Journal of Organometallic Chemistry, 192 (1980) 75—81

THE ISOCYANIDE-INDUCED FORMATION OF DICYCLOPENTADIENYLTANTALUM MONOALKYL SPECIES FROM HYDRIDE OLEFIN COMPLEXES

A.H. KLAZINGA and J.H. TEUBEN

Laboratorium voor Anorganische Chemie, Rijksuniversiteit, Nijenborgh 16, 9747 AG Groningen (The Netherlands)

(Received November 25th, 1979)

Summary

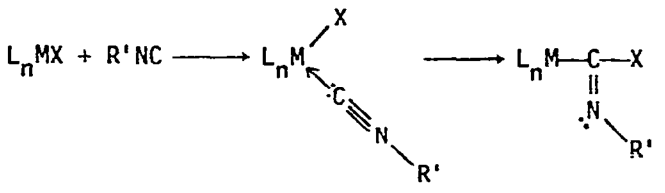
Reaction of *endo* $Cp_2Ta(H)L$ ($L = C_3H_6$, C_4H_8 (1-butene)) with aryl- and alkyl-isocyanides R'NC ($R' = 2{,}6\text{-}(CH_3)_2C_6H_3$, cyclo-$C_6H_{11}$, CH_3 and t-C_4H_9) gives the thermally stable isocyanide adducts of Cp_2TaR ($R = C_3H_7$, C_4H_9). The extraordinarily strong metal—isocyanide interaction leads to a non-linear "carbene-like" structure for these complexes and gives rise to the possibility of reactions at the nitrogen lone-pair electrons. The tantalocene isocyanide complexes react with Lewis acids, such as $AlEt_3$ to give 1/1 adducts $Cp_2TaR \cdot R'NC : AlEt_3$.

Introduction

Low-pressure carbonylation of *endo* hydride olefin complexes of tantalocene leads to thermally stable tantalum alkyl species $Cp_2Ta(CO)R$, whereas *exo* isomers undergo replacement of the olefin to give the carbonyl hydride $Cp_2Ta(CO)H$ [1]. Insertion of the CO molecule into the metal—alkyl bond is not observed under the relatively mild conditions used, probably because of the extraordinarily strong bonding of the CO ligand. In the hope of inducing insertion of a coordinated ligand into the metal—alkyl bond, we examined the reaction of hydride olefin complexes of tantalocene with isocyanides, which are structurally similar and isoelectronic with carbon monoxide. Many transition metal complexes give adducts with isocyanides. Depending on the thermal stability [2] and the nature of other ligands [3,4], the isocyanide may insert into a metal—ligand bond to give iminoacyl complexes (Scheme 1).

No isocyanide or iminoacyl complexes of tantalocene or niobocene were previously known. In this paper we describe the preparation and properties of some isocyanide adducts of tantalocene alkyls.

SCHEME 1



Results and discussion

The compounds $Cp_2TaR \cdot R'NC$ ($R = C_3H_7$, C_4H_9; $R' = 2,6\text{-}(CH_3)_2C_6H_3$, cyclo-$C_6H_{11}$, CH_3) were prepared in good yields by reaction of equivalent amounts of R'NC with *endo* $Cp_2Ta(H)L$ ($L = C_3H_6$, C_4H_8 (1-butene)) in toluene. The dark green ($R' = 2,6\text{-}(CH_3)_2C_6H_3$) or red brown adducts are obtained analytically pure by recrystallization from pentane (Table 1).

They are air-sensitive and readily soluble in pentane, ether and toluene. The elemental analyses, molecular weights (in benzene) and mass spectra are as expected for monomeric $Cp_2TaR \cdot R'NC$. The t-C_4H_9NC adducts could not be obtained pure, but their presence was established by IR spectroscopy. In contrast to the reaction with CO, *exo* hydride olefin complexes do not react with aryl and alkyl isocyanides under the mild conditions used for the synthesis of tantalocene alkyls from *endo* hydride olefin complexes.

Spectroscopic properties of isocyanide adducts

The IR spectra of the isocyanide adducts $Cp_2TaR \cdot R'NC$ show the characteristic absorptions of the groups η^5-C_5H_5 (at about 3100, 1000 and 800 cm^{-1}), R and R'. In addition, a strong, rather broad, absorption is found between

TABLE 1

ANALYTICAL DATA FOR THE COMPOUNDS $Cp_2TaR.R'NC$

Compound	Yield (%)	Analysis found (calc.) (%)			
		C	H	Ta	N
$R = C_3H_7$					
$R' = 2,6\text{-}(CH_3)_2C_6H_3$	54	54.37 (54.44)	5.38 (5.40)	37.40 (37.28)	3.07 (2.89)
$R' = C_6H_{11}$	38	51.70 (51.84)	6.12 (6.09)	39.05 (39.01)	3.10 (3.02)
$R' = CH_3$	60	[a] (45.58)	[a] (5.10)	46.5 (45.78)	[a] (3.54)
$R = C_4H_9$					
$R' = 2.6\text{-}(CH_3)_2C_6H_3$	32	55.15 (55.31)	5.64 (5.65)	36.41 (36.23)	3.02 (2.81)
$R' = C_6H_{11}$	30	51.58 (52.83)	6.28 (6.33)	38.05 (37.90)	[a] (2.94)
$R' = CH_3$	40	46.52 (46.95)	5.43 (5.44)	44.24 (44.21)	3.42 (3.42)

[a] Not determined.

TABLE 2

IR DATA FOR THE COMPOUNDS $Cp_2TaR.R'NC$ (ν(NC) in cm^{-1})[a]

R'	R = C_3H_7	R = C_4H_9	free ligand
2,6-$(CH_3)_2C_6H_3$	1800(1792)[b]	1807	2117
C_6H_{11}	1770	1765	2138
CH_3	1745(1780)	1766(1781)	2163
t-C_4H_9	1778	1779	2135

[a] KBr/Nujol. [b] Pentane solution.

1750—1800 cm^{-1}; it is assigned to the NC stretching vibration. The values of ν(NC) (Table 2) are very low compared with the free isocyanides and close to those of bridging or π-coordinated isocyanides [5,6].

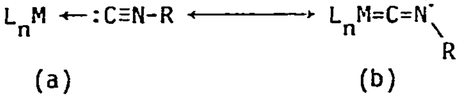
A similar large decrease in ν(NC) is observed for the low-valent metal complexes *trans*-$[M(CNR)_2(dppe)_2]$ (M = Mo, W) [7] and $[Ru(Ph_3P)(t\text{-}BuNC)_4]$ [8].

An X-ray structure determination of the latter compound shows that the isocyanide ligand is "end-on" coordinated, and that the originally linear C—N—R arrangement is distorted. From these data we infer that in the tantalocene adducts, the isocyanide ligand is also "end-on" coordinated. The extensive back donation into the isocyanide π^*-system, as indicated by the low value of ν(NC), causes a strong bonding of the isocyanide ligand and suggests a large contribution of the "carbene-like" structure (Scheme 2) to the electronic structure of these adducts.

The ^1H NMR spectra show the expected resonances of the groups Cp, R and R' (Table 3). The signals of group R show exactly the pattern observed for the corresponding alkyls in $Cp_2Ta(CO)R$ [1] and demonstrate the presence of n-alkyl groups. The similarity between the ^1H NMR spectra of the carbonyl and isocyanide adducts supports the idea that the isocyanide is "end-on" coordinated, just like the CO ligand.

In the ^{13}C NMR spectrum of $Cp_2TaC_3H_7 \cdot 2,6\text{-}(CH_3)_2C_6H_3NC$ two triplets at δ 1.75 ppm (J 119 Hz) and δ 33.39 ppm (J 122 Hz) and a quartet at δ 23.07 ppm (J 126 Hz) originate from a n-C_3H_7 group. The cyclopentadienyl carbons resonate at δ 92.09 ppm (J 178 Hz) and the methyl carbons of the xylyl group at δ 19.13 ppm (J 127 Hz). The signals due to the aromatic carbons of the latter group partly coincide with the resonances of the solvent C_6D_6. The isocyanide carbon is not observed, probably because of the long relaxation time of this carbon atom.

SCHEME 2



$$L_nM \leftarrow :C{\equiv}N\text{-}R \longleftrightarrow L_nM{=}C{=}\ddot{N}\text{-}R$$

(a) (b)

TABLE 3

^{1}H NMR DATA FOR $Cp_2TaC_3H_7.R'NC$ [a]

R'	δCp	δC_3H_7	δR'
$2,6\text{-}(CH_3)_2C_6H_3$	4.71	0.5—1.7	CH_3: 2.42, C_6H_3: 6.9
C_6H_{11}	4.73	0.5—2.4	
CH_3	4.69	0.5—1.5	CH_3: 3.04

[a] Internal standard TMS, C_6D_6, 35°C.

Thermal properties

As in the carbonyl alkyl complexes, the tantalocene alkyl species are stabilized by the strong π-acceptor properties of the isocyanide ligand. This results in relatively high thermal stabilities. as is illustrated by the decomposition temperatures of the isocyanide adducts (Table 4).

Decomposition of this type of transition metal alkyl species probably proceeds via β-hydrogen abstraction and formation of hydride olefin complexes [11]. The strong bonding between tantalum and the isocyanide ligand prevents the formation of a free coordination site on tantalum which can take part in a β-H abstraction process, and is thus responsible for the high thermal stability of the isocyanide adducts.

Chemical properties

Despite the fact that the thermal stabilities are lower than those observed for the corresponding carbonyl adducts, the isocyanide alkyl complexes do not form iminoacyl complexes, even on heating. In experiments aimed directly towards forcing insertion by the action of an additional ligand (isocyanide or phosphine) the adducts were completely recovered. Apparently, the strong metal—isocyanide interaction prevents the formation of iminoacyl products. As a consequence of this strong interaction the isocyanide adducts should show a "carbene-like" structure (Scheme 2) with a relatively high electron density on the nitrogen atom. In order to confirm this we carried out reactions with Lewis acids; dinitrogen complexes of Re, Mo, W and Os are known to react with Lewis acids via the nitrogen lone-pair electrons to give 1/1 adducts [10,11].

$Cp_2TaC_3H_7 \cdot CH_3NC$ (in pentane solution) undergoes a similar reaction with

TABLE 4

DTA DATA FOR $Cp_2TaR.R'NC$ COMPLEXES

Compound	M.p. (°C)	Decomposition temp. (°C)
$Cp_2TaC_3H_7.2,6\text{-}(CH_3)_2C_6H_3NC$	135	150
$Cp_2TaC_4H_9.2,6\text{-}(CH_3)_2C_6H_3NC$	106	152
$Cp_2TaC_3H_7.C_6H_{11}NC$	—	91
$Cp_2TaC_4H_9.C_6H_{11}NC$	82	88
$Cp_2TaC_3H_7.CH_3NC$	104	111
$Cp_2TaC_4H_9.CH_3NC$	93	98

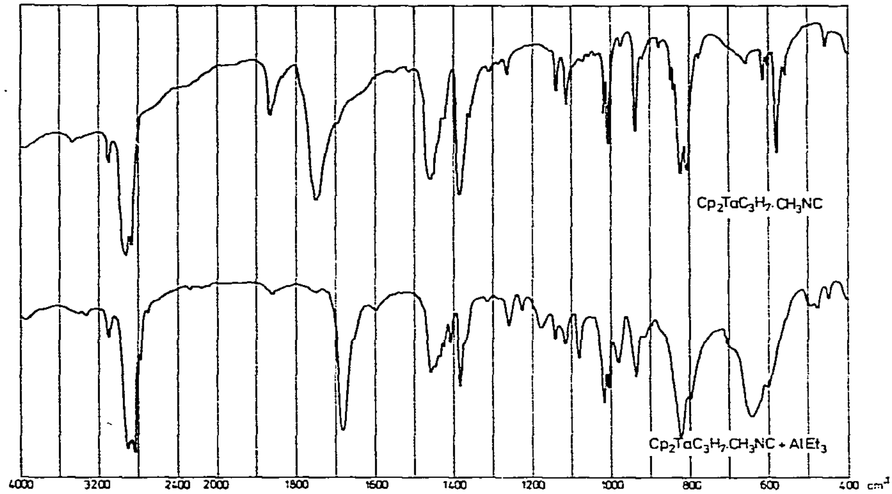


Fig. 1. IR spectra of $Cp_2TaC_3H_7.CH_3NC$ and the adduct $Cp_2TaC_3H_7.CH_3NC:AlEt_3$.

$AlEt_3$. The orange-yellow, oily reaction product is very air-sensitive and shows an intense infrared absorption at 1680 cm^{-1} (Fig. 1), which is assigned to $\nu(NC)$. The further decrease of $\nu(NC)$ (1745 → 1680 cm^{-1}) is most probably due to the coordination of the nitrogen lone-pair electrons at the Lewis acid $AlEt_3$. For $Cp_2TaC_3H_7 \cdot 2,6\text{-}(CH_3)_2C_6H_3NC$ (in pentane solution) only partial formation of an 1/1 adduct with $AlEt_3$ ($\nu(NC)$ 1670 cm^{-1}) is observed. This indicates that the coordination of the nitrogen atom at $AlEt_3$ is hindered by the bulky xylyl group. The ^1H NMR spectrum of $Cp_2TaC_3H_7 \cdot CH_3NC : AlEt_3$ (in C_6D_6) suggests the presence of two isomers A and B (2/1) (A: δ Cp 4.78, δ CH_3 3.01; B: δ Cp 4.68, δ CH_3 2.79 ppm) and indicates that free rotation about the Ta—C—N axis is hindered by the addition of $AlEt_3$. No interconversion of these two isomers (Fig. 2) is observed even at higher temperatures. Reactions of *endo* hydride olefin complexes with isocyanides proceed as expected on the basis of the Lauher and Hoffmann concept for bent metallocene derivatives [12]. The highest occupied molecular orbital $1a_1$ in Cp_2TaR (R = alkyl) is lowered in energy by interaction with the isocyanide π^*-orbitals. The large stabilization of

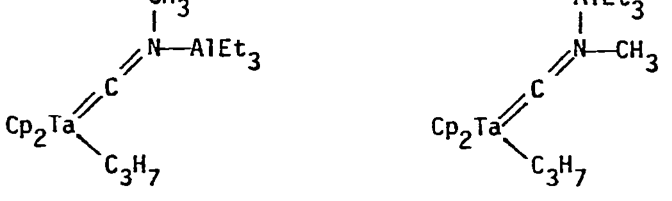


Fig. 2. Possible structures for $Cp_2TaC_3H_7.CH_3NC:AlEt_3$.

the ($1a_1 + \pi^*$) orbital indicates that Cp_2TaR is a very good π-donor, which readily reacts with π-acceptor ligands such as olefins [13], carbon monoxide [1] or isocyanides. The adducts formed in this way are very stable.

We are continuing our studies concerning the conversion of tantalocene hydride olefin complexes into tantalocene alkyl products in the presence of unsaturated substrates, and are extending the research of the corresponding, more reactive niobium complexes.

Experimental

All experiments were carried out under nitrogen. Solvents were distilled from benzophenoneketylsodium. Tantalocene hydride olefin complexes were prepared by the reaction of Cp_2TaCl_2 with appropriate alkyl Grignard reagents [14].

$2,6\text{-}(CH_3)_2C_6H_3NC$ and cyclo-$C_6H_{11}NC$ were prepared by the carbylamine reaction [15], whereas CH_3NC and t-C_4H_9NC were obtained by dehydration of the *N*-alkylformamides [16]. IR spectra were measured on a Jasco-IRA-2 spectrophotometer using a Nujol mull between KBr discs. The ^{13}C NMR spectrum of $Cp_2TaC_3H_7 \cdot 2,6\text{-}(CH_3)_2C_6H_3NC$ (in C_6D_6) was recorded on a Varian XL-100 instrument by Drs. D.M. Kok, whereas the ^1H NMR spectra were run on a Perkin-Elmer R-24B (60 MHz) instrument. The melting points and decomposition temperatures of the isocyanide adducts were determined by differential thermal analysis (DTA); heating rate 2—3°C/min. Elemental analyses were performed at the Microanalytical Department of this University under supervision of Mr. A.F. Hamminga.

Preparation of $Cp_2TaC_3H_7 \cdot 2,6\text{-}(CH_3)_2C_6H_3NC$

A solution of *endo* $Cp_2Ta(H)C_3H_6$ (450 mg, 1.27 mmol) and $2,6\text{-}(CH_3)_2C_6H_3$-NC (167 mg, 1.27 mmol) in 8 ml of toluene was stirred for 6 h at 70°C. After completion of the reaction (when the colour had changed from red to dark green) the solvent was evaporated and the residue extracted with 50 ml of n-pentane. The pentane solution was slowly cooled to —78°C and brown-green crystals separated. After decanting off the mother liquor the crystals were washed with n-pentane at —20°C and dried in vacuo. Yield: 333 mg Cp_2Ta-$C_3H_7 \cdot 2,6\text{-}(CH_3)_2C_6H_3NC$ (54%). Other $Cp_2TaR \cdot R'NC$ products were prepared by the same procedure.

Preparation of a 1/1 $Cp_2TaC_3H_7 \cdot CH_3NC : AlEt_3$ adduct

To a solution of $Cp_2TaC_3H_7 \cdot CH_3NC$ (200 mg, 0.51 mmol) in 15 ml of pentane 0.8 ml of $AlEt_3$ in hexane (0.6 *N*) was added at 0°C. The colour of the mixture immediately changed from red to orange-yellow. After evaporation, an orange, somewhat oily product was obtained. IR and ^1H NMR spectra showed the presence of the 1/1 adduct.

Acknowledgements

The authors thank Prof. Dr. F. Jellinek and Dr. H.J. de Liefde Meijer for stimulating discussions.

References

1 A.H. Klazinga and J.H. Teuben, J. Organometal. Chem., 165 (1979) 31.
2 E.J.M. de Boer and J.H. Teuben, J. Organometal. Chem., 166 (1979) 193.
3 D.W. Kuty and J.J. Alexander, Inorg. Chem., 17 (1978) 1489.
4 B. Crociani and R.L. Richards, J. Chem. Soc. Chem. Commun., (1973) 127.
5 F.A. Cotton and B.A. Frenz, Inorg. Chem., 13 (1974) 253.
6 L.S. Benner, M.M. Olmstead and A.L. Balch, J. Organometal. Chem., 159 (1978) 289.
7 J. Chatt, C.M. Elson, A.J.L. Pombeiro, R.L. Richards and G.H.D. Royston, J. Chem. Soc. Dalton, (1978) 165.
8 G.R. Barker, A.M.R. Galas, M. Green, J.A.K. Howard, F.G.A. Stone, T.W. Turney, A.J. Welch and P. Woodward, J. Chem. Soc. Chem. Commun., (1977) 256.
9 D.L. Reger and E.C. Culbertson, Inorg. Chem., 16 (1977) 3104.
10 J. Chatt, J.R. Dilworth, G.J. Leigh and R.L. Richards, J. Chem. Soc. Chem. Commun., (1970) 955.
11 J. Chatt, R.H. Crabtree, E.A. Jeffery and R.L. Richards, J. Chem. Soc. Dalton, (1973) 1167.
12 J.W. Lauher and R. Hoffmann, J. Amer. Chem. Soc., 98 (1976) 1729.
13 F.N. Tebbe and G.W. Parshall, J. Amer. Chem. Soc., 93 (1971) 3793.
14 A.H. Klazinga and J.H. Teuben, J. Organometal. Chem., 157 (1978) 413.
15 T. Shengaki and M. Takebayashi, Bull. Soc. Chim. Japan., 36 (1963) 617.
16 J. Casanova, R.E. Schuster and N.D. Werner, J. Chem. Soc., (1963) 4280.