Journal of Organometallic Chemistry, 258 (1983) 181–187
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

BROMODICYCLOPENTADIENYLNIOBIUM COMPLEXES

L. ACEDO, A. OTERO and P. ROYO

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Alcalá de Henares (Madrid) (Spain)

(Received June 29th, 1983)

Summary

The reaction of NbX_5 (X = Cl, Br) with an excess of NaCp ($Cp = C_5H_5$) followed by the addition of HBr gives $(\eta^5\text{-}C_5H_5)_2NbBr_2$ (I) in low yield. The reduction of I with Na/Hg or NaNaph in a molar ratio 1/1 gives $(\eta^5\text{-}C_5H_5)_2NbBr$ (II), whereas the same reaction in the presence of π-acid ligands gives $(\eta^5\text{-}C_5H_5)_2NbBrL$ (III, L = CO; IV, L = PMe_2Ph; V, L = $P(OMe)_3$; VI, L = PhC≡CPh; VIII, L = PhC≡CH). Finally, the reduction of I with Na/Hg in a molar ratio 2/1 gives the dimer $(\eta^5\text{-}C_5H_5)_4Nb_2Br_3$ (VIII), which contains both niobium(III) and niobium(IV). The chemical and structural characteristics of all these compounds are described.

Introduction

The chemistry of cyclopentadienyl-niobium and -tantalum derivatives has been an expanding field in the last years. Only a few complexes of the type $(\eta^5\text{-}C_5H_5)_2MXL$ (M = Nb, Ta; X = halogen; L = π-acid ligand) have been reported [1–4], in spite of their possible utility as starting products for the preparation of bis-cyclopentadienyl-niobium and -tantalum(III) complexes.

We describe below a method for the preparation of $(\eta^5\text{-}C_5H_5)_2NbBr_2$ (I) and the results obtained in reductions of I with Na/Hg or NaNaph in various molar ratios. The reductions have given a new organoniobium(III)–niobium(IV) complex and several new $(\eta^5\text{-}C_5H_5)_2NbXL$ compounds, where X = Br and L = CO, PMe_2Ph, $P(OMe)_3$, PhC≡CPh or PhC≡CH. All the compounds described have been characterised by IR, ^1H NMR spectroscopy and magnetic susceptibility measurements.

Results and discussion

The complex $(\eta^5\text{-}C_5H_5)_2NbBr_2$ (I) was prepared by treatment of NbX_5, (X = Cl, Br) with a large excess of NaC_5H_5. (This compound has previously been mentioned by other authors [5].) This method is analogous to that reported by De Liefde Meijer

0022-328X/83/$03.00

[6] for the preparation of $(\eta^5\text{-}C_5H_5)_2NbCl_2$. The formation of I is the result of the reduction of Nb^V to Nb^{IV}, and subsequent treatment with HBr yields the final product, according to eq. 1 and 2:

$$NbX_5 + 5\ NaC_5H_5 \xrightarrow{THF} (\eta^5\text{-}C_5H_5)_2Nb(\sigma\text{-}C_5H_5)_2 + C_5H_5^{\cdot} + 5\ NaCl \qquad (1)$$

$(X = Cl, Br)$

$$(\eta^5\text{-}C_5H_5)_2Nb(\sigma\text{-}C_5H_5)_2 + 2\ HBr \xrightarrow{\text{chloroform}} (\eta^5\text{-}C_5H_5)_2NbBr_2 + 2\ C_5H_6 \qquad (2)$$

Complex I is an air sensitive green or brown crystalline solid which can be stored unchanged under nitrogen. I is oxidised in air, to give the binuclear niobium(V) complex $[(\eta^5\text{-}C_5H_5)_2NbBr_2]_2O$ (IX) after two weeks of exposure. I is insoluble in the common organic solvents and only slightly soluble in dichloromethane, chloroform and acetone. The solutions are stable under nitrogen but decompose in the presence of air to give a yellow solution of IX. Complex I has a μ_{eff} of 1.82 BM at 20°C, revealing the presence of one unpaired electron. Complex IX is diamagnetic and its ^1H NMR spectrum shows a single resonance for $\eta^5\text{-}C_5H_5$ at δ 6.70 ppm, in agreement with the previously chemical shift observed for cyclopentadienylniobium(V) complexes [7]. The IR spectrum of IX shows a strong absorption due to the ν(Nb–O–Nb) at 680 cm^{-1} (See Table 2).

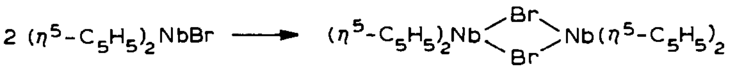
Complex II was obtained as grey crystals by reducing a THF solution of I with

$$(\eta^5\text{-}C_5H_5)_2NbBr_2 + Na/Hg \rightarrow (\eta^5\text{-}C_5H_5)_2NbBr + NaBr \qquad (3)$$

sodium amalgam (molar ratio 1/1), according to eq. 3. Similar results were obtained using NaNaph as reducing agent.

Complex II is very air sensitive, and rigourous precautions must be taken during its handling to avoid decomposition. It is soluble in organic solvents such as benzene and toluene.

The behaviour of II towards π-acid ligands is different from that observed for $(\eta^5\text{-}C_5H_5)_2NbCl$. Thus, $(\eta^5\text{-}C_5H_5)_2NbCl$ behaves as a Lewis acid and reacts readily with π-acid ligands [1–3], whereas complex II does not react with ligands such as CO or PMe_2Ph. This unusual behaviour for a 16 electrons species suggests the formation of a binuclear compound with a double bromine bridge between the two niobium atoms



(4)

Complex II is diamagnetic and shows a ^1H NMR spectrum with a single resonance due to both $(\eta^5\text{-}C_5H_5)$ rings similar to spectra previously reported for $(\eta^5\text{-}C_5H_5)_2NbCl$ [1] (See Table 3).

If I is reduced by Na/Hg in THF (1/1 molar ratio) in the presence of π-acid ligands the 18 electrons compounds $(\eta^5\text{-}C_5H_5)_2NbBrL$ are obtained, according to eq. 5. Reduction in the presence of phosphorus donor ligands yields very air-sensi-

$$(\eta^5\text{-}C_5H_5)_2NbBr_2 + L + Na/Hg \rightarrow (\eta^5\text{-}C_5H_5)_2NbBrL \qquad (5)$$

(III, L = CO; VI, L = PhC≡CPh;
IV, L = PMe_2Ph; VII, L = PhC≡CH)
V, L = $P(OMe)_3$;

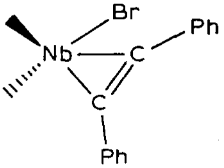
tive green crystals of IV and V. They are soluble in the common organic solvents and the solutions decompose in a few hours even under nitrogen. Complex IV has been described previously [8].

The ^1H NMR spectra of IV and V show the resonances due to the phosphorus ligands coordinated to the niobocene bromide moiety, as revealed by the splitting of the (η^5-C_5H_5) signals (See Table 3). The IR spectra show the absorptions due to the (η^5-C_5H_5) rings and the phosphorus donor ligands.

When the reduction is carried out in the presence of CO a maroon-grey solution is obtained, which gives a grey crystalline precipitate upon partial removal of solvent. III is a moderately air-sensitive solid and can be stored under nitrogen several days. This behaviour is analogous to that of (η^5-C_5H_5)$_2$NbCl(CO) [1]. The ^1H NMR spectrum of III shows a single resonance due to the (η^5-C_5H_5) rings (see Table 3) and the IR spectrum shows the ν(C≡O) at 1930 cm^{-1}.

Similarly the reduction in the presence of PhC≡CPh or PhC≡CH gives red solutions from which yellow solids of VI and VII are isolated. These solids are the most stable bromine complexes of niobium(III) isolated. Solid samples remain unchanged for several days in air. The remarkable stability of these acetylene complexes contrasts sharply with that of the phosphine and phosphite complexes mentioned above.

The ^1H NMR spectra of VI and VII show a single resonance due to the (η^5-C_5H_5) rings; in addition both show a complex resonance due to the phenyl rings, and VII shows a single resonance for acetylenic hydrogen (See Table 3). These results indicate that the two ends of the acetylene molecule are inequivalent, in agreement with a structure containing both the Br and the C=C group in the reflection plane of the rings:

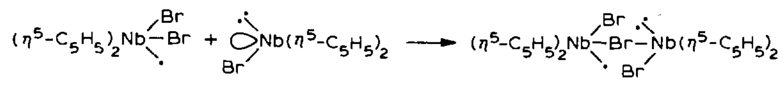


On the other hand the ν(C≡C) stretching frecuencies in these acetylene complexes VI and VII are 448 and 523 cm^{-1} lower than the value in the free acetylene (2223 cm^{-1} for Raman PhC≡CPh). This is an indication of extensive back donation of electronic density from the HOMO $a'(1a_1)$ of the (η^5-C_5H_5)$_2$NbBr moiety into the acetylene $\pi_{\|}^{\star}$ orbital [9,10]. These values suggest that the acetylene acts as a two electron donor primarily by interaction of its filled $\pi_{\|}$ molecular orbitals with the LUMO $a'(b_2)$ orbital of (η^5-C_5H_5)$_2$NbBr [9,11], behaviour similar to that observed for the analogous chloro derivatives [4].

The reduction of (η^5-C_5H_5)$_2$NbBr$_2$ in THF with sodium amalgam in a 2/1 molar ratio produces a red solution from which complex VIII is obtained as red-brown crystals, according to eq. 6.

$$2(\eta^5\text{-}C_5H_5)_2NbBr_2 + Na/Hg \rightarrow (\eta^5\text{-}C_5H_5)_2NbBr_2 \cdot (\eta^5\text{-}C_5H_5)_2NbBr + NaBr \quad (6)$$

Complex VIII has a μ_{eff} of 1.98 BM at 20°C which reveals the presence of one unpaired electron for each dimeric unit. This value is similar to that found for the analogous (η^5-C_5H_5)$_4$Nb$_2$Cl$_3$ [12]. We suggest that the most reasonable structure for this compound must contain a single bromine bridge, since this places 18 and 17 electrons, respectively, on the niobium(III) and niobium(IV) atoms, although other structures with two or three bromine bridges cannot be excluded. In this case the formation of complex VIII is the consequence of the acidic character of complex II, which achieves 18 electrons by accepting one pair from the bromine atom of complex I, as depicted in eq. 7.



All the complexes described give satisfactory analytical data (See Table 1).

Experimental

All operations were carried out under vacuum or in an inert atmosphere using Schlenk-type glassware. IR spectra (Table 2) were recorded on a Perkin–Elmer spectrophotometer (over the range 4000–200 cm^{-1}) using Nujol mulls between CsI plates. Magnetic measurements were carried out by the Faraday method with a Bruker magnet system. ^{1}H NMR spectra (Table 3) were determined on a Varian FT 80A spectrometer. C,H analysis (Table 1) were made with a Perkin–Elmer 240B microanalyzer. Solvents were dried and distilled before use. $NbBr_5$ was prepared by a standard method [13]. Bromine was determined by White's method [14].

TABLE 1

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

Complex	C	H	Br
$(\eta^5\text{-}C_5H_5)_2NbBr_2$	31.16	2.77	41.35
(I)	(31.33)	(2.61)	(41.77)
$(\eta^5\text{-}C_5H_5)_2NbBr$	40.45	3.41	25.80
(II)	(39.60)	(3.30)	(26.38)
$(\eta^5\text{-}C_5H_5)_2NbBr(CO)$	39.43	3.20	23.98
(III)	(39.88)	(3.02)	(24.15)
$(\eta^5\text{-}C_5H_5)_2NbBr(PMe_2Ph)$	48.73	4.91	18.02
(IV)	(48.92)	(4.75)	(18.12)
$(\eta^5\text{-}C_5H_5)_2NbBr(P(OMe)_3)$	36.89	4.90	18.54
(V)	(36.53)	(4.44)	(18.72)
$(\eta^5\text{-}C_5H_5)_2NbBr(PhC{\equiv}CPh)$	60.06	4.65	16.36
(VI)	(59.87)	(4.16)	(16.61)
$(\eta^5\text{-}C_5H_5)_2NbBr(PhC{\equiv}CH)$	53.72	4.02	19.45
(VII)	(53.32)	(3.95)	(19.73)
$(\eta^5\text{-}C_5H_5)_4Nb_2Br_3$	35.19	2.40	34.45
(VIII)	(34.98)	(2.90)	(34.96)
$[(\eta^5\text{-}C_5H_5)_2NbBr_2]_2O$	30.59	2.65	39.97
(IX)	(30.71)	(2.55)	(40.92)

TABLE 2

SELECTED IR ABSORPTIONS FOR CYCLOPENTADIENYLNIOBIUM COMPLEXES (cm^{-1})

Complex	ν(C≡O)	ν(C≡C)	ν(Nb–O–Nb)
$(\eta^5\text{-}C_5H_5)_2NbBr(CO)$ (III)	1930		
$(\eta^5\text{-}C_5H_5)_2NbBr(PhC{\equiv}CPh)$ (VI)		1775	
$(\eta^5\text{-}C_5H_5)_2NbBr(PhC{\equiv}CH)$ (VII)		1700	
$[(\eta^5\text{-}C_5H_5)_2NbBr_2]_2O$ (IX)			680

TABLE 3

^{1}H NMR DATA FOR CYCLOPENTADIENYLNIOBIUM COMPLEXES (multiplicity; rel.int.)

Complex	Cp	L
$(\eta^5\text{-}C_5H_5)_2NbBr$ (II)	5.74(s) [a]	
$(\eta^5\text{-}C_5H_5)_2NbBr(CO)$ (III)	4.73(s) [a]	
$(\eta^5\text{-}C_5H_5)_2NbBr(PMe_2Ph)$ (IV)	4.64 [a](d, J(P–H) 2.1 Hz; 10)	1.34(d, J(P–H) 10 Hz; 6) Me 7.30(m) [c]Ph
$(\eta^5\text{-}C_5H_5)_2NbBr(P(OMe)_3)$ (V)	4.89 (d, J(P–H) 1.6 Hz; 10) [a]	3.35(d, J(P–H) 10.4 Hz; 9) Me
$(\eta^5\text{-}C_5H_5)_2NbBr(PhC{\equiv}CPh)$ (VI)	5.89(s,10) [b]	7.37(m,10) Ph
$(\eta^5\text{-}C_5H_5)_2NbBr(PhC{\equiv}CH)$ (VII)	5.71(s,10) [b]	7.45(m,5) Ph; 8.20(s,1) CH
$[(\eta^5\text{-}C_5H_5)_2NbBr_2]_2O$ (IX)	6.70(s) [b]	

[a] Benzene-d_6. [b] Acetone-d_6. [c] Partially overlapped with solvent signals. Chemical shifts with respect to TMS, positive signs downfield.

$(\eta^5\text{-}C_5H_5)_2NbBr_2$ (I)

$NbBr_5$ (19 g, 0.03 mol) or $NbCl_5$ (8.11 g, 0.03 mol) was added to a freshly solution of NaC_5H_5 (13.20 g, 0.15 mol) in 250 ml of THF. A rapid exothermic reaction was observed and the initially colourless solution became purple and a bulky precipitate separated. After 12 h of stirring the solvent was evaporated off under vacuum and the remaining purple solid was extracted with 3 × 100 ml of hot chloroform saturated with HBr. The resulting deep green solution was concentrated under reduced pressure and then cooled to give brown-green crystals of I, which were dried under vacuum. Yield 25%.

$[(\eta^5\text{-}C_5H_5)_2NbBr_2]_2O$ (IX)

A solution of $(\eta^5\text{-}C_5H_5)_2NbBr_2$ (0.300 g, 0.78 mmol) in 50 ml of freshly distilled acetone was treated with oxygen. After 1 h of stirring at room temperature a yellow solution was obtained. The solution was concentrated under reduced pressure to give orange crystals of IX, which were washed with diethyl ether and dried under vacuum. Yield 90%.

$(\eta^5\text{-}C_5H_5)_2NbBr$ (II)

THF (50 ml) was added to a mixture of $(\eta^5\text{-}C_5H_5)_2NbBr_2$ (0.300 g, 0.783 mmol) and sodium amalgam (0.018 g, 0.783 mmol of sodium). After 1 h of stirring at room temperature a violet solution and a bulky precipitate were obtained. The solution was filtered, concentrated under reduced pressure, and cooled, to give maroon-grey crystals of II, which were washed with diethyl ether and dried under vacuum. Yield 50%. The yield was better when the initial residue was extracted several times with THF and the washings were combined with the filtrate. Similar results were obtained with NaNaph as reducing agent.

$(\eta^5\text{-}C_5H_5)_2NbBrL$ (III, $L = CO$; IV, $L = PMe_2Ph$; V, $L = P(OMe)_3$; VI, $L = PhC{\equiv}CPh$; VII, $L = PhC{\equiv}CH$)

The procedure was similar in all cases.

A solution of the appropriate ligand (0.783 mmol, except with CO for which the solvent was saturated with gaseous CO) in 50 ml of THF was added to a mixture of $(\eta^5\text{-}C_5H_5)_2NbBr_2$ (0.300 g, 0.783 mmol) and Na/Hg (0.018 g, 0.783 mmol of Na). In the case of III a maroon-grey solution and a bulky precipitate were formed; the solution was filtered and then concentrated under reduced pressure to give grey crystals of III. In the case of IV and V a deep green solution and a bulky precipitate were formed, the solution was filtered and then concentrated to give green crystals, which were washed with diethyl ether and dried under vacuum. For VI and VII a red solution and a bulky precipitate were obtained; the solution was filtered and the solvent was removed under reduced pressure to yield a yellow oil. The oils were treated with pentane to give VI and VII as yellow solids. Yields were 70–80%.

$(\eta^5\text{-}C_5H_5)_2NbBr_2.(\eta^5\text{-}C_5H_5)_2NbBr$ (VIII)

$(\eta^5\text{-}C_5H_5)_2NbBr_2$ (0.300 g, 0.783 mmol) was added to sodium amalgam (0.391 mmol of sodium) in THF (50 ml). After 6 h of stirring at room temperature a red solution and a grey precipitate were formed. The solution was filtered and then concentrated under reduced pressure to give red-brown crystals of VIII, which were washed with diethyl ether and dried under vacuum. Yield 70%.

Acknowledgements

We express our great appreciation of financial support from the Comisión Asesora de Investigación Científica y Técnica (Spain).

References

1 D.A. Lemenovskii, T.V. Baukova and V.P. Fedin, J. Organomet. Chem., 132(1977)C14.
2 M.L.H. Green and B. Jousseaume, J. Organomet. Chem., 193(1980)339.
3 A. Antiñolo, M. Fajardo, A. Otero and P. Royo, J. Organomet. Chem., 246(1983)269.
4 P. Royo and R. Serrano, J. Organomet. Chem., 247(1983)33.

5 I.H. Elson and J.K. Kochi, J. Am. Chem. Soc., 97(1975)1263; A.N. Nesmeyanov, D.A. Lemenovskii, V.P. Fedin and E.G. Perevalova, Dokl. Akad. Nauk. SSSR, 245(1979)609.
6 F.W. Siegert and H.J. de Liefde Meijer, J. Organomet. Chem., 23(1970)177.
7 W.E. Douglas and M.L.H. Green, J. Chem. Soc. Dalton Trans., (1972)1796.
8 M.L.H. Green and C.R. Lucas, J. Chem. Soc. Chem. Commun., (1972)1005.
9 J.W. Lahuer and R. Hoffmann, J. Am. Chem. Soc., 98(1976)1729.
10 K. Tatsumi, R. Hoffmann and J.L. Templeton, Inorg. Chem., 21(1981)466.
11 B.C. Ward and J.L. Templeton, J. Am. Chem. Soc., 102(1980)1532.
12 A. Antiñolo, M. Fajardo, A. Otero and P. Royo, J. Organomet. Chem., 234(1982)309.
13 C.H. Brubaker and R.C. Young, J. Am. Chem. Soc., 73(1951)4179.
14 D.C. White, Microchem. Acta, (1961)449.