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Synthesis of α-Amino Acidato Derivatives of Niobium and Tantalum Pentahalides and Their Conversion into Iminium Salts[⊥]

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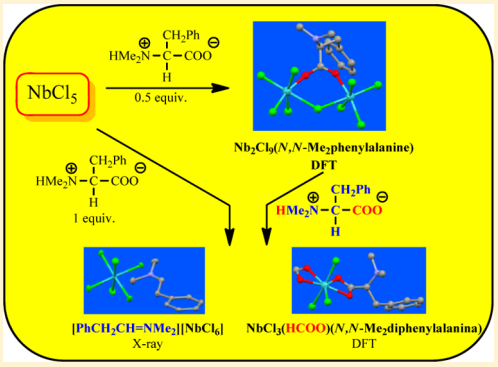
Supporting Information

ABSTRACT: Dinuclear complexes of formula $Nb_2Cl_9[O_2CCH(R)NR'R''_2\text{-}\kappa O,\kappa O]$ (R = CH_2CHMe_2, R′ = R″ = H, **1a**; R = CH_2Ph, R′ = R″ = H, **1b**; R = $CH_2CH_2SCH_3$, R′ = R″ = H, **1c**; R = R′ = H, R″ = Me, **1d**; R = CH_2Ph, R′ = R″ = Me, **1e**; $Nb_2Cl_9[O_2C[CH(CH_2)_3NH]]$, **1f**) were prepared by allowing $NbCl_5$ to react in dichloromethane with the appropriate α-amino acid in 1:2 amino acid/Nb molar ratio. The 1:1 reactions between MX_5 (M = Nb, Ta; X = Cl, Br) and a series of α-amino acids resulted in the formation of the iminium salts $[(R)CH{=}NR'R''_2][MX_6]$ (R = CH_2Ph, R′ = R″ = Me: M = Nb, X = Cl, **2a**; M = Nb, X = Br, **2b**; M = Ta, X = Cl, **2c**; M = Ta, X = Br, **2d**; R = CH_2Ph, R′ = R″ = H, M = Nb: X = Cl, **3a**; X = Br, **3b**; R = CH_2CHMe_2, R′ = R″ = H, M = Nb, X = Cl, **4**; R = R′ = H, R″ = Me, M = Nb, X = Cl, **5**). The formate/amino acidate derivative $NbCl_3(O_2CH)[O_2CCH(CH_2Ph)NMe_2]$, **6**, was isolated and identified as coproduct of the 1:1 reaction between $NbCl_5$ and *N*,*N*-dimethyl-L-phenylalanine, leading to **2a**. All of the compounds were characterized by analytical and spectroscopic methods and by X-ray diffractometry in the cases of **2a**, **2b**, and **2d**. Moreover, density functional theory studies were carried out to shed light on mechanistic and structural aspects.



INTRODUCTION

High-valent main group chlorides (e.g., PCl_5, $SbCl_5$, $SOCl_2$) have been typically used in reactions with α-amino acids as Cl-transfer agents, for the preparation of a wide variety of organic compounds.[1] On the other hand, studies on the interactions of high-valent transition metal halides with amino acids are surprisingly rare. This contrasts with the observation that α-amino acidato complexes of transition metals in low-to-medium oxidation state may exhibit valuable properties in very different fields such as asymmetric synthesis,[2] production of sol−gel-derived coatings,[3] anticancer therapy,[4] and bioorganometallic[5] and solid-state chemistries.[6]

Niobium and tantalum pentahalides are easily available, cheap, and nontoxic metal-based materials,[7] whose coordination chemistry has been developed in recent years.[8] Recent studies demonstrate that such compounds may be capable of unusual activation pathways, due to the high oxidation state of the metal center combined with relatively strong metal-halide bonds.[9] These features have encouraged their increasing application as efficient Lewis acid catalysts,[10] also in organic reactions involving natural products.[11] Otherwise, no information is still available about the reactivity of niobium and tantalum pentahalides with amino acids, and only a few reports have appeared with reference to high-valent Nb/Ta compounds in general.[12]

In the framework of our interest in the chemistry of high-valent transition metal halides,[13] herein we report the results of our synthetic, spectroscopic, crystallographic, and computational work on the reactions of MX_5 (M = Nb, Ta, X = Cl, Br)[14] with a selection of α-amino acids, performed in dichloromethane. The formation of α-amino acidato complexes and the possible occurrence of activation processes will be discussed.

EXPERIMENTAL SECTION

(1). General Considerations. *Warning! The metal compounds reported in this paper are highly moisture sensitive; thus, rigorously anhydrous conditions were required for the reaction, crystallization, and separation procedures. The reaction vessels were oven-dried at 150 °C prior to use, evacuated (1 × 10^{-2} mmHg), and then filled with argon.* $NbCl_5$ (99+%) and $TaCl_5$ (Strem, 99.9%) were purchased from Strem and stored under argon atmosphere as received. $NbBr_5$ and $TaBr_5$ were prepared according to literature procedures and stored under argon atmosphere.[15] The organic reactants were commercial products (Apollo Sci.) of the highest purity available, dried over P_4O_{10}, and stored under argon atmosphere. Solvents (Sigma-Aldrich) were distilled from P_4O_{10} under argon atmosphere before use. Infrared spectra were recorded at 298 K on an FT IR-PerkinElmer Spectrometer, equipped with UATR sampling accessory. NMR spectra

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were recorded at 298 K on a Bruker Avance DRX400 instrument equipped with a BBFO broadband probe. The chemical shifts for ^{1}H and ^{13}C were referenced to the nondeuterated aliquot of the solvent, while the chemical shifts for ^{93}Nb were referenced to external $[NEt_4][NbCl_6]$. The ^{1}H and ^{13}C NMR spectra were assigned with the assistance of ^{1}H,^{13}C correlation measured through *gs*-HSQC and *gs*-HMBC experiments.[16] Carbon, hydrogen, and nitrogen analyses were performed on a Carlo Erba model 1106 instrument. The halide content was determined by the Mohr method[17] on solutions prepared by dissolution of the solid in aqueous KOH at boiling temperature, followed by cooling to room temperature and addition of HNO_3 to neutralization. The metal (M = Nb, Ta) was analyzed as M_2O_5, obtained by hydrolysis of the samples followed by calcination in a platinum crucible.

(2). Reactions of $NbCl_5$ with α-Amino Acids in 2:1 Molar Ratio: Isolation of $Nb_2Cl_9[O_2CCH(R)NH_2$-κO,κO] (R = CH_2CHMe_2, 1a; CH_2Ph, 1b; $CH_2CH_2SCH_3$, 1c), $Nb_2Cl_9[O_2CCH_2NHMe]$, 1d, and $Nb_2Cl_9[O_2CCH(CH_2Ph)NMe_2$-κO,κO], 1e. *General Procedure.* A suspension of $NbCl_5$ in CH_2Cl_2 (15 mL) was treated with the appropriate α-amino acid. The mixture was stirred at room temperature for 18 h, during which gas (HCl) release was observed. Bubbling this gas into an aqueous solution of $AgNO_3$ determined the precipitation of a white solid (AgCl). The final reaction mixture was concentrated to ca. 5 mL and then added to pentane (30 mL). The abundant precipitate was recovered by filtration and dried in vacuo at room temperature.

$Nb_2Cl_9[O_2CCH(CH_2CHMe_2)NH_2$-κO,κO], 1a. From $NbCl_5$ (0.475 g, 1.760 mmol) and L-leucine (0.115 g, 0.880 mmol). Yellow solid, 72% yield. Anal. Calcd for $C_6H_{12}Cl_9NNb_2O_2$: C, 11.35; H, 1.90; N, 2.21; Cl, 50.24; Nb, 29.26. Found: C, 11.33; H, 2.03; N, 2.18; Cl, 49.72; Nb, 29.35%. IR (solid state): 3128m-br, 2961w, 2926w, 1594m, 1555s ($\nu_{asym,COO}$), 1472s ($\nu_{sym,COO}$), 1438m, 1392w, 1371w, 1361w, 1333s, 1280w, 1246w, 1225w, 1166m, 1131w, 1108w-m, 1053w, 968w, 958w, 739w, 656w cm^{-1}.

$Nb_2Cl_9[O_2CCH(CH_2Ph)NH_2$-κO,κO], 1b. From $NbCl_5$ (0.367 g, 1.360 mmol) and L-phenylalanine (0.112 g, 0.680 mmol). Yellow solid, 77% yield. Anal. Calcd for $C_9H_{10}Cl_9NNb_2O_2$: C, 16.16; H, 1.51; N, 2.09; Cl, 47.67; Nb, 27.77. Found: C, 16.42; H, 1.60; N, 2.13; Cl, 47.54; Nb, 27.83%. IR (solid state): 3066br-m, 2926w, 1574vs ($\nu_{asym,COO}$), 1470m-s ($\nu_{sym,COO}$), 1428w, 1357m, 1262s, 1086s, 752w-m, 698m cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 7.52, 7.37 (m, 5H, Ph); 6.73 (s, 2H, NH_2); 5.12 (m, 1H, *CH*); 3.70 (dd, $^{2}J_{HH}$ = 15.3 Hz, $^{3}J_{HH}$ = 5.1, 6.4 Hz, 2H, CH_2) ppm. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ = 172.4 (OCO); 132.3 (*ipso*-Ph); 130.7, 130.0, 129.5, (Ph); 63.6 (*CH*); 35.5 (CH_2) ppm. ^{93}Nb NMR (CD_2Cl_2): δ = 34.9 ($\Delta\nu1/2 = 2.0 \times 10^3$ Hz), −56.7 ($\Delta\nu1/2 = 3.5 \times 10^3$ Hz) ppm.

$Nb_2Cl_9[O_2CCH(CH_2CH_2SMe)NH_2$-κO,κO], 1c. From $NbCl_5$ (0.330 g, 1.220 mmol) and L-methionine (0.091 g, 0.610 mmol). Yellow solid, 80% yield. Anal. Calcd for $C_5H_{10}Cl_9NNb_2O_2S$: C, 9.20; H, 1.54; N, 2.14; Cl, 48.86; Nb, 28.45. Found: C, 9.33; H, 1.98; N, 2.22; Cl, 48.73; Nb, 28.30%. IR (solid state): 3109m-br, 3012w, 2926w, 1765w, 1694w, 1606s ($\nu_{asym,COO}$), 1566m-s, 1480vs ($\nu_{sym,COO}$), 1415m, 1366m, 1342w, 1264w-m, 1113w, 1097w, 1039 w,1014 m, 958w, 860w, 781m, 735w cm^{-1}.

$Nb_2Cl_9[O_2CCH_2NHMe]$, 1d. From $NbCl_5$ (0.405 g, 1.500 mmol) and *N*-methylglycine (0.067 g, 0.750 mmol). Yellow solid, 67% yield. Anal. Calcd for $C_3H_6Cl_9NNb_2O_2$: C, 6.08; H, 1.02; N, 2.36; Cl, 53.81; Nb, 31.34. Found: C, 6.21; H, 1.19; N, 2.15; Cl, 53.72; Nb, 31.46%. IR (solid state): 3158m-br, 3058w-sh, 2992w, 2956w, 1744w, 1694w, 1608s ($\nu_{asym,COO}$), 1574m-s, 1453s ($\nu_{sym,COO}$), 1427m, 1397m-s, 1371w, 1315w, 1264w, 1158w, 1049w, 1029w, 943m, 934w, 851m, 796m, 738w, 704w-m, 666w cm^{-1}.

$Nb_2Cl_9[O_2CCH(CH_2Ph)NMe_2$-κO,κO], 1e. From $NbCl_5$ (0.594 g, 2.200 mmol) and *N*,*N*-dimethyl-L-phenylalanine (0.213 g, 1.100 mmol). Orange microcrystalline solid, 75% yield. Anal. Calcd for $C_{11}H_{14}Cl_9NNb_2O_2$: C, 18.95; H, 2.02; N, 2.01, Cl, 45.77; Nb, 26.65;. Found: C, 18.45; H, 1.84; Cl, 46.00; Nb, 25.59%. IR spectrum (solid state): 3092m, 2962w, 1583vs ($\nu_{asym,COO}$), 1496w, 1455m-s ($\nu_{sym,COO}$), 1413w, 1370m, 1262s, 1081w, 1041w, 925w, 799m, 747w-m, 697m-s cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 7.51−7.37 (5H, Ph); 4.78 (br, 1H, *CH*), 3.62 (m, 2H, CH_2), 3.33, 3.23 (s, 6H, NMe_2) ppm. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ = 174.3 (OCO); 133.0 (*ipso*-Ph); 130.0, 129.4, 129.1 (Ph); 71.0 (*CH*); 44.2, 43.4 (NMe_2); 34.3 (CH_2) ppm. ^{93}Nb NMR (CD_2Cl_2): δ = −61.7 ($\Delta\nu1/2 = 4 \times 10^3$ Hz) ppm.

$Nb_2Cl_9[O_2C\lceil CH(CH_2)_3NH\rceil$-κO,κO], **1f**. From $NbCl_5$ (0.367 g, 1.360 mmol) and L-proline (0.078 g, 0.680 mmol). Pale yellow solid, 82% yield. Anal. Calcd for $C_5H_8Cl_9NNb_2O_2$: C, 9.70; H, 1.30; N, 2.26; Cl, 51.55; Nb, 30.02. Found: C, 9.81; H, 1.25; N, 2.16; Cl, 51.36; Nb, 30.33%. IR (solid state): 3167m-br, 1626m, 1557s ($\nu_{asym,COO}$), 1435m-s ($\nu_{sym,COO}$), 1367m-s, 1335m, 1226w, 1180w, 1084w, 1035w, 814s, 737w, 666w cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 7.80 (br, 1H, *NH*); 5.23 (m, 1H, *CH*); 3.93, 3.80 (m, 2H, CH_2); 2.85, 2.55 (m, 2H, CH_2); 2.38, 2.28 (m, 2H, CH_2) ppm. ^{13}C NMR$\{^{1}H\}$ (CD_2Cl_2): δ = 173.5 (OCO);68.7 (*CH*); 49.9, 29.5, 24.1 (CH_2) ppm.^{93}Nb NMR (CD_2Cl_2): δ = 64.7 ($\Delta\nu1/2 = 2.0 \times 10^3$ Hz), −49.1 ($\Delta\nu1/2 = 3.5 \times 10^3$ Hz) ppm.

(3). Reactions of MX_5 (M = Nb, Ta; X = Cl, Br) with α-Amino Acids in 1:1 Molar Ratio: Synthesis of Iminium Salts. *(A). Synthesis and Isolation of $[(C_6H_5CH_2)CH{=}NMe_2][MX_6]$, **2a−d**, $[(PhCH_2)CH{=}NH_2][NbCl_6]$, **3a**, $[(C_6H_5CH_2)CH{=}NH_2][NbBr_6]$, **3b**, $[(CH_2CHMe_2)CH{=}NH_2][NbCl_6]$, **4**, and $[CH_2{=}NHMe][NbCl_6]$, **5**.* A suspension of MX_5 (0.50 mmol) in CH_2Cl_2 (15 mL) was allowed to react with *N*,*N*-dimethyl-L-phenylalanine (0.50 mmol) at room temperature for 24 h. The yellowish-green colored suspension progressively turned to a yellow-brown mixture. A dark yellow solution was separated by filtration, layered with hexane, and set aside at room temperature (−30 °C in the case of **4**) to settle overnight. Microcrystalline (compound **4**) or crystalline materials (compounds **2a−d**, **3**, **5**) were recovered and then dried in vacuo at room temperature. Gas (HX) release was observed during the reaction. Bubbling this gas into an aqueous solution of $AgNO_3$ determined the precipitation of a white solid (AgX).

$[(C_6H_5CH_2)CH{=}NMe_2][NbCl_6]$, ***2a***. From $NbCl_5$ (0.165 g, 0.61 mmol) and *N*,*N*-dimethyl-L-phenylalanine (0.124 g, 0.61 mmol). Yellow crystals, 0.114 g (41% yield based on Nb). Anal. Calcd for $C_{10}H_{14}Cl_6NNb$: C, 26.46; H, 3.11; N, 3.09; Cl, 46.87; Nb, 20.47. Found: C, 26.20; H, 3.20; N, 2.92; Cl, 46.01; Nb, 19.40%. IR spectrum (solid state): 3014w, 2850w, 1689s ($\nu_{C=N}$), 1598w, 1497m, 1453m, 1409w, 1373w, 1261w, 1162m, 1084m, 1024m, 950w, 916w, 818vs, 785s, 746m, 727m, 695vs cm^{-1}. ^{1}H NMR (CD_3CN): δ = 8.34 (s, 1H, N=C*H*); 7.58−7.19 (m, 5H, Ph); 4.08 (s, 2H, CH_2); 3.67, 3.60 (s, 6H, NMe_2) ppm. $^{13}C\{^{1}H\}$ NMR (CD_3CN): δ = 180.4 (N=CH); 134.2 (*ipso*-Ph); 131.3, 129.0, 128.7 (Ph); 50.3 (NMe_2); 37.1 (CH_2) ppm. ^{93}Nb NMR (CD_3CN): δ = 6.3 ($\Delta\nu1/2 = 2.8 \times 10^2$) ppm.

$[(C_6H_5CH_2)CH{=}NMe_2][NbBr_6]$, ***2b***. From $NbBr_5$ (0.275 g, 0.55 mmol) and *N*,*N*-dimethyl-L-phenylalanine (0.113 g, 0.55 mmol). Dark brown crystals, 0.168 g (42% yield based on Nb). Anal. Calcd for $C_{10}H_{14}Br_6NNb$: C, 16.67; H, 1.96; N, 1.94, Br, 66.53; Nb, 12.89. Found: C, 16.47; H, 1.70; N, 1.75; Br, 65.99; Nb, 12.00%. IR spectrum (solid state): 3003w, 2835w, 1683s ($\nu_{C=N}$), 1599w, 1496m, 1454m, 1429m, 1407w, 1371m, 1262w, 1196w, 1156m, 1083m, 1059w, 1029m, 949w, 914m-s, 803s, 781s, 726vs, 695vs cm^{-1}.^{1}H NMR (CD_3CN): δ = 8.32 (s, 1H, N=C*H*); 7.45−7.36 (m, 5H, Ph); 4.05 (s, 2H, CH_2); 3.66, 3.58 (s, 6H, NMe_2) ppm. $^{13}C\{^{1}H\}$ NMR (CD_3CN): δ = 180.5 (N=CH); 134.0 (*ipso*-Ph); 131.5, 129.3, 128.2 (Ph); 50.3 (NMe_2); 37.4 (CH_2) ppm.

$[(C_6H_5CH_2)CH{=}NMe_2][TaCl_6]$, ***2c***. From $TaCl_5$ (0.260 g, 0.72 mmol) and *N*,*N*-dimethyl-L-phenylalanine (0.147 g, 0.72 mmol). Colorless microcrystalline solid, 0.183 g (47% yield based on Ta). Anal. Calcd for $C_{10}H_{14}Cl_6NTa$: C, 22.16; H, 2.60; N, 2.58, Cl, 39.25; Ta, 33.39. Found: C, 22.00; H, 2.40; N, 2.75; Cl, 38.70; Ta, 32.40%. IR spectrum (solid state): 3016w, 1691s ($\nu_{C=N}$), 1598w, 1493m, 1453m, 1410w, 1262w, 1241w, 1173m, 1084m, 1024m, 964w, 918w, 787m-s, 747vs, 695vs cm^{-1}. ^{1}H NMR (CD_3CN): δ = 8.34 (s, 1H, N=C*H*); 7.57−7.38 (m, 5H, Ph); 4.03 (s, 2H, CH_2); 3.65, 3.57 (s, 6H, NMe_2) ppm. $^{13}C\{^{1}H\}$ NMR (CD_3CN): δ = 180.4 (N=CH); 134.2 (*ipso*-Ph); 131.6, 129.3, 128.2 (Ph); 50.3 (NMe_2); 37.4 (CH_2) ppm.

$[(C_6H_5CH_2)CH{=}NMe_2][TaBr_6]$, ***2d***. From $TaBr_5$ (0.312 g, 0.53 mmol) and *N*,*N*-dimethyl-L-phenylalanine (0.109 g, 0.53 mmol). Dark brown crystals, 0.201 g (47% yield based on Ta). Anal. Calcd for

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$C_{10}H_{14}Br_6NTa$: C, 14.85; H, 1.75; N, 1.73, Cl, 59.29; Ta, 22.38. Found: C, 14.29; H, 1.60; N, 1.59; Cl, 59.45; Ta, 21.95%. IR spectrum (solid state): 2962w, 2838w, 1683s ($\nu_{C=N}$), 1581w, 1496m, 1452w, 1428m, 1407w, 1371m, 1260m-s, 1196w, 1155w, 1084m, 1022m, 914m, 803w, 781vs, 726vs, 690vs cm^{-1}.^{1}H NMR (CD_3CN): δ = 8.32 (s, 1H, N=C*H*); 7.45−7.30 (m, 5H, Ph); 4.04 (s, 2H, CH_2); 3.66, 3.58 (s, 6H, NMe_2) ppm. $^{13}C\{^1H\}$ NMR (CD_3CN): δ = 180.3 (N=*C*H); 134.6 (*ipso*-Ph); 131.7, 129.3, 128.9 (Ph); 50.5 (NMe_2); 37.6 (CH_2) ppm.

[(PhCH$_2$)CH=NH$_2$][NbCl$_6$], ***3a***. From $NbCl_5$ (0.288 g, 1.06 mmol) and L-phenylalanine (0.174 g, 1.06 mmol). Yellow solid, 0.204 g (45% yield based on Nb). Anal. Calcd for $C_8H_{10}Cl_6NNb$: C, 22.57; H, 2.37; N, 3.29; Cl, 49.96; Nb, 21.82. Found: C, 22.20; H, 2.20; N, 372; Cl, 49.01; Nb, 21.29%. IR spectrum (solid state): 3110w-br, 2924w, 1685s ($\nu_{C=N}$), 1587m-s, 1492s, 1453m, 1438w, 1381s, 1288s, 1245m, 1208vs, 1133w, 1090w, 1068s, 918m, 852m, 810m-s, 752s, 735vs, 697vs, 671s cm^{-1}. ^{1}H NMR (CD_3CN): δ = 10.40 (s, 1H, N=C*H*); 7.3 (5H, Ph); 6.7 (br, 2H, NH_2); 4.32 (m, 1H, C*H*); 3.31 (m, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (CD_3CN): δ = 167.8 (N=*C*H); 133.2 (*ipso*-Ph); 129.8, 129.4, 128.2 (Ph); 35.2 (CH_2) ppm.

[(PhCH$_2$)CH=NH$_2$][NbBr$_6$], ***3b***. From $NbBr_5$ (0.246 g, 0.50 mmol) and L-phenylalanine (0.082 g, 0.50 mmol). Orange solid, 0.166 g (48% yield based on Nb). Anal. Calcd for $C_8H_{10}Br_6NNb$: C, 13.88; H, 1.46; N, 2.02; Br, 69.23; Nb, 13.42. Found: C, 13.40; H, 1.20; N, 2.32; Br, 69.01; Nb, 13.00%. IR spectrum (solid state): 3090m-br, 2956w, 2916w, 1681s ($\nu_{C=N}$), 1589m-s, 1491s, 1455m, 1439w-m, 1380s, 1286s, 1260s, 1240s, 1206vs, 1068vs, 1037s, 918m, 810vs, 751s, 695vs, 671s cm^{-1}.

[(Me$_2$CHCH$_2$)CH=NH$_2$][NbCl$_6$], ***4***. From $NbCl_5$ (0.269 g, 1.00 mmol) and L-leucine (0.131 g, 1.00 mmol). Yellow solid, 0.176 g (45% yield based on Nb). Anal. Calcd for $C_5H_{12}Cl_6NNb$: C, 15.33; H, 3.09; N, 3.58; Cl, 54.30; Nb, 23.71. Found: C, 15.08; H, 3.20; N, 3.92; Cl, 53.91; Nb, 23.10%. IR spectrum (solid state): 3180m-br, 3134m-br, 2961w-m, 2929w, 1698s ($\nu_{C=N}$), 1578m, 1478vs, 1362w, 1341w, 1320w, 1276m, 1261m, 1222s, 1166m, 1104s, 1036m, 1022m, 936m, 890w, 802s, 730m cm^{-1}.

[CH$_2$=NHMe][NbCl$_6$], ***5***. From $NbCl_5$ (0.270 g, 1.00 mmol) and *N*-methylglycine (0.089 g, 1.00 mmol). Yellow crystalline solid, 0.154 g (44% yield based on Nb). Anal. Calcd for $C_2H_6Cl_6NNb$: C, 6.87; H, 1.73; N, 4.01; Cl, 60.83; Nb, 26.57. Found: C, 6.30; H, 1.50; N, 3.92; Cl, 60.03; Nb, 25.99%. IR spectrum (solid state): 3160br, 2996w, 2952w, 1691vs ($\nu_{C=N}$), 1456m-s, 1402m, 1371s, 1264vs, 1161m, 1102w, 1037m, 956s, 807s, 715s cm^{-1}.

(B). Isolation of NbCl$_3$(O$_2$CH)[O$_2$CCH(CH$_2$Ph)NMe$_2$], ***6***. Following the procedure for the synthesis of **2a**, a dark yellow solution was obtained from $NbCl_5$ (0.420 g, 1.55 mmol) and *N*,*N*-dimethyl-L-phenylalanine (0.300 g, 1.55 mmol). The solution was layered with hexane and settled aside at −30 °C for 72 h. The resulting solution was separated from the crystalline precipitate (**2a**) and dried in vacuo at room temperature. The orange residue was washed with toluene (2 × 20 mL) and dried in vacuo. Compound **6** was recovered as an orange solid. Yield 0.197 g, 30% based on Nb. Anal. Calcd for $C_{11}H_{14}Cl_3NNbO_4$: C, 31.20; H, 3.33; N, 3.31, Cl, 25.11; Nb, 21.94. Found: C, 30.95; H, 3.11; N, 3.15; Cl, 25.45; Nb, 21.20%. IR spectrum (solid state): 3093w, 3069w, 2966w, 1604m ($\nu_{asym,COO,\ formate}$), 1584m ($\nu_{asym,COO,\ amino\ acidato}$), 1478m, 1442m, 1415m ($\nu_{sym,COO,\ amino\ acidato}$), 1378m ($\nu_{sym,COO\ formate}$), 1354w, 1343w, 1316w, 1266vs, 1195w, 1157w, 1144vs, 1078m, 1052w, 1031w-m, 989s, 959s, 945m, 887w, 862w, 816s, 753m, 736w, 698s, 674s cm^{-1}. ^{1}H NMR (CD_3CN): δ = 11.6 (br, 1H, *H*COO); 7.6−7.4 (5H, Ph); 4.40 (br, 1 H, CH); 3.93, 3.83 (s, 6H, NMe_2), 3.35 (br, 1 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (CD_3CN): δ = 182.3 (HCOO); 170.0 (OCO); 134.1−129.6 (Ph); 69.1 (CH); 52.5 (NMe_2); 39.2 (CH_2) ppm.

(4). X-ray Crystallography. Crystal data and collection details for **2a**, **2b**, and **2d** are reported in Table 1. The diffraction experiments were performed on a Bruker APEX II diffractometer equipped with a CCD detector using Mo Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[18] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[19] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were fixed at calculated positions and refined by a riding model, except H(1) in **2a**, which was located in the Fourier map and refined isotropically. The asymmetric unit of the unit cell of **2a** contains two $[(C_6H_5CH_2)CH{=}NMe_2]^+$ cations and one $[NbCl_6]^-$ anion located on general positions and two halves of two $[NbCl_6]^-$ anions located on inversion centers. The crystals of **2a** are pseudomerohedrally twinned with twin matrix −1 0 0 0−1 0 0 0 1 and refined batch factor 0.0482(4). The crystals of **2b** and **2d** are isomorphous, and their asymmetric units contain three $[(C_6H_5CH_2)$-$CH{=}NMe_2]^+$ cations and three $[MBr_6]^-$ anions located on general positions. The crystals of **2b** are racemically twinned with refined batch factors 0.49(2) and 0.49(3), respectively. Similar *U* restraints were applied to the C and N atoms of **2b** (s.u. 0.005) and the C atoms of **2c** (s.u. 0.01). All the C and N atoms of **2b** and some C and N atoms of **2d** were restrained to an isotropic-like behavior (ISOR line in SHELXL, s.u. 0.01). Some high residual electron densities are present in the structures of **2b** and **2d** (ALERT A and B in the checkcif file) close to the heavier atoms (Nb, Ta, and Br). These are due to absorption effects, which have been only partially corrected by SADABS.

Table 1. Crystal Data and Experimental Details for 2a, 2b, and 2d

	2a	2b	2d
formula	$C_{10}H_{14}Cl_6NNb$	$C_{10}H_{14}Br_6NNb$	$C_{10}H_{14}Br_6NTa$
Fw	453.83	720.59	808.63
T, K	100(2)	100((2)	100((2)
λ, Å	0.71073	0.71073	0.71073
crystal system	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/c$	$Pca2_1$	$Pca2_1$
a, Å	7.1372(9)	42.613(14)	42.859(6)
b, Å	28.110(3)	7.231(2)	7.2764(11)
c, Å	16.105(2)	16.799(5)	17.012(2)
β, deg	90.3200(10)	90	90
cell volume, Å^3	3230.9(7)	5176(3)	5305.3(13)
Z	8	12	12
D_c, g cm^{-3}	1.866	2.744	3.037
μ, mm^{-1}	1.719	14.576	19.756
F(000)	1792	3984	4368
crystal size, mm	0.21 × 0.20 × 0.18	0.18 × 0.12 × 0.10	0.21 × 0.15 × 0.10
θ limits, deg	1.26−26.00	1.54−25.03	1.53−25.03
reflections collected	31800	44185	45185
independent reflections	6351 [R_{int} = 0.0330]	8820 [R_{int} = 0.0929]	8854 [R_{int} = 0.0676]
data/restraints/parameters	6531/2/335	8820/397/488	8854/223/488
goodness of fit on F^2	1.032	1.025	1.072
R_1 ($I > 2\sigma(I)$)	0.0266	0.0669	0.0469
wR_2 (all data)	0.0663	0.1672	0.1101
largest diff. peak and hole, e Å^{-3}	0.654/−0.630	1.441/−4.452	3.879/−3.397

(5). Computational Studies. The computational geometry optimizations were performed without symmetry constraints, using the hyper-GGA DFT functional M06[20] in combination with a polarized basis set composed by the 6-31G(d,p) set on the light atoms and the ECP-based LANL2TZ(f) set on the metal center.[21] The C-PCM implicit solvation model (ε = 9.08) was added.[22] Geometry optimizations were also performed using the hybrid-GGA EDF2 functional[23] and the LACVP** basis set,[24] and this method was applied for coordinate driving studies. In all the cases the "restricted" formalism was applied. The stationary points were characterized by IR simulations (harmonic approximation), from which zero-point vibrational energies and thermal corrections were obtained.[25] The software

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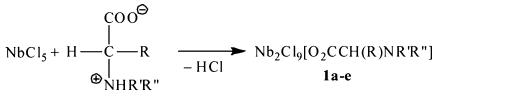
Inorg. Chem. 2015, 54, 4047−4055

used for M06/C-PCM calculations was Gaussian 09,[26] while EDF2 calculations were performed with Spartan 08.[27]

RESULTS AND DISCUSSION

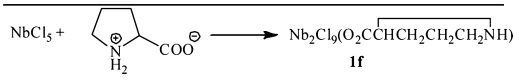
Synthesis and Characterization. *(a). α-Amino Acidato Complexes.* Niobium pentachloride slowly reacted with 0.5 equiv of α-amino acids, $O_2CCH(R)NHR'R''$, in dichloromethane with evolution of 1 equiv of HCl. After workup, yellow to orange microcrystalline solids were isolated corresponding to the general formula $Nb_2Cl_9[O_2CCH(R)NR'R''$-κO,κO], **1a−f**, Scheme 1.

Scheme 1. Synthesis of Niobium(V) Chloride α-Amino Acidato Complexes



2:1 Nb/aminoacid molar ratio

R	R'	R''	
Me_2CHCH_2	H	H	**1a**
$PhCH_2$	H	H	**1b**
$MeSCH_2CH_2$	H	H	**1c**
H	H	Me	**1d**
$PhCH_2$	Me	Me	**1e**



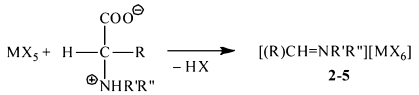
Compounds **1a−f** were characterized by analytical and spectroscopic methods. The IR spectra (solid state) are featured by one medium and one strong intensity absorption in the range of 1600−1400 cm^{-1}. These are due, respectively, to the asymmetric (ν_a) and the symmetric (ν_s) stretching vibrations of the carboxylato group. In general, the wavenumber difference ($\Delta\nu_{a-s} = \nu_a - \nu_s$) is considered as a useful parameter to discriminate between monodentate, chelating, and bridging-bidentate coordination modes. Values within the range from 100 to 150 cm^{-1} have been assigned to chelating or bidentate-bridging carboxylato groups.[28] In view of the IR data [$\Delta\nu_{a-s}$ varies between 83 (**1a**) and 155 (**1d**) cm^{-1}] and the DFT results (vide infra), we propose a bidentate-bridging coordination of the carboxylato moiety in **1a−f**.

Compounds **1a,c,d** revealed to be insoluble in non-coordinating solvents, thus preventing their NMR characterization. On the other hand, the ^1H and ^{13}C NMR spectra (CD_2Cl_2) of the more soluble **1b,e,f** displayed single sets of resonances. The major feature is represented by the ^{13}C resonance of the carboxylate carbon, occurring at 170−175 ppm.

Clear ^{93}Nb NMR spectra could be recorded on samples of **1b,e,f**. The spectra of **1b** and **1f** showed two broad resonances (e.g., at 34.9 and −56.7 ppm in the case of **1b**), presumably ascribable to two nonequivalent niobium centers within a dinuclear frame. Otherwise, only one broad resonance was clearly recognized in the spectrum of **1e** (−61.7 ppm). These features will be discussed in the DFT section in the light of computational results.

(b). Iminium Hexahalometalates. To elucidate the possible effect of the stoichiometry in the reactions of $NbCl_5$ with α-amino acids, a CD_2Cl_2 solution of the highly soluble compound **1e** was added of 1 equiv of *N,N*-dimethylalanine in a NMR tube. The ^{13}C NMR spectrum of the resulting solution indicated the disappearance of the starting material and the formation of two new products in comparable ratio. A small amount of solid sluggishly precipitated from the solution: the IR spectrum of this solid suggested the presence of one single species only. With the aim of isolating and characterizing this latter, a larger amount of $NbCl_5$ was treated with *N,N*-dimethyl-L-phenylalanine in 1:1 molar ratio in dichloromethane. A slow reaction took place with release of HCl (see Experimental Section). The mixture was filtered to remove minor amounts of insoluble material, then the resulting solution was layered with hexane. Thus, a crystalline material was collected and identified as the iminium salt $[(C_6H_5CH_2)CH{=}NMe_2][NbCl_6]$ **2a**; see Scheme 2. Analogous reactivity was observed concerning the 1:1 molar reactions of MX_5 with a series of α-amino acids, affording **2b−d**, **3a−b**, **4**, and **5** (Scheme 2).

Scheme 2. Synthesis of Iminium Salts from α-Amino Acids



1:1 Nb/aminoacid molar ratio

R	R'	R''	M	X	
$PhCH_2$	Me	Me	Nb	Cl	**2a**
$PhCH_2$	Me	Me	Nb	Br	**2b**
$PhCH_2$	Me	Me	Ta	Cl	**2c**
$PhCH_2$	Me	Me	Ta	Br	**2d**
$PhCH_2$	H	H	Nb	Cl	**3a**
$PhCH_2$	H	H	Nb	Br	**3b**
Me_2CHCH_2	H	H	Nb	Cl	**4**
H	H	Me	Nb	Cl	**5**

Compounds **2−5** were characterized by analytical and spectroscopic (IR and NMR) techniques, and by X-ray diffractometry in the cases of **2a,b,d**. A search in the literature indicated that the iminium cations $[(PhCH_2)CH{=}NMe_2]^+$ (found in **2a−d**) and $[(Me_2CHCH_2)CH{=}NH_2]^+$ (found in **4**) are described here for the first time. Instead $[(PhCH_2)CH{=}NH_2]^{+29}$ and $[CH_2{=}NHMe]^{+30}$ were previously reported, but only the latter was studied in detail by spectroscopic methods.[30a]

X-ray quality crystals of **2a**, **2b**, and **2d** were obtained by fractional crystallization procedures from CH_2Cl_2/hexane mixtures at room temperature. All of the structures (see Figure 1 and Table 2) consist of ionic packings of octahedral $[MX_6]^-$ anions and $[(C_6H_5CH_2)CH{=}NMe_2]^+$ cations. The unprecedented crystallographic characterization of the iminium $[(C_6H_5CH_2)CH{=}NMe_2]^+$ shows geometric parameters, which are as expected for such class of compounds.[31]

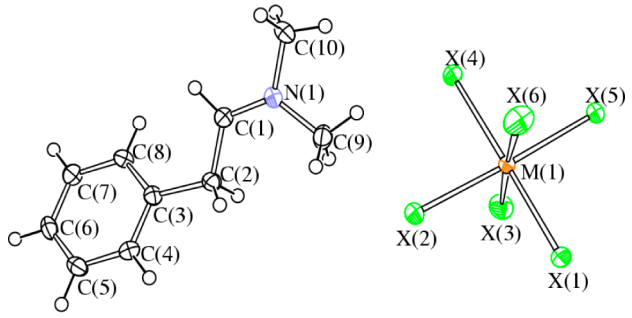


Figure 1. Molecular structure of $[(C_6H_5CH_2)CH{=}NMe_2][MX_6]$ (M = Nb, X = Cl, **2a**; M = Nb, X = Br, **2b**; M = Ta, X = Br, **2d**) with key atoms labeled. Displacement ellipsoids are at the 50% probability level.

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Inorg. Chem. 2015, 54, 4047−4055

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2a, 2b, and 2d

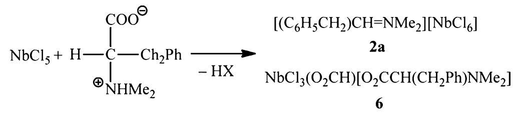
	2a	2b	2d
M(1)−X(1)	2.3547(8)	2.495(2)	2.5008(16)
M(1)−X(2)	2.3416(8)	2.500(2)	2.5125(18)
M(1)−X(3)	2.3432(8)	2.478(3)	2.5004(13)
M(1)−X(4)	2.3594(7)	2.470(3)	2.4933(16)
M(1)−X(5)	2.3546(7)	2.492(2)	2.5075(14)
M(1)−X(6)	2.3467(8)	2.489(2)	2.5085(18)
N(1)−C(1)	1.285(4)	1.32(2)	1.32(2)
N(1)−C(10)	1.476(3)	1.50(3)	1.49(2)
N(1)−C(9)	1.469(4)	1.49(2)	1.50(2)
C(1)−C(2)	1.488(4)	1.39(3)	1.44(2)
C(2)−C(3)	1.511(4)	1.54(3)	1.54(2)
X(1)−M(1)−X(4)	177.98(3)	179.70(11)	178.44(5)
X(2)−M(1)−X(5)	176.88(3)	179.21(11)	177.05(6)
X(3)−M(1)−X(6)	176.96(3)	179.26(11)	178.89(6)
C(1)−N(1)−C(9)	122.9(2)	115.3(17)	129.8(14)
C(1)−N(1)−C(10)	122.0(2)	130.9(17)	116.2(15)
C(9)−N(1)−C(10)	115.1(2)	113.7(15)	114.0(13)
N(1)−C(1)−C(2)	123.1(3)	122.9(19)	122.0(17)
C(1)−C(2)−C(3)	115.6(2)	115.2(18)	115.5(15)

The IR spectra of **2**−**5** (solid state) exhibited a strong, diagnostic absorption at 1681−1698 cm^{-1}, attributed to the iminium moiety.[30,31c,32] In the NMR spectra of **2a**−**d** (CD_3CN), containing the $[(PhCH_2)CH{=}NMe_2]^+$ cation, the salient resonances related to the iminium moiety were found at ca. 8.3 (^1H) and 180 (^{13}C) ppm. The NMR spectra of **3a** (in CD_3CN), containing $[(C_6H_5CH_2)CH{=}NH_2]^+$, exhibited the resonances due to the [CH═N] unit at 10.40 (^1H) and 167.8 (^{13}C) ppm. The ^{93}Nb NMR spectrum of **2a** consists of the typically sharp peak ascribable to the $[NbCl_6]^-$ anion, at 6.3 ppm.[13e,33] **3b**, **4**, and **5** could not be NMR-characterized due to scarce solubility.

The syntheses of **2**−**5** appear to be the result of removal of the carboxylato moiety from the amino acid substrate. In general, this transformation is accompanied by CO_2 release. For instance, naturally occurring α-amino acids are known to undergo biogenic decarboxylation by substrate-specific decarboxylase enzymes, affording amines and CO_2.[34] Moreover, electrochemical oxidation procedures[35] or appropriate oxidative synthetic systems[36] are used to convert α-amino acids into a variety of organic species (e.g., cyclic acyl-acetals, aldehydes, arylpyrrolidinones, azabicycloalkanes, amino acid esters), via the loss of CO_2 and the intermediacy of iminium ions.

We performed experiments aimed to elucidate the destiny of the [COO] moiety and, thus, the identity of the coproducts of the reactions leading to the iminium salts **2**−**5**. Unambiguous results were achieved with reference to the 1:1 reaction of $NbCl_5$ with *N*,*N*-dimethyl-L-phenylalanine. According to IR and NMR evidence, **2a** is generated from $NbCl_5$/*N*,*N*-dimethyl-L-phenylalanine in admixture with one prevalent niobium byproduct. This could be isolated as a microcrystalline material (unfortunately, we were not able to collect X-ray quality crystals), which was identified as the complex $NbCl_3(O_2CH)[O_2CCH(CH_2Ph)NMe_2]$, **6** (Scheme 3), on the basis of elemental analysis, IR (solid state) and NMR (CD_3CN solution) spectroscopy. Diagnostic IR bands at 1584/1415 and 1604/1378 cm^{-1}, respectively, were attributed to the amino acidato and the formate units, both behaving as O−O bidentate ligands.[37] Related ^{13}C NMR resonances (CD_2Cl_2 solution) were recognized at 182.3 and 170.0 ppm. The ^1H NMR resonance due to the formate proton was detected at 11.6 ppm.

Scheme 3. Reaction of $NbCl_5$ with *N*,*N*-Dimethylphenylalanine



Density Functional Theory Calculations. To give insight into the formation of the iminium salts, we performed DFT calculations on the ground state of **1e** and its reaction with *N*,*N*-dimethyl-L-phenylalanine. As reported in the Supporting Information, Figure S1, several starting structures were considered for $Nb_2Cl_9[O_2CCH(CH_2Ph)NMe_2]$, differing in the coordination mode of the α-amino acidato ligand. A comparison among the Gibbs free energies of the isomers, optimized both in gas phase and in the presence of dichloromethane as implicit solvent (C-PCM model), indicate that the most stable species (**1e-is1** in Figure 2 and Supporting Information, Figure S1) bears a bridging Cl ligand and a bridging bidentate $\kappa O,\kappa O$-carboxylate. Notwithstanding, another geometry (**1e-is2** in Figure S1) is very close in energy (ΔG = 0.6 or 2.5 kcal mol^{-1}, according to M06/C-PCM and EDF2 calculations, respectively). **1e-is2** is featured by a α-amino acidato [N,O]-coordinated to a $[NbCl_4]$ fragment, linked in turn to a second Nb center via a Cl-bridge. Supporting Information, Table S1 collects selected computed bond lengths and angles for **1e-is1** and **1e-is2**. In accordance with IR (bidentate coordination of the COO fragment) and ^{93}Nb NMR (one resonance detected) evidence, we regard **1e-is1** as the experimentally observed structure.

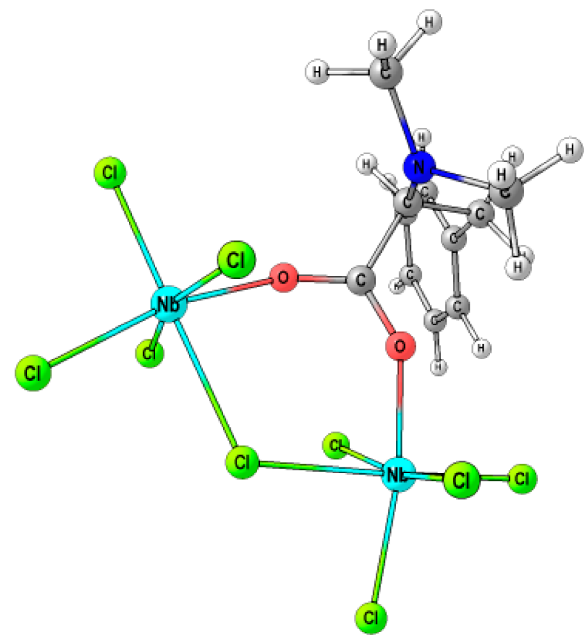


Figure 2. DFT-optimized structure of **1e** (M06/C-PCM calculations).

Since the ^{93}Nb NMR pattern of **1e** is unique in that one resonance is clearly observable, while the ^{93}Nb spectra of **1a-d,f** display two distinguishable resonances (see above), it may be concluded that the structure of the complexes is influenced by the degree of N-substitution. To elucidate this point, we

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Inorg. Chem. 2015, 54, 4047−4055

performed DFT calculations on **1a** and **1f** (see Supporting Information, Figures S2 and S3 and Tables S2 and S3). In both cases, the calculated most stable structure is featured by the α-amino acidato moiety acting at the same time as [N,O]- and [O,O]-chelating ligand toward two different niobium centers (Figures 3 and 4). This computer result might be reasonably

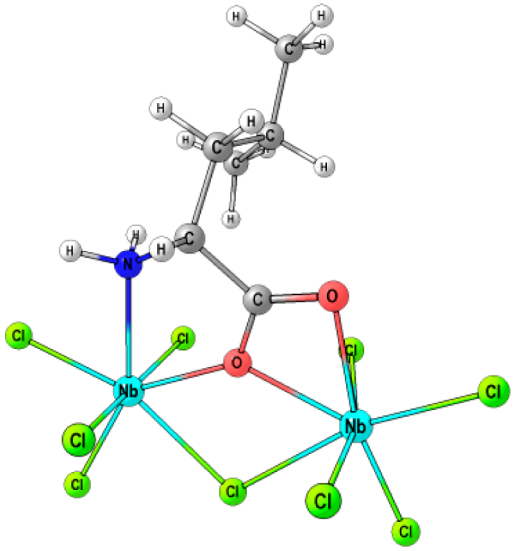

Figure 3. DFT-optimized structure of **1a** (M06/C-PCM calculations).

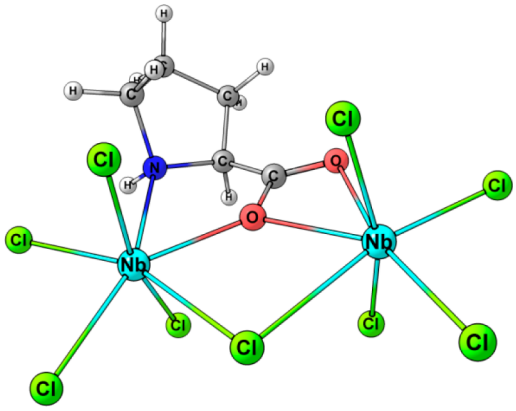

Figure 4. DFT-optimized structure of **1f** (M06/C-PCM calculations).

extended to **1b,c,d**: in fact, **1a-d,f** share spectroscopic features pointing to the presence of two nonequivalent niobium centers and a bidentate coordination of the COO fragment (see above).

We can conclude that the degree of substitution of the N atom is of paramount importance for the relative stability of the isomers: more precisely, [N,O]-chelation is favored for primary and secondary amino groups (Figures 3 and 4); in contrast, steric factors presumably exclude the dimethylamino group from coordination (Figure 2).

The reaction of the most stable isomer of **1e** with 1 equiv of *N*,*N*-dimethyl-L-phenylalanine was computationally investigated. According to the calculations, the initial result of the interaction (Supporting Information, Figure S4 and Table S4) is a change in the coordination mode of the pre-existing α-amino acidato ligand (from bridging bidentate to bidentate toward a single niobium atom). This rearrangement is accompanied by monodentate O-coordination of the α-amino acid reactant, in zwitterionic form, to the remaining metal center (Figure 5). The two resulting metal frames may be connected via NH···O hydrogen bond.

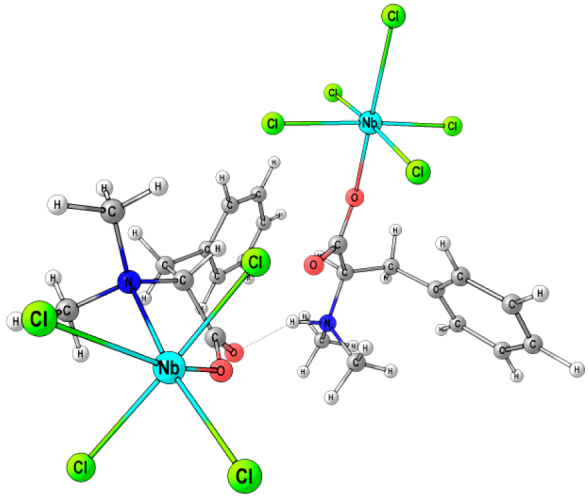

Figure 5. DFT-optimized geometry of the initial **1e**-*N*,*N*-dimethyl-phenylalanine interaction (M06/C-PCM calculations).

Such hydrogen bond interaction possibly plays a crucial role in leading to the formation of the iminium product (**2a**). To investigate this point, we performed a coordinate-driving study on two model systems based on *N*,*N*-dimethyl-L-phenylalanine, that is, $NbCl_4(N,O{-}OCOCH(CH_2Ph)NMe_2)$ and its protonated derivative $[NbCl_4(N,O{-}OCO(\mathbf{H})CH(CH_2Ph)NMe_2)]^+$, by lengthening the bond linking the carboxylate moiety to the remaining $[CH(CH_2Ph)NMe_2]$ fragment (Figure 6). In both cases, elongation of such C−C bond led to the dissociation of the Nb−N bond and the consequent formation of the $[(PhCH_2)CH{=}NMe_2]^+$ cation. Importantly, the energy variation of this process was more than 20 kcal mol^{-1} lower in the case of the O-protonated species, whose energy profile appears consistent with the experimental evidence of the facile formation of the iminium cation (Figure 6). In other terms, the conversion of α-amino acidate complexes into iminium species, promoted by the addition of further α-amino acid, is presumably viable in view of the Brönsted acidic character of the latter. This consideration triggered us to study the reactivity of **1e** with $[NH_2Et_2]Br$, which was selected for the purpose as a CH_2Cl_2-soluble Brönsted acid. Unfortunately, the reaction afforded a complicated mixture of products, which could not be separated.

The formate/α-amino acidate complex **6** is the identified coproduct of the reaction forming **2a** (see above). To propose a structure for **6**, we calculated a series of possible mono- and dinuclear isomers (see Supporting Information, Figure S5 for details). The most stable structure found for **6** consists of a heptacoordinate mononuclear complex possessing distorted pentagonal bipyramidal geometry (Figure 7). Both the formate and the amino acidato ligands are in equatorial position and exhibit κ^2 coordination by their oxygen atoms; a collection of computed bond lengths and angles is supplied in Supporting Information, Table S5.

According to the calculations, the formation of **2a** and **6** from $NbCl_5$/*N*,*N*-dimethyl-L-phenylalanine is a thermodynamically favorable reaction (eq 1).

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Inorg. Chem. 2015, 54, 4047−4055

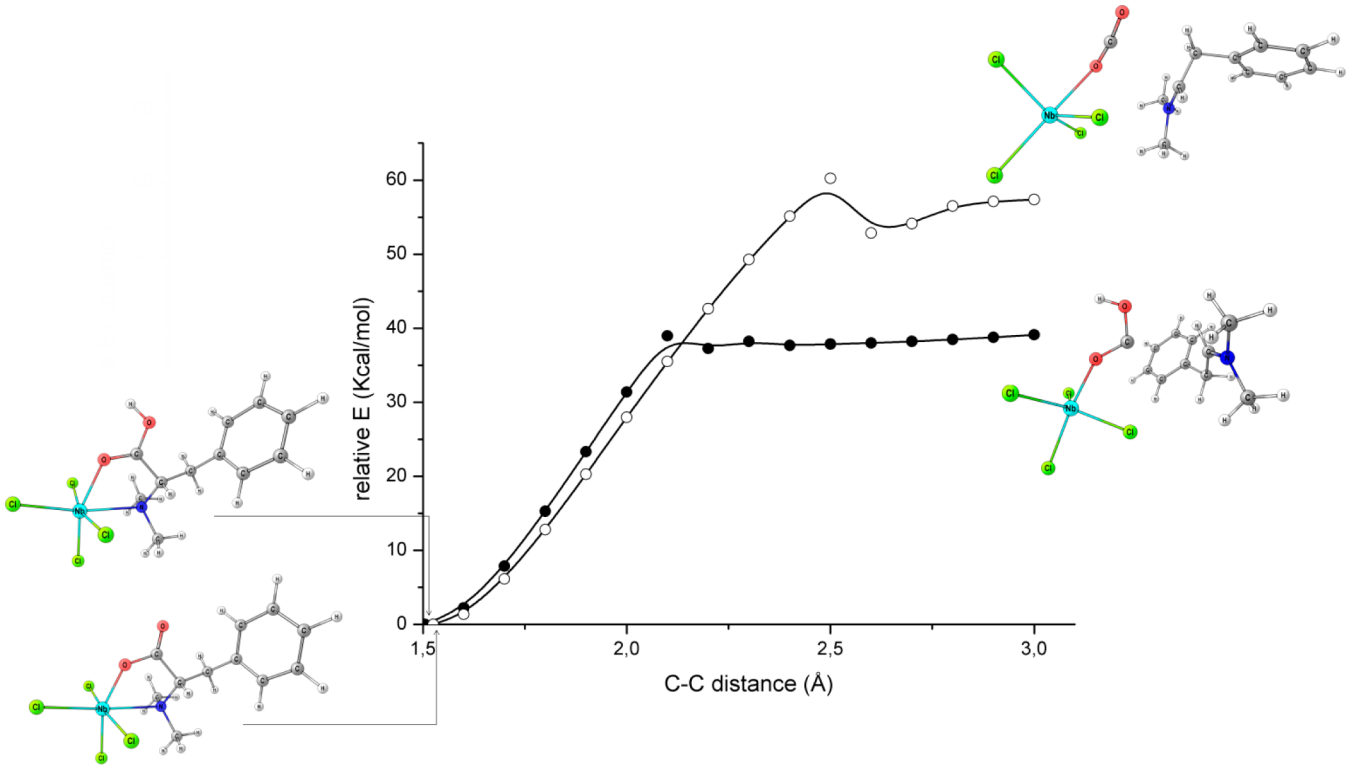

Figure 6. Energy profiles (electronic energy + nuclear repulsion; EDF2 calculations) for the elongation of the C−C bond between the carboxylate moiety and the $[CH(CH_2CHMe_2)NMe_2]$ fragment in $NbCl_4(N,O{-}OCOCH(CH_2Ph)NMe_2)$ (white dots) and $[NbCl_4(N,O{-}OCO(H)CH(CH_2Ph)NMe_2)]^+$ (black dots). Equilibrium geometries taken as references.

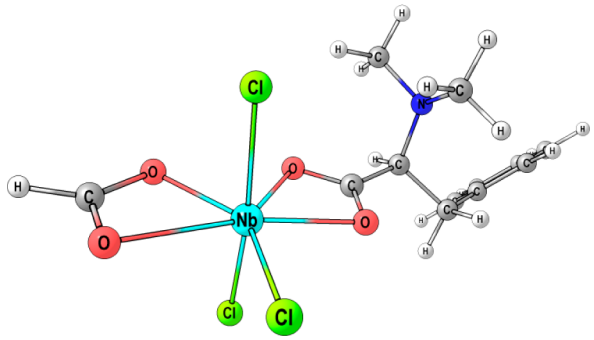

Figure 7. DFT-optimized geometry (M06/C-PCM calculations) of the most stable isomers of **6**.

$$2NbCl_5 + 2HO_2CCH(CH_2Ph)NMe_2 \rightarrow \mathbf{2a} + \mathbf{6} + HCl$$
$$\Delta G = -4.5 \text{kcal mol}^{-1} \quad (1)$$

An interesting comparison may be traced between the behavior of $NbCl_5$ and that of PCl_5. The latter has been traditionally employed as a chlorinating agent of the carboxylic function belonging to primary α-amino acids, affording $POCl_3$ and acyl chloride derivatives;[38] instead, the Cl-transfer may result in CO evolution when N-mono- or disubstituted α-amino acids are involved.[39] The different outcomes of the parallel reactions of $NbCl_5$ (and related group 5 halides) may be explained on the basis of the relatively high value of the Nb−Cl bond energy (97.5 kcal mol^{-1} in $NbCl_5$;[40] average value of P−Cl bond energy in PCl_5[41] is 60 kcal·mol^{-1}), inhibiting Cl/O interchange.

CONCLUSIONS

Information available on the interaction of α-amino acids with high-valent transition metal halides is rather sparse. Herein we have described the reactivity of $NbCl_5$ with a selection of α-amino acids: dinuclear α-amino acidate complexes are selectively generated when α-amino acid/Nb = 0.5 molar ratio is employed. By increasing the ratio to 1, activation of 0.5 equiv of organic material may be observed, consisting of selective C_{asym}−C(O) bond cleavage. This outcome has been extended by using $NbBr_5$, $TaCl_5$, or $TaBr_5$ as the metal reactant. The carboxylato group appears to be retained in the reaction system, presumably in the form of a formate ligand, as it has been demonstrated in one specific case. This contrasts with the generally known decarboxylative reactions of α-amino acids, accompanied by elimination of CO_2.

ASSOCIATED CONTENT

Supporting Information

Illustrations of the DFT-optimized isomers with relative Gibbs energies and selected bond lengths and angles of the most stable species. Structures in CIF file. Cartesian coordinates of all the computed structures are collected in a separate .xyz file (M06/C-PCM unless otherwise noted). This material is available free of charge via the Internet at http://pubs.acs.org. CCDC reference Nos. 1035988 (**2a**), 1035989 (**2b**), and 1035990 (**2d**) contain the supplementary crystallographic data for the X-ray studies reported in 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, U.K.; fax: (internat.) +44−1223/336−033; e-mail: deposit@ccdc.cam.ac.uk].

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⊥In Memoriam of Fausto Calderazzo (1930−2014).

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