

Half-sandwich isocyanide, phosphine, methyl and phosphanido pentamethylcyclopentadienylniobium(V) complexes

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Received 4 August 1994

Abstract

[NbCp*Cl₄] (Cp* = η⁵-C₅Me₅) reacts with one molar equivalent of isocyanides and phosphines to give pseudo-octahedral adducts [NbCp*Cl₄·L], (L = 2,4,6-Me₃C₆H₂NC, **1**; PMe₃, **2**; PMe₂Ph, **3**; PPh₂, **4**) and the dinuclear complex [(NbCp*Cl₄)₂(μ-dmpe)], **5**. Reactions of [NbCp*Cl₄] with appropriate amounts of MgClMe yield the corresponding dimethyl [NbCp*Cl₂Me₂], **6**, and tetramethyl [NbCp*Me₄], **7** derivatives. Similarly, when [(NbCp*Cl₃)₂(μ-O)] and **3** are treated with the alkylating magnesium reagent, [(NbCp*Me₃)₂(μ-O)], **8**, and [NbCp*Cl₃Me(PMe₂Ph)], **9**, are obtained in high yields. A new phosphanido-niobium(V) complex [NbCp*Cl₃(PPh₂)] **10**, is formed in the reaction of the starting tetrachloro complex with one equivalent of LiPPh₂. All the complexes were characterized by IR and NMR spectroscopy, and most of them were studied by mass spectrometry.

Keywords: Niobium; Pentamethylcyclopentadienyl; Isocyanide; Phosphine; Phosphanido; Half-sandwich cpds

1. Introduction

The formation of adducts of Lewis acids of group 5d metal halides has been well studied and there are many papers on the synthesis, structural characterization and chemical behaviour of these compounds. Most of them refer to the halo(alkyl) derivatives [1] [MX_{5-y}R_y] (M = Nb or Ta; X = Cl or Br; R = Me, H₂C-CMe₃, H₂C-SiMe₃, or H₂C-Ph), and some relate [2] to cyclopentadienyl derivatives. Many mono(pentamethylcyclopentadienyl)halo(alkyl)-tantalum complexes have been isolated, and their behaviour in different reactions has been reported [3]. In contrast, few analogous niobium derivatives have been described [4] and satisfactory synthetic methods are rather scarce. In this paper we report efficient methods for the synthesis of half-sandwich methyl and phosphanido niobium complexes, starting from [NbCp*Cl₄] (Cp* = η⁵-C₅Me₅), and its reactions with isocyanides and phosphines.

2. Results and discussion

When dichloromethane suspensions of [NbCp*Cl₄] are treated at room temperature with isocyanide or phosphine (L) in a 1:1 molar ratio, solutions of the complexes **1–4** are obtained, as shown in Scheme 1. The same complexes can also be prepared when L is present in the reaction of NbCl₅ with Si(C₅Me₅)Me₃. When the same reaction is carried out in the presence of one equivalent of dmpe, the dinuclear complex **5** containing the bidentate tertiary phosphine bridging both metals is formed.

The alkylation of [NbCp*Cl₄] with two equivalents of MgClMe leads to the dimethyl complex **6**, whereas the tetramethyl complex, **7**, can be isolated in 65% yield by using a 1(Nb):4(Mg) molar ratio. The alkylation by using one or three equivalents of MgClMe leads to unresolvable mixtures of different, partially alkylated compounds. These reactions were carried out under rigorously anhydrous conditions, otherwise **7** is always contaminated by the dinuclear oxo complex [(NbCp*Me₃)₂(μ-O)], **8**, resulting from its hydrolysis, because complex **7** is extremely air and light sensitive. The hydrolysis takes place with evolution of methane,

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as confirmed by GC analysis. Complex **8** can directly be prepared by alkylation of $[\{\text{NbCp}^*\text{Cl}_3\}_2(\mu\text{-O})]$ with six equivalents of MgClMe .

Complex **3** can also be alkylated when treated with one equivalent of MgClMe to give the halo(methyl) adduct, $[\text{NbCp}^*\text{Cl}_3\text{Me}(\text{PMe}_2\text{Ph})]$, **9**, although loss of L is observed in the alkylation of most of the adducts.

Similarly, reaction of the starting tetrachloro complex with one equivalent of LiPPh_2 in toluene at -78°C gave the phosphanido complex, **10**, which was isolated as a purple air-sensitive solid in 80% yield. Attempts to replace all the chlorides by phosphanido groups caused reduction to the known phosphanidoniobium(III) complex, $[(\text{NbCp}^*)_2(\mu\text{-PPh}_2)_2(\mu\text{-O})]$, [5], containing a niobium–niobium double bond.

Complexes **1–10** are air and moisture sensitive, soluble in chlorinated and aromatic solvents, and hardly soluble in hexane, except for **7** and **8** which are very soluble. They were characterized by elemental analyses and spectroscopic methods.

Characteristic pentamethylcyclopentadienyl ring $\nu_{\text{C-C}}$ and metal-chlorine $\nu_{\text{Nb-Cl}}$ vibrations are observed at $1010\text{--}1026\text{ cm}^{-1}$ and $306\text{--}337\text{ cm}^{-1}$, respectively. Complex **1** shows $\nu_{\text{C}\equiv\text{N}}$ at 2210 cm^{-1} . Complexes **6–8** show the $\nu_{\text{Nb-C}}$ IR absorption at $415\text{--}492\text{ cm}^{-1}$. The two absorptions observed at 664 cm^{-1} and 606 cm^{-1} for complex **8** could be assigned to the $\nu_{\text{Nb-O-Nb}}$, corresponding to an almost linear oxygen bridge [6].

The ^1H NMR spectra of all the complexes **1–5** show the expected resonances for the ring methyl and ligand protons, and the ^{31}P NMR spectra are consistent with the proposed pseudo-octahedral structures. Complexes **5** and **10**, could not be studied by mass spectrometry because of lack of volatility, and mononuclear or dinuclear structures cannot be assigned on the basis of its IR and NMR data.

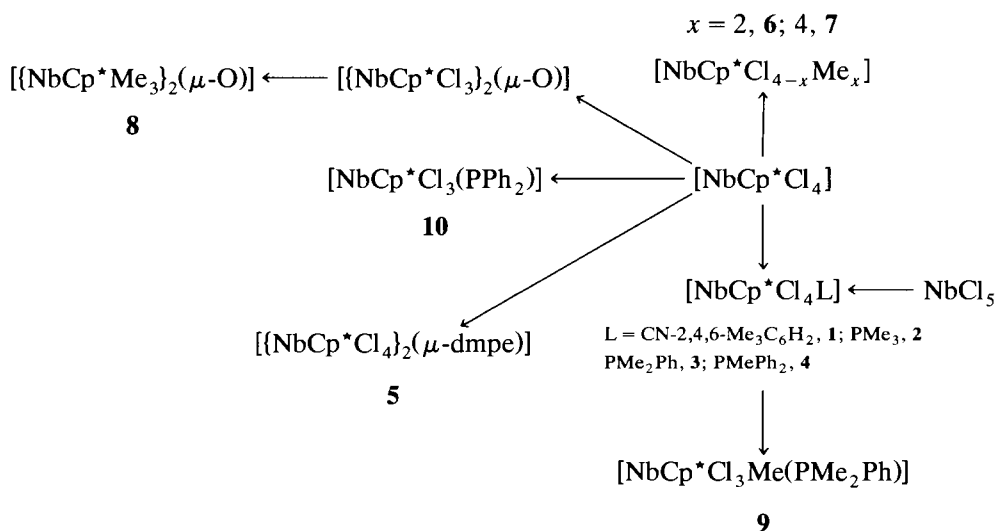
The IR and NMR spectroscopic behaviour of the methyl derivatives **6** and **7** is consistent with a four-legged piano-stool geometry similar to that observed for analogous monocyclopentadienyltantalum derivatives [7]. The singlet from the Me-Nb protons of **7** (δ 1.23) is shifted to higher fields in comparison with **6** (δ 1.36) as the number of methyl groups increases.

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of complex **8** show the signals expected for the methyl protons of the pentamethylcyclopentadienyl ring, whereas two singlets with an intensity ratio 2:1 are observed for the methyl–niobium groups, revealing that two of the methyl groups are equivalent and different from the third. This is consistent with the expected disposition of the methyl groups *trans* to the Nb-O-Nb bond [6a].

3. Experimental details

Reactions were carried out in argon using Schlenk-type glassware, and solids were handled in a glove box. Solvents were dried over appropriate reagents and distilled under argon before use, as follows: dichloromethane (P_2O_5), diethyl ether (Na-benzophenone), hexane (Na–K alloy) and toluene (Na). Literature methods were employed for the synthesis of $[\text{NbCp}^*\text{Cl}_4]$ [6c], SiCp^*Me_3 [8], $[\{\text{NbCp}^*\text{Cl}_3\}_2(\mu\text{-O})]$ [6c], 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2\text{NC}$ [9] and LiPPh_2 [10]. All other reagent-grade chemicals were purchased from commercial sources and used without further purification as follows: NbCl_5 (Fluka), phosphines (Aldrich), dmpe (Strem) and MgClMe 3M in THF (Aldrich).

IR spectra were recorded on a Perkin-Elmer 583 spectrophotometer ($4000\text{--}200\text{ cm}^{-1}$) as Nujol mulls between CsI plates. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Varian VXR-300 Unity



Scheme 1. For reagents and conditions see text.

instrument and chemical shifts are reported in δ units (positive chemical shifts to higher frequency) relative to TMS. Electron impact mass spectroscopy was carried out at 70 eV with a Hewlett-Packard 5988A instrument. C, H and N analyses were performed with a Perkin-Elmer 240C microanalyzer.

3.1. Preparation of $[NbCp^*Cl_4L]$ ($L = 2,4,6-Me_3C_6H_2NC$, **1**; PMe_3 , **2**; PMe_2Ph , **3** $PMePh_2$, **4**)

3.1.1. Method A

L (1.35 mmol) was added to a dichloromethane (50 ml) suspension of $[NbCp^*Cl_4]$ (0.50 g, 1.35 mmol) and the mixture was stirred for 30 min at room temperature. The resulting rose red suspension was decanted, filtered through Celite, and the filtrate was concentrated to ca. 10 ml and cooled to $-40^\circ C$ overnight to give **1–4** as red microcrystalline solids. Yields: **1** 70% (0.46 g); **2–4** 94% (0.56 g, 0.64 g, 0.72 g).

3.1.2. Method B

A toluene solution (20 ml) of $SiCp^*Me_3$ (2.59 ml, 10.58 mmol) was added dropwise to a dichloromethane suspension (60 ml) of $NbCl_5$ (2.86 g, 10.58 mmol) and L (10.58 mmol). The mixture was stirred vigorously for 12 h at room temperature, and then the resultant red suspension decanted and filtered through Celite. The solvent was removed in vacuum and the residue, after washing with hexane (2×10 ml), was identified as **1–4** adducts. Yields: **1** 75% (4.1 g); **2–4** 90% (4.25 g, 4.84 g, 5.43 g).

The data for **1** are as follows: IR (Nujol mull, cm^{-1}): 2210s, 1012m, 323 vs. 1H NMR (δ , ppm, in benzene- d_6 , $20^\circ C$): 6.21 (s, 2H, $H_2C_6Me_3$), 2.33 (s, 6H, $2,4,6-Me_3C_6H_2$), 2.08 (s, 15H, C_5Me_5), 1.78 (s, 3H, $2,4,6-Me_3C_6H_2$). MS(El, 70 eV): m/e 369 ($M^+ - L$, 2.1), 333 (50.8), 297 (35.5), 216 (30.2), 135 (97.2). Anal. Calc. for $C_{20}H_{26}Cl_4NNb$: C, 46.61; H, 5.05; N, 2.72. Found: C, 46.48; H, 5.05; N, 2.63%.

The data for **2** are as follows: IR(Nujol mull, cm^{-1}): 1278m, 1016m, 961m, 734m, 327s. 1H NMR (δ , ppm, in chloroform- d_1 , $20^\circ C$): 2.27 (s, 15H, C_5Me_5), 1.71 (d, 9H, $^2J_{P-H} = 11.2$ Hz, Me_3P). MS (El, 70 eV): m/e 333 (7.69), 298 (65.74), 263 (30.29), 135 (37.68). Anal. Calc. for $C_{13}H_{24}Cl_4NbP$: C, 35.06; H, 5.38. Found C, 34.85; H, 5.23%.

The data for **3** are as follows: IR (Nujol mull, cm^{-1}): 1265m, 1010m, 953m, 723m, 692m, 324s. 1H NMR (δ , ppm, in chloroform- d_1 , $20^\circ C$): 7.60m, 7.40m (5H, $PhMe_2P$), 2.25 (s, 15H, C_5Me_5), 2.07(d, 6H, $^2J_{P-H} = 10.8$ Hz, Me_2PPh). $^{31}P\{^1H\}$ NMR (δ , ppm, in chloroform- d_1 , $20^\circ C$): 2(br, PMe_2Ph). MS(El, 70 eV): m/e 333 (4.15), 298 (4.01), 263 (3.10), 135 (87.63). Anal. Calc. for $C_{18}H_{26}Cl_4NbP$: C, 42.41; H, 5.17. Found: C, 42.31; H, 5.11%.

The data for **4** are as follows: IR (Nujol mull, cm^{-1}): 1276m, 1006m, 936m, 744m, 694m, 323s. 1H NMR (δ , ppm, in chloroform- d_1 , $20^\circ C$): 7.70m, 7.35m (10H, Ph_2PMe), 2.26 (s, 15H, C_5Me_5), 2.23 (d, 3H, $^2J_{P-H} = 11.5$ Hz, $MePh_2P$). MS (El, 70 eV): m/e 333 (28.48), 298 (3.93), 263 (3.10), 135 (100). Anal. Calc. for $C_{23}H_{28}Cl_4NbP$: C, 48.41; H, 4.91. Found: C, 48.62; H, 4.89%.

3.2. Preparation of $[{NbCp^*Cl_4}_2(\mu-dmpe)]$, **5**

A solution of 0.29 mmol of dmpe (0.13 ml of a 2.2 M solution in toluene) was added to a suspension of $[NbCp^*Cl_4]$ (0.22 g, 0.59 mmol) in dichloromethane (40 ml) and stirred 30 min at room temperature. This was filtered through Celite, the solvent was removed completely from the filtrate, and the residue was washed twice with hexane (2×10 ml) to give **5** as an orange microcrystalline solid. Yield 94% (0.49 g).

The data for **5** are as follows: IR (Nujol mull, cm^{-1}): 1020m, 944m, 325s. 1H NMR (δ , ppm, in chloroform- d_1 , $20^\circ C$): 2.48 (m, 4H, $-CH_2-$), 2.27 (s, 30H, C_5Me_5), 1.70 (d, 12H, $^2J_{P-H} = 10.5$ Hz, Me_2P-). $^{13}C\{^1H\}$ NMR (δ , ppm, in chloroform- d_1 , $20^\circ C$): 136.81 (d, $^2J_{C-P} = 2.79$ Hz, C_5Me_5), 22.65 (dd, $^1J_{C-P} = 15.76$ Hz, $^2J_{C-P} = 7.40$ Hz, $-CH_2-CH_2-$), 13.09 (s, C_5Me_5), 11.76 (d, $^1J_{C-P} = 25.86$ Hz, Me_2P-). MS (El, 70 eV): m/e 333 (43.23), 298 (3.69), 263 (6.39), 135 (100). Anal. Calc. for $C_{26}H_{46}Cl_8Nb_2P_2$: C, 35.00; H, 5.17. Found: C, 34.94; H, 5.11%.

3.3. Preparation of $[NbCp^*Cl_2Me_2]$ **6**

A diethyl ether suspension (30 ml) of $[NbCp^*Cl_4]$ (0.50 g, 1.35 mmol) was cooled to $-78^\circ C$. A MgClME solution (3 M in THF, 0.9 ml, 2.70 mmol) was added dropwise. The mixture was stirred for 1 h, and then permitted to warm to room temperature. The resulting orange suspension was decanted and filtered through Celite. The solvent was removed from the filtrate by evaporation and the solid washed with hexane (2 ml) and identified as **6**. Yield 85% (0.38 g).

The data for **6** are as follows: IR (Nujol mull, cm^{-1}): 1023m, 415m, 337m, 306m. 1H NMR (δ , ppm, in benzene- d_6 , $20^\circ C$): 1.58 (s, 15H, C_5Me_5), 1.36 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (δ , ppm, in benzene- d_6 , $20^\circ C$): 125.1s, 12.5s (C_5Me_5), 71.5(br, Me). MS (El, 70 eV): m/e 313 (100), 298 (69.2), 261 (58.6), 135 (11.5). Anal. Calc. for $C_{12}H_{21}Cl_2Nb$: C, 43.79; H, 6.43. Found: C, 43.69; H, 6.34%.

3.4. Preparation of $[NbCp^*Me_4]$, **7**

This reaction was carried out in a dry box using darkened glassware for photo-sensitive materials. To a suspension of 0.70 g (1.89 mmol) of $[NbCp^*Cl_4]$ in 30

ml of hexane was added dropwise a 3 M THF solution of MgClMe (2.52 ml, 7.57 mmol). The mixture was stirred for 2 h at ambient temperature. The orange suspension was decanted, filtered through Celite, and the solvent evaporated from the filtrate to give 0.35 g (65%) of **7** as an orange solid which was characterized by IR and ^1H NMR spectroscopy.

The data for **7** are as follows: IR (Nujol mull, cm^{-1}): 1026m, 473m. ^1H NMR (δ , ppm, in benzene- d_6 , 20°C): 1.51 (s, 15H, C_5Me_5), 1.23 (s, 12H, CH_3). MS(EI, 70 eV) m/e 273 (57.3), 258 (17.1), 241 (52.8), 226 (100), 135 (43.5).

3.5. Preparation of $[\{\text{NbCp}^*\text{Me}_3\}_2(\mu\text{-O})]$, **8**

To a suspension of 0.46 g (0.67 mmol) of $[\{\text{NbCp}^*\text{Cl}_3\}_2(\mu\text{-O})]$ in 40 ml of hexane was added dropwise a 3 M THF solution of MgClMe (1.34 ml, 4.03 mmol). The mixture was stirred for 3 h and then decanted and filtered through Celite. The filtrate was concentrated to ca. 20 ml and cooled to -40°C overnight to give **8** as yellow crystals. Yield 80% (0.30 g).

The data for **8** are as follows: IR (Nujol mull, cm^{-1}): 1024m, 664s, 606s, 474m. ^1H NMR (δ , ppm, in benzene- d_6 , 20°C): 1.65 (s, 15H, C_5Me_5), 0.92 (s, 6H, 2Me), 0.87 (s, 3H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm, in benzene- d_6 , 20°C): 116.1s, 11.0s (C_5Me_5), 51.0br, 52.0br (Me). MS (EI, 70 eV): m/e 547 (11.1), 273 (100), 257 (36), 241 (68.4), 135 (3.1). Anal. Calc. for $\text{C}_{26}\text{H}_{48}\text{Nb}_2\text{O}$: C, 66.50; H, 10.30. Found: C, 66.32; H, 10.17%.

3.6. Preparation of $[\text{NbCp}^*\text{Cl}_3\text{Me}(\text{PMe}_2\text{Ph})]$, **9**

A 3 M THF solution of MgClMe (0.33 ml, 0.98 mmol) was added dropwise to a suspension of 0.50 g (0.98 mmol) of **3** in 50 ml of diethyl ether. The mixture was stirred vigorously for 30 min and the precipitate was filtered off. The clear filtrate was concentrated in vacuo to ca. half volume and cooled to -40°C overnight to give **9** as brown crystals. Yield 75% (0.36 g).

The data for **9** are as follows: IR (Nujol mull, cm^{-1}): 1015m, 945m, 747m, 695m, 492m, 323s. ^1H NMR (δ , ppm, in benzene- d_6 , 20°C): 7.60m, 7.05m (5H, PhPMe_2), 1.97 (br, 6H, Me_2PhP), 1.84 (s, 15H, C_5Me_5), 0.46 (s, 3H, Me-Nb). $^{31}\text{P}\{^1\text{H}\}$ NMR (δ , ppm, in benzene- d_6 , 20°C): -1.86 (br, PMe_2Ph). Anal. Calc. for $\text{C}_{19}\text{H}_{29}\text{Cl}_3\text{NbP}$: C, 46.79; H, 5.95. Found: C, 46.68; H, 5.90%.

3.7. Preparation of $\text{NbCp}^*\text{Cl}_3(\text{PPh}_2)$, **10**

To a mixture of $[\text{NbCp}^*\text{Cl}_4]$ (0.30 g, 0.81 mmol) and LiPPh_2 (0.15 g, 0.81 mmol), was added toluene (30 ml) at -78°C . After 1 h the suspension was warmed up to room temperature. The resulting mixture was filtered

through dry Celite and the filtrate was concentrated to ca. 15 ml and cooled to -40°C to give **10**, as purple crystals. Yield 80% (0.34 g).

The data for **10** are as follows: IR (Nujol mull, cm^{-1}): 1020m, 693s, 326s. ^1H NMR (δ , ppm, in benzene- d_6 , 20°C): 6.9m–7.8m (10H, Ph_2P), 1.92 (s, 15H, C_5Me_5). Anal. Calc. for $\text{C}_{22}\text{H}_{25}\text{Cl}_3\text{NbP}$: C, 50.81; H, 4.85. Found: C, 50.61; H, 4.74%.

Acknowledgements

We are grateful to DGICYT (Project No. PB-92-0178-C) for financial support for this research.

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