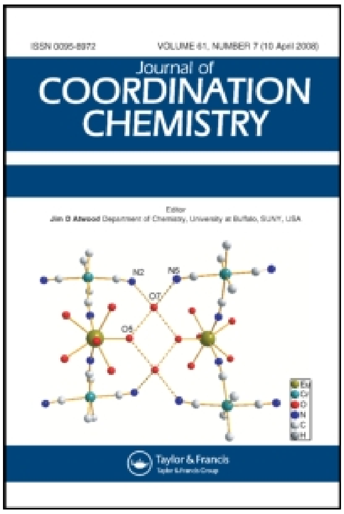

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Synthesis, characterization, and acceptor behavior of dichlorotris(2-*t*-butylphenoxo)niobium(V)

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Synthesis, characterization, and acceptor behavior of dichlorotris(2-*t*-butylphenoxo)niobium(V)

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The reaction of niobium pentachloride with three equivalents of 2-*t*-butylphenol in carbon tetrachloride afforded $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3]$. The identity of the complex has been established by elemental analyses, molar conductance, molecular weight determination, IR, ^1H, and ^{13}C-NMR and UV-Vis spectral studies. Based upon these studies, a square–pyramidal geometry around niobium has been proposed. Thermal behavior of the complex has been studied by TGA and DTA. Acceptor behavior of $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3]$ toward Ph_3P, Ph_3As, Ph_3PO, Ph_3AsO, and an uncommon ligand arsenictrithiophenoxide $As(SPh)_3$ allows the isolation of 1 : 1 addition compounds as shown by physicochemical, IR, and ^1H-NMR spectral studies. The formation of $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3]\cdot As(SPh)_3$ appears to be the first adduct of its class and suggests the suitability of $As(SPh)_3$ as a ligand.

Keywords: Niobium(V) complexes; 2-*t*-Butylphenol; Oxygen; Phosphorus; Arsenic donor ligands

1. Introduction

The chemistry of substituted phenols as ligands continues to be a fascinating area of study owing to their ability to provide complexes with rich structural diversity and potential applications in diverse fields [1–4]. Although the literature contains voluminous reports on phenoxides of main group elements, transition metals, lanthanides, and actinides, more recent interest has centered on the early and late d-block metal chemistry supported by sterically bulky aryloxide ligation [5–7]. Niobium complexes, in particular, derived from alcohols and substituted phenols [8, 9] present striking structural features and a wide range of applications in material science [10–15]. The niobium(V) catalysts bearing di-and tri-phenolic ligands polymerize ethylene, in the presence of an organoaluminum cocatalyst [16]. Metal aryloxide chemistry has been considerably enriched with complexes derived from phenols containing alkyl/aryl substituents at the 2,6-positions of the phenolic ring [17], however, reports on complexes of 2-*t*-butylphenol are rather limited. A particular interest in selection of 2-*t*-butyl as ligand stems from the fact that intermolecular dehydrogenation of alkyl

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groups or chelation might occur. In continuation of our work on niobium(V) complexes of 2-*t*-butylphenol [18, 19], in the present work we report the synthesis, characterization, and acceptor behavior of $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3]$ toward triphenylphosphine, triphenylarsine, and their oxides. In addition, the present work also explores the possible use of arsenictrithiophenoxide, $As(SPh)_3$, as a potential arsenic donor ligand toward niobium.

2. Experimental

2.1. *Materials and methods*

$NbCl_5$ (Fluka) was used without purification; its purity was checked by chlorine analysis. 2-*t*-Butylphenol (Merck b.p. 224°C) was purified by vacuum distillation. Solvents were dried before use by standard methods. The niobium content was estimated as Nb_2O_5 after decomposing the complexes with a mixture of conc. H_2SO_4 and HNO_3 followed by heating at 650–700°C. Chlorine was determined by Volhard's method. Microanalyses for carbon and hydrogen were performed on an Eager 300 NCH System Elemental Analyzer. Molar conductances (10^{-3} M solutions) in nitrobenzene were obtained at $25 \pm 0.1^\circ C$ on an Elico conductivity bridge (type CM-82T). Molecular weights were determined cryoscopically in benzene (0.0015–0.0020 M) using a Beckmann thermometer. IR spectra were recorded (KBr pellets) on a Nicolet-5700 FTIR spectrometer. ^1H- and ^{13}C-NMR spectra were recorded on a BRUKER AVANCE II 400 spectrometer using $CDCl_3$. Electronic spectra were recorded on a VARIAN CARY-100 Bio UV-Vis spectrophotometer in $CHCl_3$. Thermograms were recorded on a Perkin–Elmer thermal analyzer.

2.2. *Synthesis*

2.2.1. $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3]$. To a suspension of niobium pentachloride (3.545 g, 0.013 M) in CCl_4 (25 mL) was added three equivalents of 2-*t*-butylphenol (5.89 g, 0.039 M) in carbon tetrachloride (20 mL), resulting in the formation of clear solution and an immediate color change from light yellow to dark brown accompanied by evolution of HCl. The reaction mixture was then refluxed for 3–4 h till the evolution of hydrogen chloride ceased to ensure completion of the reaction. No solid formed during the course of the reaction. The solution was then filtered and excess solvent removed by distillation. The resultant concentrate was then evaporated under vacuum and treated thrice with petroleum ether when a dark brown complex was obtained (yield = 2.92 g, 82.37%). Anal. Calcd for $C_{30}H_{39}O_3Cl_2Nb$ (%): C, 55.82; H, 6.40; Cl, 11.62; Nb, 15.20. Found: C, 55.82; H, 4.87; Cl, 11.60; Nb, 15.15. Λ_m, ($PhNO_2$): $9.45\ S\,cm^2\,M^{-1}$. Mol wt Calcd: 611, Found: 615.

2.3. *Reactions of $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3]$ with Ph_3P, Ph_3As, Ph_3PO, Ph_3AsO, and $As(SPh)_3$*

In a typical reaction, $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3]$ dissolved in minimum of absolute ethanol was treated with an equimolar amount of Ph_3P, Ph_3As, Ph_3PO, Ph_3AsO, or

$As(SPh)_3$ in dry benzene. The contents were initially stirred for 4–5 h and then refluxed for another 5–6 h when a significant color change from the initial color was observed. The resulting solid was treated with petroleum ether and dried in vacuum. Anal. Calcd for $C_{48}H_{54}O_3Cl_2NbP$/874 (%): C, 65.96; H, 6.18; Cl, 8.13; Nb, 10.65. Found (%): C, 65.90; H, 6.15; Cl, 8.09; Nb, 10.58. Λ_m, ($PhNO_2$): 2.56 S cm^2 M^{-1}. Anal. Calcd for $C_{48}H_{54}O_3Cl_2NbAs$/917 (%): C, 62.81; H, 5.89; Cl, 7.74; Nb, 10.14. Found (%): C, 62.78; H, 5.85; Cl, 7.73; Nb, 10.10. Λ_m, ($PhNO_2$): 2.94 S cm^2 M^{-1}. Anal. Calcd for $C_{48}H_{54}O_4Cl_2NbP$/890 (%): C, 64.77; H, 6.07; Cl, 7.98; Nb, 10.46; P, 3.60. Found (%): C, 64.73; H, 6.01; Cl, 7.94; Nb, 10.42. Λ_m, ($PhNO_2$): 3.56 S cm^2 M^{-1}. Anal. Calcd for $C_{48}H_{54}O_4Cl_2NbAs$/933 (%): C, 61.72; H, 5.79; Cl, 7.60; Nb, 9.97. Found (%): C, 61.70; H, 5.74; Cl, 7.57; Nb, 9.94. Λ_m, ($PhNO_2$): 4.23 S cm^2 M^{-1}. Anal. Calcd for $C_{48}H_{54}O_3S_3Cl_2NbAs$/1013 (%): C, 56.86; H, 5.33; Cl, 7.00; Nb, 9.18. Found (%): C, 56.82; H, 5.30; Cl, 6.97; Nb, 9.15. Λ_m, ($PhNO_2$): 4.93 S cm^2 M^{-1}.

3. Results and discussion

Formation of dichlorotris(2-*t*-butylphenoxo)niobium(V) is shown in scheme 1.

Microanalytical data of the complex is consistent with the formulation. The complex is moisture sensitive and sparingly soluble in $CHCl_3$, C_6H_6, and $C_6H_5NO_2$. The molar conductance of the complex in nitrobenzene indicated a non-electrolyte. The cryoscopic molecular weight determination of the complex in benzene suggested it to be monomeric in this solvent.

3.1. *IR spectra*

The IR assignments for the complex have been made by a comparison with the infrared frequencies of ligand 2-*t*-butylphenol. The ν(OH), ν(C–O), and ν(Nb–O) modes are diagnostic for the formation of complex. The absorption band occurring at 3532 cm^{-1} [20] in 2-*t*-butylphenol is absent in the complexes, suggesting deprotonation of the phenolic proton upon complexation. The bands at 1392–1182 cm^{-1} assigned to ν(C–O) mode in free 2-*t*-butylphenol [21, 22] red shift to 1294–1190 cm^{-1} in complexes characteristic of ν(C–O–Nb) modes. Bands at 580–570 cm^{-1} assigned to ν(Nb–O) indicate bonding of phenolic oxygen to niobium, in agreement with previous reports on niobium alkoxides and phenoxides [23]. Sharp absorption bands at 380–370 cm^{-1} are assigned to ν(Nb–Cl) [24]. No band which could be assigned to bridging Nb–O–Nb or Nb–Cl–Nb was observed in the complexes, suggesting monomers.

3.2. *^{1}H-NMR spectra*

The ^{1}H-NMR spectra of $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3]$ did not display a signal for phenolic –OH which occurs at δ 4.56 in free 2-*t*-butylphenol, confirming deprotonation

$$NbCl_5 + 3HOC_6H_4C(CH_3)_3\text{-}2 \xrightarrow[\text{reflux}]{CCl_4} NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3 + 3HCl\uparrow$$

Scheme 1. Reaction scheme of formation of $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3]$.

on complexation. Signals at δ 6.65–7.12 ppm in free 2-*t*-butylphenol undergo downfield shifts to δ 6.67–7.30 ppm (table 1), ascribed to deshielding of these protons due to the transfer of electron density from the ring to the metal [25]. The signal due to *t*-butyl at δ 1.40 ppm in 2-*t*-butylphenol remained unaltered in [$NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3$].

3.3. ^{13}C-NMR spectra

The ^{13}C-NMR spectra of 2-*t*-butylphenol exhibited resonances at δ 34.48 and δ 29.65 and six signals in δ 116.76–154.16 ppm range ascribed to the quaternary and methyl carbons of the *t*-butyl group and aromatic carbons of the phenolic ring, respectively. The complex showed signals at δ 34.92 and δ 29.72 ppm due to quaternary and methyl carbons of *t*-butyl, respectively. The significant downfield shift in carbon resonances adjacent to the phenolic oxygen (C_{ipso}) and the aromatic carbons of the phenolic ring, which appeared at δ 154.7 and in δ 137.13–116.78 ppm on complexation, clearly indicated bonding through phenolic oxygen. The downfield shifts for carbon are attributed to the removal of electron density from the aromatic ring to niobium in agreement with ^{1}H-NMR spectral data.

3.4. Electronic spectra

Electronic spectra of [$NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3$] from 200 to 800 nm in acetonitrile displayed intense absorptions at 237 and 259 nm, assigned to phenolic intraligand $\pi - \pi^*$ and LMCT transitions from the π-type p-orbital of the phenolic oxygen to a 4d orbital of niobium.

On the basis of physicochemical, IR, ^{1}H- and ^{13}C-NMR, and UV-Vis spectral data, a square–pyramidal geometry (figure 1) around niobium may tentatively be suggested

Table 1. ^{1}H-NMR data of niobium (V) 2-*t*-butylphenoxides (δ ppm).

Compound	Substituent (*t*-butyl protons)	Aromatic phenolic ring protons	Aromatic protons (donor ligands)
$NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3$	1.43	6.67–7.30	–
$NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3Ph_3P$	1.25	6.73–7.21	7.46–7.69
$NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3Ph_3As$	1.37	6.73–7.22	7.67–7.84
$NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3Ph_3PO$	1.40	6.74–7.24	7.44–7.70
$NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3Ph_3AsO$	1.35	6.76–7.23	7.56–7.80
$NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3As(SPh)_3$	1.57	6.73–7.22	7.28–7.51

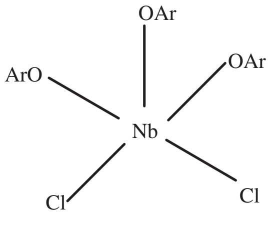

Figure 1. Proposed structure of [$NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3$]. (OAr = $OC_6H_4C(CH_3)_3\text{-}2$).

for the complex in consonance with previous report on tantalum(V) trisphenoxide complex [25].

3.5. *Thermal studies*

The thermogravimetric curve of $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3]$ recorded in air shows the complex to be thermally stable to 46.05°C. The complex decomposes in two steps. The observed weight loss of 46.15% and 16.71% in the first and second decompositional steps in the temperature range of 46.05–430.08°C and 430.08–816.49°C accounted for the loss of two phenoxide units to give $[NbOCl_2(OC_6H_4C(CH_3)\text{-}2)]$ as the likely intermediate and $[NbO_2(OC_6H_4C(CH_3)_3\text{-}2)]$ as the final product of decomposition. The two-step decomposition for $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3]$ may be represented by scheme 2.

The DTA curve of $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3]$ displayed an endothermic peak at 138.25°C and an exothermic peak at 438.63°C, thereby substantiating the two-step decomposition.

4. Reactions of $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3]$ with Ph_3P, Ph_3As, Ph_3PO, Ph_3AsO, and $As(SPh)_3$

Addition compounds of phosphorus and arsenic donors with various metal halides have been reported [26]. The formation of 1 : 1 adducts of tertiary phosphine and arsine oxide with niobium and tantalum pentachloride as well as oxytrichloro adduct $NbOCl_3 \cdot 2Ph_3PO$ have been described [27, 28]. Hence, the reactions of $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3]$ with triphenylphosphine, triphenylarsine, and their oxides have been investigated. In addition, arsenic trithiophenoxide, synthesized by various methods [29–32], was considered as a possible arsenic donor. The interaction of $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3]$ with equimolar amounts of [L]; Ph_3P, Ph_3As, Ph_3PO, Ph_3AsO, and $As(SPh)_3$ afforded 1 : 1 addition compounds (scheme 3).

The adducts are moisture sensitive, light brown to dark brown solids, and are quite stable in dry air. The compounds are soluble in benzene, nitrobenzene, and chloroform. Molar conductance values of millimolar solutions of the adducts in nitrobenzene showed non-electrolytes.

$$\left[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3\right] \xrightarrow{46.15\%} \left[NbOCl_2(OC_6H_4C(CH_3)_3\text{-}2)\right] + \text{Organic matter}$$

$$\left[NbOCl_2(OC_6H_4C(CH_3)_3\text{-}2)\right] \xrightarrow{16.71\%} \left[NbO_2(OC_6H_4C(CH_3)_3\text{-}2)\right] + \text{Organic matter}$$

Scheme 2. Thermal decomposition of $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3]$.

$$NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3 + L \longrightarrow NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3] \cdot L$$

Scheme 3. Reaction scheme of formation of $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3] \cdot L$.

4.1. *IR spectra*

Bonding of oxygen, phosphorus, and arsenic donors with niobium has been deduced from a comparison of the infrared spectra of the addition compounds with that of free ligands. Bands at 1452, 1182, 1175, 1114, 1079, 749, 520, and 430 cm^{-1} in $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3] \cdot Ph_3P$ and at 1560, 1478, 1441, 1194, 1088, 749, 611, and 471 cm^{-1} in $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3] \cdot Ph_3As$ due to ν(C–C), ν(C–H), stretching and bending of (P–C) and (As–C) bands coupled with aromatic ring vibrations indicate their formation.

Characteristic vibrations of Ph_3PO and Ph_3AsO become perturbed on coordination due to ν(P=O), ν(As=O), ν(P–C), and ν(As–C) modes. The shift of the modes to lower wave number is ascribed to overall decrease in the bond order of P=O and As=O due to decrease in $p\pi$–$d\pi$ bonding. The ν(P=O) and ν(As=O) stretching vibrations at 1192 and 879 cm^{-1} [33, 34] in triphenylphosphine oxide and triphenylarsine oxide, respectively, appear at 1187 and 852 cm^{-1} in the respective adducts. Generally, ν(P=O) of Ph_3PO is shifted to the lower frequency upon coordination to metal, while ν(As=O) of Ph_3AsO complexes may move to higher or lower wavenumbers than the free ligand. Bands at 455 and 479 cm^{-1} in Ph_3PO and Ph_3AsO, respectively, ascribed to ν(P–C) and ν(As–C) move to higher spectral regions at 465 and 490 cm^{-1} in agreement with earlier reports [33, 35]. Complexes of tertiary phosphines with a number of acceptors have been reported to be more stable than those of analogous arsines [36, 37].

IR spectra of $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3] \cdot As(SPh)_3$ display bands at 470–360 cm^{-1} and 750–690 cm^{-1} ascribed to ν(As–S) and ν(As–S–C) relative to bands known to occur at 492 s, 400 w, and 372 vs cm^{-1} due to ν(As–S) and at 744 vs and 684 vs cm^{-1} assigned to ν(As–S–C) [38] in $As(SPh)_3$, suggesting thereby its formation.

Although Ph_3P and Ph_3As are common ligands, the number of ligand vibrations exhibited in the low-frequency region makes it difficult to assign ν(M–P) or ν(M–As) vibrations for the adducts. We are not able to assign unambiguously the ν(Nb–P/As) vibrations.

4.2. *^{1}H-NMR spectra*

^{1}H-NMR spectra of the adducts are sharply divided into three ranges. The upper field signals from δ 1.25 to 1.57 ppm and δ 6.73 to 7.24 ppm refer to 2-*t*-butyl substituent and phenolic ring protons, respectively, and downfield signals from δ 7.25 to 7.84 ppm are due to L (table 1). In adducts, the phenolic protons downfield shift by δ 0.13–0.16 ppm relative to the respective signals of the parent complex. Evidence for coordination of $As(SPh)_3$ to niobium is provided by thiophenyl proton resonances at δ 7.28–7.51 ppm compared to δ 7.25–7.46 ppm in $As(SPh)_3$. The resonance corresponding to the butyl group for the adducts is in the expected region, but for $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3] \cdot As(SPh)_3$ the signal shifts appreciably downfield. Combined analytical and IR and ^{1}H-NMR spectral data suggest that a distorted-octahedral structure is likely for the dichlorotris(2-*t*-butylphenoxo)niobium(V) adducts (figure 2).

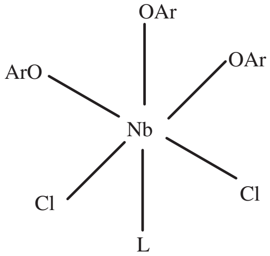

Figure 2. Proposed structure of $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3] \cdot L$. ($OAr = OC_6H_4C(CH_3)_3\text{-}2$).

5. Conclusion

Reactivity of oxygen, phosphorus, and arsenic donors toward $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3]$ afford 1:1 addition compounds corroborated by IR and ^{1}H-NMR spectral studies. To the best of our knowledge, $[NbCl_2(OC_6H_4C(CH_3)_3\text{-}2)_3] \cdot As(SPh)_3$ is the first example of an addition compound; $As(SPh)_3$ may find promise as an arsenic donor.

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