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An Efficient Reduction Process Leading to Titanium(II) and Niobium(II): Preparation and Structural Characterization of *trans*-MCl$_2$(py)$_4$ Compounds, M = Ti, Nb, and Mn

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An easy way to produce the scarcely known mononuclear divalent coordination compounds of titanium and niobium by reduction of higher-valent species with potassium graphite, KC$_8$, in THF or THF−pyridine solutions is described. Also reported is the preparation and X-ray structural characterization of several *trans*-dichlorotetrakis(pyridine)-metal(II) species: *trans*-TiCl$_2$(py)$_4$·THF, **1**·THF, and three crystal forms of *trans*-NbCl$_2$(py)$_4$. The latter crystallize unsolvated in a tetragonal, **2*t***, and a monoclinic, **2*m***, form but the third type, **2**·0.5THF, has THF in the crystals. The propeller-like arrangement of the pyridine planes in the niobium polymorphs is very similar, but differs considerably from that of **1**·THF in which the pairs of trans pyridine molecules are coplanar. For comparison purposes, we also report the structure of *trans*-MnCl$_2$(py)$_4$. The variation of the M−N bond distances for the high-spin *trans*-MCl$_2$(py)$_4$ species of the first transition series shows the pattern expected from ligand field considerations with maxima at titanium and manganese and minima at vanadium and nickel.

Introduction

The development of the low-valent coordination chemistry of the elements of groups 4 and 5 has been very slow. Such chemistry for vanadium only recently bloomed due to the synthesis of a series of new starting materials which made possible a better understanding of the chemistry of the divalent oxidation state.[1]

Except for organometallic compounds,[2] complexes of niobium(II) are rare. A few phosphine adducts are known.[3] NbCl$_2$(PMe$_3$)$_4$[3a] was produced in low yield along with Nb(III) species by reduction of NbCl$_5$ or NbCl$_4$·2PMe$_3$ with Na/Hg in the presence of excess PMe$_3$. Higher yields were obtained for the dmpe[3b] analog. The only other divalent mononuclear compounds known are those of the type Nb(OAr)$_2$(dmpe)$_2$ (OAr = 4-methylphenoxide, 3,5-dimethylphenoxide, or phenoxide).[4] A few confacial bioctahedral dinuclear species with a Nb−Nb triple bond of the formula Nb$_2$X$_6$(THT)$_3$$^{2-}$ (X = Cl or Br and THT = tetrahydrothiophene) have also been reported.[5]

Considerable effort has been devoted to the understanding of the organometallic chemistry of titanium(II), particularly that of Cp$_2$TiL$_2$ and CpTiXL$_n$[6] or aryl-containing species,[7] but other areas have not been studied as extensively. There is a wide class of relatively ill-characterized low-valent titanium species commonly used in McMurry reactions in organic synthesis.[8] In the insoluble [HTiCl(THF)$_{\sim 0.5}$]$_x$ compound, there appears to be an extended array containing Ti−H−Ti and Ti−Cl−Ti bridges.[9] A few inorganic compounds containing Na, Ti, and Cl which were recently characterized are Na$_2$Ti$_3$Cl$_8$[10] and Na$_2$TiCl$_4$.[11] Another Ti(II) species which shows an extended structure is Ti(AlBr$_4$)$_2$.[12] There are only a handful of well-characterized mononuclear coordination compounds of divalent titanium. Among them are those which contain phosphine ligands such as TiCl$_2$(dmpe)$_2$,[13] Ti(BH$_4$)$_2$(dmpe)$_2$ and Ti(CH$_3$)$_2$(dmpe)$_2$[14] or alkoxide ligands such as Ti(OAr-2,6−*i*-Pr$_2$)$_2$(bipy).[15] Tetratolylporphyrinato compounds with other ligands such as pyridine and picoline are also known.[16] An amine-containing titanium(II) compound reported is the mononuclear *trans*-(TMEDA)$_2$TiCl$_2$, which was prepared by stirring TiCl$_3$(THF)$_3$ and Li metal in TMEDA over a period of 2 days.[17]

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Table 1. Crystallographic Data for *trans*-$TiCl_2(py)_4$ (**1**·THF), *trans*-$NbCl_2(py)_4$ (**2*t***), *trans*-$NbCl_2(py)_4$ (**2*m***), *trans*-$NbCl_2(py)_4$ (**2**·0.5THF) and *trans*-$MnCl_2(py)_4$ (**3**)

	1·THF	**2*t***	**2*m***	**2**·0.5THF	**3**
formula	$C_{24}H_{28}Cl_2N_4OTi$	$C_{20}H_{20}Cl_2N_4Nb$	$C_{20}H_{20}Cl_2N_4Nb$	$C_{22}H_{42}Cl_2N_4NbO_{0.5}$	$C_{20}H_{20}Cl_2N_4Mn$
fw	507.30	480.21	480.21	516.26	442.24
space group	$C2/c$	$I4_1/acd$	$P2_1/n$	$C2/c$	$P\bar{1}$
a, Å	14.884(1)	16.006(2)	9.3344(6)	16.622(5)	9.310(4)
b, Å	9.317(3)		16.755(2)	9.033(1)	13.576(5)
c, Å	18.167(2)	16.986(4)	13.381(2)	31.469(3)	9.2091(7)
α, deg					101.22(2)
β, deg			94.30(1)	99.98(1)	102.07(2)
γ, deg					73.40(2)
V, Å^3	2505.6(9)	4351(1)	2086.9(4)	4653(2)	1079.4(6)
Z	4	8	4	8	2
d_{calc}, g cm^{-3}	1.345	1.466	1.528	1.474	1.361
μ, mm^{-1}	0.578	0.810	0.845	0.765	0.870
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
temp, K	213(2)	213(2)	213(2)	213(2)	213(2)
R1,[a] wR2[b]	0.073, 0.17	0.089, 0.147	0.059, 0.117	0.050, 0.118	0.069, 0.152
R1,[a] wR2[b] (all data)	0.087, 0.18	0.110, 0.156	0.095, 0.142	0.075, 0.145	0.082, 0.159

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $wR2 = [\Sigma w[(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$.

Our studies have shown that one of the major obstacles in the development of the chemistry of low-valent coordination chemistry of titanium and niobium is the lack of easy synthetic routes for the preparation of materials containing labile ligands. We wish to report the preparation of reactive THF solutions of $TiCl_2$ as well as the X-ray structural characterization of the product from the reaction of such a solution and pyridine, namely *trans*-$TiCl_2(py)_4$, as well as the high yield synthesis and structural characterization of *trans*-$NbCl_2(py)_4$. For comparative purposes, we also report the structure of *trans*-$MnCl_2(py)_4$.

Experimental Section

In the preparation of divalent titanium and niobium compounds, all operations were carried out under an argon atmosphere using standard Schlenk techniques. Pyridine was purified by predrying over KOH, followed by distillation from CaH_2 under nitrogen. All other solvents were purified by conventional methods and distilled under nitrogen. Immediately prior to use, the solvents were degassed by three cycles of freezing, pumping and thawing. $TiCl_3$ and $NbCl_5$ were purchased from Aldrich Chemical Co. $NbCl_4(THF)_2$ was prepared as reported in the literature.[18] The well-known *trans*-$MnCl_2(py)_4$, **3**, was easily prepared by dissolving $MnCl_2 \cdot 4H_2O$ in neat pyridine and slowly evaporating the excess solvent. Potassium–graphite (KC_8) was prepared by heating the two components under an inert atmosphere at 150–200 °C for about 30 min.[8b,19] The IR spectra were recorded on a Perkin Elmer 16PC FT-IR spectrophotometer as Nujol mulls between KBr plates. UV–vis spectra were obtained on a Cary-17D spectrometer.

Preparation of $TiCl_2(THF)_n$ Solution. $TiCl_3$ (0.50 g, 3.2 mmol) was dissolved in 10 mL of THF and KC_8 (0.53 g, 3.9 mmol) was then added. After the mixture was stirred for 10 min at room temperature, it was filtered with the aid of glass wool and a glass frit. The black residue was washed with three 10 mL portions of THF, and these were added to the filtrate. A yellow-brown solution was obtained.

Preparation of *trans*-$TiCl_2(py)_4$·THF, 1·THF. Method 1. When a mixture of pyridine and toluene (5 mL each) was added slowly to a $TiCl_2(THF)_n$ solution, the color immediately turned blue. The solvent was removed under vacuum and the blue residue redissolved in toluene (15 mL), cooled to −40 °C, layered with hexanes (containing a few drops of pyridine), and kept at −40 °C for 3 days. Air-sensitive blue crystals were isolated by filtration and washed with cold hexanes (0.41 g, 25% yield).

Preparation of 1·THF. Method 2. In a typical experiment $TiCl_3$ (0.50 g, 3.2 mmol) was added to a mixture of THF, toluene, pyridine (5 mL each), and KC_8 (0.53 g, 3.9 mmol). The color of the mixture immediately turned blue. After the mixture was stirred for 10 min at room temperature, it was filtered with the aid of glass wool and a glass frit. The black residue was washed with three 10 mL portions of toluene, and these were added to the filtrate. The solvent was removed under vacuum, and the blue residue was treated as above. Air-sensitive blue crystals were isolated by filtration and were washed with cold hexanes (0.39 g, 24% yield). IR (cm^{-1}): 1600 (w), 1526 (w), 1260 (s), 1092 (s), 1022 (s), 799 (vs), 700 (w), 668 (w). UV–vis (toluene): λ_{max} (nm): 435, 500 (sh).

Preparation of *trans*-$NbCl_2(py)_4$. To a 16 mL mixture of THF/py (15:1) were added KC_8 (0.214 g, 1.58 mmol) and $NbCl_4(THF)_2$ (0.30 g, 0.79 mmol). The yellow reaction mixture immediately turned royal blue. It was stirred at room temperature for 2 h, and the mixture was then filtered through Celite. The solvents were removed under vacuum to give a crude product which was recrystallized from Et_2O containing a few drops of pyridine at −40 °C. Finally it was washed with cold hexanes to give a yield of 0.23 g (61%). Crystals suitable for X-ray diffraction were grown by layering a solution of the compound in THF with hexanes. Slow diffusion of the hexanes at room temperature produced crystals of **2*t***, whereas diffusion at −20 °C resulted in a mixture of **2**·0.5THF and **2*m***. IR: 1605 (w), 1525 (w), 1280 (s), 1105 (s), 1050 (s), 820 (vs), 710 (w), 625 (w), 530 (w). UV–vis: λ_{max} 496 nm ($\epsilon = 1.3 \times 10^3$).

X-ray Structure Determinations

Crystals were mounted on the tip of a glass fiber and quickly placed under a stream of N_2 at −75 °C. Data were collected on an Enraf-Nonius FAST area detector system utilizing the program MADNES.[20] Detailed procedures for data collection have been described previously.[21] All calculations were performed on a local area VAX cluster. Cell indexing was accomplished by using 50 reflections taken from three 10° ω-rotations in the range $0 \leq \omega \leq 100°$. The correct Laue group was confirmed by axial images. The refined cell typically used 250 reflections for least-squares fitting in the range $20 \leq 2\theta \leq 32°$. Foi data collection, the detector was set at a distance of 40 mm and a swing angle of 22.5°. Data were corrected for Lorentz and polarization effects

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Table 2. Atomic Coordinates ($\times 10^4$)

	x	*y*	*z*		*x*	*y*	*z*
Compound **1**·THF							
Ti(1)	5000	0	5000	C(21)	9171(4)	5099(7)	3300(3)
Cl(1)	6104(1)	1183(2)	4251(1)	C(22)	8634(4)	4789(8)	2651(3)
N(1)	4266(3)	2121(5)	5084(2)	C(23)	7984(4)	3760(8)	2662(4)
N(2)	9105(3)	4426(5)	3947(2)	C(24)	7910(4)	3038(7)	3311(3)
C(1)	3764(6)	2392(8)	5616(5)	C(25)	8469(4)	3394(6)	3934(3)
C(2)	3277(7)	3637(9)	5674(6)	O(1)	−16(2)	99(1)	287(2)
C(3)	3309(6)	4688(8)	5168(5)	C(50)	490(6)	114(1)	7541(8)
C(4)	3814(9)	4426(10)	4629(6)	C(51)	−787(6)	16(1)	2614(8)
C(5)	4272(8)	3132(9)	4603(5)				
Compound **2*t***							
Nb	0	2500	1250	C(2)	702(10)	981(8)	3360(8)
Cl	1110(2)	3610(2)	1250	C(3)	1560(1)	936(1)	3330(7)
N	679(5)	1783(5)	2171(4)	C(4)	1969(7)	1285(8)	2733(7)
C(1)	296(8)	1423(8)	2781(7)	C(5)	1529(8)	1720(7)	2168(6)
Compound **2*m***							
Nb(1)	1334(1)	7509(1)	5938(1)	C(23)	−3200(9)	9014(6)	4872(7)
Cl(1)	2881(2)	8505(1)	5110(2)	C(24)	−1999(9)	9403(5)	5299(6)
Cl(2)	−266(2)	6529(1)	6744(2)	C(25)	−761(9)	8975(4)	5536(6)
N(1)	3304(7)	6826(3)	6557(5)	C(31)	1356(8)	5932(4)	4658(6)
N(2)	−650(6)	8178(3)	5380(5)	C(32)	1382(8)	5420(5)	3846(7)
N(3)	1326(6)	6736(4)	4562(5)	C(33)	1378(9)	5734(5)	2910(7)
N(4)	1374(7)	8274(4)	7307(5)	C(34)	1340(9)	6542(5)	2801(7)
C(11)	3306(9)	6390(5)	7386(6)	C(35)	1329(8)	7035(5)	3620(6)
C(12)	4490(1)	5990(6)	7794(7)	C(41)	210(9)	8341(5)	7864(6)
C(13)	5770(1)	6037(5)	7343(7)	C(42)	180(1)	8856(5)	8649(7)
C(14)	5789(9)	6478(5)	6501(7)	C(43)	1330(1)	9318(6)	8938(8)
C(15)	4554(8)	6853(5)	6124(7)	C(45)	2517(9)	8734(5)	7600(6)
C(21)	−1819(9)	7813(5)	4952(6)	C(44)	2513(1)	9238(6)	8422(8)
C(22)	−3091(9)	8203(5)	4693(6)				
Compound **2**·0.5THF							
Nb(1)	6688(1)	3163(1)	1090(1)	C(25)	5125(5)	1410(1)	605(3)
Cl(1)	5959(1)	1846(2)	1625(1)	C(31)	6381(5)	6561(8)	1214(2)
Cl(2)	7418(1)	4471(2)	555(1)	C(32)	5998(5)	7870(1)	1279(3)
N(1)	7406(3)	1115(6)	1023(2)	C(33)	5191(7)	7850(1)	1298(4)
N(2)	5658(4)	2449(7)	553(2)	C(34)	4779(6)	6520(1)	1251(4)
N(3)	5992(4)	5232(7)	1172(2)	C(35)	5187(5)	5268(9)	1196(3)
N(4)	7633(4)	4033(7)	1638(2)	C(41)	8370(4)	4529(9)	1581(3)
C(11)	7731(4)	296(8)	1371(3)	C(42)	8916(5)	5250(1)	1891(3)
C(12)	8119(4)	−1032(9)	1346(3)	C(43)	8707(6)	5450(1)	2290(3)
C(13)	8208(5)	−1566(9)	948(3)	C(44)	7954(6)	4980(1)	2355(3)
C(14)	7917(5)	−726(9)	593(3)	C(45)	7443(5)	4270(1)	2030(3)
C(15)	7532(4)	584(9)	635(2)	O(1)	0	1910(3)	2500
C(21)	5497(7)	3170(1)	188(3)	O(2)	0	−740(2)	2500
C(22)	4819(9)	2930(2)	−112(4)	C(50)	810(1)	−110(2)	2630(6)
C(23)	4270(6)	1890(1)	−59(4)	C(51)	620(1)	1090(3)	2537(8)
C(24)	4432(5)	1100(1)	306(3)				
Compound **3**							
Mn(1)	5000	0	0	Mn(2)	0	5000	5000
Cl(1)	5956(2)	1131(1)	2286(2)	Cl(2)	8015(2)	4837(1)	2691(2)
N(1)	2524(6)	1041(5)	73(6)	N(3)	−414(6)	3229(4)	5105(6)
C(11)	134(1)	698(9)	−67(1)	C(31)	−606(8)	2699(6)	4375(9)
C(12)	−15(1)	124(1)	−65(1)	C(32)	−476(9)	1673(6)	444(1)
C(13)	−432(10)	2190(9)	195(1)	C(33)	80(1)	1157(7)	528(1)
C(14)	747(10)	2534(7)	100(1)	C(34)	186(1)	1687(8)	606(1)
C(15)	2197(9)	1940(6)	920(9)	C(35)	1628(9)	2725(7)	594(1)
N(2)	4475(6)	8984(5)	1486(6)	N(4)	1845(6)	4760(4)	3536(6)
C(21)	4047(9)	9408(7)	2812(9)	C(41)	1503(9)	5108(6)	2208(9)
C(22)	382(1)	8823(8)	377(1)	C(42)	257(1)	4988(7)	1315(9)
C(23)	4019(9)	7788(8)	339(1)	C(43)	404(1)	4502(7)	177(1)
C(24)	4453(9)	7331(7)	201(1)	C(44)	4430(9)	4148(7)	311(1)
C(25)	4664(9)	7960(6)	109(1)	C(45)	3299(8)	4301(6)	3965(9)

using MADNES and processed with the ABSURD program[22] to give values of F and $\sigma(F)$ for each reflection.

For the tetragonal *trans*-$NbCl_2(py)_4$ polymorph, **2*t***, the initial structural model consisted of the independent niobium, chloride, nitrogen, and carbon atoms, which were placed at positions reported previously for the isotypic vanadium compound.[23] The structure was then refined routinely. For the monoclinic polymorph, **2*m***, and the THF adduct, **2**·0.5THF, of $NbCl_2(py)_4$ as well as *trans*-$TiCl_2(py)_4$·THF, **1**·THF, and *trans*-$MnCl_2(py)_4$, **3**, the positions of the heavy atoms were found in a direct methods E-map. The remaining atoms were found in a sequence of least-squares refinement cycles followed by difference-Fourier syntheses, using the SHELXL-93 structure refinement package.[24] In each model, the hydrogen atoms were included in calculated positions for purposes of structure factor calculations only.

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Table 3. Selected Bond Lengths (Å) and Angles (deg)[a]

	trans-TiCl$_2$(py)$_4$, **1**·THF		
Ti(1)–N(1)	2.271(4)	Ti(1)–N(1)	2.271(4)
Ti(1)–N(2)	2.278(4)	Ti(1)–Cl(1)	2.497(1)
N(1)–Ti(1)–N(1)′	179.997(1)	N(1)–Ti(1)–N(2)	89.0(2)
N(1)–Ti(1)–N(2)′	91.0(2)	N(2)–Ti(1)–N(2)′	180.0
N(1)–Ti(1)–Cl(1)	90.0(1)	N(2)–Ti(1)–Cl(1)	89.6(1)
	trans-NbCl$_2$(py)$_4$, **2*t***		
Nb–N	2.223(8)	Nb–Cl	2.512(4)
N–Nb–N′	89.4(4)	N–Nb–N″	177.8(5)
N–Nb–N‴	90.6(4)	N–Nb–Cl	88.9(2)
N–Nb–Cl′	91.1(2)	Cl–Nb–Cl′	180.0
	trans-NbCl$_2$(py)$_4$, **2*m***		
Nb(1)–N(1)	2.269(6)	Nb(1)–N(2)	2.245(6)
Nb(1)–N(3)	2.249(6)	Nb(1)–N(4)	2.234(7)
Nb(1)–Cl(2)	2.517(2)	Nb(1)–Cl(1)	2.518(2)
N(4)–Nb(1)–N(1)	91.5(2)	N(4)–Nb(1)–N(3)	179.2(2)
N(2)–Nb(1)–N(3)	93.7(2)	N(4)–Nb(1)–N(2)	87.0(2)
N(2)–Nb(1)–N(1)	177.9(2)	N(3)–Nb(1)–N(1)	87.8(2)
N(4)–Nb(1)–Cl(2)	89.8(2)	N(2)–Nb(1)–Cl(2)	88.1(2)
N(4)–Nb(1)–Cl(1)	90.3(2)	N(2)–Nb(1)–Cl(1)	90.5(2)
Cl(2)–Nb(1)–Cl(1)	178.60(8)		
	trans-NbCl$_2$(py)$_4$, **2**·0.5THF		
Nb(1)–N(1)	2.231(6)	Nb(1)–N(3)	2.236(6)
Nb(1)–N(4)	2.262(6)	Nb(1)–N(2)	2.282(6)
Nb(1)–Cl(2)	2.531(2)	Nb(1)–Cl(1)	2.535(2)
N(1)–Nb(1)–N(3)	178.5(2)	N(1)–Nb(1)–N(4)	92.7(2)
N(3)–Nb(1)–N(4)	85.8(2)	N(1)–Nb(1)–N(2)	92.3(2)
N(3)–Nb(1)–N(2)	89.1(2)	N(4)–Nb(1)–N(2)	174.8(2)
N(1)–Nb(1)–Cl(2)	89.9(1)	N(3)–Nb(1)–Cl(2)	90.2(2)
N(3)–Nb(1)–Cl(1)	89.9(2)	N(4)–Nb(1)–Cl(1)	90.3(2)
Cl(2)–Nb(1)–Cl(1)	179.83(7)		
	trans-MnCl$_2$(py)$_4$, **3**		
Mn(1)–N(1)	2.342(6)	Mn(1)–N(2)	2.326(6)
Mn(1)–Cl(1)	2.514(2)	Mn(2)–N(4)	2.314(6)
Mn(2)–N(3)	2.341(6)	Mn(2)–Cl(2)	2.529(2)
N(1)–Mn(1)–N(2)	87.0(2)	N(1)–Mn(1)–N(2)′	93.0(2)
N(2)–Mn(1)–Cl(1)	88.8(2)	N(2)–Mn(1)–Cl(1)′	91.2(2)
N(1)–Mn(1)–Cl(1)	90.1(1)	N(1)–Mn(1)–Cl(1)′	89.9(1)
N(3)–Mn(2)–N(4)	94.8(2)	N(3)–Mn(2)–N(4)′	85.2(2)
N(4)–Mn(2)–Cl(2)	91.2(2)	N(4)–Mn(2)–Cl(2)′	88.8(2)
N(3)–Mn(2)–Cl(2)	89.3(1)	N(3)–Mn(2)–Cl(2)′	90.7(1)

[a] Primed atoms are symmetry related to the corresponding unprimed atoms.

Other pertinent information regarding data collection and refinement is given in Table 1. Atomic coordinates are given in Tables 2. Selected bond distances and angles are given in Table 3.

Results and Discussion

Synthesis. The reduction of Ti(IV) or Ti(III) to the divalent state by reaction with potassium graphite in THF provides, in a rather easy manner, solutions of TiCl$_2$ which presumably contain mononuclear species. We did not encounter the commonly found highly insoluble products reported by others,[3,9,17] which are frequently associated with the formation of edge-sharing or face-sharing products and tend to frustrate further reduction. These are normally found when other reducing such as Li, Na, Mg, and Zn are used. The formation of analogous solutions of vanadium(II), namely VCl$_2$(THF)$_n$[1c] is another example in which the choice of the appropriate reducing agent is crucial in obtaining solutions instead of insoluble materials. An indication of the cleanliness of the solution of TiCl$_2$(THF)$_n$ is given by the smooth formation of a royal blue solution upon addition of pyridine and the subsequent crystallization of the very soluble *trans*-TiCl$_2$(py)$_4$ compound which has been mentioned earlier.[17] Several crystals from several batches were examined by X-ray crystallography. In each case, the unit cell parameters were the same. This is an indication of the homogeneity of the product. The absence of greenish crystals of the less soluble TiCl$_3$(py)$_3$ also points in the same direction. We believe the low yields observed during the synthesis of **1**·THF are mainly due to its relatively high solubility in solvents such as toluene, benzene, THF, diethyl ether and even hexanes. We are currently examining the reactivity in more detail by working on a series of other reactions, the results of which will be reported elsewhere.

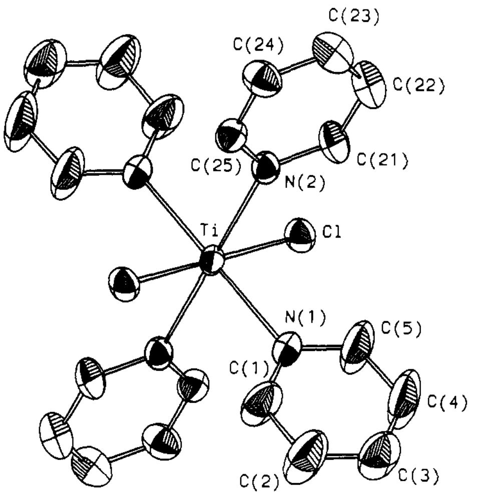

Figure 1. Thermal ellipsoid plot of *trans*-TiCl$_2$(py)$_4$ in **1**·THF showing the coplanar arrangement of each pair of trans pyridine rings. Atoms are represented by their 50% probability ellipsoids.

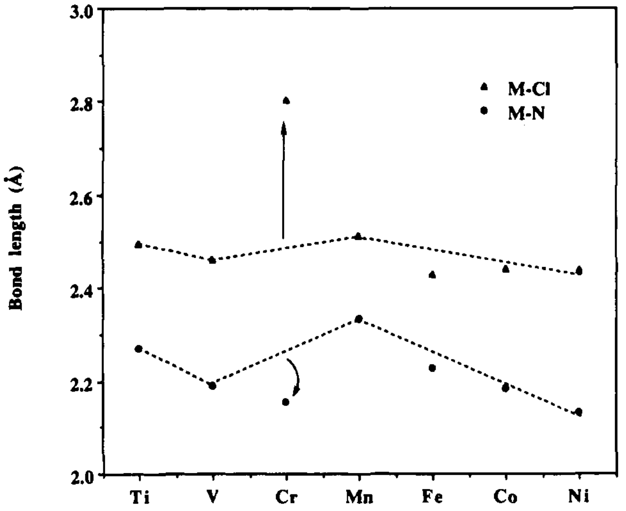

Figure 2. Variation in the metal-to-ligand distances in high spin *trans*-MCl$_2$(py)$_4$ molecules of the first transition series.

The situation is different for niobium. Its reduction to the divalent state is not as clean unless pyridine is added to the reaction flask while KC$_8$ is still present. Whenever pyridine was not added during the reduction process, the reaction mixture always contained unidentified niobium-containing solids. When the reaction mixture was filtered and pyridine was then added to the filtrate, the isolated NbCl$_2$(py)$_4$ crystals were contaminated with other species. Nevertheless, if the reduction of Nb(V) or Nb(IV) species was carried out in the presence of mixtures of

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(24) Sheldrick, G. M.; SHELXL-93: A program for Crystal Structure Refinement. University of Göttingen, Germany, 1993.

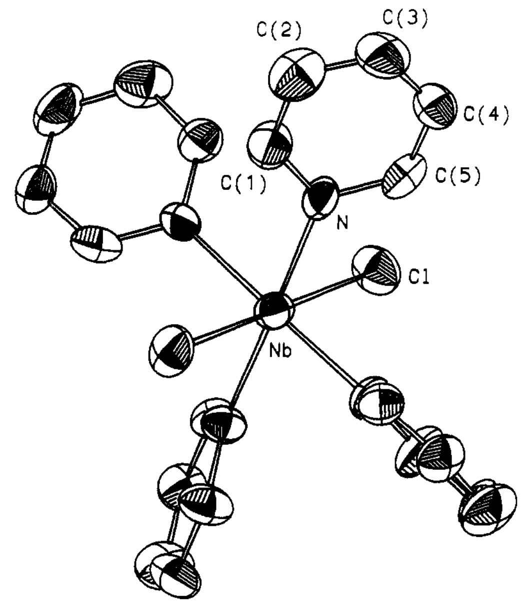

Figure 3. Structural representation of one of the polymorphs of *trans*-$NbCl_2(py)_4$, **2*t***, showing the propeller-like distribution of the pyridine molecules and the atom labelling scheme. All non-hydrogen atoms are represented by their 50% probability ellipsoids.

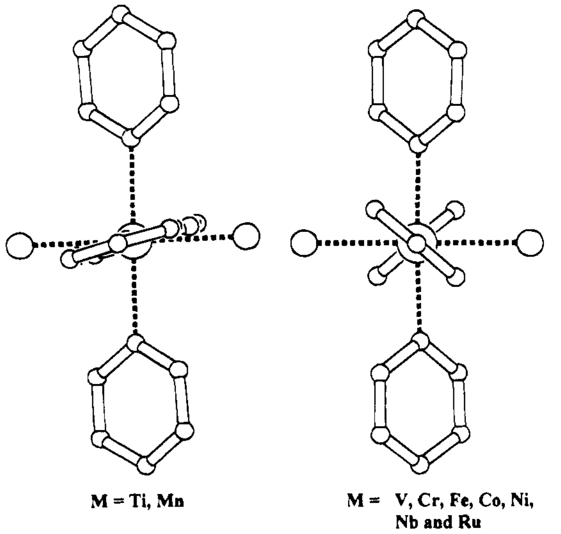

Figure 4. Idealized representation of the two structural motifs found in *trans*-$MCl_2(py)_4$ species.

THF/pyridine the product was obtained in high yields and the purity was good.

Structural Considerations. Figure 1 shows the structure of *trans*-$TiCl_2(py)_4$. The titanium atom is located on a crystallographic inversion center, requiring the two pairs of trans pyridine molecules to be coplanar. This configuration is similar to that found in the Mn analog, although for the latter there are two crystallographically independent molecules, with both manganese atoms occupying an inversion center. This type of configuration is quite different from that found in the other known $MCl_2(py)_4$ molecules formed by elements of the first transition series, namely V,[23] Cr,[25] Fe, Co, and Ni.[26] In all those compounds the pyridine molecules are arranged about the metal atoms in such a way as to provide a propeller-like configuration.

In view of the small number of structurally characterized titanium(II) compounds few comparisons can be made. The Ti−Cl bond lengths in **1** are 0.021 Å longer than those in $TiCl_2(TMEDA)_2$ while the Ti−N bond distances are *ca.* 0.10 Å shorter in **1**. This is probably due to the better π-donating ability of pyridine compared to tetramethylethylendiamine. The Ti−Cl bond distances in **1** are 0.052 Å shorter than those found in $TiCl_2(dmpe)_2$.

More interesting comparisons can be made, however, by looking at the variation of the metal-to-ligand distances as a function of the number of d electrons in the series of high-spin, divalent metal compounds of the type *trans*-$MCl_2(py)_4$. As shown in Figure 2, the M−N bond distances vary, as expected from ligand field considerations, by decreasing from Ti to V, then increasing to Mn and decreasing again until reaching Ni. The discontinuity at Cr can be attributed to a pseudo-Jahn−Teller effect. The variation of the M−Cl distances is the expected one until Fe. However, as pointed out by Long and Clark[26] those distances remain almost constant in the Fe, Co, and Ni compounds.

It is interesting to note that the longest M−N bond distances in the series are those of Ti and Mn (2.275(5) and 2.326(6) Å, respectively). Although perhaps coincidental, this might be the reason why those two compounds show a different configuration. Models indicate that the repulsion of the hydrogen atoms of adjacent pyridine groups are minimized more effectively in the propeller-like configuration found in the compounds with smaller M−N distances.

trans-$NbCl_2(py)_4$ was isolated as three different crystal forms depending on the crystallization conditions. Two of them are solvent free (true polymorphs) while the other one contains THF in the crystal. However, the molecular structure, shown in Figure 3, is similar in all cases, with bond distances and bond angles that are almost the same within experimental error. In one of the polymorphs, **2*t***, the molecule belongs to the D_4 symmetry point group. In the other two, the deviation from the idealized configuration is very slight. The arrangement of the six atoms directly bonded to the niobium atom is essentially the same as in the Ti and Mn compounds but the orientation of the four pyridine molecules about the central atom is quite different. It resembles the propeller shape found in the Cr, Fe, Co, Ni, and Ru[27] analogs. The planes defined by the two sets of trans pyridine molecules give rise to dihedral angles of 90°. Figure 4 shows both idealized configurations. In *trans*-$NbCl_2(py)_4$, the Cl−Nb−Cl atoms define a 4-fold axis (crystallographically strict in only one of the polymorphs). The Nb−N bond lengths are considerably longer than the metal-to-nitrogen bond lengths found in the low-spin compound *trans*-$RuCl_2(py)_4$ (2.223(8) vs 2.073(3) Å, respectively), but similar to those found in high-spin *trans*-$FeCl_2(py)_4$. They are shorter than those of the Ti and Mn analogs.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, complete bond distances and bond angles and anisotropic displacement parameters and calculated hydrogen coordinates for all compounds as well as ORTEP drawings of **2*m***, **2**·0.5THF, and **3** (49 pages). Ordering information is given on any current masthead page.

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