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Synthesis and Crystal Structures of Lithium and Potassium Triazenide Complexes

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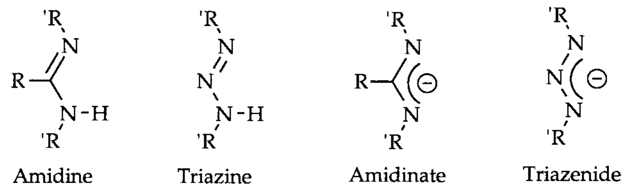
In recent years a major emphasis of organometallic chemistry has been the design and development of new monoanionic ligands which readily bind to, and stabilize, main group and transition metal complexes. The motivation behind this effort is to better control the electronic and steric properties at the metal, and thus to tailor the reactivity of the resulting complex. An example of a monoanionic ligand which has received much recent attention is the amidinate ligand (Chart 1).[1−3] This versatile ligand has been employed in the synthesis of complexes of most of the transition metals and several lanthanide, actinide, and main group elements. Amidinate-based complexes have been shown to mimic metallocene complexes as polymerization and alkyne dimerization catalysts.[4−9] Additionally, amidinate ligands stabilize early transition metal complexes containing metal−ligand multiple bonds.[10−14]

A ligand which is closely related in structure to the amidinate is the triazenide[15−18] (Chart 1). The triazenide[19] and the amidinate show similarities in their bonding to metals.[20] X-ray diffraction studies have shown that both ligands bind in monodentate, bidentate, and bridging fashions.[1−3,16] The difference between these ligands stems from the central element, which affects the electron-donating ability of the terminal nitrogens.

Insight into the effect of the central nitrogen on the electronic properties of the triazenide ligand can be understood by comparing the acidity of the N−H of the triazene to that of the amidine. Representative triazenes and their pK_a's are as follows: $H_2NN{=}NH$, 11.4;[21] (p-$C_6H_4NO_2$)NHN=N(p-$C_6H_4NO_2$), <6.4;[22,23] and benzotriazole ($C_6H_4N_3H$), 8.4−9.1.[24,25] Values for the corresponding amidines have not been determined but would be expected to be greater than that for an amide ($RCONH_2$, pK_a = 17).[26] Accordingly, triazenide ligands donate significantly less electron density to the metal than their amidinate counterparts.

Chart 1



Evaluation of the relative donor ability of the triazenide and the amidinate ligands has also been accomplished through comparison of carbonyl stretching frequencies of analogous metal carbonyl complexes containing these ligands.[27−30]

Herein we report the synthesis and structure of lithium and potassium triazenide complexes. These compounds are important starting materials for the synthesis of triazenide complexes of the transition metals.[30−34] Both structures have the dimeric core [$M_2(N_3)_2L_2$ (L = solvent)] and, to our knowledge, represent two new bonding modes for the triazenide ligand.[16]

The lithium triazenide **1** was synthesized by the dropwise addition of a hexane solution of n-butyllithium to 1,3-ditolyltriazine in ether at room temperature. Cooling to −25 °C resulted in formation of amber crystals of **1** in 81% yield. In a similar fashion, **1** was prepared by adding $LiN(SiMe_3)_2$ to an ether solution of the triazine in 85% recrystallized yield. The X-ray structure determination study revealed that the compound is the dimeric etherate.[35] An ORTEP diagram is shown in Figure 1. The bonding in the lithium triazenide, **1**, is quite similar to that in the dimeric lithium amidinates $[FcC(NCy)_2Li(Et_2O)]_2$ (Fc = Ferrocenyl, Cy = cyclohexyl), synthesized by Hagadorn and Arnold,[36] $[MeC_6H_4C(NSiMe_3)_2Li(THF)]_2$, reported by Stalke, Wedler, and Edelmann,[37] and $[PhC(NPh)_2Li(HMPA)]_2$, reported

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(1) Dehnicke, K. *Chem. Ztg.* **1990**, *114*, 295−304.
(2) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219−300.
(3) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403−481.
(4) Hagadorn, J. R.; Arnold, J. *J. Am. Chem. Soc.* **1996**, *118*, 893−894.
(5) Hagadorn, J. R.; Arnold, J. *Organometallics* **1996**, *15*, 984−991.
(6) Hagadorn, J. R.; Arnold, J. *Organometallics* **1994**, *13*, 4670−4672.
(7) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1995**, *14*, 1827−1833.
(8) Gómez, R.; Green, M. L. H.; Haggitt, J. L. *J. Chem. Soc., Dalton Trans.* **1996**, 939−946.
(9) Littke, A.; Sleiman, N.; Bensimon, C.; Richeson, D. S.; Yap, G. P. A.; Brown, S. J. *Organometallics* **1998**, *17*, 446−451.
(10) Hagadorn, J. R.; Arnold, J. *Inorg. Chem.* **1997**, *36*, 2928−2929.
(11) Dawson, D. Y.; Arnold, J. *Organometallics* **1997**, *16*, 1111−1113.
(12) Mountford, P. *J. Chem. Soc., Chem. Commun.* **1997**, 2127−2134.
(13) Hagadorn, J. R.; Arnold, J. *Organometallics* **1998**, *17*, 1355−1368.
(14) Müller, E.; Müller, J.; Olbrich, F.; Brüser, W.; Knapp, W.; Abeln, D.; Edelmann, F. T. *Eur. J. Inorg. Chem.* **1998**, 87−91.
(15) Patia, S. *The Chemistry of Diazonium and Diazo Groups*; John Wiley and Sons: New York, 1978; Vol. 1.
(16) Moore, D. S.; Robinson, S. D. *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 1−68.
(17) Campbell, T. W.; Day, B. F. *Chem. Rev.* **1951**, *48*, 299−317.
(18) Vrieze, K.; Van Koten, G. *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1987; Vol. 2, pp 189−244.
(19) Hartmen, W. W.; Dickey, J. B. *Organic Syntheses*; John Wiley and Sons: New York, 1943; Collect. Vol. II, pp 163−165.
(20) Hursthouse, M. B.; Mazid, A.; Clark, T.; Robinson, S. D. *Polyhedron* **1993**, *12*, 563−565.
(21) Sutherland, J. W. *J. Phys. Chem.* **1979**, *83*, 789−795.
(22) Dwyer, F. P. *J. Soc. Chem. Ind.* **1938**, *57*, 351−357.
(23) Sawicki, E.; Hauser, T. R.; Stanley, T. W. *Anal. Chem.* **1959**, *31*, 2063−2065.
(24) Hansen, L. D.; West, B. D.; Baca, E. J.; Blank, C. L. *J. Am. Chem. Soc.* **1968**, *90*, 6588−6592.
(25) Aten, W. C.; Büchel, K. H. *Z. Naturforsch.* **1970**, *25b*, 961−965.
(26) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley and Sons: New York, 1992.
(27) King, R. B.; Nainan, K. C. *Inorg. Chem.* **1975**, *14*, 271−274.
(28) de Roode, W. H.; Beekes, M. L.; Oskam, A.; Vrieze, K. *J. Organomet. Chem.* **1977**, *142*, 337−349.
(29) Inglis, T.; Kilner, M. *J. Chem. Soc., Dalton Trans.* **1975**, 930−934.
(30) Rossi, R.; Duatti, A.; Magon, L.; Toniolo, L. *Inorg. Chim. Acta* **1980**, *48*, 243−246.
(31) Knoth, W. H. *Inorg. Chem.* **1973**, *12*, 38−44.
(32) Gómez, M.; Muller, G.; Sales, J. *Polyhedron* **1993**, *12*, 1171−1177.
(33) Toniolo, L.; Immirzi, A.; Croatto, U.; Bombieri, G. *Inorg. Chim. Acta* **1976**, *19*, 209−214.
(34) Candeloro de Sanctis, S.; Toniolo, L.; Boschi, T.; Deganello, G. *Inorg. Chim. Acta* **1975**, *12*, 251−254.

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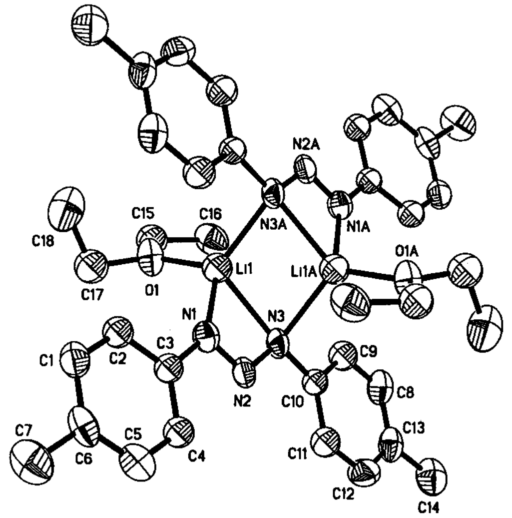

Figure 1. Molecular structure of **1**. Important distances (Å) and angles (deg): Li(1)−N(1) = 2.070(17), Li(1)−N(2) = 2.511(17), Li(1)−N(3) = 2.181(17), Li(1)−O(1) = 1.911(16), N(1)−N(2) = 1.292(10), N(2)−N(3) = 1.318(10), Li(1A)−N(3) = 2.139(15), N(1)−N(2)−N(3) = 113.6(6), N(1)−Li(1)−N(3) = 61.8(5), N(1)−Li(1)−N(3A) = 118.5(7), O(1)−Li(1)−N(3) = 126.1(7), O(1)−Li(1)−N(3A) = 119.7(8), N(3)−Li(1)−N(3A) = 104.2(6).

by Barker and co-workers[38] (although different binding modes for lithium amidinates have also been observed).[38−41] The Li1−N3−Li1A−N3A core of **1** is planar as in the dimers [FcC(NCy)$_2$Li(Et$_2$O)]$_2$ and [PhC(NPh)$_2$Li(HMPA)]$_2$ whereas the dimer [MeC$_6$H$_4$C(NSiMe$_3$)$_2$Li(THF)]$_2$ has a puckered core. The Li−N distances of **1** are from 2.070 to 2.181 Å. These distances are slightly longer than the Li−N distances found in [FcC(NCy)$_2$Li(Et$_2$O)]$_2$, which fall in the range 2.010−2.158 Å and closer to those of PhC(NPh)$_2$Li(HMPA)]$_2$, which lie between 2.046 and 2.173 Å. The longer Li−N distances of **1** are most likely a result of the decreased donor ability of the triazenide relative to the amidinate ligand. Additionally, the Li−O distance of the etherate in **1** is 1.911 Å while the ether Li−O distance in [FcC(NCy)$_2$Li(Et$_2$O)]$_2$ is slightly longer at 1.951 Å.

We have also prepared the potassium analogue by three methods. Reaction of potassium hydride with a solution of the triazine dissolved in DME resulted in the evolution of hydrogen and formation of a precipitate. The solid was dissolved on addition of THF and the solution filtered to remove a trace of insoluble material. Cooling to −25 °C resulted in formation of amber crystals of **2**, which were isolated in 74% yield. Compound **2** was also prepared by deprotonation of the triazine with KN(SiMe$_3$)$_2$ or KO-*t*-Bu in a similar fashion in 86 and 82% recrystallized yield, respectively. X-ray quality crystals were grown from THF/DME at −25 °C.[42] An ORTEP drawing is shown in Figure 2. The bonding of the triazenide to the potassium in **2** is significantly different from that of the lithium triazenide dimer **1** and more closely related to the dimeric sodium amidinate [PhC(NSiMe$_3$)$_2$Na(Et$_2$O)]$_2$. Each potassium is bonded to two triazenide ligands; however, unlike the geometry in the lithium dimer, the potassium atoms are positioned above and below the plain defined by the three nitrogens of the triazenide ligand. The K−N bond distances range from 2.824 to 2.978 Å, with the K1−N2 distance significantly longer at 3.230 Å. The coordination sphere of the seven-coordinate potassium is completed by an η^2-DME and the oxygen of a DME which is bridged to a neighboring potassium of a K$_2$(N$_3$)$_2$ unit. The bridging DME makes the structure polymeric. The K1−O2 distance is 2.755 while the bridging oxygen has a K1−O1 distance of 2.845 Å and a K1B−O1 distance of 2.779 Å.

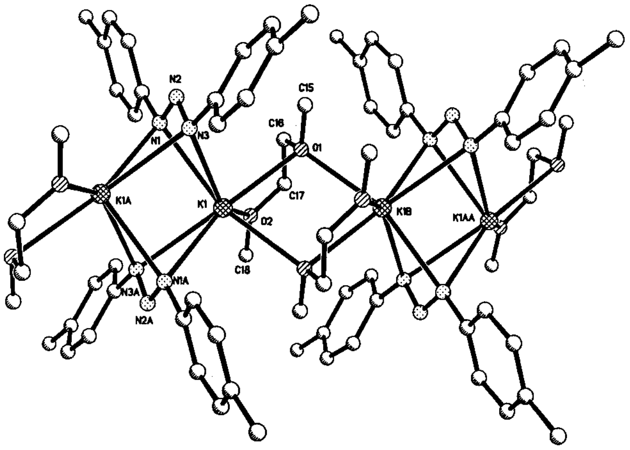

Figure 2. Molecular structure of **2**. Important distances (Å) and angles (deg): K(1)−N(1) = 2.824(3), K(1)−N(2) = 3.302(3), K(1)−N(3) = 2.978(2), K(1)−O(1) = 2.845(2), K(1)−O(2) = 2.755(2), K(1)−O(1A) = 2.799(2), K(1A)−N(1) = 2.826(2), K(1A)−N(2) = 3.230(2), K(1A)−N(3) = 2.916(2), N(1)−N(2) = 1.313(2), N(2)−N(3) = 1.315(2), K(1)−N(3A) = 2.916(2), N(1)−N(2)−N(3) = 113.6(6), N(1)−K(1)−N(3) = 61.8(5), N(1)−K(1)−N(3A) = 118.5(7), O(1)−K(1)−N(3) = 126.1(7), O(1)−K(1)−N(3A) = 119.7(8), N(3)−K(1)−N(3A) = 104.2(6).

In conclusion, we have synthesized and structurally characterized two triazenide complexes which both contain the [M(N$_3$)]$_2$ subunit. We are currently using these compounds as precursors for the synthesis of main group and transition metal derivatives as well as developing modified triazene ligands.

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Supporting Information Available: Characterization and X-ray crystal structure data for **1** and **2** (19 pages). Ordering information is given on any current masthead page.

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(35) **X-ray Data for 1**. Data were collected at 193 K using highly oriented graphite crystal monochromated Mo Kα radiation. There were 2702 reflections collected in the 2θ range 3.0−45.0°, of which 2307 were unique (R_{int} = 1.89%). The structure was solved by direct methods, and non-hydrogen atoms were refined anisotropically. In the final least-squares refinement cycle on F, R = 9.05%, R_w = 10.88%, and GOF = 2.02 for 1103 reflections with $F > 4.0\sigma(F)$ and 139 parameters. The crystal data are a = 11.12(2) Å, b = 9.293(7) Å, c = 17.102(16) Å, β = 92.16(11)°, V = 1766(4) Å^3, space group $P2_1/c$, Z = 4, MW = 305.3, and ρ(calcd) = 1.148 g/cm^3.

(36) Hagadorn, J. R.; Arnold, J. *Inorg. Chem.* **1997**, *36*, 132−133.

(37) Stalke, D.; Wedler, M.; Edelmann, F. T. *J. Organomet. Chem.* **1992**, *431*, C1−C5.

(38) Barker, J.; Barr, D.; Barnett, N. D. R.; Clegg, W.; Cragg-Hine, I.; Davidson, M. G.; Davies, R. P.; Hodgson, S. M.; Howard, J. A. K.; Kliner, M.; Lehmann, C. W.; Lopez-Solera, I.; Mulvey, R. E.; Raithby, P. R.; Snaith, R. *J. Chem. Soc., Dalton Trans.* **1997**, 951−955.

(39) Cragg-Hine, I.; Davidson, M. G.; Mair, F. S.; Raithby, P. R.; Snaith, R. *J. Chem. Soc., Dalton Trans.* **1993**, 2423−2424.

(40) Eisen, M. S.; Kapon, M. *J. Chem. Soc., Dalton Trans.* **1994**, 3507−3510.

(41) Gebauer, T.; Dehmicke, K.; Goesmann, H.; Fenske, D. *Z. Naturforsch., B* **1994**, *49*, 1444.

(42) **X-ray Data for 2**. Data were collected at 192 K using highly oriented graphite crystal monochromated Mo Kα radiation. There were 4681 reflections collected in the 2θ range 3.0−55.0°, of which 4478 were unique (R_{int} = 2.41%). The structure was solved by direct methods, and non-hydrogen atoms were refined anisotropically. In the final least-squares refinement cycle on F, R = 4.66%, R_w = 7.08%, and GOF = 1.38 for 3820 reflections with $F > 4.0\sigma(F)$ and 222 parameters. The crystal data are a = 7.633(5) Å, b = 10.664(6) Å, c = 13.360(8) Å, α = 108.750(10)°, β = 91.490(10)°, γ = 107.360(10)°, V = 973.8(11) Å^3, space group $P\bar{1}$, Z = 2, MW = 353.5, and ρ(calcd) = 1.206 g/cm^3.