Azolato Coordination Modes

# Coordination of 3,5-Diisopropyl-1,2,4-triazolato and 5-Phenyltetrazolato Ligands to the $[K([18]crown-6)]^+$ Fragment: Structural Insight into the Coordination of Nitrogen-Rich Azolato Ligands to Single Metal Centers**

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There is considerable interest in the coordination chemistry of anionic, five-membered, heterocyclic N ligands.[1–6] Much of this activity has centered on pyrazolato ligands,[1] and many new and unexpected coordination modes have been documented recently.[2] Theoretical predictions regarding the high stability of the pentazolate ($N_5^-$) ion suggest that metal complexes of this ligand might be stable enough to allow isolation.[5] Recent tantalizing results in this area include the first experimental detection of the $N_5^-$ ion (in the gas phase),[6] as well as isolation and characterization of metal complexes containing the isoelectronic $P_5^-$ ligand.[7] As experimental work moves inexorably toward ligands with higher nitrogen content,[3,4,6,8–10] a considerable barrier to development remains the formation of insoluble oligomeric or polymeric complexes in which the nitrogen atoms of the heterocyclic ligands bridge metal ions.[3,9,10] Coordination modes of 1,2,4-triazolato and tetrazolato ligands to single metal centers remain poorly developed so far. Several examples of $\eta^1$ coordination of 1,2,4-triazolato and tetrazolato ligands are known.[3,4,11] However, $\eta^2$ coordination of 1,2,4-triazolato ligands to single metal centers has only recently been reported for $[(t\mathrm{Bu_2pz})_3\mathrm{Ti}(\eta^2\text{-}\mathrm{Me_2tz})]$ ($t\mathrm{Bu_2pz}$ = 3,5-di-*tert*-butylpyrazolato, $\mathrm{Me_2tz}$ = 3,5-dimethyltriazolato)[4] and $[\mathrm{Ti}(\eta^2\text{-}i\mathrm{Pr_2tz})_4]$ ($i\mathrm{Pr_2tz}$ = 3,5-diisopropyl-1,2,4-triazolato).[8] A related compound, benzotriazolatopotassium, contains $\eta^2$ bonding interactions within a more complex bridging structure.[9] $\eta^2$ Bonding interactions within more complex bridging coordination modes of tetrazolato ligands are restricted to $[\{(C_5H_4(CH_3))_2\mathrm{Ln}(\mu\text{:}\eta^2(N,N'),\eta^1(N')\text{-Phttz})\}_2]$ (Ln = Yb, Gd, Dy, Er; Phttz = 5-phenyltetrazolato)[12a] and 5-cyanotetrazolatocesium.[12b] Other structurally authenticated coordination modes of 1,2,4-triazolato and tetrazolato ligands have not been reported to date.

Herein, we report the synthesis, structure, and properties of 3,5-diisopropyl-1,2,4-triazolato and 5-phenyltetrazolato complexes of the ([18]crown-6)potassium fragment. These complexes exhibit slipped terminal $\eta^2$ coordination of the

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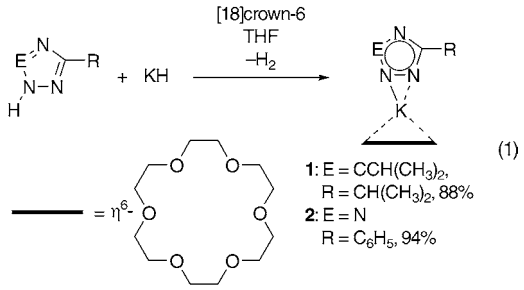
heterocyclic ligands to the metal centers. The potassium ion normally bonds to anionic five-membered nitrogen heterocyclic ligands with a variety of bridging coordination modes,[9,13,14] so the terminal coordination described herein is particularly novel. In addition, the results suggest that (pentazolato)([18]crown-6)potassium is a potential target for stabilization of the pentazolate ion on a metal center.

Treatment of 3,5-diisopropyltriazole[15a] or 5-phenyltetrazole[15b] with potassium hydride and [18]crown-6 in THF at ambient temperature led to slow hydrogen evolution and formation of (3,5-diisopropyl-1,2,4-triazolato)([18]crown-6)potassium (**1**, 88%) and (5-phenyltetrazolato)([18]crown-6)potassium (**2**, 94%) as white crystalline solids [Eq. (1)]. Complexes **1** and **2** can be alternatively prepared by a two-




(1)

step sequence in which the potassium salts are formed first, and are then treated with [18]crown-6. Both **1** and **2** are very soluble in alcohols and hot THF, and are easily crystallized from the latter. The microanalytical data are consistent with the proposed formulations, and the $^1$H and $^{13}$C{$^1$H} NMR spectroscopy data in [D$_4$]methanol show the expected signals for the nitrogen heterocycles and [18]crown-6 ligands. The single set of signals for the isopropyl groups in **1** and the sharp single resonances of the [18]crown-6 ligands in **1** and **2** suggest that the ligands are involved in dynamic exchange processes in solution at room temperature.

Complexes **1** and **2** exist in the solid state as monomers that contain $\eta^6$-[18]crown-6 ligands[2c,16] and slipped $\eta^2$-3,5-diisopropyl-1,2,4-triazolato (in **1**) or slipped $\eta^2$-phenyltetrazolato (in **2**) ligands (Figures 1 and 2).[17] There are no intermolecular bonding interactions. The K–N bond lengths in **1** (2.709(3), 3.304(3) Å) and **2** (2.744(2), 3.102(3) Å) indicate slipped $\eta^2$ bonding,[19] as opposed to the more common idealized $\eta^2$ bonding. Roesky, Mösch-Zanetti and co-workers previously documented a difference in bond length of 0.475 Å as an example of extreme slippage in an aluminum complex containing an $\eta^2$-pyrazolato ligand.[19c] The bond-length difference of 0.595 Å in **1** is similar to, or slightly shorter than, that in the aforementioned aluminum pyrazolato complex, given the difference in ionic radii between potassium (1.38 Å) and aluminum (0.535 Å).[20] By the same argument, the bond-length difference in **2** of 0.358 Å clearly places it within the regime of slipped $\eta^2$ bonding. The shorter K–N bond lengths in **1** and **2** are comparable to those in [K(Ph$_2$pz)(thf)]$_6$ (2.76–2.87 Å),[13] while the longer K–N bond lengths are comparable to or longer than the related values in structurally characterized [K([18]crown-6)(en)]$^+$ fragments (2.88–3.08 Å; en = ethylenediamine).[16d,e] The K–O bond lengths (**1**, 2.789–2.934 Å; **2**, 2.777–2.926 Å) are similar to those in other potassium complexes containing $\eta^6$-[18]crown-6 ligands.[2c,16] In **1**, the KN$_2$ plane and triazolato ligand core are nearly coplanar (angle between least-squares planes: 2.1°). By contrast, the corresponding planes in **2** deviate from coplanarity by 19.5°. Interestingly, **2** exists as the $\eta^2$-1,2 isomer, as opposed to the $\eta^2$-2,3 isomer. We have previously reported molecular orbital calculations that predict the $\eta^2$-1,2 and $\eta^2$-2,3 isomers to differ in energy by less than 0.8 kcal mol$^{-1}$ in model titanium complexes.[4a] In the case of **2**, formation of the 1,2 isomer may be a result of the higher basicity of the N atoms.

Complexes **1** and **2** contain slipped $\eta^2$-azolato ligands, in which one K–N bond is 0.36–0.60 Å longer than the other. Slipped $\eta^2$-pyrazolato ligands have been documented in several different metal complexes,[19] but the asymmetry in

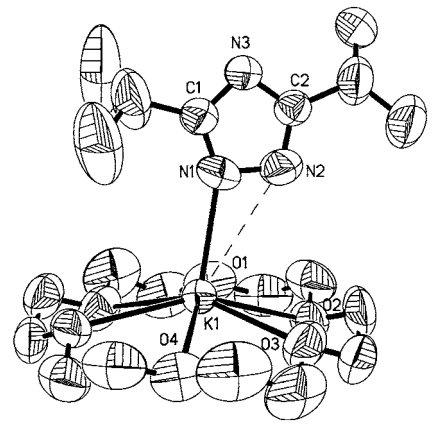



***Figure 1.*** Perspective view of **1**. Selected interatomic distances [Å] and angles [°]: K1–N1 2.709(3), K1–N2 3.304(3), K1···N3 4.902(3), K1–O1 2.789(2), N1–N2 1.380(4), C1–N1 1.293(4), C1–N3 1.329(4); C1-N1-K1 151.0(3), C2-N2-K1 157.3(2), N1-K1-O1 91.19(10), N2-K1-O2 73.31(8), N2-K1-O1 84.29(9), N1-K1-N2 24.02(9).

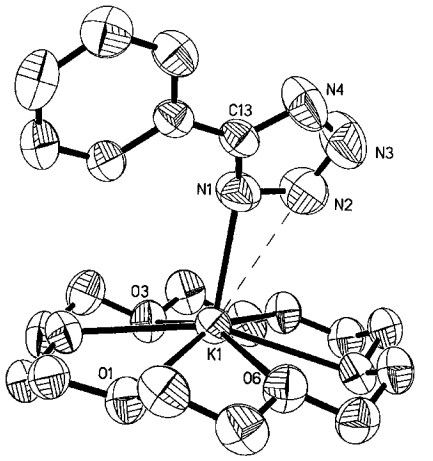



***Figure 2.*** Perspective view of **2**. Selected bond lengths [Å] and angles [°]: K1–N1 2.744(2), K1–N2 3.102(3), K1–O1 2.926(3), N1–N2 1.341(3), N2–N3 1.299(3), N3–N4 1.342(3); K1-N2-N3 160.22(17), K1-N1-C13 153.62(13), N1-K1-N2 25.60(5).

the metal–nitrogen bond lengths was clearly attributable to steric crowding. In **1** and **2**, the steric demands of the C-bound substituents of the azolato ligands are not particularly high, and so the slipped $\eta^2$ bonding cannot be a result of to steric crowding. The structural distortions observed in **1** and **2**, that is, the slipped $\eta^2$ coordination modes and the bending in **2**, must reflect optimization of the bonding interactions between the azolato ligands and the potassium center. The bending in **2** suggests that the basicity of the in-plane nitrogen lone pairs is reduced in tetrazolato ligands to the point where the out-of-plane $\pi$ orbitals may be similar in energy. The results of this study are of fundamental importance, and have implications for efforts to prepare metal complexes containing pentazolato ligands. In particular, **2** is thermally stable and shows no tendency to undergo cycloreversion to benzonitrile and (azido)([18]crown-6)potassium.[21] Accordingly, it is possible that (pentazolato)([18]crown-6)potassium may exhibit a similar stability toward loss of dinitrogen, and might therefore possess sufficient thermal stability to allow its isolation. The slipped $\eta^2$-azolato ligands in **1** and **2** suggest that a similar coordination mode could be present in (pentazolato)([18]-crown-6)potassium. However, extrapolation of the bending observed in **2** to the pentazolato ligand raises the intriguing possibility that (pentazolato)([18]crown-6)potassium may exist with a facial $\eta^2$-pentazolato ligand or even an $\eta^5$-pentazolato ligand. In this vein, similar bending features have been found in related 1,2,4-di-*tert*-butyltriphospholylato and 1,4,2-di-*tert*-butylstibadiphospholylato complexes of lanthanide ions.[22] Additionally, recent theoretical studies predicted that bis($\eta^5$-pentazolato)iron(II) is stable thermodynamically and may have sufficiently thermal stability to allow isolation.[5a,b]

## Experimental Section

Complexes **1** and **2** were not noticeably affected by short exposure to air, but were hygroscopic upon extended exposure. Accordingly, all manipulations were performed under a purified argon atmosphere using standard Schlenk techniques.

**1**: A mixture of 3,5-diisopropyl-1,2,4-triazole (1.53 g, 10.0 mmol), potassium hydride (0.42 g, 10.5 mmol), and [18]crown-6 (2.77 g, 10.5 mmol) in THF (100 mL) was stirred at ambient temperature for 5 h until hydrogen evolution was complete. The volatile components were then removed under reduced pressure, and the resulting residue was washed with hexane to afford **1** as an analytically pure white solid (4.01 g, 88%); m.p. 167°C; $^1$H NMR (400 MHz, $CD_3OD$, 23°C, TMS): $\delta = 3.61$ (s, 24H; $OCH_2$), 3.01 (septet, $^2J = 7.2$ Hz, 2H; CH), 1.27 ppm (d, $^2J = 7.2$ Hz, 12H; $CH_3$); $^{13}$C{$^1$H} NMR (100 MHz, $CD_3OD$, 23°C, TMS): $\delta = 168.23$ (s; NCCH), 71.33 (s; $OCH_2$), 29.15 (s; *C*$HCH_3$), 22.59 ppm (s; $CH_3$); MS (EI): *m*/*z* (%): 303 (100) [K([18]crown-6)]$^+$; Elemental analysis (%) calcd for $C_{20}H_{38}KN_3O_6$: C 52.72, H 8.41, N 9.22; found: C 52.59, H 8.34, N 9.24. Single crystals suitable for X-ray diffraction analysis were obtained from THF/hexane (1/1) at −20°C.

**2**: In a fashion similar to the preparation of **1**, reaction of 5-phenyltetrazole (1.46 g, 10.0 mmol), potassium hydride (0.42 g, 10.5 mmol), and [18]crown-6 (2.77 g, 10.5 mmol) afforded **2** as a white solid (4.22 g, 94%); m.p. 157°C; $^1$H NMR (400 MHz, $CD_3OD$, 23°C, TMS): $\delta = 7.27$, 7.28 (m, 5H; aromatic CH), 3.41 ppm (s, 24H; $OCH_2$); $^{13}$C{$^1$H} NMR (100 MHz, $CD_3OD$, 23°C, TMS): $\delta = 162.93$ (s; tetrazolato ring CN), 131.42 (s; Ph ring CH), 129.71 (s; overlapping Ph ring CH and *ipso*-C), 127.73 (s; Ph ring CH), 71.31 ppm (s; $CH_2$); MS (EI): *m*/*z* (%): 303 (100) [K([18]crown-6)]$^+$; Elemental analysis (%) calcd for $C_{19}H_{29}KN_4O_6$: C 50.88, H 6.52, N 12.49; found: C 50.32, H 6.46, N 12.55. Single crystals suitable for X-ray diffraction analysis were obtained from THF at ambient temperature.

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[1] For reviews on pyrazolato complexes, see a) F. Nief, *Eur. J. Inorg. Chem.* **2001**, 891–904; b) J. E. Cosgriff, G. B. Deacon, *Angew. Chem.* **1998**, *110*, 298–299; *Angew. Chem. Int. Ed.* **1998**, *37*, 286–287; c) G. La Monica, G. A. Ardizzoia, *Prog. Inorg. Chem.* **1997**, *46*, 151–238; d) A. P. Sadimenko, S. S. Basson, *Coord. Chem. Rev.* **1996**, *147*, 247–297; e) S. Trofimenko, *Prog. Inorg. Chem.* **1986**, *34*, 115–210; f) S. Trofimenko, *Chem. Rev.* **1972**, *72*, 497–508.

[2] For selected recent examples of pyrazolato coordination modes to single metal centers, see a) $\eta^1$: L. R. Falvello, J. Fornies, A. Martin, R. Navarro, V. Sicilia, P. Villarroya, *Chem. Commun.* **1998**, 2429–2430 (C-bonded); W. Zheng, H. W. Roesky, M. Noltemeyer, *Organometallics* **2001**, *20*, 1033–1035 (N-bonded); b) $\eta^2$: G. B. Deacon, C. M. Forsyth, A. Gitlits, R. Harika, P. C. Junk, B. W. Skelton, A. H. White, *Angew. Chem.* **2002**, *114*, 3383–3385; *Angew. Chem. Int. Ed.* **2002**, *41*, 3249–3251; G. B. Deacon, E. E. Delbridge, B. W. Skelton, A. H. White, *Angew. Chem.* **1998**, *110*, 2373–2373; *Angew. Chem. Int. Ed.* **1998**, *37*, 2251–2252; I. A. Guzei, A. G. Baboul, G. P. A. Yap, A. L. Rheingold, H. B. Schlegel, C. H. Winter, *J. Am. Chem. Soc.* **1997**, *119*, 3387–3388; c) $\eta^3$: G. B. Deacon, E. E. Delbridge, C. M. Forsyth, *Angew. Chem.* **1998**, *110*, 1880–1882; *Angew. Chem. Int. Ed.* **1999**, *38*, 1766–1767; d) $\eta^5$: J. R. Perera, M. J. Heeg, H. B. Schlegel, C. H. Winter, *J. Am. Chem. Soc.* **1999**, *121*, 4536–4537; A. Steiner, G. T. Lawson, B. Walfort, D. Leusser, D. Stalke, *J. Chem. Soc. Dalton Trans.* **2001**, 219–221; G. B. Deacon, A. Gitlits, P. W. Roesky, M. R. Bürgstein, K. C. Lim, B. W. Skelton, A. H. White, *Chem. Eur. J.* **2001**, *7*, 127–138.

[3] Recent review on the coordination chemistry of 1,2,4-triazole-derived ligands: J. G. Haasnoot, *Coord. Chem. Rev.* **2000**, *200–202*, 131–185.

[4] For leading references to the coordination chemistry of 1,2,4-triazolato and tetrazolato ligands, see a) C. Yélamos, K. R. Gust, A. G. Baboul, M. J. Heeg, H. B. Schlegel, C. H. Winter, *Inorg. Chem.* **2001**, *40*, 6451–6462; b) N. C. Mösch-Zanetti, M. Ferbinteanu, J. Magull, *Eur. J. Inorg. Chem.* **2002**, 950–956.

[5] Selected recent papers describing theoretical studies on $N_5^-$ ions and metal complexes thereof: a) J. Frunzke, M. Lein, G. Frenking, *Organometallics* **2002**, *21*, 3351–3359; b) M. Lein, J. Frunzke, A. Timoshkin, G. Frenking, *Chem. Eur. J.* **2001**, *7*, 4155–4163; c) L. A. Burke, R. N. Butler, J. C. Stephens, *J. Chem. Soc. Perkin Trans. 2* **2001**, 1679–1684; d) S. Fau, K. J. Wilson, R. J. Bartlett, *J. Phys. Chem. A* **2002**, *106*, 4639–4644; e) L. Gagliardi, G. Orlandi, S. Evangelisti, B. O. Roos, *J. Chem. Phys.* **2001**, *114*, 10733–10737; f) X. Wang, H.-R. Hu, A. Tian, N. B. Wong, S.-H. Chien, W.-K. Li, *Chem. Phys. Lett.* **2000**, *329*, 483–489; g) S. A. Perera, R. J. Bartlett, *Chem. Phys. Lett.* **1999**, *314*, 381–387; h) M. N. Glukhovtsev, P. von R. Schleyer, C. Maerker, *J. Phys. Chem.* **1993**, *97*, 8200–8206.

[6] A. Vij, J. G. Pavlovich, W. W. Wilson, V. Vij, K. O. Christie, *Angew. Chem.* **2002**, *114*, 3177–3180; *Angew. Chem. Int. Ed.* **2002**, *41*, 3051–3054.

[7] For selected leading references to $P_5^-$ complexes, see E. Urzenius, W. W. Brennessel, C. J. Cramer, J. E. Ellis, P. von R. Schleyer, *Science* **2002**, *295*, 832–834; P. Sekar, M. Scheer, A.

  

Voigt, R. Kirmse, *Organometallics* **1999**, *18*, 2833 – 2837; O. J. Scherer, T. Hilt, G. Wolmershäuser, *Organometallics* **1998**, *17*, 4110 – 4112; M. Detzel, G. Friedrich, O. J. Scherer, G. Wolmershäuser, *Angew. Chem.* **1995**, *107*, 1454 – 1456; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1321 – 1325; A. K. Hughes, V. J. Murphy, D. O'Hare, *J. Chem. Soc. Chem. Commun.* **1994**, 163 – 164; B. Rink, O. J. Scherer, G. Wolmershäuser, *Chem. Ber.* **1995**, *128*, 71 – 73; B. Rink, O. J. Scherer, G. Heckmann, G. Wolmershäuser, *Chem. Ber.* **1992**, *125*, 1011 – 1016.

[8] N. C. Mösch-Zanetti, M. Hewitt, T. R. Schneider, J. Magull, *Eur. J. Inorg. Chem.* **2002**, 1181 – 1185.

[9] P. C. Andrews, W. Clegg, R. E. Mulvey, P. A. O'Neil, H. M. M. Wilson, *J. Chem. Soc. Chem. Commun.* **1993**, 1142 – 1143.

[10] For leading references to complexes with bridging tetrazolato ligands, see L. Carlucci, G. Ciani, D. M. Proserpio, *Angew. Chem.* **1999**, *111*, 3700 – 3704; *Angew. Chem. Int. Ed.* **1999**, *38*, 3488 – 3492; E. O. John, R. D. Willett, B. Scott, R. L. Kirchmeier, J. M. Shreeve, *Inorg. Chem.* **1989**, *28*, 893 – 897.

[11] Crystallographically characterized $\eta^1$-1,2,4-tetrazolato and $\eta^1$-tetrazolato ligands coordinated to single metal centers from a Cambridge Crystallographic Database search (version 5.23, April 2002): R. Hage, J. G. Haasnoot, J. Reedijk, R. Wang, E. M. Ryan, J. G. Vos, A. L. Spek, A. J. M. Duisenberg, *Inorg. Chim. Acta* **1990**, *174*, 77 – 85; B. E. Buchanan, J. G. Vos, M. Kaneko, W. J. M. van der Putten, J. M. Kelly, R. Hage, R. A. G. de Graaff, R. Prins, J. G. Haasnoot, J. Reedijk, *J. Chem. Soc. Dalton Trans.* **1990**, 2425 – 2431; R. Hage, J. P. Turkenburg, R. A. G. De Graaff, J. G. Haasnoot, J. Reedijk, *Acta Crystallogr. Sect. C* **1989**, *45*, 381 – 383; S. Bhandari, C. G. Frost, C. E. Hague, M. F. Mahon, K. C. Molloy, *J. Chem. Soc. Dalton Trans.* **2000**, 663 – 669; S. Bhandhari, M. F. Mahon, K. C. Molloy, J. S. Palmer, S. F. Sayers, *J. Chem. Soc. Dalton Trans.* **2000**, 1053 – 1060; T. M. Becker, J. A. Krause-Bauer, C. L. Homrighausen, M. Orchin, *Polyhedron* **1999**, *18*, 2653 – 2571; K. D. Demadis, E.-S. El Samanody, T. J. Meyer, P. S. White, *Inorg. Chem.* **1998**, *37*, 838 – 839; B. Morosin, R. G. Dunn, R. Assink, T. M. Massis, J. Fronaberger, E. N. Duesler, *Acta Crystallogr. Sect. C* **1997**, *53*, 1609 – 1611; R. Guilard, I. Perrot, A. Tabard, P. Richard, C. Lecomte, Y. H. Liu, K. M. Kadish, *Inorg. Chem.* **1991**, *30*, 27 – 37; R. Das, P. Paul, K. Nag, K. Venkatsubramanian, *Inorg. Chim. Acta* **1991**, *185*, 221 – 227.

[12] a) X.-G. Zhou, Z.-E. Huang, R.-F. Cai, L.-X. Zhang, X.-F. Hou, X.-J. Feng, X.-Y. Huang, *J. Organomet. Chem.* **1998**, *563*, 101 – 112; b) H. P. H. Arp, A. Decken, J. Passmore, D. J. Wood, *Inorg. Chem.* **2000**, *39*, 1840 – 1848.

[13] C. Yélamos, M. J. Heeg, C. H. Winter, *Inorg. Chem.* **1998**, *37*, 3892 – 3894.

[14] For potassium complexes of tris(pyrazolyl)borate and related ligands, see Z. Hu, S. M. Gorun, *Inorg. Chem.* **2001**, *40*, 667 – 671; C. Janiak, S. Temizdemir, S. Dechert, *Inorg. Chem. Commun.* **2000**, *3*, 271 – 275; H. V. R. Dias, J. D. Gorden, *Inorg. Chem.* **1996**, *35*, 318 – 324; H. V. R. Dias, W. Jin, H.-J. Kim, H.-L. Lu, *Inorg. Chem.* **1996**, *35*, 2317 – 2328; C. Janiak, *Chem. Ber.* **1994**, *127*, 1379 – 1385.

[15] a) R. Grüner, Z. Benes, E. Schuber, M. Arman, *Monatsh. Chem.* **1927**, *48*, 37 – 46; b) Purchased commercially.

[16] For selected recent reports on structurally characterized complexes containing the $[K([18]crown-6)]^+$ fragment, see a) S. Neander, F. E. Tio, R. Buschumann, U. Behrens, F. Olbrich, *J. Organomet. Chem.* **1999**, *582*, 58 – 65; b) S. Neander, U. Behrens, F. Olbrich, *J. Organomet. Chem.* **2000**, *604*, 59 – 67; c) M. C. Cassani, Y. K. Gun'ko, P. B. Hitchcock, A. G. Hulkes, A. V. Khvostov, M. F. Lappert, A. V. Protechenko, *J. Organomet. Chem.* **2002**, *647*, 71 – 83; d) C. Downie, Z.-J. Tang, A. M. Guloy, *Angew. Chem.* **2000**, *112*, 346 – 348; *Angew. Chem. Int. Ed.* **2000**, *39*, 338 – 340; e) T. F. Fässler, R. Hoffmann, *Angew. Chem.* **1999**, *111*, 526 – 529; *Angew. Chem. Int. Ed.* **1999**, *38*, 543 – 545.

[17] X-ray structure determinations: The data were collected on a Siemens/Bruker P4-CCD instrument at 295(2) K with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved and refined on all $F^2$ with the programs of SHELXS-97.[18] **1**: $C_{20}H_{38}KN_3O_6$, $M_r = 455.63$, monoclinic, space group $P2(1)/c$, $a = 14.2681(15)$, $b = 9.8984(12)$, $c = 18.767(2)$ Å, $\beta = 103.605(3)°$, $V = 2576.1(5)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.175$ g cm$^{-3}$, crystal size: $0.50 \times 0.40 \times 0.20$ mm, $F(000) = 984$, $\mu(Mo_{K\alpha}) = 0.242$ mm$^{-1}$. The total number of reflections measured was 18035 in the range $4 \le 2\theta \le 57°$, of which 5968 were unique. Final $R$ indices: $R_1 = 0.0624$ ($I > 2\sigma(I)$) and $wR_2 = 0.2221$ (all data). Max./min. residual electron density: 0.61/−0.30 e Å$^{-3}$. **2**: $C_{19}H_{29}KN_4O_6$, $M_r = 448.56$, monoclinic, space group $Cc$, $a = 14.309(14)$, $b = 10.584(10)$, $c = 16.512(16)$ Å, $\beta = 114.93(2)°$, $V = 2268(4)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.314$ g cm$^{-3}$, crystal size: $0.40 \times 0.40 \times 0.20$ mm, $F(000) = 952$, $\mu(Mo_{K\alpha}) = 0.275$ mm$^{-1}$. The total number of reflections measured was 8049 in the range $5 \le 2\theta \le 56.60°$, of which 4406 were unique. Final $R$ indices: $R_1 = 0.0247$ ($I > 2\sigma(I)$) and $wR_2 = 0.0611$ (all data). Max./min. residual electron density: 0.12/−0.10 e Å$^{-3}$. CCDC-196712 (**1**) and CCDC-196713 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[18] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, **1997**.

[19] a) I. A. Guzei, G. P. A. Yap, C. H. Winter, *Inorg. Chem.* **1997**, *36*, 1738 – 1739; b) D. Pfeiffer, M. J. Heeg, C. H. Winter, *Angew. Chem.* **1998**, *110*, 2674 – 2676; *Angew. Chem. Int. Ed.* **1998**, *37*, 2517 – 2519; c) W. Zheng, N. C. Mösch-Zanetti, T. Blunck, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt, *Organometallics* **2001**, *20*, 3299 – 3303.

[20] N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Butterworth-Heinemann, Oxford, **1997**, pp. 75, 222.

[21] T. Koritsanszky, J. Buschmann, P. Luger, A. Knöchel, M. Patz, *J. Am. Chem. Soc.* **1994**, *116*, 6748 – 6756.

[22] G. B. Deacon, E. E. Delbridge, G. D. Fallon, C. Jones, D. E. Hibbs, M. B. Hursthouse, B. W. Skelton, A. H. White, *Organometallics* **2000**, *19*, 1713 – 1721; unpublished results described in G. K. Clentsmith, F. G. N. Cloke, P. B. Hitchcock, M. D. Francis, J. F. Nixon, A. G. Avent, *Eur. J. Inorg. Chem.* **2001**, 898.

  