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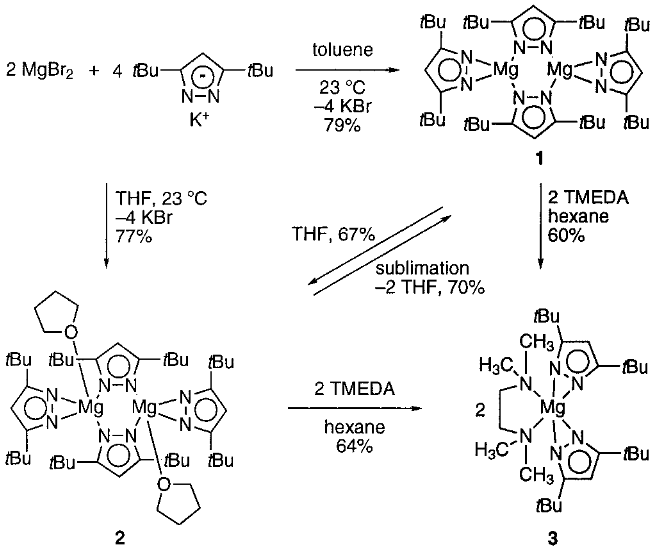
Magnesium Complexes Bearing η^2-Pyrazolato Ligands[**]

Dirk Pfeiffer, Mary Jane Heeg, and Charles H. Winter[*]

Pyrazolato ligands are commonly employed in complexes of the middle to late d-block metals, and either exhibit η^1 bonding to a single metal ion or bridge two metal centers.[1] η^2-Pyrazolato bonding is generally observed in lanthanide(III) complexes as a consequence of the more ionic bonding and larger size of the metal centers, relative to the d-block metals.[2] We have described several titanium(IV) and tantalum(V) complexes that contain η^2-pyrazolato ligands, and demonstrated that this binding mode is significantly favored over η^1 binding unless the coordination sphere is sterically congested.[3–5] Very recently, we reported the crystal structure of a hexameric potassium pyrazolato complex that contains bridging η^2-pyrazolato ligands.[6] Since the η^2 coordination mode was observed in the potassium complex it seemed very likely that this coordination mode would be observed in other main group metal complexes.

Our motivation for exploring pyrazolato complexes concerns the development of improved source compounds for chemical vapor deposition (CVD) applications. Volatile metal complexes composed of Group 2 or lanthanide metals with 1,3-diketonate ligands are widely used in CVD processes.[7] However, the presence of oxygen makes diketonate-based precursors inappropriate for the deposition of non-oxide materials, such as magnesium-doped gallium nitride.[8] With these considerations in mind, we report the synthesis, structure, and reactivity of several magnesium pyrazolato complexes. Surprisingly, η^2-pyrazolato coordination is observed in these complexes, despite the small size of the magnesium ion. This study gives the first structural documentation of terminal η^2-pyrazolato ligands with the main group metals and offers new insight into the design of volatile Group 2 compounds for use in film depositions through CVD methods.

Treatment of magnesium bromide with potassium 3,5-di-*tert*-butylpyrazolate[6] (2 equiv) in toluene led to the formation of bis[bis(3,5-di-*tert*-butylpyrazolato)magnesium] (**1**, 79%; Scheme 1) as colorless crystals after workup. If the reaction of magnesium bromide with potassium 3,5-di-*tert*-butylpyrazolate was carried out in tetrahydrofuran (THF), workup afforded bis[bis(3,5-di-*tert*-butylpyrazolato)(tetrahydrofuran)magnesium] (**2**, 77%) as colorless crystals. Treatment of **1** or **2** with *N,N,N'N'*-tetramethylethylene diamine (TMEDA, 1 equiv per magnesium) led to the formation of bis(3,5-di-*tert*-butylpyrazolato)(*N,N,N',N'*-tetramethylethylenediamine)magnesium (**3**, 60–64%). Dissolution of **1** in THF followed by workup, afforded **2** (67%), while sublimation of **2** at 150 °C (0.1 torr) afforded **1** (70%) with loss of the



Scheme 1. Synthesis and reactions of the pyrazolatomagnesium complexes **1**–**3**.

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[*] Prof. Dr. C. H. Winter, D. Pfeiffer, Dr. M. J. Heeg
Department of Chemistry, Wayne State University
Detroit, MI 48202 (USA)
Fax: +(1)313-577-1377
E-mail: cwinter@sun.science.wayne.edu

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coordinated THF ligand. Sublimation of **3** (ca. 150 °C, 0.1 torr) afforded variable mixtures of **1** and **3** (3:1 – 4:1). The structures of **1** – **3** were established by spectroscopic and analytical techniques as well as by X-ray crystal structure determinations. In the ^{1}H and ^{13}C{^{1}H} NMR spectra of **1** in [D$_8$]toluene signals were observed for only one type of pyrazolato ligand between −80 and 20 °C, suggesting fast exchange between the terminal and bridging pyrazolato ligands in this temperature range.

To establish the solid-state structure, the X-ray crystal structures of **1** – **3** were determined.[9] The structure of **2** was of lower precision than **1** and **3**, because of disorder of the THF ligands and the *tert*-butyl groups. However, the gross structure of **2** was unambiguously established from the X-ray data. Perspective views of **1** and **3** are presented in Figures 1 and 2, respectively.

Complex **1** exists as a dimeric complex with two η^2-pyrazolato ligands and two bridging pyrazolato ligands (Figure 1). Each binuclear molecule occupies a crystallographic inversion center. The plane containing the η^2-pyrazolato ligands is approximately perpendicular to the plane containing the bridging ligands. The η^2-pyrazolato ligands are characterized by Mg – N bond lengths of 1.987(4) and 2.050(4) Å, while the corresponding values for the bridging pyrazolato ligands are 2.001(3) and 2.047(3) Å. The bonding of the η^2-pyrazolato ligand is unsymmetrical, with a difference in the Mg – N bond lengths of 0.06 Å. We have previously documented similar "slipped" η^2-pyrazolato coordination in a tantalum complex.[4] The coordination geometry about each magnesium atom can be envisioned as distorted trigonal planar if the center of the η^2-pyrazolato ligand is considered to be a monodentate donor (N1-Mg-N3 124.04(13), N1-Mg-N4′ 112.03(13), N2-Mg-N3 125.10(14), N2-Mg-N4′ 128.31(14), N3-Mg-N4′ 106.56°). The dihedral angle between the planes described by N1-Mg1-N2 and Mg1-N3-N4 is 52.95°.

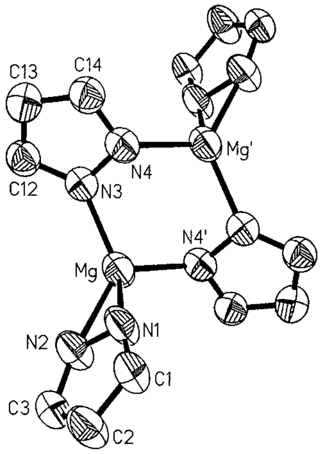

Figure 1. Structure of **1** in the solid state. The *tert*-butyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mg – N1 1.987(4), Mg – N2 2.050(4), Mg – N3 2.001(3), Mg – N4′ 2.047(3), Mg – N4 2.690(4), Mg – Mg′ 3.322(2), N1 – N2 1.397(4), N3 – N4 1.397(4); N1-Mg-N2 40.47(11), Mg-N1-N2 72.2(2), Mg-N2-N1 67.3(2), N1-Mg-N3 124.04(13), N1-Mg-N4′ 112.03(13), N2-Mg-N3 125.10(14), N2-Mg-N4′ 128.31(14), Mg-N3-N4 103.3(2), N3-Mg-N4′ 106.56(13).

Complex **3** exists as a six-coordinate monomeric complex with two η^2-pyrazolato ligands and one TMEDA ligand (Figure 2). The bonding of the pyrazolato ligands to magnesium is asymmetric with one short and one long Mg – N bond (Mg – N1 2.047(3), Mg – N2 2.140(3), Mg – N3 2.054(3), Mg – N4 2.144(3) Å). The pyrazolato Mg – N bond lengths in **3** are longer than those in **1**, probably as a consequence of the increased coordination number about the magnesium center. The asymmetry associated with the pyrazolato ligands in **3** is more pronounced than in **1**, again probably because of the increased steric interactions present in **3**. The Mg – N bond lengths associated with the TMEDA ligand are 2.235(3) and 2.221(3) Å. The coordination geometry about the magnesium atom can be described as distorted tetrahedral if the center of each pyrazolato ligand is considered as a monodentate donor.

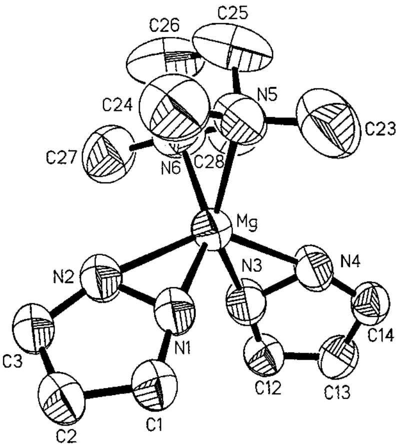

Figure 2. Perspective view of one independent molecule of **3**. The *tert*-butyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mg – N1 2.047(3), Mg – N2 2.140(3), Mg – N3 2.054(3), Mg – N4 2.144(3), Mg – N5 2.235(3), Mg – N6 2.221(3), N1 – N2 1.390(4), N3 – N4 1.397(4); N1-Mg-N2 38.70(10), N3-Mg-N4 38.78(11), N5-Mg-N6 80.65(14), N1-Mg-N3 103.55(13), N1-Mg-N4 112.76(12), N2-Mg-N3 110.05(13), N2-Mg-N4 140.75(12), N1-Mg-N5 95.06(12), N1-Mg-N6 146.75(13), N2-Mg-N5 99.76(12), N2-Mg-N6 109.14(13), N3-Mg-N5 149.32(14), N3-Mg-N6 95.81(13), N4-Mg-N5 111.32(13), N4-Mg-N6 99.31(13).

Complexes **1** – **3** are the first main group metal complexes with terminal η^2-pyrazolato ligands. The η^2-pyrazolato coordination is markedly asymmetric in **1** and **3**, with differences in Mg – N bond length of 0.06 – 0.09 Å within each pyrazolato ligand. The "slipped" η^2 bonding may originate from steric interactions between the bulky 3,5-di-*tert*-butylpyrazolato ligands, since the differences were larger for the six-coordinate metal center in **3** than for the four-coordinate magnesium center in **1**. The observation of η^2-pyrazolato bonding in **1** – **3** is surprising in view of the small size of Mg^{2+} (ionic radius of 0.72 Å[10] for a six-coordinate Mg^{2+} ion) and the rarity of this coordination mode among metals in general.[3–5] We have recently reported that potassium (3,5-diphenylpyrazolate)(tetrahydrofuran) exists as a hexamer in which each potassium atom is bonded to the nitrogen atoms of one diphenylpyrazolato ligand in an η^2 fashion and to the nitrogen atoms of two adjacent diphenylpyrazolato ligands with η^1 interactions.[6] This precedent, coupled with the results of the present work, implies that η^2-pyrazolato ligand coordination should be common in many main group metal complexes. Such a prediction is important because of the structural similarities between η^2-pyrazolato and 1,3-diketonate complexes. Since 1,3-diketonate complexes are employed as precursors for film depositions by CVD techniques,[8] it is likely that pyrazolato complexes can be used in applications where oxygen contamination is detrimental. To this end, we are studying the use of **1** (sublimes at 150 °C, 0.1 torr without decomposition) as a CVD precursor for the fabrication of magnesium-doped Group 13 semiconductors.[11]

Experimental Section

1: A 200-mL Schlenk flask was charged with magnesium bromide (0.500 g, 2.71 mmol), potassium 3,5-di-*tert*-butylpyrazolate (1.18 g, 5.42 mmol), and toluene (50 mL). The resultant mixture was stirred at ambient temperature for 72 h, during which time a fine white precipitate formed. The volatile components were removed under reduced pressure to afford a colorless, sticky solid. This solid was extracted with hexane (60 mL), and the resultant solution filtered through a 2-cm pad of Celite on a coarse glass frit. The resultant clear, colorless solution was concentrated under vacuum to approximately 20 mL and then stored at −20 °C for 18 h to afford **1** as colorless crystals (0.82 g, 79 %): m.p. 148–152 °C; IR (Nujol) $\tilde{\nu} = 1531$ (m), 1508 (s), 1412 (m), 1360 (s), 1317 (s), 1254 (vs), 1226 (m), 1202 (m), 1059 (m), 1040 (s), 1016 (s), 987 (s), 786 cm^{-1} (s); ^1H NMR ([D_6]benzene, 23 °C): $\delta = 6.09$ (s, 2H, pyrazolato C−*H*), 1.26 (s, 36H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR ([D_6]benzene, 23 °C): $\delta = 165.66$ (s, $C{-}C(CH_3)_3$), 100.34 (s, pyrazolato *C*−H), 31.91 (s, $C(CH_3)_3$), 30.75 (s, $C(CH_3)_3$); elemental analysis calcd for $C_{44}H_{76}Mg_2N_8$: C 69.02, H 10.00, N 14.63; found: C 69.05, H 10.17, N 14.65.

2: In a similar fashion to the preparation of **1**, magnesium bromide (0.500 g, 2.71 mmol) and potassium 3,5-di-*tert*-butylpyrazolate (1.18 g, 5.42 mmol) were allowed to react in THF (40 mL) to afford **2** as colorless crystals (0.95 g, 77 %): m.p. 114–122 °C (decomp.); IR (Nujol) $\tilde{\nu} = 1501$ (s), 1410 (m), 1359 (vs), 1308 (s), 1249 (s), 1225 (s), 1205 (s), 1052 (s), 1034 (s), 1015 (s), 997 (s), 896 (m), 784 cm^{-1} (s); ^1H NMR ([D_6]benzene, 23 °C): $\delta = 6.04$ (s, 2H, pyrazolato C−*H*), 3.48 (m, 4H, OCH_2CH_2), 1.40 (s, 36H, $C(CH_3)_3$), 1.31 (m, 4H, OCH_2CH_2); $^{13}C\{^1H\}$ NMR ([D_6]benzene, 23 °C): $\delta = 161.88$ (s, $C{-}C(CH_3)_3$), 97.08 (s, pyrazolato *C*−H), 67.99 (s, OCH_2CH_2), 31.91 (s, $C(CH_3)_3$), 30.38 (s, $C(CH_3)_3$), 25.18 (s, OCH_2CH_2); elemental analysis calcd for $C_{52}H_{92}Mg_2N_8O_2$: C 68.64, H 10.19, N 12.31; found: C 68.78, H 10.21, N 12.54.

3: A 200-mL Schlenk flask was charged with **1** (0.500 g, 0.654 mmol), TMEDA (0.152 g, 1.31 mmol), and hexane (40 mL). The reaction was stirred for 18 h at ambient temperature and then filtered through a 2-cm pad of Celite on a coarse glass frit. The clear, colorless hexane solution was concentrated to about 20 mL and then stored at −20 °C for 18 h to afford **3** as colorless crystals (0.39 g, 60 %): m.p. 163–165 °C; IR (Nujol) $\tilde{\nu} = 3110$ (m), 2799 (s), 1514 (vs), 1494 (vs), 1413 (m), 1355 (vs), 1325 (s), 1287 (s), 1248 (vs), 1226 (s), 1205 (s), 1189 (m), 1163 (m), 1123 (m), 1058 (m), 1014 (vs), 996 (vs), 949 (s), 797 (s), 770 cm^{-1} (vs); ^1H NMR ([D_6]benzene, 23 °C): $\delta = 6.07$ (s, 2H, pyrazolato C−*H*), 2.03 (s, 12H, $N{-}CH_3$), 1.86 (s, 4H, $N{-}CH_2$), 1.39 (s, 36H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR ([D_6]benzene, 23 °C): $\delta = 159.65$ (s, $C{-}C(CH_3)_3$), 96.05 (s, pyrazolato *C*−H), 55.84 (s, $N{-}CH_2$), 46.31 (s, $N{-}CH_3$), 31.79 (s, $C(CH_3)_3$), 31.54 (s, $C(CH_3)_3$); elemental analysis calcd for $C_{28}H_{54}MgN_6$: C 67.39, H 10.91, N 16.84; found: C 66.77, H 10.62, N 16.52.

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[9] X-ray crystal data for **1**: $C_{44}H_{76}Mg_2N_8$, $M_r = 765.75$, monoclinic, $P2_1/c$, $a = 12.0348(14)$, $b = 11.7684(12)$, $c = 18.159(2)$ Å, $\beta = 101.661(2)°$, $V = 2518.8(5)$ $Å^3$, $Z = 2$, $\rho_{calcd} = 1.010$ $g\,cm^{-3}$, $\mu = 0.083$ mm^{-1}, 5278 independent reflections harvested from 1390 frames of data containing 13076 integrated intensities, $R_{int} = 0.12$. All data were included in the refinement. For $I \geq 2\sigma(I)$, $R_1 = 0.0721$ and $wR_2 = 0.1507$; including weak data $R_1 = 0.2709$ and $wR_2 = 0.2114$. Siemens/Bruker P4-CCD, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite monochromator, $2\theta_{max} = 56.6°$, $T = 295(2)$ K. X-ray crystal data for **3**: $C_{28}H_{54}MgN_6$, $M_r = 499.08$, triclinic, $P\bar{1}$, $a = 9.5463(7)$ A, $b = 10.3431(9)$, $c = 19.471(2)$ Å, $\alpha = 98.200(2)$, $\beta = 97.488(2)$, $\gamma = 116.013(2)°$, $V = 1669.5(2)$ $Å^3$, $Z = 2$, $\rho_{calcd} = 0.993$ $g\,cm^{-3}$, $\mu = 0.076$ mm^{-1}, 6418 independent reflections were harvested from 1470 frames of data containing 9490 integrated intensities, $R_{int} = 0.035$. All data were included in the refinement. For $I \geq 2\sigma(I)$, $R_1 = 0.082$ and $wR_2 = 0.242$; including weak data, $R_1 = 0.165$ and $wR_2 = 0.287$. Siemens/Bruker P4-CCD, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite monochromator, $2\theta_{max} = 56.5°$, $T = 295(2)$ K. Suitable crystals for single-crystal X-ray analysis were selected and mounted inside thin-walled capillaries in a dry box under a nitrogen atmosphere. Data collection and integration used the Bruker SMART and SAINT software. Empirical absorption corrections were calculated using the program SADABS.[12] Solution and refinement used the programs SHELXS[12] and SHELXL-93.[12] All non-hydrogen atoms were described anisotropically. Hydrogen atoms were placed in calculated positions. The 3,5-di-*tert*-butylpyrazolato ligands typically show severe disorder in the *tert*-butyl groups, which results in modeling difficulties and high *R* values. However, other criteria of chemical and crystallographic reasonableness show these to be acceptable structural models. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-101335. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +(44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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