Journal of Organometallic Chemistry, 247 (1983) 33–37
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

NIOBIUM(III) COMPLEXES CONTAINING ACETYLENE, ISOCYANIDE, PHOSPHINE OR PHOSPHITE LIGANDS

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(Received November 29th, 1982)

Summary

The reduction of THF solutions of $(\eta\text{-}C_5H_5)_2NbCl_2$ with Na/Hg in the presence of various phosphines, phosphites, acetylenes or isocyanides gives complexes of the type $(\eta\text{-}C_5H_5)_2NbClL$, where L = PMe_2Ph, $P(OMe)_3$, PhC≡CPh, PhC≡CH, HC≡CH, CNPh, or CNCy. A complex is also formed in solution from PEt_3 but cannot be isolated as a solid. For L = $P(OPh)_3$ no stable compound can be obtained. The IR, ^1H and ^{13}C NMR spectra of the complexes are described.

Introduction

The chemistry of dicyclopentadienyl-transition metal complexes has been an expanding field in recent years. Although several hydridoniobium(III) derivatives $(\eta\text{-}C_5H_5)_2NbHL$ have been reported [1–5], few examples of halo derivatives $(\eta\text{-}C_5H_5)_2NbXL$ are known, in spite of their potential utility as starting products for the isolation of dicyclopentadienylniobium(III) complexes [2,3,6,7]. The complex $(\eta\text{-}C_5H_5)_2NbBr(PMe_2Ph)$ is the only halophosphineniobium(III) complex to be isolated to date, and was made from $(\eta\text{-}C_5H_5)_2NbCl_2$ in a five-step syntheses [2].

The reduction of $(\eta\text{-}C_5H_5)_2NbCl_2$ has been reported previously [6], such reduction in the presence of the appropriate ligand L is the simplest method of obtaining chlorodicyclopentadienylniobium(III) complexes $(\eta\text{-}C_5H_5)_2NbClL$. In this way, we have isolated and characterized several new compounds of this type, with L = PMe_2Ph, $P(OMe)_3$, PhC≡CPh, PhC≡CH, HC≡CH, CNPh or CNCy.

Results and discussion

Although the reduction of $(\eta\text{-}C_5H_5)_2NbCl_2$ has been reported to proceed in several solvents and with various reducing agents [6,7], we have found that the Na/Hg-THF system is the best, due to the greater solubility of both the initial and final products in this solvent. If $(\eta\text{-}C_5H_5)_2NbCl_2$ is reduced by Na/Hg in THF in the presence of a phosphine, a green solution is always obtained, but its subsequent

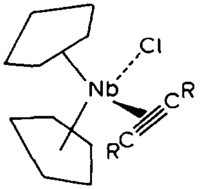
0022-328X/83/$03.00

work-up gives varying results depending on the phosphine used. When L = PMe_2Ph, complex I is obtained in good yield; its analytical and ^1H NMR data (Tables 1 and 2) support its formulation. When L = PEt_3, a green crystalline solid is again isolated; its ^1H NMR spectrum in benzene-d_6 indicates the presence of the ligand (two multiplets at δ 1.2 and 0.7 ppm) effectively coordinated to the niobocene chloride moiety, as revealed by the splitting of the (η-C_5H_5) signal (doublet at δ 4.76 ppm, J(P–H) 1.5 Hz). The IR spectrum also shows a single band at 245 cm^{-1}, due to ν(Nb–Cl) (Table 3). These results suggest the formation of $(\eta$-$C_5H_5)_2NbCl(PEt_3)$, although satisfactory analytical data could not be obtained, and attempts at recrystallization resulted in the decomposition of the sample.

Complex II is obtained from $P(OMe)_3$, but no stable compound could be obtained from $P(OPh)_3$.

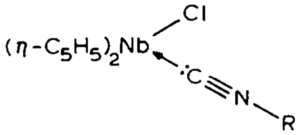
Similarly PhC≡CPh and PhC≡CH give compounds III and IV in good yield, but the same reaction made under acetylene gas gives an unidentified solid and a brown solution from which the acetylene complex V can be isolated in low yield. The ν(C≡C) stretching frequencies in the acetylene complexes III–V, (Table 3), are lowered by 448, 411 and 349 cm^{-1}, respectively, with respect to the value in the free acetylene (2223 cm^{-1} for Raman PhC≡CPh). This is an indication of the extensive back donation of electronic density from the HOMO $a'(1a_1)$ of the $(\eta$-$C_5H_5)_2NbCl$ moiety into the acetylene $\pi_{\|}^*$ orbital [8,9]. This back donation increases with increasing aryl substitution. The ^{13}C chemical shifts of the acetylenic carbon atoms lie between 103.6 and 108 ppm, and the ^1H resonances of the hydrogen atoms attached to them in IV and V appear between 6 and 8 ppm. These values suggest that the acetylene molecules act as two electron donors, primarily by interaction of the filled $\pi_{\|}$ molecular orbitals with the LUMO $a'(b_2)$ of $(\eta$-$C_5H_5)_2NbCl$ [8–10].

In this model, the two ends of the acetylene molecule are non-equivalent, and this is in agreement with the observed ^1H NMR spectrum, which shows two ^1H signals for V whereas only one terminal acetylenic hydrogen resonance is observed for IV. This means that only one isomer has been formed, probably due to the large difference in bulk between the hydrogen atom and the phenyl ring.

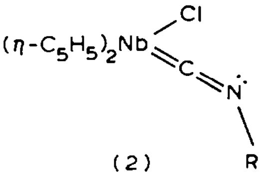


The remarkable stability of these acetylene complexes contrasts sharply with that of the corresponding phosphine and phosphite complexes, IV being the most stable. It remains unchanged in air as a solid for at least one year, and in benzene solution for several days. It is slowly decomposed in $CHCl_3$-d_1 as shown by the greenish colour of the solution and the appearance in its ^1H NMR spectra of an additional (η-C_5H_5) peak at δ 6.34 ppm.

Isocyanides may also coordinate to niobiocene chloride, as shown by the reduction in the presence of CNPh and CNCy which gives compounds VI and VII. The ν(C≡N) stretching frequency in these complexes is lowered by 370 and 280 cm^{-1} with respect to the free ligand. This large decrease is due to the extensive electronic donation from the $a'(a_1)$ orbital of the isocyanide, which enhances the contribution of structure **2**.



(1)



(2)

The ^{13}C chemical shift of the isocyanide carbon atom, which might give evidence for carbenoid character, could not be observed, probably due to a long relaxation time. Similar low $\nu(C{\equiv}N)$ values associated with a bent arrangement of the isocyanide ligand have been previously observed [11], and also postulated in niobocene and tantalocene hydride isocyanide adducts [12].

Experimental

All experiments were performed under nitrogen in Schlenk-type glassware. All solvents were distilled under nitrogen from benzophenoneketyl sodium, except toluene which was dried with calcium hydride. $(\eta\text{-}C_5H_5)_2NbCl_2$ was prepared as described in ref. 2b and phenyl and cyclohexyl isocyanides by the carbylamine reaction [13]. IR spectra (Table 3) were taken as Nujol mulls in a Perkin-Elmer 457 spectrophotometer. The ^1H and $\{^1H\}^{13}C$ NMR spectra (Table 2) were run on a Varian FT-80A. The C, H and N analyses were made with a Perkin-Elmer 240B microanalyzer (Table 1).

The experimental procedure was similar in all cases. A mixture of 0.30 g (1 mmol) of $(\eta\text{-}C_5H_5)_2NbCl_2$, 1.05 mmol of sodium amalgam, and 1 mmol of the appropriate ligand in 30 ml of THF was stirred overnight. The green (L = PMe_2Ph, $P(OMe)_3$), orange (L = $PhC{\equiv}CPh$, $PhC{\equiv}CH$), or brown or brick red (L = CNPh, CNCy)

TABLE 1

ANALYTICAL DATA FOR Cp_2NbClL COMPLEXES (Found (Calcd.)(%))

Complex	C	H	N
$Cp_2NbCl(PMe_2Ph)$	55.04	5.50	
(I)	(54.45)	(5.33)	
$Cp_2NbCl(P(OMe)_3)$	40.79	4.91	
(II)	(40.80)	(4.97)	
$Cp_2NbCl(PhC{\equiv}CPh)$	65.40	4.59	
(III)	(65.99)	(4.58)	
$Cp_2NbCl(PhC{\equiv}CH)$	61.01	4.66	
(IV)	(59.94)	(4.47)	
$Cp_2NbCl(HC{\equiv}CH)$	50.53	4.29	
(V)	(50.64)	(4.25)	
$Cp_2NbCl(CNPh)$	56.24	4.28	3.82
(VI)	(55.92)	(4.14)	(3.84)
$Cp_2NbCl(CNCy)$	55.83	6.17	3.81
(VII)	(55.37)	(6.01)	(3.80)

TABLE 2

^1H AND $\{^1H\}^{13}C$ NMR DATA FOR Cp_2NbClL COMPLEXES (multiplicity; rel. int.)

Complex	Cp		L	
	^1H	$\{^1H\}^{13}C$	^1H	$\{^1H\}^{13}C$
$Cp_2NbCl(PMe_2Ph)$ (I)	4.66(d, J(P–H) 1.8; 10)		7.56(m)^b Ph 1.28(d, J(P–H) 7.5; 6)Me	
$Cp_2NbCl(P(OMe)_3)$ (II)	5.12(d, J(P–H) 1.9; 10)		3.63(d, J(P–H), 10.5; 9)Me	
$Cp_2NbCl(PhC{\equiv}CPh)$ (III)	5.34(s)	107.8	7.39(m), 7.22(m)^b Ph	107≡C 128.1–131.6^b, several Ph
$Cp_2NbCl(PhC{\equiv}CH)$ (IV)	5.32(s; 10)	107.5	8.16(s; 1) ≡CH 7.30(m) Ph	108 ≡CPh; 106.5≡CH 127–130.9^b, several Ph
$Cp_2NbCl(HC{\equiv}CH)$ (V)	5.12(s; 10)	107.5	8.41(s; 1) ≡CH 7.74(s; 1) ≡CH	103.6 ≡CH
$Cp_2NbCl(CNPh)$ (VI)	4.93(s)	103	7.25^b Ph	127.8–131.2^b several Ph
$Cp_2NbCl(CNCy)$ (VII)	5.06(s; 10)	96.3	1.52, 1.14(m, 11)CH_2	34.2; 25.4; 23.6 CH_2

^{a} In benzene-d_6. Chemical shifts with respect to TMS, positive signs downfield. ^{b} Partially overlapped with solvent signals.

TABLE 3

SELECTED IR VIBRATIONS OF Cp_2NbClL COMPLEXES (cm^{-1})

Complex	$\nu(C\equiv C)$	$\nu(C\equiv N)$	$\nu(Nb-Cl)$
$Cp_2NbCl(PMe_2Ph)$ (I)			245
$Cp_2NbCl(P(OMe)_3)$ (II)			250
$Cp_2NbCl(PhC\equiv CPh)$ (III)	1775		250
$Cp_2NbCl(PhC\equiv CH)$ (IV)	1700		247
Cp NbCl(HC≡CH) (V)	1625		250
$Cp_2NbCl(CNPh)$ (VI)		1750(br)	250
$Cp_2NbCl(CNCy)$ (VII)		1850(br)	240

solutions were filtered, and the solvent evaporated under reduced pressure to a volume of ca. 5 ml. On addition of 1–2 ml of diethyl ether and subsequent cooling, compounds I–IV and VI crystallized out. They were repeatedly washed with ether and recrystallized from toluene/pentane. Yields were 60–70%.

The reaction with acetylene was carried in a similar way, but with the reaction flask saturated with the gas. The work-up of the resulting brown solution was similar. The yield was 15%.

Acknowledgements

The authors gratefully acknowledge financial support from the Comisión Asesora de Investigación Científica y Técnica.Spain.

References

1 F.N.Tebbe and G.W.Parshall, J. Am. Chem. Soc., 93(1971)3793.
2 (a) C.R. Lucas and M.L.H. Green, J. Chem. Soc. Dalton, (1973) 1005; (b) C.R. Lucas, Inorg. Synthesis, 16(1976)107.
3 E.E.H. Otto and H.H. Brintzinger, J. Organometal. Chem., 148(1978)29.
4 J.A. Labinger and J. Schwartz, J. Am. Chem. Soc., 97(1975)1596.
5 A.H. Klazinga and J.H. Teuben, J. Organometal. Chem., 165(1979)31.
6 D.A. Lemenovskii, T.V. Baukova and V.P. Fedin, J. Organometal. Chem., 132(1977)C14.
7 S. Fredericks and J.L. Thomas, J. Am. Chem. Soc., 100(1978)350.
8 J.W. Lauher and R. Hoffmann, J. Am. Chem. Chem., 98(1976)1729.
9 K. Tatsumi, R. Hoffmann and J.L. Templeton, Inorg. Chem., 21(1982)466.
10 B.C. Ward and J.L. Templeton, J. Am. Chem. Soc., 102(1980)1532.
11 (a) J.M. Basset, D. E. Berry, G.K. Barker, M. Green, J.A.K. Howard and F.G.A. Stone, J. Chem. Soc. Dalton, (1979)1003; (b) J.M. Basset, G.K. Barker, M. Green, J.A.K. Howard, F.G.A. Stone and W.C. Wolsey, ibid., (1981)219.
12 A.H. Klazinga and J.H. Teuben, J. Organometal Chem., 192(1980)75. (b) 194(1980)309.
13 J. Casanova, R.E. Schuster and N.D. Werner, J. Chem. Soc., (1963)4280.