New Complexes of Niobium(V) and Tantalum(V) with Monoanionic NNO Heteroscorpionate Ligands

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A new synthetic route based on bis(3,5-dimethylpyrazol-1-yl)acetic acid (Hbdmpza) (**1**) has afforded the alcohol 2,2-bis(3,5-dimethylpyrazol-1-yl)ethanol (Hbdmpze) in good yield. This alcohol and the related lithium compound $[\{Li(bdmpza)(H_2O)\}_4]$ are excellent precursors for introducing these scorpionate ligands into transition metal complexes. For example, the lithium compound and Hbdmpze (the latter after prior addition of *n*BuLi) react with a solution of MCl_5 (M = Nb, Ta) in THF to give, after stirring for 12 h at –70 °C, a solution from which the complexes $[MCl_4(\kappa^3\text{-bdmpz}x)]$ (x = a, M = Nb **2**, Ta **3**; x = e, M = Nb **4**, Ta **5**) have been isolated. When solutions of **2**–**5** in THF were stirred at ca. 20 °C for 48 h, the oxo complexes $[MCl_2(O)(\kappa^3\text{-bdmpz}x)]$ (x = a, M = Nb **6**, Ta **7**; x = e, M = Nb **8**, Ta **9**) were isolated. The structures of these complexes have been determined by spectroscopic methods and the X-ray crystal structure of **8** has been established. Finally, a new class of heteroscorpionate-metal complexes containing an alkoxide ligand has been prepared. Direct reaction of the complexes $[MCl_4(\kappa^3\text{-bdmpza})]$ (M = Nb **2**, Ta **3**) with several alcohols gave the complexes $[MCl_3(\kappa^3\text{-bdmpza})(OR)]$ (M = Nb, R = Me **10**, Et **11**, *i*Pr **12**, *t*Bu **13**; M = Ta, R = Me **14**, Et **15**, *i*Pr **16**, *t*Bu **17**) after the appropriate workup.

Introduction

Several classes of poly(pyrazol-1-yl)borato niobium complexes containing halide, alkoxide, alkyl, imido, oxo, or alkyne ancillary ligands have been prepared.[1] We have reported the preparation of several complexes of the type $TpNb(Cl)_2(RC{\equiv}CR')$ or $Tp^*Nb(O)(Cl)(OR)$ [Tp = hydridotris(pyrazol-1-yl)borate and Tp* = hydridotris(3,5-dimethylpyrazol-1-yl)borate],[2] and have recently examined the synthesis of new "heteroscorpionate" ligands[3] that incorporate pyrazole rings. The target compounds are related to the tris(pyrazol-1-yl)methane system,[4] where one pyrazole group is replaced by a carboxylate, dithiocarboxylate or ethoxide group; i.e. bis(3,5-dimethylpyrazol-1-yl)acetate (bdmpza), bis(3,5-dimethylpyrazol-1-yl)dithioacetate (bdmpzdta) and 2,2-bis(3,5-dimethylpyrazol-1-yl)ethoxide (bdmpze). The aim is to provide a small degree of steric hindrance and considerable coordinative flexibility in the ligand. These compounds are excellent reagents for the introduction of scorpionate ligands into niobium complexes and a series of alkyne-containing niobium(III) complexes has been isolated and characterized.[5] More recently, we extended the range of complexes to include group 4 metals.[6]

In continuing such research we have further studied the synthesis of heteroscorpionate-containing niobium(V) and tantalum(V) species, where any compounds have been reported in the literature. We describe here the synthesis and characterization of new classes of heteroscorpionate-niobium and -tantalum complexes containing halide, oxo and alkoxide ancillary ligands.

Results and Discussion

The alcohol 2,2-bis(3,5-dimethylpyrazol-1-yl)ethanol (Hbdmpze) was obtained by reduction of the lithium compound $[\{Li(bdmpza)(H_2O)\}_4]$ with a 2.0 M solution of $(CH_3)_2S{\cdot}BH_3$ (borane-methyl sulfide complex) in THF at reflux in a 1:1 molar ratio (Scheme 1).[5] However, to increase the low yield (46%) of this method we proposed a new route based on the use of bis(3,5-dimethylpyrazol-1-yl)acetic acid (Hbdmpza) (**1**), which was also synthesized and characterized in this work. The lithium compound $[\{Li(bdmpza)(H_2O)\}_4]$ reacted at room temperature in a 1:1 molar ratio (Scheme 1) with hydrochloric acid to give, after appropriate workup, the acid **1** (97% yield). Reduction of this acid with a 2.0 M solution of $(CH_3)_2S{\cdot}BH_3$ gave the alcohol 2,2-bis(3,5-dimethylpyrazol-1-yl)ethanol (Hbdmpze) in 84% yield (Scheme 1). The mass spectrum (FAB) of **1** indicates a mononuclear formulation (Exp. Sect.). The IR spectrum shows two strong bands at 1578 and 1414 cm^{-1}, which are assigned to $\nu_{as}(CO_2^-)$ and

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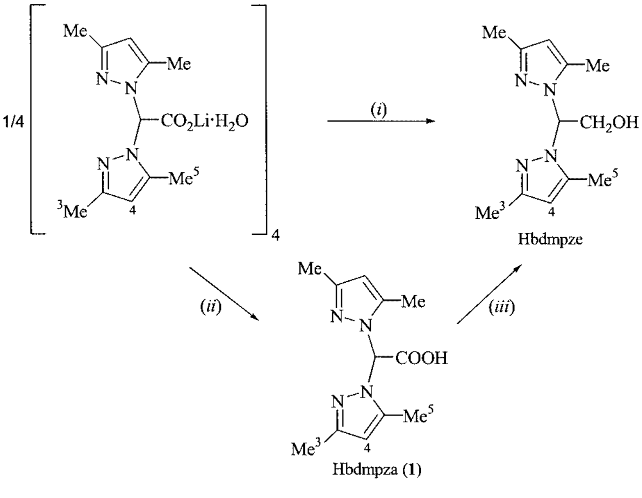
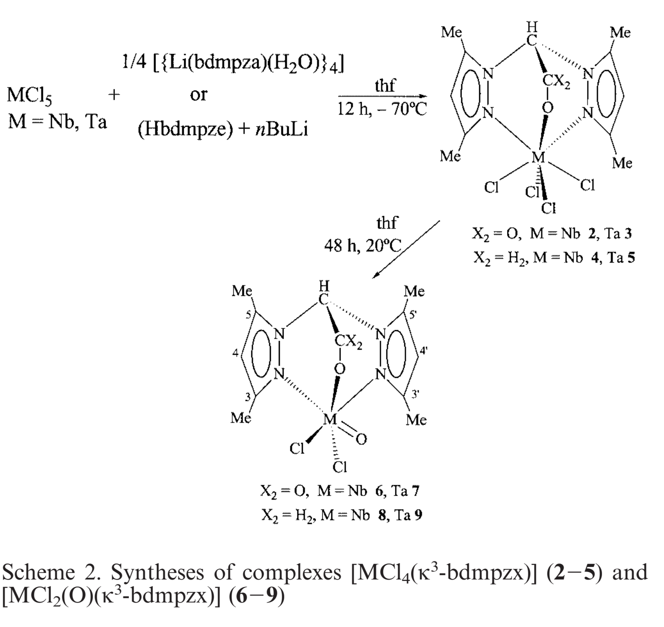


Scheme 1. Summary of reactions leading to compound **1**. Reagents and conditions: (i) $(CH_3)_2S{\cdot}BH_3$, THF, reflux, 12 h under an atmosphere of dry nitrogen, yield 46%; (ii) HCl, THF, 1 h, 20 °C, yield 97%; (iii) $(CH_3)_2S{\cdot}BH_3$, THF, reflux, 12 h under an atmosphere of dry nitrogen, yield 84%.

$\nu_s(CO_2^-)$, respectively. The ^1H NMR spectrum shows a set of resonances for H^4, Me^3 and Me^5, indicating that both pyrazole rings are equivalent in solution. In addition, all the resonances are shifted to lower fields than those for the lithium compound $[\{Li(bdmpza)(H_2O)\}_4]$. The $^{13}C\{^1H\}$ NMR spectra exhibit the corresponding signals for CH, C^3, C^4, C^5, Me^3, Me^5 and CO_2^- (Exp. Sect.).

$[\{Li(bdmpza)(H_2O)\}_4]$ and (Hbdmpze) were used in the complexation of some niobium and tantalum fragments, initially with MCl_5 (M = Nb, Ta). Thus, $[\{Li(bdmpza)(H_2O)\}_4]$ and (Hbdmpze) (the latter with prior addition of *n*BuLi) reacted with a solution of MCl_5 (Scheme 2) in THF to give, after stirring for 12 h at −70 °C, a solution from which the complexes $[MCl_4(\kappa^3\text{-bdmpzx})]$ (*x* = *a*, M = Nb **2**, Ta **3**; *x* = *e*, M = Nb **4**, Ta **5**) were isolated as red, (**2**) yellow (**3, 4**) and white (**5**) solids after the appropriate workup. When solutions of **2−5** in THF were stirred at ca. 20 °C for 48 h, the oxo complexes $[MCl_2(O)(\kappa^3\text{-bdmpzx})]$ (*x* = *a*, M = Nb **6**, Ta **7**; *x* = *e*, M = Nb **8**, Ta **9**) were isolated as white solids after the appropriate workup (Scheme 2). Although rigorously anhydrous experimental conditions were used, hydrolysis still occurred.



Scheme 2. Syntheses of complexes $[MCl_4(\kappa^3\text{-bdmpzx})]$ (**2−5**) and $[MCl_2(O)(\kappa^3\text{-bdmpzx})]$ (**6−9**)

The complexes were characterised spectroscopically. The mass spectra of **2−9** indicate a mononuclear formulation (Exp. Sect.). The ir spectra of **2−3** and **6−7** show two strong bands at ca. 1750 and 1500 cm^{-1}, which are assigned to $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$, respectively. In the lithium compound $[\{Li(bdmpza)(H_2O)\}_4]$, $\Delta\nu_{as\text{-}s}$ $[\nu_{as}(CO_2^-) - \nu_s(CO_2^-)]$ is 180 cm^{-1}, and the carboxylate forms a coordinating bridge between two lithium atoms. IR spectroscopy is a good indicator of the bonding mode of carboxylate ligands:[7] bonding through the two oxygen atoms (chelate mode) leads to a decrease in $\Delta\nu_{as\text{-}s}$ in comparison to the absorptions of a bridge mode, and bonding through the single oxygen atom leads to an increase in $\Delta\nu_{as\text{-}s}$, again in comparison to a bridging mode. The $\Delta\tilde{\nu}_{as\text{-}s}$ (ca. 235 cm^{-1}) for these compounds accords with an *O*-coordination (monodentate) mode. The IR spectra of **4**, **5**, **8** and **9** contain a strong band at ca. 570 cm^{-1} that is assigned to ν(M−O). Complexes **2−9** show other bands of interest at ca. 420 and 315 cm^{-1}, which are assigned to ν(M−Cl) of the terminal group for a mononuclear disposition, with a seven-coordinate model or octahedral environment for each niobium atom. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **2−5** show a single set of resonances for the pyrazole rings, indicating that the pyrazoles are equivalent. These data confirm a seven-coordinate model (Scheme 2), with κ^3-NNO coordination for the bdmpza or bdmpze.

The ^1H NMR spectra of **6−9** exhibit two resonances for each H^4, Me^3 and Me^5 pyrazole protons, indicating that the two pyrazole rings are non-equivalent (Exp. Sect.). These results are consistent with a proposed octahedral disposition in which the two pyrazole rings are located in *cis* and *trans* positions with respect to the oxo ligand (Scheme 2). Homonuclear NOE (nuclear Overhauser enhancement) difference spectroscopy confirmed these assignments for each pyrazole ring. In addition, the $^{13}C\{^1H\}$ NMR spectra of complexes **6−9** exhibit two resonances for the different pyrazole carbon atoms C^3, C^4, C^5, Me^3, Me^5 which have been assigned on the basis of $^1H-^{13}C$ HETCOR correlation experiments (Exp. Sect.). The chiral centre of the metal atom in these complexes was confirmed by the presence in solution of the two enantiomers upon addition of the chiral shift reagent (*R*)-(−)-(9-anthryl)-2,2,2-trifluoroethanol. This process gave rise to two signals for each proton in the ^1H NMR spectra, resulting from the two diastereoisomers of the corresponding two enantiomers (Figure 1).

The molecular structure of complex **8** was determined by X-ray diffraction. It crystallizes in the orthorhombic space group *Pbca* with eight molecules per unit cell, and consists of a monomeric unit with a heteroscorpionate ligand bonded to the niobium atom through the two nitrogen atoms and the oxygen from the alkoxide group (Figure 2).

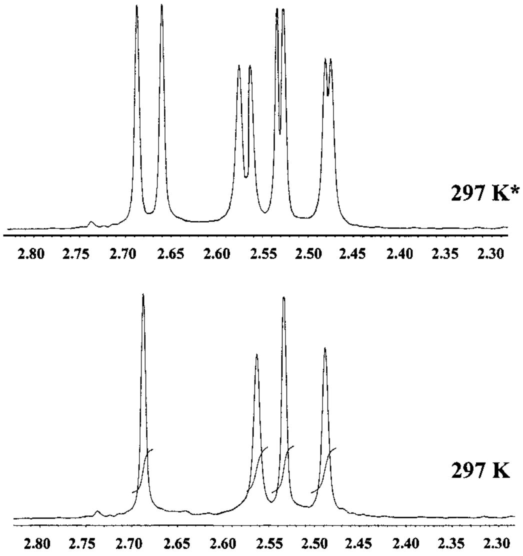


Figure 1. ^{1}H. NMR spectra in the region of the Me group of the complex [NbCl$_2$(O)(κ^3-bdmpza)] (**6**); *with chiral shift reagent

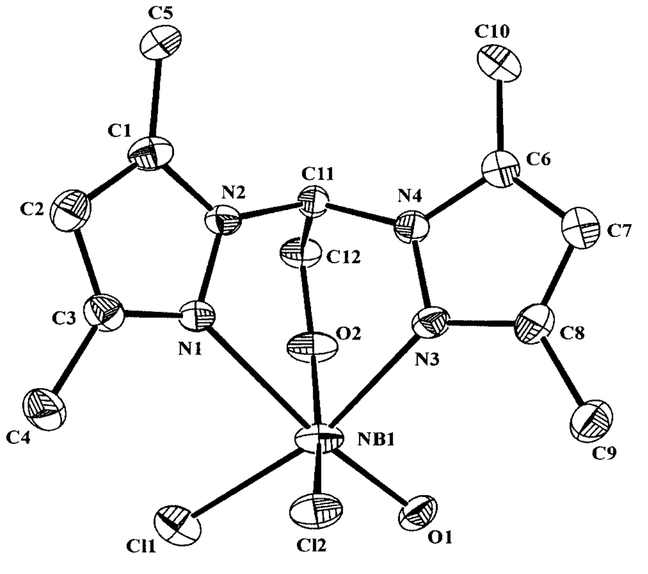


Figure 2. ORTEP drawing of the complex [NbCl$_2$(O)(κ^3-bdmpze)] (**8**)

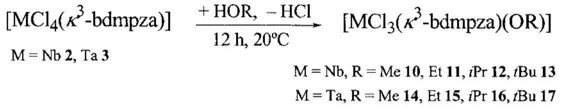
In addition, the niobium centre is coordinated to two chloride atoms and one oxygen, rendering the niobium atom a chiral centre. In the solid state, due to the centrosymmetric space group, both enantiomers are present and one, *OC*−6−43(C), is depicted in Figure 2.

This complex has a pseudooctahedral geometry with an equatorial plane defined by the N1, N3, O1 and Cl1 atoms and two apical positions defined by O2 and Cl2. The major distortion appears in the O2−Nb1−Cl2 angle [157.7(2)°, Table 1]. The Nb1−N3 bond length [2.263(6) Å] is as expect for an Nb pyrazolyl complex[2] but the elongated Nb1−N1 [2.456(5) Å] indicates that O1 exerts a strong *trans* influence. The Nb1−O1 [1.796(5) Å] is as expected for a double bond.[8]

Table 1. Bond lengths (Å) and angles (°) for **8**

Nb(1)−O(1)	1.796(5)	O(1)−Nb(1)−O(2)	99.9(2)
Nb(1)−O(2)	1.903(5)	O(1)−Nb(1)−N(3)	96.7(2)
Nb(1)−N(3)	2.263(6)	O(2)−Nb(1)−N(3)	79.2(2)
Nb(1)−Cl(1)	2.337(2)	O(1)−Nb(1)−Cl(1)	97.4(2)
Nb(1)−Cl(2)	2.412(2)	O(2)−Nb(1)−Cl(1)	96.2(2)
Nb(1)−N(1)	2.456(5)	N(3)−Nb(1)−Cl(1)	165.7(1)
O(2)−C(12)	1.402(8)	O(1)−Nb(1)−Cl(2)	98.1(2)
		O(2)−Nb(1)−Cl(2)	157.7(2)
		N(3)−Nb(1)−Cl(2)	85.7(1)
		Cl(1)−Nb(1)−Cl(2)	94.49(8)
		O(1)−Nb(1)−N(1)	172.2(2)
		O(2)−Nb(1)−N(1)	78.7(2)
		N(3)−Nb(1)−N(1)	75.5(2)
		Cl(1)−Nb(1)−N(1)	90.3(1)
		Cl(2)−Nb(1)−N(1)	81.8(1)
		C(12)−O(2)−Nb(1)	136.0(4)

To extend the range of alkoxide-containing niobium and tantalum species we prepared a new class of heteroscorpionate-metal complex, which contains an alkoxide ancillary ligand. Direct reaction of complexes [MCl$_4$(κ^3-bdmpza)] (M = Nb **2**, Ta **3**) with several alcohols (Scheme 3) gave, after appropriate workup, the complexes [MCl$_3$(κ^3-bdmpza)(OR)] (M = Nb, R = Me **10**, Et **11**, *iPr* **12**, *t*Bu **13**; M = Ta, R = Me **14**, Et **15**, *iPr* **16**, *t*Bu **17**), which were isolated as yellow solids. The mass spectra of complexes **10−17** indicate a mononuclear formulation (Exp. Sect.). In the IR spectra $\Delta\tilde{\nu}_{as\text{-}s}$ is ca. 225 cm^{-1}, which accords with coordination by a single oxygen. Three strong bands are also observed at ca. 550, 370 and 300 cm^{-1}, and the first of these was assigned to ν(M−OR) and the latter two to ν(M−Cl). The ^{1}H NMR spectra of these complexes exhibit a single set of resonances for H^4, Me^3 and Me^5, indicating that the pyrazole rings are equivalent. These results are consistent with the proposed seven-coordinate disposition in which the alkoxide and chloride ligands bisect the plane of the scorpionate ligand (Figure 3). In addition, the ^{13}C{^{1}H} NMR spectra show the corresponding signals for C^3, C^4, C^5, Me^3 and Me^5 and the different carbon atoms of the corresponding alkoxide ligand (Exp. Sect.).



Scheme 3. Synthesis of complexes [MCl$_3$(κ^3-bdmpza)(OR)] **10−17**

Conclusion

A new synthetic route has provided the alcohol 2,2-bis(3,5-dimethylpyrazol-1-yl)ethanol (Hbdmpze) in good yield. Both this alcohol and the related lithium compound

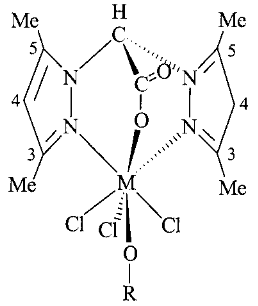


Figure 3. Proposed structure for complexes **10−17**

[{Li(bdmpza)(H_2O)}$_4$] are excellent precursors for introducing these scorpionate ligands into transition metal complexes, as confirmed by the preparation of different niobium and tantalum complexes. New classes of heteroscorpionte-niobium(V) and tantalum(V) complexes, containing halide, oxo and alkoxide ancillary ligands have also been isolated.

Experimental Section

All reactions were performed using standard Schlenk-tube techniques under an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. Microanalyses were carried out with a Perkin−Elmer 2400 CHN analyser. Mass spectra were recorded on a VG Autospec instrument using the FAB technique and 3-nitrobenzyl alcohol as matrix. Infrared spectra were recorded in the region 4000−200 cm^{-1} using a Perkin−Elmer 883 spectrophotometer. ^1H and ^{13}C NMR spectra were registered on a Varian Unity FT-300 and 200 spectrometers referenced to the residual deuterated solvent. The NOE difference spectra were recorded with the acquisition parameters: spectrum width 5000 Hz, acquisition time 3.27 s, pulse width 90°, relaxation delay 4 s, irradiation power 5−10 dB, number of scans 120. Two-dimensional NMR spectra were acquired using standard VARIANT-FT software and processed using an IPC-Sun computer.

The complexes $NbCl_5$ and $TaCl_5$ were purchased from Aldrich. The compounds [{Li(bdmpza)(H_2O)}$_4$] and Hbdmpze were prepared as reported previously.[3,5]

Preparations

Hbdmpza (1): A 10% solution of HCl (4.50 mL, 11.02 mmol) in water was added to [Li(bdmpza)(H_2O)}$_4$] (3.00 g, 11.02 mmol) dissolved in dry THF (30 mL) in a Schlenk tube (250 mL), and the resultant reaction mixture was stirred for 1 h at room temperature. The mixture was then separated and the organic layer dried with $MgSO_4$ and subsequently concentrated to afford the white solid **1**, which was washed with hexane and crystallized from a mixture of THF/hexane. Yield 97%. $C_{12}H_{16}N_4O_2$ (248.3): calcd. C 58.05, H 6.49, N 22.56; found C 58.12, H 6.65, N 22.31. ^1H NMR ($CDCl_3$, 297 K): δ = 6.89 (s, 1 H, CH), 5.91 (s, 2 H, H^4), 2.15 (s, 6 H, Me^3), 2.30 (s, 6 H, Me^5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 69.3 (CH), 149.6, 142.6 (C^3 or C^5), 106.9 (C^4), 13.5 (Me^3), 11.1 (Me^5), 168.2 (CO_2^-) ppm. IR (Nujol): $\tilde{\nu}$ = 1562 ν(C=N), 1578 $\nu_{as}(CO_2^-)$, 1414 $\nu_s(CO_2^-)$ cm^{-1}. Mass spectrum (*m/z* assignment, % intensity): 248 [Hbdmpza]$^+$, 100.

[NbCl$_4$(κ^3-bdmpza)] (2): An equimolar quantity of [{Li(bdmpza)(H_2O)}$_4$] (1.01 g, 0.92 mmol) was added dropwise to a THF (100 mL) solution of $NbCl_5$ (1.00 g, 3.70 mmol). The resultant solution was then stirred for 12 h at −70 °C, and the solvent then removed under vacuum to give a solid that was extracted with CH_2Cl_2. The solvent was then removed to give a red solid. Yield 92%. $C_{12}H_{15}Cl_4N_4NbO_2$ (482.0): calcd. C 29.90, H 3.13, N 11.66; found C 30.02, H 3.13, N 11.72. ^1H NMR ($CDCl_3$, 297 K), δ = 6.85 (s, 1 H, CH), 6.18 (s, 2 H, H^4), 2.55 (s, 6 H, Me^3), 2.70 (s, 6 H, Me^5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 72.1 (CH), 149.2, 142.3 (C^3 or C^5), 106.5 (C^4), 12.1 (Me^3), 11.6 (Me^5), 168.3 (CO_2^-) ppm. IR (Nujol): $\tilde{\nu}$ = 1575 ν(C=N), 1760 $\nu_{as}(CO_2^-)$, 1525 $\nu_s(CO_2^-)$, 429, 304 ν(Nb−Cl) cm^{-1}. Mass spectrum (*m/z* assignment, % intensity): 446 [M − Cl], 100.

[TaCl$_4$(κ^3-bdmpza)] (3): The synthetic procedure was the same as for complex **2**, using $TaCl_5$ (1.00 g, 2.79 mmol) and [{Li(bdmpza)(H_2O)}$_4$] (0.76 g, 0.70 mmol). The solution was stirred for 12 h at −70 °C, and the solvent was then removed under vacuum and the solid extracted with CH_2Cl_2. The latter solvent was then removed to give a yellow solid. Yield 91%. $C_{12}H_{15}Cl_4N_4O_2Ta$ (570.0): calcd. C 25.31, H 2.61, N 9.82; found C 25.34, H 2.65, N 9.86. ^1H NMR ($CDCl_3$, 297 K): δ = 7.83 (s, 1 H, CH), 6.01 (s, 2 H, H^4), 2.33 (s, 6 H, Me^3), 2.42 (s, 6 H, Me^5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 73.4 (CH), 148.7, 141.2 (C^3 or C^5), 105.8 (C^4), 12.3 (Me^3), 11.1 (Me^5), 168.7 (CO_2^-) ppm. IR (Nujol): $\tilde{\nu}$ = 1572 ν(C=N), 1712 $\nu_{as}(CO_2^-)$, 1498 $\nu_s(CO_2^-)$, 405, 315 ν(Ta−Cl) cm^{-1}. Mass spectrum (*m/z* assignment, % intensity): 534 [M − Cl], 100.

[NbCl$_4$(κ^3-bdmpze)] (4): A 1.6 M solution of *n*BuLi in hexane (2.3 mL, 3.70 mmol) was added to a cooled (−70 °C) solution of Hbdmpze (0.87 g, 3.70 mmol) in dry THF (100 mL). After 30 min a solution of $NbCl_5$ (1.00 g, 3.70 mmol) in THF (50 mL) was added and the reaction mixture was stirred for 12 h at −70 °C. The so obtained product was then extracted into CH_2Cl_2 (50 mL) and the solvent removed under vacuum to give a yellow solid. This solid was then crystallised from a mixture of THF/hexane. Yield 90%. $C_{12}H_{17}Cl_4N_4NbO$ (468.0): calcd. C 30.73, H 3.63, N 11.91; found C 30.83, H 3.92, N 12.12. ^1H NMR ($CDCl_3$, 297 K): δ = 7.29 (t, $^3J_{H,H}$ = 5.4 Hz, 1 H, CH), 4.50 (d, $^3J_{H,H}$ = 5.4 Hz, 2 H, CH_2O), 6.04 (s, 2 H, H^4), 2.17 (s, 6 H, Me^3), 2.36 (s, 6 H, Me^5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 71.7 (CH), 62.8 (CH_2O), 149.1, 141.1 (C^3 or C^5), 108.4 (C^4), 12.4 (Me^3), 11.2 (Me^5) ppm. IR (Nujol): $\tilde{\nu}$ = 1574 ν(C=N), 585 ν(Nb−O), 425, 325 ν(Nb−Cl) cm^{-1}. Mass spectrum (*m/z* assignment, % intensity): 432 [M − Cl], 100.

[TaCl$_4$(κ^3-bdmpze)] (5): The synthetic procedure was the same as for complex **4**, using $TaCl_5$ (1.00 g, 2.79 mmol), Hbdmpze (0.65 g, 2.79 mmol) and *n*BuLi (1.7 mL, 2.79 mmol), to give **5** as a white solid (85% yield). $C_{12}H_{17}Cl_4N_4OTa$ (556.1): calcd. C 25.92, H 3.18, N 10.08; found C 25.92, H 3.22, N 10.12. ^1H NMR ($CDCl_3$, 297 K): δ = 7.59 (t, $^3J_{H,H}$ = 4.4 Hz, 1 H, CH), 4.55 (d, $^3J_{H,H}$ = 4.4 Hz, 2 H, CH_2O), 6.06 (s, 2 H, H^4), 2.14 (s, 6 H, Me^3), 2.38 (s, 6 H, Me^5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 71.3 (CH), 63.1 (CH_2O), 149.3, 141.8 (C^3 or C^5), 106.1 (C^4), 12.3 (Me^3), 11.2 (Me^5) ppm. IR (Nujol): $\tilde{\nu}$ = 1570 ν(C=N), 564 ν(Ta−O), 409, 312 ν(Ta−Cl) cm^{-1}. Mass spectrum (*m/z* assignment, % intensity): 520 [M − Cl], 100.

[NbCl$_2$(O)(κ^3-bdmpza)] (6): A THF (100 mL) solution of [NbCl$_4$(κ^3-bdmpza)] (**2**) (0.50 g, 1.03 mmol) was stirred for 48 h at 20 °C. The solvent was then removed under vacuum to give a white solid, which was crystallised from a mixture of THF/hexane. Yield 92%. $C_{12}H_{15}Cl_2N_4NbO_3$ (427.1): calcd. C 33.72, H 3.51, N 13.13; found C 33.72, H 3.51, N 13.13. ^1H NMR ($CDCl_3$, 297 K): δ = 6.74 (s, 1 H, CH), 6.18, 6.04 (s, 2 H, H^4 or $H^{4'}$), 2.70, 2.55 (s, 6 H, Me^3 or $Me^{3'}$), 2.54, 2.49 (s, 6 H, Me^5 or $Me^{5'}$) ppm. $^{13}C\{^1H\}$ NMR

(CDCl$_3$): δ = 66.3 (CH), 156.1, 154.9, 143.0, 141.3 (C^3 or C$^{3'}$, C^5 or C$^{5'}$), 108.9, 108.7 (C^4 or C$^{4'}$), 11.3, 10.8 (Me^3 or Me$^{3'}$), 15.3, 14.4 (Me^5 or Me$^{5'}$), 162.3 (CO$_2^-$) ppm. IR (Nujol): ṽ = 1579 ν(C=N), 1761 ν$_{as}$(CO$_2^-$), 1525 ν$_s$(CO$_2^-$), 926 ν(Nb=O), 429, 324 ν(Nb−Cl) cm^{-1}. Mass spectrum (*m*/*z* assignment, % intensity): 426 [M], 100.

[TaCl$_2$(O)(κ^3-bdmpza)] (7): The synthetic procedure was the same as for complex **6**, using [TaCl$_4$(κ^3-bdmpza)] **3** (0.50 g, 0.88 mmol). The solvent was removed under vacuum to give a white solid, which was crystallised from a mixture of THF/hexane. Yield 85%. C$_{12}$H$_{15}$Cl$_2$N$_4$O$_3$Ta (515.1): calcd. C 27.92, H 2.92, N 10.81; found C 27.93, H 2.97, N 10.83. ^{1}H NMR (CDCl$_3$, 297 K): δ = 6.61 (s, 1 H, CH), 6.23, 6.08 (s, 2 H, H^4 or H$^{4'}$), 2.76, 2.57 (s, 6 H, Me^3 or Me$^{3'}$), 2.54, 2.49 (s, 6 H, Me^5 or Me$^{5'}$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 66.5 (CH), 157.0, 155.5, 143.3, 141.3 (C^3 or C$^{3'}$, C^5 or C$^{5'}$), 109.4, 109.2 (C^4 or C$^{4'}$), 11.4, 10.9 (Me^3 or Me$^{3'}$), 15.7, 14.6 (Me^5 or Me$^{5'}$), 161.1 (CO$_2^-$) ppm. IR (Nujol): ṽ = 1569 ν(C=N), 1712 ν$_{as}$(CO$_2^-$), 1488 ν$_s$(CO$_2^-$), 897 ν(Ta=O), 405, 315 ν(Ta−Cl) cm^{-1}. Mass spectrum (*m*/*z* assignment, % intensity): 514 [M], 100.

[NbCl$_2$(O)(κ^3-bdmpze)] (8): The synthetic procedure was the same as for complex **6**, using [NbCl$_4$(κ^3-bdmpze)] (**4**) (0.50 g, 1.07 mmol). The product was extracted into CH$_2$Cl$_2$ and the solvent was then removed under vacuum to give a white solid that was crystallised from a mixture of THF/hexane. Yield 87%. C$_{12}$H$_{17}$Cl$_2$N$_4$NbO$_2$ (413.1): calcd. C 34.82, H 4.11, N 13.51; found C 34.84, H 4.14, N 13.53. ^{1}H NMR (CDCl$_3$, 297 K): δ = X 6.42, A 4.91, B 4.72 (ABX, J_{AB} = 12.2, $^3J_{AX}$ = 1.2, $^3J_{BX}$ = 2.4 Hz, 3 H, CHCH$_2$O), 6.09, 5.97 (s, 2 H, H^4 or H$^{4'}$), 2.65, 2.55 (s, 6 H, Me^3 or Me$^{3'}$), 2.48, 2.44 (s, 6 H, Me^5 or Me$^{5'}$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 72.6 (CH), 65.8 (CH$_2$O), 153.8, 153.1, 142.8, 141.8 (C^3 or C$^{3'}$, C^5 or C$^{5'}$), 108.1, 108.0 (C^4 or C$^{4'}$), 11.5, 11.0 (Me^3 or Me$^{3'}$), 15.2, 14.5 (Me^5 or Me$^{5'}$) ppm. IR (Nujol): ṽ = 1574 ν(C=N), 570 ν(Nb−O), 930 ν(Nb=O), 421, 325 ν(Nb−Cl) cm^{-1}. Mass spectrum (*m*/*z* assignment, % intensity): 412 [M], 100.

[TaCl$_2$(O)(κ^3-bdmpze)] (9): The synthetic procedure was the same as for complex **6**, using [TaCl$_4$(κ^3-bdmpze)] (**5**) (0.50 g, 0.89 mmol). The product was extracted into CH$_2$Cl$_2$ and the solvent was then removed under vacuum to give a white solid, which was crystallised from a mixture of THF/hexane. Yield 83%. C$_{12}$H$_{17}$Cl$_2$N$_4$O$_2$Ta (501.1): calcd. C 28.72, H 3.41, N 11.11; found C 28.77, H 3.42, N 11.13. ^{1}H NMR (CDCl$_3$, 297 K): δ = X 7.19, A 4.57, B 4.50 (ABX, J_{AB} = 22.4, $^3J_{AX}$ = $^3J_{BX}$ = 4.3 Hz, 3 H, CHCH$_2$O), 6.06, 5.97 (s, 2 H, H^4 or H$^{4'}$), 2.49, 2.34 (s, 6 H, Me^3 or Me$^{3'}$), 2.49, 2.13 (s, 6 H, Me^5 or Me$^{5'}$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 72.1 (CH), 63.1 (CH$_2$O), 147.9, 144.8, 144.7, 143.5 (C^3 or C$^{3'}$, C^5 or C$^{5'}$), 107.9, 106.0 (C^4 or C$^{4'}$), 11.0, 10.9 (Me^3 or Me$^{3'}$), 12.6, 10.9 (Me^5 or Me$^{5'}$) ppm. IR (Nujol): ṽ = 1570 ν(C=N), 550 ν(Ta−O), 899 ν(Ta=O), 399, 316 ν(Ta−Cl) cm^{-1}. Mass spectrum (*m*/*z* assignment, % intensity): 465 [M], 100.

[NbCl$_3$(κ^3-bdmpza)(OMe)] (10): A MeOH (100 mL) solution of [NbCl$_4$(κ^3-bdmpza)] (**2**) (0.5 g, 1.03 mmol) was stirred for 12 h at 20 °C. The solvent was then removed under vacuum and the solid extracted into toluene. The toluene was then removed to give a yellow solid. Yield 81%. C$_{13}$H$_{18}$Cl$_3$N$_4$NbO$_3$ (477.6): calcd. C 32.78, H 3.64, N 11.77; found C 32.94, H 3.81, N 11.92. ^{1}H NMR (CDCl$_3$, 297 K): δ = 8.08 (s, 1 H, CH), 6.02 (s, 2 H, H^4), 2.34 (s, 6 H, Me^3), 2.46 (s, 6 H, Me^5), 3.91 (s, 3 H, OMe) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 69.9 (CH), 148.0, 145.4 (C^3 or C^5), 108.4 (C^4), 12.3 (Me^3), 12.0 (Me^5), 162.8 (CO$_2^-$), 54.2 (OMe) ppm. IR (Nujol): ṽ = 1574 ν(C=N), 1751 ν$_{as}$(CO$_2^-$), 1515 ν$_s$(CO$_2^-$), 579 ν(Nb−OMe), 385, 305 ν(Nb−Cl) cm^{-1}. Mass spectrum (*m*/*z* assignment, % intensity): 442 [M − Cl], 100.

[NbCl$_3$(κ^3-bdmpza)(OEt)] (11): A solution of [NbCl$_4$(κ^3-bdmpza)] (**2**) (0.5 g, 1.03 mmol) in EtOH (100 mL) was stirred for 12 h at 20 °C, and the solvent was then removed under vacuum and the solid extracted with toluene. The toluene was then removed to give a yellow solid. Yield 80%. C$_{14}$H$_{20}$Cl$_3$N$_4$NbO$_3$ (491.6): calcd. C 34.32, H 3.81, N 11.44; found C 34.35, H 3.82, N 11.46. ^{1}H NMR (CDCl$_3$, 297 K): δ = 7.89 (s, 1 H, CH), 5.99 (s, 2 H, H^4), 2.31 (s, 6 H, Me^3), 2.41 (s, 6 H, Me^5), 4.36 (q, $^3J_{H,H}$ = 7.0 Hz, 2 H, O*CH$_2$*CH$_3$), 1.30, (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, OCH$_2$*CH$_3$*) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 70.4 (CH), 147.9, 144.9 (C^3 or C^5), 108.2 (C^4), 12.5 (Me^3), 11.9 (Me^5), 162.7 (CO$_2^-$), 63.8 (O*CH$_2$*CH$_3$), 13.8 (OCH$_2$*CH$_3$*) ppm. IR (Nujol): ṽ = 1573 ν(C=N), 1710 ν$_{as}$(CO$_2^-$), 1480 ν$_s$(CO$_2^-$), 561 ν(Nb−OEt), 374, 306 ν(Nb−Cl) cm^{-1}. Mass spectrum (*m*/*z* assignment, % intensity): 456 [M − Cl], 100.

[NbCl$_3$(κ^3-bdmpza)(O*i*Pr)] (12): A solution of [NbCl$_4$(κ^3-bdmpza)] (**2**) (0.5 g, 1.03 mmol) in *i*PrOH (100 mL) was stirred for 12 h at 20 °C. The solvent was then removed under vacuum and the solid extracted with toluene; the toluene was then removed to give a yellow solid. Yield 75%. C$_{15}$H$_{22}$Cl$_3$N$_4$NbO$_3$ (505.6): calcd. C 35.77, H 4.25, N 11.17; found C 35.63, H 4.35, N 11.23. ^{1}H NMR (CDCl$_3$, 297 K): δ = 7.56 (s, 1 H, CH), 5.94 (s, 2 H, H^4), 2.27 (s, 6 H, Me^3), 2.33 (s, 6 H, Me^5), 5.19 [m, $^3J_{H,H}$ = 7.0 Hz, 1 H, O*CH*(CH$_3$)$_2$], 1.28 [d, $^3J_{H,H}$ = 7.0 Hz, 6 H, OCH*(CH$_3$)$_2$*] ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 71.0 (CH), 147.9, 144.2 (C^3 or C^5), 108.2 (C^4), 12.6 (Me^3), 11.7 (Me^5), 162.6 (CO$_2^-$), 72.1 [O*CH*(CH$_3$)$_2$], 21.4 [OCH*(CH$_3$)$_2$*] ppm. IR (Nujol): ṽ = 1569 ν(C=N), 1680 ν$_{as}$(CO$_2^-$), 1464 ν$_s$(CO$_2^-$), 552 ν(Nb−O*i*Pr), 368, 298 ν(Nb−Cl) cm^{-1}. Mass spectrum (*m*/*z* assignment, % intensity): 470 [M − Cl], 100.

[NbCl$_3$(κ^3-bdmpza)(O*t*Bu)] (13): A solution of [NbCl$_4$(κ^3-bdmpza)] (**2**) (0.5 g, 1.03 mmol) in *t*BuOH (100 mL) was stirred for 12 h at 20 °C. The solvent was then removed under vacuum and the solid extracted with toluene; the toluene was then removed to give a yellow solid. Yield 90%. C$_{16}$H$_{24}$Cl$_3$N$_4$NbO$_3$ (519.7): calcd. C 37.04, H 4.42, N 10.82; found C 37.17, H 4.54, N 10.94. ^{1}H NMR (CDCl$_3$, 297 K): δ = 7.63 (s, 1 H, CH), 6.01 (s, 2 H, H^4), 2.30 (s, 6 H, Me^3), 2.42 (s, 6 H, Me^5), 1.57 [s, 9 H, OC(Me)$_3$] ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 70.3 (CH), 147.8, 144.9 (C^3 or C^5), 108.3 (C^4), 12.4 (Me^3), 11.8 (Me^5), 162.4 (CO$_2^-$), 29.3 [O*C*(CH$_3$)$_3$], 24.9 [OC*(CH$_3$)$_3$*] ppm. IR (Nujol): ṽ = 1564 ν(C=N), 1652 ν$_{as}$(CO$_2^-$), 1442 ν$_s$(CO$_2^-$), 543 ν(Nb−O*t*Bu), 358, 295 ν(Nb−Cl) cm^{-1}. Mass spectrum (*m*/*z* assignment, % intensity): 484 [M − Cl], 100.

[TaCl$_3$(κ^3-bdmpza)(OMe)] (14): A solution of [TaCl$_4$(κ^3-bdmpza)] (**3**) (0.5 g, 0.88 mmol) in MeOH (100 mL) was stirred for 12 h at 20 °C. The solvent was then removed under vacuum and the solid extracted with toluene that was then removed to give a yellow solid. Yield 82%. C$_{13}$H$_{18}$Cl$_3$N$_4$O$_3$Ta (565.6): calcd. C 27.62, H 3.03, N 9.92; found C 27.74, H 3.06, N 9.85. ^{1}H NMR (CDCl$_3$, 297 K): δ = 7.86 (s, 1 H, CH), 6.01 (s, 2 H, H^4), 2.31 (s, 6 H, Me^3), 2.42 (s, 6 H, Me^5), 3.90 (s, 3 H, OMe) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 70.5 (CH), 148.3, 145.1 (C^3 or C^5), 108.4 (C^4), 12.5 (Me^3), 11.9 (Me^5), 163.2 (CO$_2^-$), 54.2 (OMe) ppm. IR (Nujol): ṽ = 1570 ν(C=N), 1710 ν$_{as}$(CO$_2^-$), 1503 ν$_s$(CO$_2^-$), 554 ν(Ta−OMe), 365, 301 ν(Ta−Cl) cm^{-1}. Mass spectrum (*m*/*z* assignment, % intensity): 530 [M − Cl], 100.

[TaCl$_3$(κ^3-bdmpza)(OEt)] (15): A solution of [TaCl$_4$(κ^3-bdmpza)] (**3**) (0.5 g, 0.88 mmol) in EtOH (100 mL) was stirred for 12 h at 20 °C. The solvent was then removed under vacuum and the solid extracted with toluene that was then removed to give a yellow solid. Yield 87%. $C_{14}H_{20}Cl_3N_4O_3Ta$ (579.6): calcd. C 29.03, H 3.21, N 9.70; found C 29.05, H 3.22, N 9.73. ^1H NMR ($CDCl_3$, 297 K): δ = 7.82 (s, 1 H, CH), 6.00 (s, 2 H, H^4), 2.30 (s, 6 H, Me^3), 2.42 (s, 6 H, Me^5), 4.35 (q, $^3J_{H,H}$ = 7.0 Hz, 2 H, $O\mathit{CH_2}CH_3$), 1.30 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, $OCH_2\mathit{CH_3}$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 71.0 (CH), 148.0, 144.9 (C^3 or C^5), 108.2 (C^4), 12.5 (Me^3), 11.9 (Me^5), 162.7 (CO_2^-), 63.8 ($O\mathit{CH_2}CH_3$), 13.8 ($OCH_2\mathit{CH_3}$) ppm. IR (Nujol): $\tilde{\nu}$ = 1563 ν(C=N), 1680 $\nu_{as}(CO_2^-)$, 1468 $\nu_s(CO_2^-)$, 541 ν(Ta−OEt), 354, 298 ν(Ta−Cl) cm^{-1}. Mass spectrum (*m/z* assignment, % intensity): 544 [M − Cl], 100.

[$TaCl_3(\kappa^3$-bdmpza)(O*i*Pr)] (16): A solution of [$TaCl_4(\kappa^3$-bdmpza)] (**3**) (0.5 g, 0.88 mol) in *i*PrOH (100 mL) was stirred for 12 h at 20 °C. The solvent was then removed under vacuum and the solid extracted with toluene that was subsequently removed to give a yellow solid. Yield 68%. $C_{15}H_{22}Cl_3N_4O_3Ta$ (593.7): calcd. C 30.46, H 3.53, N 9.42; found C 30.62, H 3.66, N 9.65. ^1H NMR ($CDCl_3$, 297 K): δ = 7.77 (s, 1 H, CH), 5.98 (s, 2 H, H^4), 2.30 (s, 6 H, Me^3), 2.40 (s, 6 H, Me^5), 5.18 [m, $^3J_{H,H}$ = 7.0 Hz, 1 H, $O\mathit{CH}(CH_3)_2$], 1.28 [d, $^3J_{H,H}$ = 7.0 Hz, 6 H, $OCH\mathit{(CH_3)_2}$] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 70.6 (CH), 147.8, 144.7 (C^3 or C^5), 108.1 (C^4), 12.5 (Me^3), 11.8 (Me^5), 162.3 (CO_2^-), 72.3 [$O\mathit{CH}(CH_3)_2$], 21.4 [$OCH\mathit{(CH_3)_2}$] ppm. IR (Nujol): $\tilde{\nu}$ = 1568 ν(C=N), 1658 $\nu_{as}(CO_2^-)$, 1455 $\nu_s(CO_2^-)$, 539 ν(Ta−O*iPr*), 345, 294 ν(Ta−Cl) cm^{-1}. Mass spectrum (*m/z* assignment, % intensity): 558 [M − Cl], 100.

[$TaCl_3(\kappa^3$-bdmpza)(O*t*Bu)] (17): A solution of [$TaCl_4(\kappa^3$-bdmpza)] (**3**) (0.5 g, 0.88 mmol) in *t*BuOH (100 mL) was stirred for 12 h at 20 °C. The solvent was then removed under vacuum and the solid extracted with toluene that was subsequently removed to give a yellow solid. Yield 91%. $C_{16}H_{24}Cl_3N_4O_3Ta$ (607.7): calcd. C 31.61, H 3.82, N 9.22; found C 31.63, H 3.86, N 9.26. ^1H NMR ($CDCl_3$, 297 K): δ = 7.80 (s, 1 H, CH), 6.00 (s, 2 H, H^4), 2.31 (s, 6 H, Me^3), 2.41 (s, 6 H, Me^5), 1.55 [s, 9 H, $OC(Me)_3$] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 70.3 (CH), 147.5, 144.3 (C^3 or C^5), 108.2 (C^4), 12.5 (Me^3), 11.7 (Me^5), 163.1 (CO_2^-), 30.1 [$O\mathit{C}(CH_3)_3$], 26.3 [$OC\mathit{(CH_3)_3}$] ppm. IR (Nujol): $\tilde{\nu}$ = 1573 ν(C=N), 1643 $\nu_{as}(CO_2^-)$, 1438 $\nu_s(CO_2^-)$, 529 ν(Ta−O*t*Bu), 334, 289 ν(Ta−Cl) cm^{-1}. Mass spectrum (*m/z* assignment, % intensity): 572 [M − Cl], 100.

Crystal Data for 8: Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a solution of **8** in dichloromethane. The crystals were mounted on fine glass fibres with epoxy cement. The diffractions were measured on a four-circle diffractometer (Nonius-MACH3) at 200 K using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and a $\omega/2\theta$ scan. Two standard diffractions were monitored every hour and showed no significant intensity variation. The lattice parameters were refined by least-squares fitting from 25 automatically centred diffractions. An empirical absorption correction was made. The structure was solved by direct methods[9] yielding the positions of all non-hydrogen atoms. Refinement on F^2 was carried out by full-matrix least-squares techniques.[10] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions and were refined isotropically (Table 2). CCDC-208238 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystal data and structure refinement for **8**

Empirical formula	$C_{12}H_{17}Cl_2N_4NbO_2$
Molecular weight	413.11
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	*Pbca*
Unit cell dimensions	
	a = 13.106(1) Å
	b = 16.463(3) Å
	c = 14.650(2) Å
Volume	3160.8(8) $Å^3$
Z	8
Density (calculated)	1.736 g/cm^3
Absorption coefficient	11.08 cm^{-1}
$F(000)$	1664
Crystal size	$0.3 \times 0.2 \times 0.2$ mm^3
Index ranges	$0 \le h \le 17$, $0 \le k \le 21$, $0 \le l \le 19$
Reflections collected	3787
Independent reflections	3787 [R(int) = 0.0000]
Data/restraints/parameters	3787/0/191
Goodness-of-fit on F^2	1.045
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0758, $wR2$ = 0.1973
R indices (all data)	$R1$ = 0.0931, $wR2$ = 0.2062
Extinction coefficient	0.0001(2)
Largest diff. peak and hole	3.711 and −2.442 $e\cdot Å^{-3}$

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