Published in final edited form as:

Dalton Trans. 2006 August 28; (32): 3855–3857.

A dinucleating ligand related to the β -diketiminates

Travis J. Hebden, William W. Brennessel, Christine J. Flaschenriem, and Patrick L. Holland

Department of Chemistry, University of Rochester, Rochester, NY 14627, USA. E-mail:

holland@chem.rochester.edu

Abstract

A new ligand conceptually creates two sites reminiscent of β -diketiminates, and upon deprotonation the salts exist in oligomeric forms with potassium ions linking multiple ligands.

Sterically demanding β -diketimate ligands have come into wide use as tools for forming low-coordinate inorganic and organometallic complexes.¹ In many cases multimetallic complexes or intermediates are formed that have interesting properties. For example, zinc β -diketimate complexes catalytically copolymerise ² We CO₂ and epoxides through a bimetallic mechanism. have reported the cleavage of N–N single bonds and N=N double bonds using diiron(II) complexes.^{3,4} One way of understanding these bimetallic reactions is to create dinucleating ligands incorporating multiple β -diketimate units.⁵

One conceptually can fuse two β -diketimate groups by attaching two deprotonated enamines to a heterocycle such as pyridazine or phthalazine. Other workers have reported dinucleating ligands based on these scaffolds.⁶ Following this strategy, 1,4-dichlorophthalazine was treated with four equivalents of a deprotonated *t*-butyl methyl imine precursor to give 1,4-bis-(2-(2,6-diisopropylphenylimino)-3,3-dimethylbutyl)-phthalazine (**1**, Scheme 1).[†] It is necessary to use four equivalents because the deprotonated imine is a strong enough base to deprotonate the product. The imine byproduct may be recovered through distillation.

The molecular structure of **1** is shown in Fig. 1. The bond distances in **1** are consistent with a C1–C2 single bond and a C1=N1 double bond: this molecule exists as the imine tautomer shown in Scheme 1 rather than the enamine tautomer that predominates in the β -diketiminates.⁷ The ¹H NMR spectrum of **1** includes a singlet corresponding to four hydrogen atoms on C2 per molecule, and no N–H peak is observed. This suggests that if the enamine/imine or bisenamine tautomers of **1** exist in solution they are minor species. To test whether the minor tautomer is formed, a solution of **1** in THF-*d*₈ with a drop of D₂O was sonicated for several days at room temperature. Proton NMR spectroscopy showed no decrease in the integration for the methylene protons, indicating that the hydrogen atom on C2 does not exchange with solvent. We conclude that enamines are not formed under these conditions.

Correspondence to: Patrick L. Holland.

[†]**1**: Under an atmosphere of N₂, a slurry of lithiated imine was prepared according to ref. ⁹ (159 mmol in 250 mL pentane) and cooled to –55 °C. A solution of 1,4-dichlorophthalazine (7.93 g, 39.8 mmol) in THF (300 mL) was added dropwise, and the mixture was warmed to room temperature and stirred overnight. The solution was quenched with aqueous HCl (0.08 M, 100 mL). The organic phase was dried over Na₂ SO₄ and concentrated to a sticky orange solid, which was dissolved in hot toluene (250 mL) and cooled to –20 °C. The light yellow solid was isolated by filtration and rinsed with cold hexanes. Yield: 15.17 g, 59%; mp 249 °C; Elem. Anal. C, 81.9; H, 9.4; N, 8.6 (C₄₄ H₆₀ N₄ requires C, 81.9; H, 9.4; N, 8.7%); IR: ν_{max} (KBr) 1659 cm^{–1} (imine CN); δ_{H} (400 MHz; C₆ D₆) 1.19 (12H, d, *J* = 7 Hz, CH(CH₃)₂), 1.28 (12H, d, *J* = 7 Hz, CH(CH₃)₂), 1.43 (18H, s, C(CH₃)₃), 3.20 (4H, septet, *J* = 7 Hz, CH(CH₃)₂), 3.96 (4H, s, C2–H₂), 6.92 (2H, t, *J* = 8 Hz, *p*-Ar), 6.95 (8H, m, *m*-Ar and phthalazine); δ_{C} (161 MHz; C₆ D₆) 22.4, 24.2, 28.7, 29.7, 33.2, 41.8, 123.3, 123.9, 124.0, 125.4, 131.5, 136.6, 147.2, 156.0, 175.2. Crystal data: C₄₄ H₆₀ N₄, *M* = 645, monoclinic, *a* = 17.384(3) Å, *b* = 17.457(3) Å, *c* = 13.119(2) Å, β = 100.347(3)°, *V* = 3916.3(11) Å³, *T* = 100 K, space group C2/c (#15), *Z* = 4, μ (Mo–K α) = 0.064 mm^{–1}, 25674 reflections measured, 4921 unique (*R*_{int} = 0.0501), *R* 0.0529, *wR*₂ 0.1381.

Compound **1** was deprotonated by heating a THF solution to 60 °C overnight with four molar equivalents of KH to ensure complete deprotonation.[‡] Proton NMR spectra of the red product **2** show a compound with a singlet for the C2–H protons, one on each arm. An intense peak in the infrared spectrum of **1** at 1659 cm^{−1} is absent from **2**, indicating that the imine functionality has been altered. These data suggest an azaallyl anion from delocalisation of the negative charge generated by methylene deprotonation.

X-Ray quality crystals of **2** were grown by vapour diffusion of a diethyl ether solution into toluene under a N₂ atmosphere. The crystal structure indicates that **2** has two azaallyl anions (N1–C1–C2), consistent with the spectroscopic data. The conjugation does not extend into the phthalazine ring due to twisting of the azaallyl arms out of the plane of the phthalazine.¹ This contrasts with known lithium and potassium β-diketiminato complexes, which are usually planar.⁸ Fig. 2 shows that instead of a simple dipotassium salt, the product is a dimer of two dinucleating ligands with four potassium ions. The two phthalazine rings are twisted 50.61(5)° relative to one another. The potassium environments fall into two classes. Two potassium ions (K2, K3) bind to lone pairs of two heterocyclic nitrogen atoms and to two azaallyl π-systems (Fig. 3a), giving eight coordinate potassium. The other two potassium ions (K1, K1A) bind to the lone pairs of two arm nitrogen atoms, and to the N–N bonds of both phthalazines, giving six coordination (Fig. 3b).

A persistent impurity in samples of **2** was also crystallographically characterised (Fig. 4), showing that it contains **3**, a monoanionic version of the ligand coordinated to potassium. The potassium ions are bound in an η³-benzyl interaction with an azaallyl group and in an η² interaction with the phthalazine of another ligand, linking each anion to two others. The bond lengths in the remaining imine indicate a double bond between C1 and N1, and two hydrogen atoms are attached to C2. Therefore, **3** represents a protonation level between **1** and **2**. Each potassium ion in **3** is also coordinated by a diethyl ether solvent molecule, giving six coordinate potassium.

In conclusion, we have created a dinucleating analogue of the β-diketiminato ligands with a phthalazine core. The high coordination number of potassium gives nonplanar conformations of the anionic ligands, and further studies will explore whether these ligands lead to discrete bimetallic complexes of transition metals.

Acknowledgements

We acknowledge support from the University of Rochester, the National Institutes of Health (GM65313), Boehringer-Ingelheim Pharmaceuticals (Master's Fellowship) and Xerox Corp. (REACH funding).

References

1. Bourget-Merle L, Lappert MF, Severn JR. Chem Rev 2002;102:3031. [PubMed: 12222981]A review on β-diketiminates

[‡]**2**: Under an atmosphere of N₂, **1** (0.563 g, 0.873 mmol) and KH (0.0140 g, 3.49 mmol) were weighed into a bomb flask and cooled to −45 °C. Cold THF (−45 °C, 20 mL) was added while stirring. After 30 min, the red slurry was stirred for 14 h at 60 °C. The resulting dark blue mixture was filtered through Celite and reduced *in vacuo* to give **2** as a dark red solid. Yield: 0.561 g, 89%. Compound **2** is highly sensitive and slowly decomposes even in the glove box as a solid. Elem. Anal. C, 73.5; H, 8.3; N, 7.6 (C₈₈H₁₁₆N₈K₄ requires C, 73.3; H, 8.1; N 7.8%); δ_H (500 MHz; THF-*d*₈) 0.90 (12H, d, *J* = 7 Hz, CH(CH₃)₂), 1.01 (12H, d, *J* = 7 Hz, CH(CH₃)₂), 1.37 (18H, s, C(CH₃)₃), 3.37 (4H, septet, *J* = 7 Hz, CH(CH₃)₂), 5.01 (2H, s, C2–H), 6.30 (2H, t, *J* = 7 Hz, *p*-Ar), 6.70 (4H, d, *J* = 7 Hz, *m*-Ar), 7.22 (2H, dd, *J* = 6, 3 Hz, phthalazine), 7.72 (2H, dd, *J* = 6, 3 Hz, phthalazine); δ_C (161 MHz; THF-*d*₈) 21.6, 22.8, 26.3, 29.6, 39.6, 77.6, 112.1, 120.1, 122.6, 126.1, 126.2, 135.4, 147.6, 150.9, 162.2; crystal data for **2**·Et₂O: C₉₂H₁₂₆N₈K₄O, *M* = 1516, trigonal, *a* = *b* = 14.1939(7) Å, *c* = 37.812(4) Å, *V* = 6597.2(8) Å³, *T* = 223 K, space group *P*3₂21 (#152), *Z* = 3, μ(Mo-Kα) = 0.251 mm^{−1}, 64 605 reflections measured, 13 293 unique (*R*_{int} = 0.0562), *R* 0.0512, *wR*₂ 0.1184. Compound **3** crystallized as a toluene solvate, crystal data: C_{51.5}H₇₃N₄KO, *M* = 803, monoclinic, *a* = 9.480(1) Å, *b* = 32.013(4) Å, *c* = 15.899(2) Å, *V* = 4758.6(9) Å³, *T* = 100 K, space group *P*2₁/n (#14), *Z* = 4, μ(Mo-Kα) = 0.151 mm^{−1}, 55 151 reflections measured, 13 796 unique (*R*_{int} = 0.0429), *R* 0.0624, *wR*₂ 0.1609. CCDC reference numbers 608908–608910. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b607440e

2. Moore DR, Cheng M, Lobkovsky EB, Coates GW. *J Am Chem Soc* 2003;125:11911. [PubMed: 14505413]
3. Smith JM, Lachicotte RJ, Holland PL. Vela J, Stoian S, Flaschenreim CJ, Münck E, Holland PL. *J Am Chem Soc* 2003;2004;125:126:15752. 4522. [PubMed: 14677959]
4. Holland PL. *Can J Chem* 2005;83:296. The use of β -diketiminato complexes as mimics of nitrogenase
5. Allen SD, Moore DR, Lobkovsky EB, Coates GW. Bourget-Merle L, Hitchcock PB, Lappert MF. Lee SY, Na SJ, Kwon HY, Lee BY, Kang SO. Lee BY, Kwon HY, Lee SY, Na SJ, Han S, Yun H, Lee H, Park YW. *J Organomet Chem J Organomet Chem Organometallics J Am Chem Soc* 2003;2004;2004;2005;683:68923:127:137. 4357, 5382, 3031.
6. Manzur J, García AM, Letelier R, Spodine E, Peña O, Grandjean D, Olmstead MM, Noll BC. Spodine E, Atria AM, Manzur J, García AM, Garland MT, Hocquet A, Sanhueza E, Baggio R, Peña O, Saillard JY. Barrios AM, Lippard SJ. Gavrilova AL, Bosnich B. *J Chem Soc, Dalton Trans J Chem Soc, Dalton Trans J Am Chem Soc Chem Rev* 1993;1997;1999;2004;121:104:905. 3683, 11751, 349.
7. Wright RJ, Power PP, Scott BL, Kiplinger JL. *Organometallics* 2004;23:4801.
8. Clegg W, Cope EK, Edwards AJ, Mair FS. Stender M, Wright RJ, Eichler BE, Prust J, Olmstead MM, Roesky HW, Power PP. Carey DT, Cope-Eatough EK, Vilaplana-Mafé E, Mair FS, Pritchard RG, Warren JE, Woods RJ. *Inorg Chem J Chem Soc, Dalton Trans Dalton Trans* 1998;2001;2003;37:2317. 3465, 1083. [PubMed: 11670390]
9. Budzelaar PHM, van Oort AB, Orpen AG. *Eur J Inorg Chem* 1996:3539. Lithiated imine preparation

Fig. 1. Thermal-ellipsoid plot of **1** showing 50% probability ellipsoids. Hydrogen atoms and *iso*-propyl groups have been omitted for clarity.

Fig. 2. Thermal-ellipsoid plot of compound **2**, which has two dianions connected by four K^+ ions. Hydrogen atoms, *tert*-butyl and *iso*-propyl groups have been omitted for clarity.

Fig. 3.

(a) Two of the four K^+ ions in **2** are bound η^3 to two azallyl anions and η^1 to a phthalazine nitrogen. (b) Two of the four K^+ ions in **2** are bound η^1 to two azallyl anions and η^2 to the phthalazine nitrogens. R = $CHC(tBu)N(2,6-diisopropylphenyl)$.

Fig. 4. Thermal-ellipsoid plot of the X-ray crystal structure of **3**, the monodeprotonated product from compound **1**. *iso*-Propyl groups are omitted for clarity, and a second molecule is shown to indicate bridging.

Scheme 1.
Preparation of **1**. Ar = 2,6-diisopropylphenyl.