb(CO)C_2R_2H$ [10] and for the formation of $Cp_2Nb(C_2H_5)C_2H_4$ from Cp_2NbH_3 and C_2H_4 [4].

The preferential formation of n-alkyl products in the carbonylation reactions may be due either to a stereospecific reaction step or to rapid isomerization of initially formed isoalkyl products [11,12]. In our previous paper we reported the existence of *endo*- and *exo*-hydride-olefin isomers (established for propene and 1-butene), denoted as (a) and (b), which differ in the position of the alkyl part of the coordinated olefin relative to the hydride ligand. A preliminary assignment was made on the basis of the ${}^1H$ NMR spectra. Our reasoning is along the lines followed by Labinger et al. for the structure of the hydrideacetylene complexes $Cp_2M(H)C_2R_2$ (M = Nb, Ta) [10,13]. The *endo*- and *exo*-isomers show a quite different behaviour towards CO: the *endo*-isomer $Cp_2Ta(H)L$ gives the alkylcarbonyl derivative $Cp_2Ta(CO)R$ exclusively, whereas the *exo*-isomer under the same conditions yields the hydridecarbonyl complex $Cp_2Ta(H)CO$ (δ(Cp) 4.50 ppm, δ(H) —6.75 ppm). Apparently, the sterically unfavourable position of the alkyl part in the *exo*-isomer inhibits the insertion of the olefin into the metal—hydride bond and leads to substitution of the olefin, whereas in the *endo*-isomer the sterical conditions are such that insertion is promoted. A rationalization of these observations is attempted in Scheme 1 on the basis of the bonding concept of Lauher and Hoffmann [14].

The CO-ligand is assumed to enter the coordination sphere of Ta opposite to
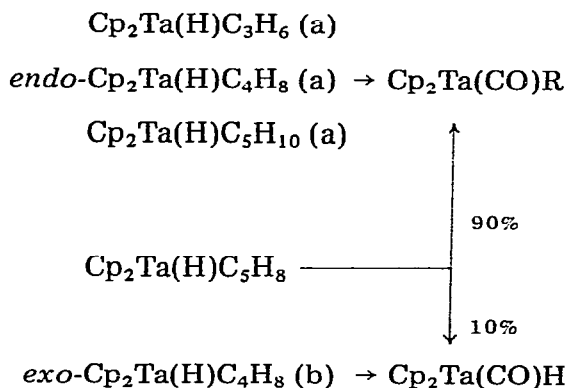
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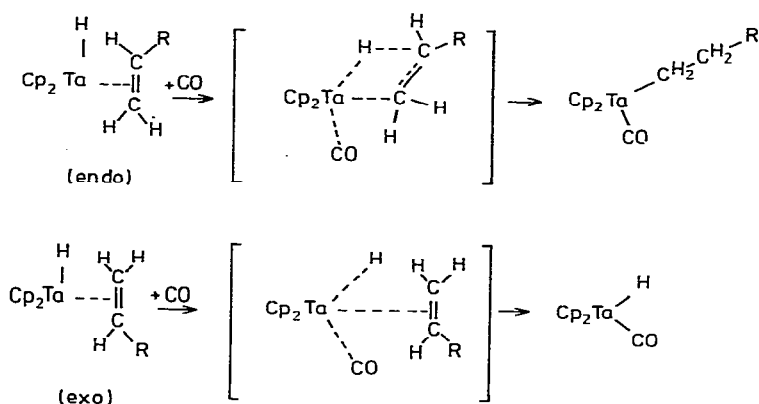
the hydride ligand. The competition between H and CO leads to a weakening of the Ta—H bond, making it more susceptible to insertion. In addition, the *endo*-olefin is sterically pushed towards the hydride. For the *exo*-isomer, the approaching CO molecule loosens the olefin by steric interaction with the protruding substituent before the weakening of the Ta—H bond is sufficient to give insertion.

The cyclopentene ligand in the complex $Cp_2Ta(H)C_5H_8$ combines the *endo*- and *exo*-configurations. In agreement with our view, carbonylation of $Cp_2Ta(H)C_5H_8$ yields both $Cp_2Ta(CO)C_5H_9$ and $Cp_2Ta(CO)H$. The products can be separated by careful sublimation (85°C/0.001 mmHg) of the pentane extract. The reactions mentioned above are summarized in Scheme 2.

SCHEME 2

$$Cp_2Ta(H)C_3H_6 \text{ (a)}$$

$$endo\text{-}Cp_2Ta(H)C_4H_8 \text{ (a)} \rightarrow Cp_2Ta(CO)R$$

$$Cp_2Ta(H)C_5H_{10} \text{ (a)}$$

$$Cp_2Ta(H)C_5H_8 \quad\quad\quad 90\%$$

$$10\%$$

$$exo\text{-}Cp_2Ta(H)C_4H_8 \text{ (b)} \rightarrow Cp_2Ta(CO)H$$

In order to explore an alternative method for the synthesis of alkylcarbonyl complexes and to test the idea that the preferential formation of the n-alkylcarbonyl compounds is due to a rapid isomerization of the corresponding isoalkyl compounds, we tried to prepare the latter from $Cp_2Ta(CO)Cl$ and RMgX or RLi. This method was also used by Fredericks and Thomas for the preparation of $Cp_2Nb(CO)CH_3$ [2]. The preparation of chlorocarbonylniobocene via the reduction of Cp_2NbCl_2 under CO does not proceed smoothly. Strong reduc-

tants such as sodium amalgam give only small amounts of $Cp_2Nb(CO)Cl$ [2], whereas milder reducing agents, such as zinc, probably produce an adduct of $Cp_2Nb(CO)Cl$ and $ZnCl_2$ [3].

The previously unknown corresponding tantalum derivative $Cp_2Ta(CO)Cl$ was prepared in moderate yields (40%) from Cp_2TaCl_2 using potassium as reductant. The reaction of Cp_2TaCl_2 with t-BuMgCl in ether under CO also gives $Cp_2Ta(CO)Cl$, in about the same yield. The chlorocarbonyl compound is characterized by a sharp singlet in its ^1H NMR spectrum at δ 4.75 ppm due to the C_5H_5 protons and a strong IR absorption at 1885 cm^{-1} due to the carbonyl group. Elemental analyses (Table 1) are in agreement with the composition $Cp_2Ta(CO)Cl$. The grey-green product is soluble in toluene and THF and shows a high thermal stability (m.p. 221°C: decomposition temperature 229°C). In contrast to the corresponding niobium compound, $Cp_2Ta(CO)Cl$ is rather inert; reagents such as $LiAlH_4$, CH_3Li, RMgX and strong reducing agents such as sodium and potassium do not affect the chlorocarbonyltantalocene. Although substitution reactions starting from $Cp_2Ta(CO)Cl$ seem not to be very successful, we are continuing our studies of alkyltantalum carbonyl complexes. In addition, reactions of hydride-olefin complexes and ligands with electron-donating and -accepting properties, such as cyanides and isocyanides, are under investigation.

Experimental

All experiments were carried out under purified nitrogen. Solvents were distilled from benzophenoneketylsodium under nitrogen or dried over sodium wire (toluene). Cp_2TaCl_2 and compounds $Cp_2Ta(H)L$ were prepared by published procedures [15,5]. IR spectra were measured on a Jasco IRA-2 spectrophotometer using Nujol mulls between KBr plates. The ^{13}C NMR spectrum of $Cp_2Ta(CO)C_3H_7$ (in C_6D_6) was recorded on a Varian XL-100 instrument by Drs. O. Piepers . The PMR spectra (in C_6D_6) were recorded on a Hitachi Perkin—Elmer 60 MHz instrument. The melting points and decomposition temperatures of the hydride-olefin and alkylcarbonyl complexes were determined by differential thermal analysis (DTA); heating rate 1.5°C/min (the data are listed in Table 2). Elemental analyses were performed at the Microanalytical Department of this University under the supervision of Mr. A.F. Hamminga.

Preparation of $Cp_2Ta(CO)C_4H_9$

A solution of $Cp_2Ta(H)C_4H_8$ (a) (320 mg, 0.87 mmol) in 6 ml of toluene was stirred at 75°C under 1 atm carbon monoxide. After the colour of the solution had changed from red to dark blue (7—8 h), the solvent was removed under reduced pressure and the residue extracted with pentane. The pentane solution was concentrated and cooled to —78°C. Blue-green crystals separated. Yield: 220 mg $Cp_2Ta(CO)C_4H_9$ (64%). The other complexes $Cp_2Ta(CO)R$ were prepared in essentially the same way. All alkylcarbonyl compounds can be purified by vacuum sublimation (80—120°C, 0.001 mmHg).

Reaction of $Cp_2Ta(H)C_4H_8(b)$ with CO

A solution of $Cp_2Ta(H)C_4H_8$ (b) (300 mg, 0.82 mmol) in 6 ml of toluene

was stirred for 7 h at 70°C under CO (1 atm). After evaporation the residue was extracted with ether. Crystallization from pentane/ether (1/1) gave purple crystalline material. Yield: 118 mg $Cp_2Ta(CO)H$ (42%).

Preparation of $Cp_2Ta(CO)Cl$

Procedure 1. To a stirred suspension of Cp_2TaCl_2 (690 mg, 1.8 mmol) in 50 ml of THF under CO (1 atm) an excess of potassium sand (120 mg) was added at room temperature. After completion of the reaction (10 h), the green solution was allowed to stand for 3 h and filtered. The solvent was removed under reduced pressure. After washing with pentane a grey-green product was isolated. Yield: 280 mg $Cp_2Ta(CO)Cl$ (40%).

Procedure 2. To a stirred suspension of Cp_2TaCl_2 (650 mg, 1.7 mmol) in 40 ml of ether under CO (1 atm) 1—2 equivalents of t-BuMgCl in ether were slowly added at room temperature. After 20 h the solvent was removed and the residue extracted with toluene. The green product was dried in vacuo. A further purification finally gave 254 mg $Cp_2Ta(CO)Cl$ (40%).

Acknowledgements

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