Synthesis, Structure, and Reactivity of Potassium Pyrazolato Complexes: The First Structurally Documented η^2-Pyrazolato Coordination by a Main Group Metal

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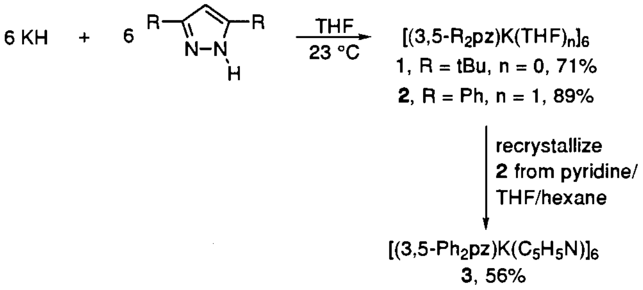
Introduction

Pyrazolato ligands have been widely employed in complexes of the middle to late d-block metals and exhibit either η^1-bonding to a single metal ion or bridge between two metal centers.[1] In lanthanide(III) ions, η^2-pyrazolato bonding is generally observed due to the more ionic bonding and larger size of the metal centers, compared to the d-block metals.[2] We have recently reported that titanium(IV) and tantalum(V) centers bind pyrazolato ligands in an η^2-fashion and that this binding mode is significantly favored over η^1-binding unless the coordination sphere is sterically congested.[3,4] Our interest for exploring the coordination chemistry of pyrazolato ligands is motivated by the isoelectronic relationship between metal complexes bearing η^2-pyrazolato ligands and analogous complexes with 1,3-diketonate ligands. 1,3-Diketonate ligands are widely used to prepare volatile metal complexes for use in chemical vapor deposition (CVD) processes, especially among the group 2 and lanthanide metals.[5] Unfortunately, the presence of oxygen or fluorine (fluorinated 1,3-diketonate complexes are commonly used to enhance volatility) degrades the properties of many thin film materials and is especially detrimental when non-oxide materials are desired (e.g., lanthanide-doped group 13−15 semiconductors[6]). Moreover, nitrogen donor ligands are more basic than common oxygen donors and may bond more strongly to metal centers, leading to source compounds with enhanced thermal stability.[7] Finally, synthetic reagents that allow access to new pyrazolato complexes are required for advances in this area. With these considerations in mind, we have begun to examine the preparation and properties of main group metal pyrazolato complexes. To date, there are no structurally characterized η^2-pyrazolato complexes of main group metals. Since many main group metal ions are as large or larger than lanthanide(III) ions, it is very likely that η^2-pyrazolato coordination will be common in the main group elements. Herein we report the synthesis, structure, and reactivity of several potassium pyrazolato complexes. These complexes are easily prepared by deprotonation of pyrazoles with potassium hydride in tetrahydrofuran. The crystal structure of one complex reveals a hexameric formulation in which each potassium ion is bonded to a pyrazolato ligand in an η^2-fashion but also bridges to two adjacent pyrazolato ligands with η^1-interactions. This type of pyrazolato bonding is unprecedented. The potassium pyrazolato complexes serve as excellent pyrazolato transfer reagents for the preparation of other metal complexes.

Scheme 1. Preparation of **1**−**3**



Results

The synthetic chemistry is outlined in Scheme 1. Treatment of 3,5-di-*tert*-butylpyrazole with potassium hydride (1 equiv) in tetrahydrofuran at ambient temperature led to vigorous evolution of hydrogen. Upon cessation of gas evolution, (3,5-di-*tert*-butylpyrazolato)potassium (**1**, 71%) was isolated as colorless needles after crystallization from hexane/tetrahydrofuran. In a similar fashion, treatment of 3,5-diphenylpyrazole with potassium hydride led to (3,5-diphenylpyrazolato)(tetrahydrofuran)potassium (**2**, 89%) after recrystallization. Addition of pyridine (30−40 equiv) to a tetrahydrofuran solution of **2**, followed by crystallization from hexane/tetrahydrofuran, afforded (3,5-diphenylpyrazolato)(pyridine)potassium (**3**, 56%) as colorless crystals. Complexes **1**−**3** were characterized by spectral and analytical techniques. Additionally, the X-ray crystal structure of **2** was determined. Due to the low solubility of **1**−**3** in benzene and cyclohexane, it was not possible to determine solution molecular weights by freezing point depression techniques. While **2** was found to be hexameric in the solid state, we were unable to gain detailed information about the solution structures of **1**−**3**. The solubilities of **1**−**3** in organic solvents afford some insight into the solution structures. Complex **1** was soluble in tetrahydrofuran but was insoluble in benzene and toluene. Complexes **2** and **3** were very soluble in

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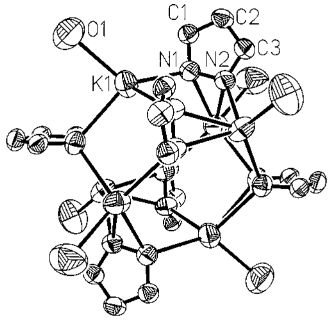


Figure 1. Perspective view of **2** with thermal ellipsoids at the 50% probability level. The phenyl groups and tetrahydrofuran carbon atoms have been removed for clarity.

Table 1. Crystallographic Data for **2**

empirical formula	$C_{114}H_{114}K_6N_{12}O_6$
fw	1982.85
space group	$R\bar{3}$
a (Å)	25.693(2)
c (Å)	14.4195(10)
V (Å^3)	8243.2(9)
Z	3
T (K)	295(2)
λ (Å)	Mo Kα (λ = 0.710 73 Å)
ρ_{calcd} (g cm^{-3})	1.199
μ (mm^{-1})	0.295
$R(F)^a$ (%)	10.39
$R_w(F)^b$ (%)	18.51

^{a} $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w(F)^2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**

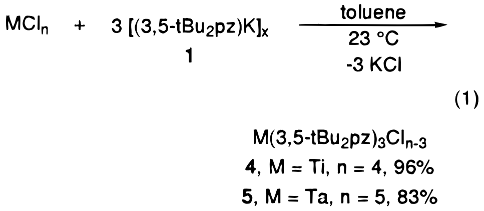
K(1)−N(1)#1 2.869(4)	K(1)−N(2)#2 2.801(3)
K(1)−N(2)#1 2.763(4)	K(1)−O(1) 2.716(5)
K(1)−N(1) 2.854(4)	N(1)−N(2) 1.370(4)

O(1)−K(1)−N(2)#1 88.7(2)	N(2)#2−K(1)−N(1) 92.30(11)
O(1)−K(1)−N(2)#2 112.9(2)	O(1)−K(1)−N(1)#1 93.8(2)
N(2)#1−K(1)−N(2)#2 92.00(8)	N(2)#1−K(1)−N(1)#1 28.08(9)
O(1)−K(1)−N(1) 129.2(2)	N(2)#2−K(1)−N(1)#1 115.05(11)
N(2)#1−K(1)−N(1) 135.58(11)	N(1)−K(1)−N(1)#1 115.09(13)

tetrahydrofuran and moderately soluble in benzene and toluene. Dissolution of **2** and **3** in the aromatic solvents suggests that the ionic bonds are not accessible to the solvent and implies a hexameric or other oligomeric structure in which only the organic groups can interact with the solvent.

To understand the bonding involved in **1**−**3**, we attempted to determine their X-ray crystal structures. Of **1**−**3**, only **2** afforded crystals of sufficient quality to allow a structure solution. Its perspective view is given in Figure 1. Table 1 gives a summary of the data collection and structure solution, while Table 2 lists selected bond lengths and angles. Compound **2** exists as a hexamer in which each potassium atom is bonded to the nitrogen atoms of one diphenylpyrazolato ligand in an η^2-fashion, to the nitrogen atoms of two adjacent diphenylpyrazolato ligands with η^1-interactions, and to the oxygen atom of one tetrahydrofuran ligand. The asymmetric unit contains one potassium ion, one tetrahydrofuran ligand, and one diphenylpyrazolato ligand. The η^2-interaction is characterized by potassium−nitrogen bond lengths of 2.763(4) (K(1)−N(2)#1) and 2.869(4) Å (K(1)−N(1)#1). The η^1-pyrazolato interactions have potassium−nitrogen bond lengths of 2.854(4) (K(1)−N(1)) and 2.801(3) Å (K(1)−N(2)#2). The potassium−oxygen bond distance is 2.716(5) Å. The bonding of potassium to the nitrogens can be envisioned as maximizing ionic contacts between the potassium ion and the lone pairs on the nitrogens. A potassium−nitrogen bond length of about 2.83 Å is predicted, based upon the van der Waals radii of potassium and nitrogen.[8,9] The "slipped" η^2-pyrazolato interaction with potassium, with one potassium−nitrogen distance about 0.1 Å shorter than the other, is similar to the situation observed in tantalum(V) pyrazolato complexes that we have recently reported.[4] The coordination geometry about each potassium atom in **2** can be viewed as distorted tetrahedral, if the center of each η^2-pyrazolate ligand is considered to be a monodentate donor (range of angles 88.7−129.2°).

The utility of **1** as a pyrazolato transfer reagent was probed. Treatment of titanium tetrachloride with **1** (3 equiv) in toluene for 20 h afforded the new complex chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV) (**4**, 96%) as a yellow crystalline solid. Treatment of tantalum pentachloride with **1** (3 equiv) afforded dichlorotris(3,5-di-*tert*-butylpyrazolato)tantalum(V) (**5**, 83%) as a colorless crystalline solid. Reaction of the metal chlorides with ≥4 equiv of **1** did not lead to further chloride substitution, and only **4** or **5** were isolated. The compositions of **4** and **5** were established from their spectral and analytical data.



$$\underset{}{MCl_n} + \underset{\mathbf{1}}{3\,[(3,5\text{-}tBu_2pz)K]_x} \xrightarrow[\substack{23\ °C \\ -3\ KCl}]{toluene} \qquad (1)$$

$$M(3,5\text{-}tBu_2pz)_3Cl_{n-3}$$

4, M = Ti, n = 4, 96%

5, M = Ta, n = 5, 83%

Discussion

Complex **2** features an unusual hexameric structure in which each potassium atom is bonded to the nitrogens of a pyrazolato ligand in a "slipped" η^2-fashion and to the nitrogens of two adjacent pyrazolato ligands with η^1-interactions. This is the first main group metal pyrazolato complex that has a structurally authenticated η^2-interaction. Observation of such a bonding mode suggests that η^2-pyrazolato bonding should be common in many main group metal derivatives. The synthesis of bis(3,5-dimethylpyrazolato)barium has been reported, but it is apparently not soluble in tetrahydrofuran and was not structurally characterized.[10] It is likely that this complex contains η^2-pyrazolato ligands. A significant implication of the present work is that a broad range of main group metal pyrazolato complexes that are structurally related to 1,3-diketonate complexes should be readily prepared. Pyrazolato complexes may therefore lead to alternative classes of volatile source compounds for film depositions using CVD techniques. While **1**−**3** are not volatile, the hexameric aggregation in **2** is substantially reduced from the infinite polymeric structure observed for (acetylacetonato)potassium hemihydrate.[11] Finally, we have demonstrated that the complexes described herein are extremely useful in the synthesis of new metal pyrazolato species.

Experimental Section

General Considerations. All manipulations were carried out under argon using Schlenk line or glovebox techniques. Hexane and toluene were distilled from sodium under a nitrogen atmosphere immediately

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prior to use. Tetrahydrofuran was distilled from sodium/benzophenone ketyl immediately prior to use. Titanium tetrachloride, tantalum pentachloride, and 3,5-diphenylpyrazole were purchased from Aldrich Chemical Co. and were used as received. Pyridine (Aldrich Chemical Co.) was dried over calcium hydride and distilled under vacuum. Potassium hydride (35% dispersion in mineral oil, Aldrich Chemical Co.) was washed with hexane before being used, to remove the mineral oil. 3,5-Di-*tert*-butylpyrazole was prepared according to a published procedure.[12]

Samples for infrared spectroscopy were prepared as Nujol mulls. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 500, 300, 125, or 75 MHz. Chemical shifts are given relative to residual protons or carbons of the indicated solvent. Melting points were determined in sealed capillary tubes under argon and are uncorrected. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN.

Preparation of 3,5-Di-*tert*-butylpyrazolatopotassium (1). A 100-mL Schlenk flask was charged with 3,5-di-*tert*-butylpyrazole (1.00 g, 5.55 mmol), potassium hydride (0.44 g, 10.97 mmol), and tetrahydrofuran (40 mL) at room temperature. Vigorous gas evolution ensued. After stirring for 2 h, the reaction solution was filtered through a 2-cm pad of Celite on a coarse glass frit to afford a colorless solution. The volume of the solution was concentrated to ca. 15 mL, and hexane (40 mL) was carefully layered on the tetrahydrofuran solution. The system was allowed to equilibrate for 48 h. The solvent was decanted by cannula, and the resultant crystals were vacuum-dried to afford **1** as colorless needles (0.86 g, 71%): mp >300 °C; IR (Nujol, cm^{-1}) 1495 (s), 1358 (s), 1304 (m), 1248 (m), 1212 (m), 1052 (w), 1017 (w), 1003 (m), 993 (w), 777 (s), 733 (m); **1** was not soluble in benzene or toluene, so ^1H and $^{13}C\{^1H\}$ NMR spectra were not recorded. Anal. Calcd for $C_{11}H_{19}KN_2$: C, 60.50; H, 8.77; N, 12.83. Found: C, 60.07; H, 8.72; N, 12.79.

Preparation of (3,5-Diphenylpyrazolato)(tetrahydrofuran)-potassium (2). In a fashion similar to the preparation of **1**, 3,5-diphenylpyrazole (1.00 g, 4.54 mmol) and potassium hydride (0.360 g, 8.98 mmol) were allowed to react in tetrahydrofuran (50 mL) to afford **1** as colorless crystals (1.34 g, 89%) after crystallization from tetrahydrofuran/hexane at ambient temperature: mp 236 °C; ^1H NMR (C_6D_6, 22 °C, δ) 7.65 (d, $J = 7.5$ Hz, 24 H, o-$C_5\mathit{H}_2H_2'H''$), 7.25 (m, 24 H, m-$C_5H_2\mathit{H}_2'H''$), 7.07 (m, 12 H, p-$C_5H_2H_2'\mathit{H}''$), 7.02 (s, 6H, pz ring C*H*), 3.53 (m, 24 H, $OC\mathit{H}_2CH_2$), 1.39 (m, 24 H, $OCH_2C\mathit{H}_2$); $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C, ppm) 153.99 (s, *C*-Ph), 137.41 (s, ipso *C* of Ph ring), 129.51 (s, ortho *C*H of Ph ring), 126.06 (s, para *C*H of Ph ring), 125.07 (s, meta *C*H of Ph ring), 99.57 (s, pz ring *C*H), 67.74 (s, $O\mathit{C}H_2CH_2$), 25.7 (s, $OCH_2\mathit{C}H_2$); IR (Nujol, cm^{-1}) 1599 (s), 1523 (m), 1508 (w), 1260 (m), 1216 (m), 1155 (w), 1067 (s), 1024 (w), 968 (s), 915 (m), 802 (w), 757 (s), 699 (s), 688 (s). Anal. Calcd for $C_{114}H_{114}K_6N_{12}O_6$: C, 69.06; H, 5.80; N, 8.48. Found: C, 66.96; H, 5.92; N, 8.60.

Preparation of (3,5-Diphenylpyrazolato)(pyridine)potassium (3). A solution of **2** (0.40 g, 0.20 mmol) in tetrahydrofuran (25 mL) was treated with pyridine (0.60 mL, 7.4 mmol). After being stirred for 6 h at ambient temperature, the colorless solution was concentrated under reduced pressure to 20 mL and was layered with hexane (25 mL). After 10 days at ambient temperature, large colorless crystals of **3** were isolated by decanting the solvent (0.23 g, 56%): dec range 144−150 °C; ^1H NMR (C_6D_6, 22 °C, δ) 8.49 (m, 12 H, o-$C_5\mathit{H}_2H_2'H''N$), 7.67 (d, $J = 8.4$ Hz, 24 H, o-$C_5\mathit{H}_2H_2'H''$), 7.23 (m, 24 H, m-$C_5H_2\mathit{H}_2'H''$), 7.06 (m, 12 H, p-$C_5H_2H_2'\mathit{H}''$), 7.02 (s, 6 H, pz ring C*H*), 6.96 (m, 6 H, p-$C_5H_2H_2'\mathit{H}''N$), 6.64 (m, 12 H, m-$C_5H_2\mathit{H}_2'H''N$); $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C, ppm) 153.90 (s, *C*-Ph), 150.25 (s, ortho *C*H of Py), 137.15 (s, ipso *C* of Ph ring), 135.13 (s, para *C*H of Py), 129.50 (s, ortho *C*H of Ph ring), 126.15 (s, para *C*H of Ph ring), 125.07 (s, meta *C*H of Ph ring), 123.40 (s, meta *C*H of Py), 99.53 (pz ring *C*H); IR (Nujol, cm^{-1}) 1600 (m), 1587 (m), 1522 (m), 1506 (w), 1439 (m), 1318 (w), 1260 (m), 1216 (m), 1145 (w), 1068 (m), 1032 (w), 996 (w), 969 (s), 913 (w), 799 (w), 757 (s), 745 (m), 698 (s), 688 (m). Anal. Calcd for $C_{120}H_{96}K_6N_{18}$: C, 71.18; H, 4.78; N, 12.45. Found: C, 70.07; H, 5.06; N, 12.45.

Preparation of Chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV) (4). A solution of titanium tetrachloride (0.21 mL, 1.9 mmol) in toluene (30 mL) was added to a suspension of **1** (1.40 g, 6.41 mmol) in toluene (50 mL) at 0 °C. The reaction mixture was allowed to warm to ambient temperature and was stirred for 20 h. Filtration of the reaction mixture through a 1-cm pad of Celite on a coarse glass frit afforded a yellow solution. The volatile components were removed under reduced pressure to afford **4** as a yellow solid (1.17 g, 96%): mp 169 °C; ^1H NMR (C_6D_6, 22 °C, δ) 6.41 (s, 3H, pz ring C*H*), 1.14 (s, 54 H, $C(C\mathit{H}_3)_3$); $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C, ppm) 158.55 (s, $\mathit{C}C(CH_3)_3$), 110.63 (s, pz ring *C*H), 32.33 ($C\mathit{C}(CH_3)_3$), 30.57 ($CC(\mathit{C}H_3)_3$); IR (Nujol, cm^{-1}) 1507 (m), 1364 (m), 1254 (m), 1234 (m), 1205 (w), 1092 (m), 1020 (m), 994 (w), 813 (s), 717 (w). Anal. Calcd for $C_{33}H_{57}ClN_6Ti$: C, 63.81; H, 9.25; N, 13.53. Found: C, 63.63; H, 9.34; N, 13.53.

Preparation of Dichlorotris(3,5-di-*tert*-butylpyrazolato)tantalum(V) (5). A 100-mL Schlenk flask was charged with tantalum pentachloride (0.30 g, 0.84 mmol), **1** (1.00 g, 4.58 mmol), and toluene (50 mL). After being stirred for 2 h at ambient temperature, the reaction mixture was refluxed for 48 h. The volatile components were removed under reduced pressure, and the resultant pale yellow solid was extracted with hexane (80 mL). Filtration of the hexane extract through a 1-cm pad of Celite on a coarse glass frit gave a colorless solution. This solution was cooled to −20 °C. After 24 h, large colorless crystals of **5** were isolated by decanting the solvent (0.55 g, 83%): mp 211 °C; ^1H NMR ($CDCl_3$, 22 °C, δ) 6.76 (s, 3H, pz ring C*H*), 1.29 (s, 54 H, $C(C\mathit{H}_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22 °C, ppm) 156.84 (s, $\mathit{C}C(CH_3)_3$), 115.24 (s, pz ring *C*H), 32.07 ($C\mathit{C}(CH_3)_3$), 30.56 ($CC(\mathit{C}H_3)_3$); IR (Nujol, cm^{-1}) 1520 (m), 1363 (s), 1256 (s), 1236 (s), 1201 (w), 1093 (m), 1034 (w), 984 (m), 819 (s), 800 (s), 715 (w). Anal. Calcd for $C_{33}H_{57}Cl_2N_6Ta$: C, 50.19; H, 7.28; N, 10.64. Found: C, 50.30; H, 7.39; N, 10.44.

Crystal Structure Determination of 2. A crystal of **2** suitable for the diffraction experiment was grown by diffusion of hexane into a tetrahydrofuran solution of **2** at ambient temperature. The crystal was mounted in a thin-walled capillary tube under a nitrogen atmosphere. Crystallographic data were collected at room temperature on a Siemens/Bruker automated P4/CCD diffractometer with monochromated Mo radiation. A total of 1390 frames were collected at 10 s and integrated with the manufacturer's SMART and SAINT software. Absorption corrections were applied with the SADABS program, and the structure was solved and refined using the programs of SHELXS-86 and SHELXL-93.[13] Crystal data are presented in Table 1. Results are presented in Table 2 and Figure 1. Other data are available in the Supporting Information. Although all atoms occupy general crystallographic positions, the center of the cage has site symmetry $\bar{3}$. The potassium ions are arranged at octahedral vertexes around the cage center. Hydrogen atoms were placed in observed positions and were refined in the pyrazolato ligands. All non-hydrogen atoms were described anisotropically. The tetrahydrofuran ligands were severely disordered. Alternate partially occupied positions were included for C(16) (C(22)), C(17) (C(21)), and C(19) (C(20)). Hydrogen atoms in the tetrahydrofuran groups were placed in calculated positions. The tetrahydrofuran disorder persisted in the lower symmetry space group $R3$, and the Flack parameter indicated a racemic mix, so the space group $R\bar{3}$ was deemed correct.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for **2** are available on the Internet only. Ordering information is given on any masthead page.

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