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Synthesis and characterization of monocyclopentadienylniobium(V) derivatives with nitrogen and phosphorus donor ligands

A.M. Andreu, F.A. Jalón and A. Otero

Departamento de Química Inorgánica, Universidad de Alcalá de Henares, Campus Universitario, Alcalá de Henares (Spain)

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Abstract

$\{[(\eta^5\text{-}C_5H_4Me)NbCl_2]_2(\mu\text{-}O)(\mu\text{-}Cl)_2\}$ (I) has been obtained by hydrolysis of complex $Nb(\eta^5\text{-}C_5H_4Me)Cl_4$. The reactions of $\{[(\eta^5\text{-}C_5H_4R)NbCl_2)]_2(\mu\text{-}O)(\mu\text{-}Cl)_2\}$ (I: R = Me; II: R = H; III: R = $SiMe_3$ with an 0.5 molar proportions of the nitrogen donor ligands 2,2′-bipyridine (bipy) or 1,10-phenanthroline (*o*-phen) give the complexes $\{[(\eta^5\text{-}C_5H_4R)NbCl_3(N\text{–}N)]_2\text{-}(\mu\text{-}O)\}$ (IV: R = CH_3, N–N = bipy; V: R = CH_3, N–N = *o*-phen; VI: R = H, N–N-bipy; VII: R = H, N–N = *o*-phen; VIII: R = $SiMe_3$, N–N-bipy; IX: R = $SiMe_3$, N–N = *o*-phen), whereas the similar reactions of complex III with the phosphorus donor ligands dppe and dppm give the complexes $\{[(\eta^5\text{-}C_5H_4SiMe_3)NbCl_3]_2(P\text{–}P)(\mu\text{-}O)\}$ (X: P–P = dppe; XI: P–P = dppm). The complexes have been characterized by IR and ^1H NMR spectroscopy.

Introduction

Several monocyclopentadienylniobium complexes have been reported previously [1], and the hydrolysis reactions of $Nb(\eta\text{-}C_5H_4R)Cl_4$ to give different oxo binuclear niobium(V) compounds have been described [2,3]. We report here the reactions of $\{[(\eta^5\text{-}C_5H_4R)NbCl_2)]_2(\mu\text{-}O)(\mu\text{-}Cl)_2\}$ with nitrogen (N–N) and phosphorus (P–P) donor ligands to give new niobium(V) binuclear complexes $\{[(\eta^5\text{-}C_5H_4R)NbCl_3\text{-}(N\text{–}N)]_2(\mu\text{-}O)\}$ and $\{[(\eta^5\text{-}C_5H_4SiMe_3)NbCl_3]_2$ $(\mu\text{-}P\text{–}P)(\mu\text{-}O)\}$ by displacement of the bridging chloride ligands.

Results and discussion

Synthetic studies

Complex I was obtained by hydrolysis of $Nb(\eta^5\text{-}C_5H_4Me)Cl_4$ in wet dichloromethane, according to eq. 1.

$$Nb(\eta^5\text{-}C_5H_4Me)Cl_4 \xrightarrow{H_2O} \{[(\eta^5\text{-}C_5H_4Me)NbCl_2]_2(\mu\text{-}O)(\mu\text{-}Cl)_2\} + 2HCl \qquad (1)$$

We have described previously the preparation of similar complexes [3]. Complex I was isolated as a yellow solid, stable in a dry atmosphere, and like complex II, insoluble in the common organic solvents. Complexes I–III react with 2,2′-bipyridine(bipy) or 1,10-phenanthroline (*o*-phen) with the displacement of the two chloride bridges and the coordination of a molecule of the ligand to each metal center, as in eq. 2.

$$\{[(\eta^5\text{-}C_5H_4R)NbCl_2]_2(\mu\text{-}O)(\mu\text{-}Cl)_2\} + 2N\text{–}N \xrightarrow{THF} \{[(\eta^5\text{-}C_5H_4R)NbCl_3(N\text{–}N)]_2(\mu\text{-}O)\} \quad (2)$$

(IV–IX)

(IV: $R = CH_3$, N–N = bipy; V: $R = CH_3$, N–N = *o*-phen;
VI: R = H, N–N = bipy; VII: R = H, N–N = *o*-phen;
VIII: $R = SiMe_3$, N–N = bipy; IX: $R = SiMe_3$, N–N = *o*-phen)

Complexes IV–IX were isolated as air-stable white solids. They are insoluble in THF and only slightly soluble in chloroform and dichloromethane. Complexes containing the η^5-$C_5H_4SiMe_3$ group are more soluble than the η^5-C_5H_5 and η^5-C_5H_4Me derivatives. We observed in the course the reactions the formation of intermediate red solutions, which presumably contain the corresponding adducts with the solvent THF. All attempts to isolate these adducts in the solid state were unsuccessful, and upon evaporation of the solvent unidentified green solids were always obtained. Complexes IV–IX are 18 electron niobium(V) binuclear species if the bipy or *o*-phen acts as a chelate ligand, but the possibility of a polymeric structure with nitrogen bridging ligands cannot be excluded. Dicyclopentadienylniobium(V) complexes with various bipy or *o*-phen chelate ligands have been described previously [4].

We have also studied the behaviour of the more soluble complex III with dppm and dppe. In these cases complexes X and XI were obtained, as shown in eq. 3.

$$\{[(\eta^5\text{-}C_5H_4SiMe_3)NbCl_2]_2(\mu\text{-}O)(\mu\text{-}Cl)_2\} + P\text{–}P \xrightarrow{THF} \{[(\eta^5\text{-}C_5H_4SiMe_3)NbCl_3]_2(\mu\text{-}O)(\mu\text{-}(L\text{–}L))\} \quad (3)$$

(X: L–L = dppe; XI: L–L = dppm)

Complexes X and XI were isolated as air-stable pale yellow solids. They are soluble in THF, chloroform, and dichloromethane, and insoluble in diethyl ether and aromatic and aliphatic hydrocarbons.

The most notable feature of these complexes is the presence of a diphosphine (dppe or dppm) as a bridging ligand between the two metal centers, to give binuclear 16 electron niobium(V) species. (The behaviour as bridging ligands of various diphosphines, mainly dppm, in many binuclear complexes has been extensively studied [5].) All the new compounds were characterized by microanalysis (see Table 1).

IR spectroscopy

The IR spectra of all the complexes show the absorptions expected for the η^5-cyclopentadienyl ligand [6], and those of the $SiMe_3$ group [7] also in complexes

Table 1

Analyses and physical properties of the binuclear monocyclopentadienylniobium(V) complexes

Complex	Analysis (Found (calcd.) (%))			Colour	Yield(%)
	C	H	N		
$\{[(\eta^5\text{-}C_5H_4Me)NbCl_2]_2(\mu\text{-}O)(\mu\text{-}Cl_2)\}$	29.8 (30.0)	2.8 (2.9)	–	Yellow	90
$\{[(\eta^5\text{-}C_5H_4Me)NbCl_3(bipy)]_2(\mu\text{-}O)\}$	42.9 (43.4)	3.5 (3.4)	6.5 (6.3)	White	80
$\{[(\eta^5\text{-}C_5H_4Me)NbCl_3(o\text{-}phen)]_2(\mu\text{-}O)\}$	46.5 (46.3)	3.4 (3.2)	6.3 (6.0)	White	80
$\{[(\eta^5\text{-}C_5H_5)NbCl_3(bipy)]_2(\mu\text{-}O)\}$	42.1 (42.0)	3.1 (3.0)	6.4 (6.5)	White	80
$\{[(\eta^5\text{-}C_5H_5)NbCl_3(o\text{-}phen)]_2(\mu\text{-}O)\}$	45.3 (45.1)	3.2 (2.9)	6.1 (6.1)	White	80
$\{[(\eta^5\text{-}C_5H_4SiMe_3)NbCl_3(bipy)]_2(\mu\text{-}O)\}$	42.8 (43.1)	4.5 (4.2)	5.3 (5.6)	White	80
$\{[(\eta^5\text{-}C_5H_4SiMe_3)NbCl_3(o\text{-}phen)]_2(\mu\text{-}O)\}$	45.5 (45.7)	3.8 (4.0)	5.4 (5.3)	White	80
$\{[(\eta^5\text{-}C_5H_4SiMe_3)NbCl_3]_2(dppe)(\mu\text{-}O)\}$	46.9 (46.4)	4.7 (4.6)	–	Pale yellow	85
$\{[(\eta^5\text{-}C_5H_4SiMe_3)NbCl_3]_2(dppm)(\mu\text{-}O)\}$	46.6 (46.7)	4.7 (4.5)	–	Pale yellow	82

containing the η^5-$C_5H_4SiMe_3$ ring. The IR spectrum of complex I shows the ν_{asym}(NbONb) absorption band (see Table 2) at 640 cm^{-1}, in accord with a non-linear Nb–O–Nb linkage [8] previously described [3] for the analogous complexes II and III. This situation has been confirmed by X-ray analysis for complex III. On the other hand, the IR spectra of complexes IV–XI show the ν_{asym}(NbONb) absorption bands (see Table 2) at ca. 750 cm^{-1}, in accord with a Nb–O–Nb linear structure [8]. The presence of this linear NbONb linkage in complexes X and XI is compatible with the presence of the postulated diphosphine bridging because in

Table 2

Selected IR data for the binuclear monocyclopentadienylniobium(V) complexes

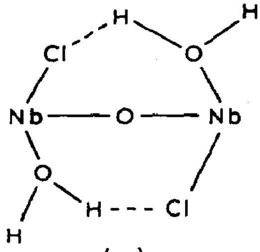
Complex	ν_{asym}(NbONb)	ν(Nb–Cl)	L	
			bipy(or dppe)	o-phen (or dppm)
I	640(vs)			
IV	760(vs)	320(s)	1600(s); 1590(s)	
V	720(vs)	320(s)		1510(s)
VI	770(vs)	320(s)	1620(s); 1610(s)	
VII	735(vs)	320(s)		1520(w); 1550(w)
VIII	770(vs)	320(s)	1620(s); 1610(s)	
IX	740(vs)	330(s)		1530(m)
X	750(vs)	310(m)	1540(w); 1170(m); 1110(m) 770(s); 700(s)	
XI	750(vs)	320(m)		1590(w); 1170(m); 1130(m); 770(s); 700(s); 505(m)

Table 3

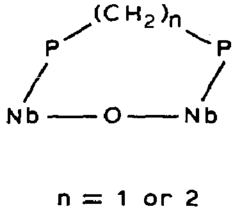
NMR spectra for binuclear monocyclopentadienyl niobium(V) complexes (solvent $CDCl_3$)

Compound	^1H (internal standard TMS)			^{31}P
	δ(ppm) (int.)(mult).	Assignment		δ(ppm)(H_3PO_4)
VIII	0.33(18)(s)	$SiMe_3$		
	6.54–6.78(8)(mc)	C_5H_4		
	7.65–9.00(16)(m)	bipy		
IX	0.41(18)(s)	$SiMe_3$		
	6.72–6.84(8)(mc)	C_5H_4		
	7.81–10.11(16)(mc)	*o*-phen		
X	0.30(18)(s)	$SiMe_3$		48.0(s)
	6.70–7.00(8)(mc)	C_5H_4		
	7.40(20)(m)	Ph	dppe	
	2.10(4)(m)	CH_2–CH_2		
XI	0.30(18)(s)	$SiMe_3$		34.8(s)
	6.70–7.00(8)(mc)	C_5H_4		
	7.40(20)(m)	Ph	dppm	
	3.50(2)(m)	CH_2		

complex $[(\eta^5\text{-}C_5H_4Me)NbCl_3(H_2O)]_2(\mu\text{-}O)$, with a ring made up of six bonds (see Fig. 1a) the Nb–O–Nb angle is 171.8(1) Å [9] and in our complexes the corresponding rings must contain six and seven bonds, respectively (Fig. 1b).



(a)



(b)

The IR spectra of complexes IV–XI also show ν(Nb–Cl) absorptions at ca. 350 cm^{-1} and the corresponding absorptions due to the ligands (see Table 2).

NMR spectroscopy

The low solubility of the complexes containing the $\eta^5\text{-}C_5H_4Me$ and $\eta^5\text{-}C_5H_5$ rings hinders ^1H NMR studies. As shown in Table 3, all the complexes containing the $\eta^5\text{-}C_5H_4SiMe_3$ exhibit ^1H NMR spectra containing the expected singlet for the $SiMe_3$ group and several broad peaks due to the non-equivalent $\eta^5\text{-}C_5H_4$ protons [10]. Complexes VIII and XI also show the characteristic ^1H signals for the bipy, *o*-phen, dppe, and dppm, respectively (see Table 3). The ^{31}P NMR spectra for X and XI show a singlet (see Table 3), indicating that the two phosphorus atoms in the dppe or dppm ligand are equivalent, in accord with the view that they act as bridging ligands. However, the ^{31}P NMR data do not exclude the possibility that the diphosphine acts as bridging ligand between two metal centers of the two different binuclear fragments, to give polynuclear species.

Experimental

All operations were carried out under vacuum or under an inert atmosphere with Schlenk-type glassware. Solvents were dried and distilled under N_2 and degassed before use. $Nb(\eta^5\text{-}C_5H_4Me)Cl_4$, II and III were prepared as previously described [2,3]. IR spectra were recorded with Nujol mulls between CsI plates in the region 4000–200 cm^{-1} on a Perkin–Elmer 599 spectrophotometer. Carbon, hydrogen and nitrogen analysis were carried out with a Perkin–Elmer 240B microanalyzer. ^1H and ^{31}P NMR spectra were recorded on Varian FT 80A instrument.

$\{[(\eta^5\text{-}C_5H_4Me)NbCl_2]_2(\mu\text{-}O)(\mu\text{-}Cl)_2](I)$

A red suspension of $Nb(\eta^5\text{-}C_5H_4Me)Cl_4$ (0.500 g, 0.87 mmol) in wet dichloromethane (50 ml) was stirred at room temperature for 3 h. The yellow complex I was filtered off and dried under vacuum. Yield 90%.

$\{[(\eta^5\text{-}C_5H_4R)NbCl_3(N\text{-}N)]_2(\mu\text{-}O)\}$ (IV, V, VI, VII, VIII, IX)

Bipy (0.220 g, 1.45 mmol) was added to a red solution of III (0.500 g, 0.72 mmol) in THF (50 ml). After 2 h stirring at room temperature a white precipitate was present, and this was filtered off, washed several times with hexane, and dried under vacuum. It was identified as complex VIII. Yield 80%. The other complexes were prepared similarly.

$\{[(\eta^5\text{-}C_5H_4SiMe_3)NbCl_3]_2(P\text{-}P)(\mu\text{-}O)\}$, (X, XI)

The ligand dppm (0.110 g, 0.29 mmol) was added to a red solution of complex III and the mixture was stirred for 24 h at room temperature. The resulting yellow solution was evaporated to dryness under vacuum, and the pale yellow solid residue was washed several times with hexane then dried under vacuum. It was identified as complex XI. Yield 82%. Complex X was prepared similarly.

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