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Synthesis, characterization and reactivity of tetracyclopentadienylniobium(IV), a precursor to organometallic derivatives of niobium(IV)

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Abstract

In toluene as medium, tetra(cyclopentadienyl)niobium(IV), $NbCp_4$, has been prepared in satisfactory yields from the reaction of NaCp with: (a) Nb_2Cl_{10}, (b) $NbCl_4(THF)_2$, or (c) $NbCp_2Cl_2$. Tetracyclopentadienylniobium(IV) has been characterized by X-ray diffraction. Crystal data: $C_{20}H_{20}Nb$, $M = 353.29$ g mol^{-1}, hexagonal, space group $P6_5$ (no. 170), $a = b = 9.396(2)$, $c = 31.23(3)$ Å, $V = 2388(2)$ Å^3, $Z = 6$, $d_{calc} = 1.48$ g cm^{-3}, $\lambda(Cu{-}K_\alpha) = 1.54184$ Å, $T = 291$ K, $\mu = 62.04$ cm^{-1}, $F(000) = 1686$. Two of the four cyclopentadienyl ligands are bonded to niobium in a pentahapto fashion, the other two being monohapto. $NbCp_4$ undergoes cyclopentadiene elimination in the presence of species containing active protons such as Ph_3SiOH or strong acids, the products being tris- or biscyclopentadienyl compounds depending on the molar ratio of the reagents.

Keywords: Niobium; Cyclopentadienyl; Structures; Complexes

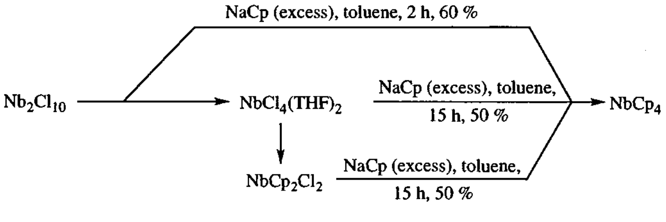
1. Introduction

By reaction of the pentachlorides with excess NaCp in benzene, Fischer and coworkers obtained low yields of the tetracyclopentadienyl derivatives of niobium(IV) and tantalum(IV) (9.3 and 10.9% for niobium and tantalum, respectively) [1]. With reduced reaction times, the yield of the niobium compound was increased to ca. 60% [2]. On the basis of IR and hydrogenation data, a structure consisting of two pentahapto and two monohapto cyclopentadienyl ligands was proposed [1]. As for the reactivity of these systems, little is known [3] except the reaction with hydrogen chloride yielding $NbCp_2Cl_2$.

In the framework of our studies concerning the synthesis and the reactivity of polycyclopentadienyl derivatives of early transition elements, we wish to report an improved synthetic route to and the crystal and molecular structure of $NbCp_4$. In addition, a study of the reactivity of this system with respect to substances containing active protons has been carried out.

2. Results and discussion

We started our approach to the chemistry of tetracyclopentadienylniobium(IV) with a reinvestigation of the known synthetic procedures, see Scheme 1. Although preferable from the point of view of the availability of the starting material, the reaction involving Nb_2Cl_{10} requires some care because when the reaction times are longer than 2–3 h, the yield decreases to ca. 10–20%.



Scheme 1.

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On the other hand, when using niobium(IV) derivatives [$NbCl_4(THF)_2$ or $NbCp_2Cl_2$] reactions are slower but the required longer reaction times are not detrimental for the yield. This suggests that the higher Lewis acidity of niobium(V) intermediates affects their stabilities in some unknown way.

Similar to what is observed in the case of the tetracyclopentadienyls of Group 4, $NbCp_4$ is affected by Lewis bases; red–violet solutions of $NbCp_4$ in THF or Et_2O turn deep blue–green after some hours. Moreover, a reaction with deposition of brown solids occurs in the presence of chlorinated hydrocarbons.

Due to the paramagnetism of the compound both in the solid state [1] and in solution [4], an NMR study was precluded and we decided to solve the structure of $NbCp_4$ by X-ray diffraction. Due to its reactivity towards oxygen and/or moisture both in solution or in the solid state, we had difficulty in obtaining single crystals of the compound; after several attempts, small single crystals were obtained by layering heptane on a toluene solution of $NbCp_4$. Although the quality of the crystals did not allow an accurate solution of the structure, the crystallographic data have established that $NbCp_4$ is mononuclear and, in agreement with earlier suggestions [1], it presents two pentahapto and two monohapto cyclopentadienyl ligands, Fig. 1. It is rather surprising that the structure of niobium is similar to that of $TiCp_4$ and $HfCp_4$ [5] and substantially different from that of $ZrCp_4$, the latter presenting three pentahapto- and one monohaptocyclopentadienyl ligands [6]. Table 1 reports the bond distances and angles. The cyclopentadienyl ligands are coordinated to niobium in a distorted tetrahedral geometry; the angle at niobium between the two monohapto ligands is 83.4(6)° and that between the centroids of the two η^5-cyclopentadienyls is 131.1°, values similar to those observed in $NbCp_2(CH_2Ph)_2$ (79.3 and 133°) [7], $NbCp_2(CH_2SiMe_2)_2$ (83.0 and 135.4°) [8], $TiCp_4$ (86.3 and 129.9°) and $HfCp_4$ (88.0 and 130.0°) [5]. The centroid–Nb distances are 2.082 and 2.019 Å. The two η^5-cyclopentadienyls are almost planar with a maximum deviation from the least-square plane of 0.008 and 0.026 Å with C–C bond distances in the range 1.37(2)–1.41(2) Å. According to the data observed for MCp_4 (M = Ti, Hf) [5] and for the niobium(V) derivative $Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(N^tBu)$ [9], we could expect two different types of C–C bonds; however, the high standard deviations of the C–C bond distances do not allow any significant trend to be observed.

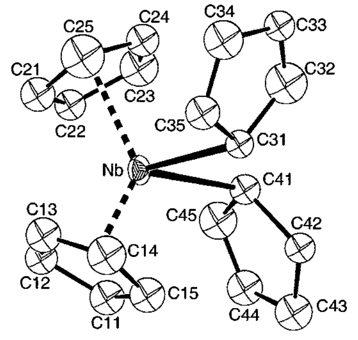
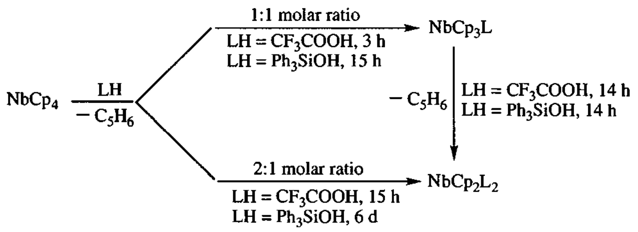


Fig. 1. View of the molecular structure of $NbCp_4$.

Table 1
Bond distances (Å) and angles (°) in $NbCp_4$. Estimated standard deviations in parentheses refer to the least significant digit

Nb–C(21)	2.29(3)	Nb–C(11)	2.39(3)
Nb–C(22)	2.33(3)	Nb–C(15)	2.40(3)
Nb–C(24)	2.35(2)	Nb–C(23)	2.42(3)
Nb–C(25)	2.36(3)	Nb–C(14)	2.44(3)
Nb–C(13)	2.36(3)	Nb–C(41)	2.46(3)
Nb–C(12)	2.37(3)	Nb–C(31)	2.48(2)
C(41)–Nb–C(31)	83.4(6)		
C(31)–Nb–$Cp_{cent(1)}$	105.4(5)	C(41)–Nb–$Cp_{cent(1)}$	114.3(6)
C(31)–Nb–$Cp_{cent(2)}$	109.1(4)	C(41)–Nb–$Cp_{cent(2)}$	103.2(6)

$Cp_{cent(1)}$ and $Cp_{cent(2)}$ refer to the computed η^5-C_5H_5 centroids for atoms C(11)–C(15) and C(21)–C(25), respectively.



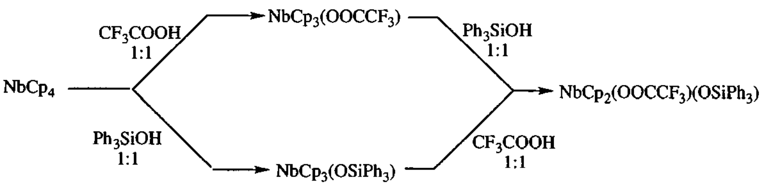
Scheme 2.

The availability of $NbCp_4$ allowed its reactivity to be studied, mainly towards substances containing active protons. The niobium compound $NbCp_4$ reacts with CF_3COOH or Ph_3SiOH to give 1:1 or 1:2 derivatives depending on the molar ratio, see Scheme 2. The large difference in the reaction times necessary to convert quantitatively the tetracyclopentadienyl into the products allowed isolation of the tricyclopentadienyl derivatives, $NbCp_3L$ (L = CF_3COOH, Ph_3SiOH) and of the mixed-ligand compound $NbCp_2(OOCCF_3)(OSiPh_3)$, see Scheme 3.

Similarly, $NbCp_3Cl$ can be isolated from the reaction of $NbCp_4$ with PyHCl in toluene as medium. As in the case of LH, the use of a PyHCl/Nb molar ratio of 2 slowly produces the dichloride $NbCp_2Cl_2$. On the other hand, no tricyclopentadienyl has been obtained in a pure state by using pyridinium bromide or iodide. In this case, independent of the molar ratio, the dihalides $NbCp_2X_2$ have been obtained, see Scheme 4.

$NbCp_4$ reacts with 9,10-dihydroxyphenanthrene with protonolysis of two cyclopentadienyl rings and formation of $NbCp_2(C_{14}H_8O_2)$, see Eq. (1).

$$NbCp_4 + C_{14}H_8O_2 \rightarrow NbCp_2(C_{14}H_8O_2) + 2C_5H_6 \qquad (1)$$



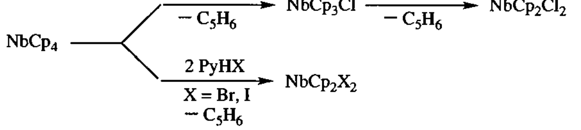
Scheme 3.

$NbCp_2(C_{14}H_8O_2)$ shows an IR spectrum in the solid state characterized by the absorptions typical of the phenanthrenediolato ligand, similar to what is observed for the analogous compounds of zirconium(IV) and hafnium(IV) [10] thus suggesting that we are dealing with a niobium(IV) derivative containing the 9,10-phenanthrenediolato *O*-*O*′ ligand.

3. Conclusions

This paper has filled a gap in our knowledge of solid state data for tetracyclopentadienyls of early transition elements, showing that the titanium, hafnium, niobium and probably tantalum (based on the Debye diagrams already reported in the literature [1]) have similar molecular structures, i.e. two of the four cyclopentadienyl ligands are bonded to the metal in a pentahapto fashion, the other two being monohapto bonded. At variance with these compounds, three cyclopentadienyl ligands are pentahapto bonded, and one is monohapto bonded in the zirconium derivative, $ZrCp_4$.

Moreover, the study of the reactivity of $NbCp_4$ towards substances containing active protons has allowed the isolation of the triscyclopentadienyl compounds $NbCp_3L$. It is noteworthy that the corresponding compounds of Group 4 elements appear to be transient species: the biscyclopentadienyl derivatives MCp_2L_2 are obtained independent of the LH/M molar ratio. Although much work is necessary in order to clarify the solid-state structure of the paramagnetic $NbCp_3L$ derivatives, we may tentatively assume that the different reactivity observed on going from $ZrCp_4$ to $NbCp_4$ depends on a different hapticity of the cyclopentadienyl ligands in MCp_3L. As a matter of fact, the known examples of structurally characterized $[ZrcCp_3L]^{n+}$ systems ($L = H\cdots AlEt_3$, $n = 0$ [11]; $L = Me$, $n = 0$ [11]; CO, acetonitrile, Bu^tNC, $n = 1$ [12,13]), present a pentahaptocoordination of the cyclopentadienyl ligands corresponding to a formal 20-e counting. The lower reactivity of the $NbCp_3L$ systems may be tentatively assigned to the fact that they are in fact 17-e compounds containing two η^5- and one η^1-cyclopentadienyl groups.



Scheme 4.

4. Experimental

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified argon. Solvents were dried by conventional methods prior to use.

IR spectra were recorded on a FT-1725X instrument on solutions or Nujol or polychlorotrifluoroethylene (PCTFE) mulls prepared under rigorous exclusion of moisture and air. Magnetic susceptibilities were measured with a magnetic balance (Sartorius 4104, electromagnet Varian V 2900) according to the Faraday method using $CuSO_4 \cdot 5H_2O$ for calibration at three different field strengths (9400, 10 200, 10 800 G) and averaging the observed values. Diamagnetic corrections were calculated using Pascal contributions [14].

Toluene suspensions of NaCp were obtained in the following way: a suspension of NaH in THF was treated with freshly distilled cyclopentadiene at room temperature (r.t.). The solution was dried in vacuo and the colourless residue was suspended in toluene.

Trifluoroacetic acid, CF_3COOH, was used in admixture with the corresponding anhydride. The total amount of trifluoroacetate groups was determined by acid–base titration in aqueous solution, while the $CF_3COOH/(CF_3CO)_2$ molar ratio was obtained from the ^{19}F-NMR spectrum. Triphenylsilanol, Ph_3SiOH (Aldrich) was dried over P_4O_{10} in vacuo for 24 h. Pyridinium halides, PyHX, X = Cl, Br, I, were prepared by reaction of pyridine with the appropriate hydrogen halide in heptane. 9,10-dihydroxyphenanthrene was prepared by reduction of 9,10-phenanthrenequinone with dihydrogen in the presence of Pd/C in toluene at r.t. Large scale preparations of $NbCp_2Cl_2$ [15] and $NbCl_4(THF)_2$ [16] were carried out according to the literature. Nb_2Cl_{10} (Fluka) was sublimed prior to use.

4.1. Preparation of $NbCp_4$

From Nb_2Cl_{10}. A suspension of NaCp (obtained from 6.10 g, 254 mmol of NaH) in toluene (500 ml) was

Table 2
Crystallographic data and details of the structure refinement for $NbCp_4$

Empirical formula	$C_{20}H_{20}Nb$
Formula weight	353.29
Crystal size (mm)	$0.30 \times 0.30 \times 0.10$
Temperature (K)	291
Wavelength (Å)	1.54184
Crystal system	Hexagonal
Space group	$P6_5$ (no. 170)
Unit cell dimensions	
$a = b$ (Å)	9.396(2)
c (Å)	31.23(3)
Volume (Å^3)	2388(2)
Z	6.00
D_{calc} (g cm^{-3})	1.48
Absorption coefficient (cm^{-1})	62.04
$F(000)$	1086
θ Range for data collection (°)	1.4–65.0
Index ranges	$-11 \leq h \leq 9$, $-9 \leq k \leq 11$, $-36 \leq l \leq 36$
Reflections collected	10445
Independent reflections	2691 [$R_{int} = 0.289$]
Completeness to $\theta = 64.95°$ (%)	99.9
Absorption correction	Numerical
Max. and min. transmission	0.354 and 0.128
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2691/21/90
Goodness-of-fit on F^2	0.946
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1093$, $wR_2 = 0.1517$
R indices (all data)	$R_1 = 0.2882$, $wR_2 = 0.1749$
Absolute structure parameter	0.00(9)
Largest difference peak and hole (e A^{-3})	0.657 and -0.632

treated at r.t. with Nb_2Cl_{10} (6.62 g, 12.2 mmol). The suspension turned brown on mixing the reagents and violet after stirring for a few minutes. The suspension was stirred for 2 h, filtered, and the solid washed with toluene until the washings were almost colourless (ca. 6×25 ml). The red–violet solution was evaporated to dryness in vacuo at r.t. affording a dark brown residue which was treated with heptane (50 ml). The black microcrystalline solid was collected by filtration and dried in vacuo at r.t. affording 5.12 g (52% yield) of $NbCp_4$ in the form of an oxygen- and moisture-sensitive solid. Anal. Found: C, 68.5; H, 4.7; Nb, 25.9. Calc. for $C_{20}H_{20}Nb$: C, 68.1; H, 5.7; Nb, 26.3%. IR (Nujol, cm^{-1}): 3076m, 1591w, 1433w, 1123w, 1009w, 818m, 749m, 720s, 669w, 619m-w, 601m-w.

From $NbCl_4(THF)_2$. A suspension of NaCp (5.0 g, 51 mmol) in toluene (250 ml) was treated at r.t. with $NbCl_4(THF)_2$ (3.15 g, 8.3 mmol). The suspension turned brown on mixing the reagents. The reaction mixture was stirred for 15 h at r.t. obtaining a violet suspension. Isolation of the product was similarly carried out yielding 1.45 g (49% yield) of $NbCp_4$.

From $NbCp_2Cl_2$. A suspension of NaCp (1.96 g, 20 mmol) in toluene (100 ml) was treated at r.t. with $NbCp_2Cl_2$ (1.0 g, 3.4 mmol). The reaction mixture was stirred for 15 h at r.t. obtaining a violet suspension. By a procedure similar to the preceding one, 0.63 g (53% yield) of $NbCp_4$ were obtained.

4.2. $NbCp_4$: crystal structure solution and refinement

Crystals of $NbCp_4$ ($NbCp_2Cl_2$ as starting material) were obtained from toluene–heptane solution. Crystallographic data and details of the structure refinement for $NbCp_4$ are in Table 2. Data were collected at 291 K on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. The crystals are thin, weakly diffracting platelets; hence intensity data were collected with Cu–K_α radiation. A numerical absorption correction (minimum transmission 0.128, maximum transmission 0.354) was applied before averaging symmetry-equivalent data. After merging, 2691 independent reflections remained for structure solution by direct methods [17a]. The structure model was completed by Fourier difference syntheses. It was kept as simple as possible with isotropic displacement parameters for the C atoms and refined with full-matrix least-squares on F^2 [17b]. Convergence was reached for 2691 reflections and 90 variables at agreement factors of $wR_2 = 0.1749$ (all data), $R_1 = 0.1093$ [$I > 2\sigma(I)$].

4.3. Reaction of $NbCp_4$ with CF_3COOH

CF_3COOH/Nb molar ratio 1.1. A 10:1 (v/v) mixture of CF_3COOH and $(CF_3CO)_2O$ (0.07 ml, 0.82 mmol of CF_3COOH) was added at r.t. to a red–violet suspension of $NbCp_4$ (0.30 g, 0.78 mmol). Immediate reaction with formation of a violet solution was observed. After 3 h stirring at r.t., the volume of the solution was reduced to ca. 5 ml and heptane (25 ml) was added. Upon cooling at ca. -30 °C, a blue–black microcrystalline solid separated out which was recovered by filtration and dried in vacuo affording 0.15 g (46% yield) of $NbCp_3(OOCCF_3)$ as a moisture- and oxygen-sensitive product. Anal. Found: C, 50.3; H, 4.0; Nb, 24.1. Calc. for $C_{17}H_{15}F_3NbO_2$: C, 50.8; H, 3.7; Nb, 23.2%. IR (Nujol, cm^{-1}): 3092m, 1695s (ν_{as} COO), 1576w, 1410s (ν_s COO), 1262w, 1196s (ν_{as} CF_3), 1143 5 (ν_s CF_3), 1016m, 978w, 823s, 786m-s, 721s, 669m, 614m, 523m, 489w, 419m. Magnetic measurement: diamagnetic correction -187×10^{-6} cgsu, $\chi_{mol}^{corr} = 1.8 \times 10^{-3}$ cgsu, μ_{eff} (298 K) 2.08 BM.

CF_3COOH/Nb molar ratio 2:1. A 10:1 (v/v) mixture of CF_3COOH and $(CF_3CO)_2O$ (0.5 ml, 5.8 mmol of CF_3COOH) was added at r.t. to a red–violet suspension of $NbCp_4$ (1.19 g, 2.9 mmol) in toluene (20 ml). Immediate reaction with formation of a violet solution was observed which turned dark brown. After 15 h stirring at r.t., the volume of the suspension was reduced to ca. 5 ml and heptane (25 ml) was added. The microcrystalline solid which separated out was recovered by filtration and dried in vacuo affording 1.14 g (88% yield) of $NbCp_2(OOCCF_3)_2$ as a moisture- and oxygen-sensitive product. Anal. Found: C, 38.5; H, 2.7; Nb, 20.3. Calc. for $C_{14}H_{10}F_6NbO_4$: C, 37.4; H, 2.2; Nb, 20.7%. IR (Nujol, cm^{-1}): 3120m, 1699vs (ν_{as} COO), 1578w, 1405s (ν_s COO), 1188s (ν_{as} CF_3), 1143 5 (ν_s CF_3), 1016m, 954w, 827s, 790m, 723s, 669m, 614m, 521w, 493w, 413m. Magnetic measurement: diamagnetic correction -180×10^{-6} cgsu, $\chi^{corr}_{mol} = 1.9 \times 10^{-3}$ cgsu, μ_{eff} (298 K) 2.16 BM.

The same compound (IR and analytical data) was obtained after a 14 h reaction at r.t. between $NbCp_3(OOCCF_3)$ and trifluoroacetic acid in toluene.

4.4. Reaction of $NbCp_4$ with Ph_3SiOH

Ph_3SiOH/Nb molar ratio 1.1. A red–violet suspension of $NbCp_4$ (0.53 g, 1.3 mmol) in toluene (20 ml) was treated with solid Ph_3SiOH (0.36 g, 1.3 mmol). A slow reaction was observed. After 15 h stirring at r.t. the deep brown solution was partially evaporated in vacuo and heptane (20 ml) was added. The resulting suspension was filtered and the solid was dried in vacuo affording 0.39 g (54% yield) of $NbCp_3(OSiPh_3)$ as a moisture- and oxygen-sensitive product. Anal. Found: C, 69.9; H, 5.1; Nb, 16.8; Si, 4.6. Calc. for $C_{33}H_{30}NbOSi$: C, 70.3; H, 5.0; Nb, 16.5; Si, 4.9%. IR (Nujol, cm^{-1}): 3082m, 1463s, 1428m, 1377s, 1113m, 958m, 812mw, 759w, 741w, 720m, 699m, 512m. Magnetic measurement: diamagnetic correction -319×10^{-6} cgsu, $\chi^{corr}_{mol} = 1.8 \times 10^{-3}$ cgsu, μ_{eff} (298 K) 2.08 BM.

Ph_3SiOH/Nb molar ratio 1:2. A red–violet suspension of $NbCp_4$ (0.43 g, 1.1 mmol) in toluene (20 ml) was treated with solid Ph_3SiOH (0.59 g, 2.2 mmol). A slow change of colour to deep brown and deep green was observed. After 6 days stirring at r.t. the suspension was dried in vacuo at r.t. and heptane (20 ml) was added. The resulting suspension was filtered and the solid was dried in vacuo affording 0.39 g (70% yield) of $NbCp_2(OSiPh_3)_2$ as a moisture- and oxygen-sensitive product. Anal. Found: C, 68.2; H, 5.4; Nb, 12.4; Si, 7.1. Calc. for $C_{46}H_{40}NbO_2Si_2$: C, 71.5; H, 5.0; Nb, 12.0; Si, 7.2.%. IR (Nujol, cm^{-1}): 3080m, 1464s, 1427m-s, 1378s, 11 12m, 910m-w, 809m-w, 699s, 508m-s. Magnetic measurement: diamagnetic correction -444×10^{-6} cgsu, $\chi^{corr}_{mol} = 1.9 \times 10^{-3}$ cgsu, μ_{eff} (298 K) 2.14 BM.

The same compound (IR and analytical data) was obtained after a 15 h reaction at r.t. between $NbCp_3(OSiPh_3)$ and triphenylsilanol in toluene.

4.5. Preparation of $NbCp_2(OOCCF_3)(OSiPh_3)$

This compound was obtained either from the reaction of $NbCp_3(OOCCF_3)$ with Ph_3SiOH or from $NbCp_3(OSiPh_3)$ and CF_3COOH. Only the procedure relative to the former reaction is described in detail, the latter being performed in a similar way. A solution of $NbCp_3(OOCCF_3)$ (0.46 g, 1.2 mmol) in toluene (20 ml) was treated with Ph_3SiOH (0.34 g, 1.2 mmol). After 14 h stirring at r.t., the solution was partially evaporated in vacuo and heptane (20 ml) was added. The suspension was filtered and the solid was dried in vacuo at r.t. affording 0.55 g of $NbCp_2(OOCCF_3)(OSiPh_3)$ as a microcrystalline solid sensitive to moisture and oxygen. Anal. Found: C, 58.6; H, 4.5; Nb, 15.0; Si, 4.8. Calc. for $C_{30}H_{25}NbO_3Si$: C, 58.9; H, 4.1; Nb, 15.2; Si, 4.6%. IR (Nujol, cm^{-1}): 3113w, 1695s, 1428s, 1410m, 1191vs, 1157w, 1138m-s, 1111m-s, 967s, 512s. Magnetic measurement: diamagnetic correction -329×10^{-6} cgsu, $\chi^{corr}_{mol} = 1.18 \times 10^{-3}$ cgsu, μ_{eff} (298 K) 1.68 BM.

4.6. Reaction of $NbCp_4$ with pyridinium halides

(a) PyHCl/Nb molar ratio 1:1. A suspension of $NbCp_4$ (0.63 g, 1.6 mmol) in toluene (30 ml) was treated at r.t. with PyHCl (0.19 g, 1.6 mmol). Formation of a deep red solution was observed upon mixing the reagents. After 15 h stirring at r.t., the suspension was filtered, the volume of the solution was reduced to ca. 10 ml and heptane (20 ml) was added. The suspension was filtered and the solid was dried in vacuo at r.t. affording 0.32 g (62% yield) of $NbCp_3Cl$ as a dark brown microcrystalline solid sensitive to moisture and oxygen. Anal. Found: C, 55.0; H, 4.9; Cl, 11.0; Nb, 26.6. Calc. for $C_{15}H_{15}ClNb$: C, 55.6; H, 4.6; Cl, 10.9; Nb, 28.7%. IR (Nujol, cm^{-1}): 3079m, 1418w, 1305w, 1017mw, 1009mw, 817m-s, 798w, 729s.

(b) PyHCl/Nb molar ratio 2:1. A suspension of $NbCp_4$ (0.46 g, 1.2 mmol) in toluene (25 ml) was treated at r.t. with PyHCl (0.28 g, 2.4 mmol). The resulting brown suspension was stirred for 60 h at r.t. The suspension was filtered and the pale brown solid was washed with toluene (3 × 10 ml) and dried in vacuo at r.t. affording 0.22 g (63% yield) of $NbCp_2Cl_2$ [15,18] which was identified by analytical and spectroscopic methods.

(c) PyHX (X = Br, I)/Nb molar ratio 2:1. Only the reaction of PyHBr with $NbCp_4$ is described in detail, the others being performed in a similar way. A suspension of $NbCp_4$ (0.44 g, 1.15 mmol) in toluene (25 ml) was treated at r.t. with PyHBr (0.37 g, 2.3 mmol). The resulting red–brown suspension was stirred for 14 h at r.t. After filtration the brown solid was washed with toluene (3 × 10 ml) and dried in vacuo at r.t. affording 0.37 g (76% yield) of $NbCp_2Br_2$ [15,18] which was identified by analytical and spectroscopic methods. The iodo derivative, $NbCp_2I_2$ [15,18], was obtained as a red–brown solid (77% yield).

4.7. Reaction of $NbCp_4$ with 9,10-dihydroxyphenanthrene: preparation of $NbCp_2(C_{14}H_8O_2)$

A suspension of $NbCp_4$ (0.355 g, 1.0 mmol) in toluene (25 ml) was treated at r.t. with 9,10-dihydroxyphenanthrene (0.205 g, 1.0 mmol). Immediate reaction with formation of a deep red solution was observed. After 15 h at r.t., the volume of the solution was reduced to ca. 10 ml and heptane (20 ml) was added. The suspension was filtered and the solid was dried in vacuo at r.t. affording 0.32 g (75% yield) of $NbCp_2(C_{14}H_8O_2)$ as a red–brown microcrystalline solid sensitive to moisture and oxygen. Anal. Found: C, 66.0; H, 4.4; Nb, 21.0. Calc. for $C_{24}H_{18}NbO_2$: C, 66.8; H, 4.2; Nb, 21.5%. IR (Nujol; cm^{-1}): 3102m-w, 1600m-w, 1580m, 1511w, 1487m, 1338s, 1262w, 1223w, 1112w, 1055s, 1029s, 929w, 808s, 790vs, 754s, 723s, 687m, 574m, 544mw. Magnetic measurement: diamagnetic correction -222×10^{-6} cgsu, $\chi_{mol}^{corr} = 1.31 \times 10^{-3}$ cgsu, μ_{eff} (298 K) 1.70 BM.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 160280 for compound $NbCp_4$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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