Inorganic Chemistry

Communication

pubs.acs.org/IC

Photoinduced Reactivity of the Soft Hydrotris(6-*tert*-butyl-3-thiopyridazinyl)borate Scorpionate Ligand in Sodium, Potassium, and Thallium Salts

Michael Tüchler,[†] Ferdinand Belaj,[†] Georg Raber,[‡] Dmytro Neshchadin,[§] and Nadia C. Mösch-Zanetti*,[†]

[†]Institute of Chemistry, Inorganic Chemistry, and [‡]Institute of Chemistry, Analytical Chemistry, University of Graz, Schubertstrasse 1, 8010 Graz, Austria

[§]Institute of Physical and Theoretical Chemistry, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria

Supporting Information

ABSTRACT: The soft scorpionate ligand hydrotris(6-*tert*-butyl-3-thiopyridazinyl)borate (**Tn**) was found to exhibit pronounced photoreactivity. Full elucidation of this process revealed the formation of 6-*tert*-butylpyridazine-3-thione (**PnH**) and 4,5-dihydro-6-*tert*-butylpyridazine-3-thione (**H_2PnH**). Under exclusion of light, no solvolytic reactions occur, allowing the development of high-yield preparation protocols for the sodium, potassium, and thallium salts and improving the yield for their derived copper boratrane complex. The photoreactivity is relevant for all future studies with electron-deficient scorpionate ligands.

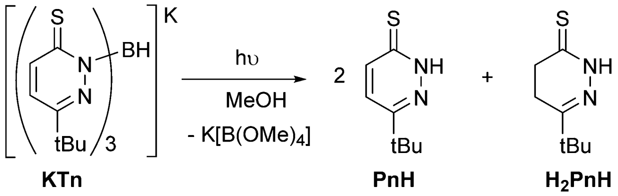
Scorpionate ligands were introduced with Trofimenko's hydrotris(pyrazolyl)borate (**Tp**) ligand in 1966.[1] It refers to an anionic, tridentate ligand that is capable of facially coordinating the metal center. The widespread use of scorpionate ligands in bioinorganic chemistry is due to their steric and electronic tunability by variation of the substituents in the backbone of the heterocycle.[2−5] The scope was further expanded with the introduction of the soft coordinating hydrotris(mercaptoimidazolyl)borate (**Tm**) ligand by Reglinski and co-workers.[6] Analogous mercapto-substituted scorpionate ligands based on benzoimidazole,[7] thiadiazole,[8,9] benzothiadiazole,[10] thiazolidine,[10,11] triazole,[12] tetrazole,[13] pyridine,[14] or pyridazine backbones[15,16] were likewise prepared. They all show significantly different chemical behavior compared to the nitrogen-based Tp ligands and are widely applied in coordination and bioinorganic chemistry.[17−24] The larger sulfur atom, as well as the larger chelate ring (8- vs 6-membered), leads to a larger coordination pocket for the metal center, allowing more flexibility of the ligand binding. This is illustrated by the occurrence of complexes with inverted boron centers, where the hydride ion points toward the coordinated metal, or the formation of direct metal (M)−B bonds.[25−27] However, the solvolytic cleavage of scorpionate ligands, especially when attached to a Lewis acidic transition metal, has been a recurrent issue.[6,22,28] It is assumed that the B−N bond weakens with decreasing electron density of the heterocycle.

We have recently developed hydrotris(3-thiopyridazinyl)borate scorpionate ligands featuring electron-deficient pyridazine heterocycles. The derived higher electrophilic complexes are prone to diverse reactivity in comparison to other scorpionate ligands, allowing isolation of the first copper boratrane complex bearing a sulfur rich environment.[15,16] However, our studies were hampered by relatively low yields, which were not accounted for by the stability of the products.

Herein, the photoinduced reactivity of the hydrotris(6-*tert*-butyl-3-thiopyridazinyl)borate (**KTn**) ligand is reported and fully elucidated. Exclusion of light allowed the development of reproducible high-yield preparation protocols for **NaTn**, **KTn**, and **TlTn**, as well as for their copper boratrane complex. Furthermore, the molecular structure of **TlTn** is reported to exhibit an unusual octanuclear array.

Upon exposure to light, a solution of **KTn** in protic solvents is transformed into 2 equiv of 6-*tert*-butylpyridazine-3-thione (**PnH**) and 1 equiv of 4,5-dihydro-6-*tert*-butylpyridazine-3-thione (**H_2PnH**), as shown in Scheme 1. Upon exclusion of light, also in protic solvents no transformation is observed.

Scheme 1. Photoreactivity of KTn



To identify the products, 0.30 g (0.54 mmol) of **KTn** was dissolved in methanol and irradiated at 365 nm for 12 h. After workup, 86 mg (0.5 mmol) of **H_2PnH** and 161 mg (0.96 mmol) of **PnH** could be isolated after column chromatography. ^{1}H and ^{13}C NMR spectra clearly identify the formation of **PnH** and **H_2PnH**. The latter reveals resonances for the aliphatic C4 and C5 and their attached protons, which are particularly distinctive as two triplets at 2.37 and 2.84 ppm integrating for two protons each.

The exclusive formation of **PnH** and **H_2PnH** is demonstrated by repeated ^{1}H NMR measurements during the reaction. A solution of **KTn** in dry methanol was irradiated at 365 nm, and samples were taken after 5, 15, 35, and 65 min, respectively. After

Received: June 24, 2015
Published: August 11, 2015

DOI: 10.1021/acs.inorgchem.5b01417
Inorg. Chem. 2015, 54, 8168−8170

evaporation of the solvent, ^{1}H NMR spectra in $CDCl_3$ were recorded [see the Supporting Information(SI), Figure S1]. The progressive decrease of **KTn** and increase of **PnH** and **H_2PnH** are demonstrated by the resonances of the *tert*-butyl groups. Furthermore, the distinct triplets for **H_2PnH** are apparent. However, no resonances for other species could be detected.

The reaction shown in Scheme 1 was also monitored by high-pressure liquid chromatography (HPLC), again showing the exclusive formation of **PnH** and **H_2PnH** (Figure 1).

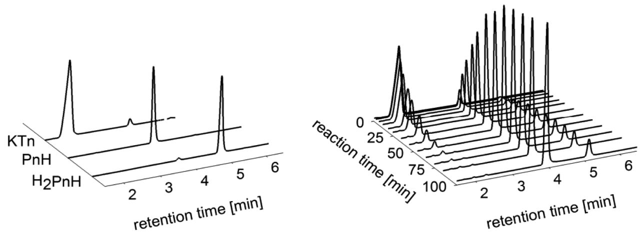


Figure 1. HPLC traces showing the retention times for **KTn**, **PnH**, and **H_2PnH** and the photoreaction of **KTn** in 65:35 (v/v) MeCN/H_2O, followed by HPLC measurements.

Furthermore, kinetic analysis revealed a first-order reaction on **KTn** with a reaction constant $k = 0.0457$ s^{-1} and a half-life time of 15.2 min (see the SI).

This points to a pronounced and fast reactivity upon UV irradiation and is consistent with our observation that even daylight induces the photoreaction. However, NMR spectroscopy of a **KTn** sample in methanol-d_4 exposed to daylight revealed only 50% conversion after 24 h. Interestingly, the ratio of **PnH** and **H_2PnH** was found to be 8:1, which is significantly higher than the expected 2:1. Apparently, hydrolysis of the B−N bond is faster than reduction of the **Pn** heterocycle. Nevertheless, no hydrolysis, even in protic solvents such as methanol, is observed under exclusion of light (see the SI). Naturally, hydrolysis of the B−N bond is also prevented by working in dry aprotic solvents, explaining the fact that in anhydrous $CHCl_3$ no reaction occurs even under irradiation. Thus, the study reported here not only fully elucidates the photochemical behavior but also shows that, upon exclusion of light, electron-deficient scorpionates are inert toward solvolysis.

The UV−vis spectrum of **KTn** in methanol (Figure 3) reveals two bands at 363 nm ($\varepsilon = 1.03 \times 10^4$ L mol^{-1} cm^{-1}) and 283 nm ($\varepsilon = 3.72 \times 10^4$ L mol^{-1} cm^{-1}). The long-wave transition can provisionally be ascribed to an n−π* excitation according to published data.[29] In situ irradiation with a Nd:YAG laser at 355 nm coupled to NMR indicated the cleavage reaction, whereas irradiation at 280 (±10) nm (high-pressure Hg−Xe lamp, monochromator) showed no conversion (see the SI, Figure S7). This is corroborated by the **Tm** ligand only featuring one absorption maximum at 258 nm, implying that the band at 363 nm is responsible for the photoreactivity.

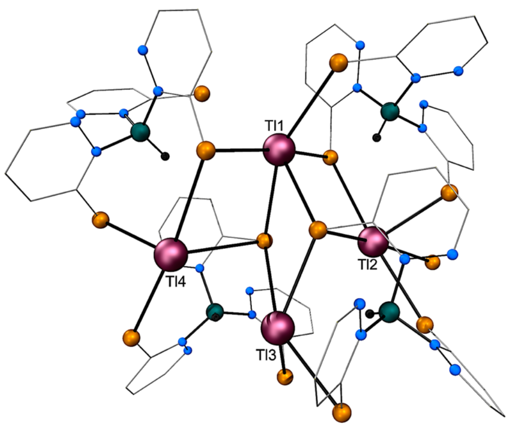


Figure 2. Molecular view of the tetrameric unit Tl1−Tl4 of **TlTn**. Hydrogen atoms, except for those located at the boron atoms, *tert*-butyl groups, and solvents are omitted for clarity.

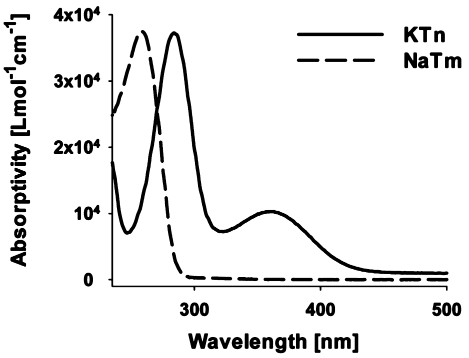


Figure 3. UV−vis spectra of 2.5 μM solutions of **KTn** and **NaTm** in methanol.

Electron-deficient scorpionate ligands are relatively rare despite their potentially interesting electronic behavior.[7,14−16,30−32] This might be due to their reactivity toward light, hampering widespread use. For example, recently Parkin and co-workers reported the preparation of oxygen-coordinating scorpionate ligands. In one example, namely, hydrotris(2-oxo-1-*tert*-butylimidazolyl)borate, low yields (7%) are reported. Interestingly, one of the isolated decomposition products was found to be the reduced 2-oxo-1-*tert*-butylimidazole,[7] which has a similar structure to **H_2PnH**. Possibly a similar photochemical influence is responsible in the mentioned example and might point to a photochemical influence in oxoimidazolyl systems.

Not only did the above-described observations allow us to significantly improve the yield in **KTn** synthesis, but also the yield for the copper boratrane complex [Cu{B(Pn)$_3$}Cl] could be increased from 36% to 84%.[16] Furthermore, we were able to prepare to date unknown **NaTn** and **TlTn** salts. Upon exclusion of light, **NaTn** could be prepared in 85% yield and **TlTn** almost quantitatively. Their photochemical behavior is identical with that of **KTn**, also requiring exclusion of light for the preparation and handling (see the SI). All three salts represent important starting materials that will widen the application of pyridazine-based scorpionate ligands in coordination chemistry.

The molecular structure of **TlTn** was determined by single-crystal X-ray diffraction analysis (Figure 2). The molecular structure of **TlTn** consists of interconnected alternating tetramers (Tl1−Tl4 and Tl5−Tl8; Figure 2), resulting in sinusoidal tubes parallel to the *a* axis (see the SI, Figure S1). Interestingly, the ligands shows three different coordination modes, as illustrated in Figure 4.

Four scorpionate ligands that are involved in bridging the two tetrameric units display a μ_4-(κ^2,κ^2,κ,κ)-coordination mode (Figure 4, motif A). Three of the nonbridging ligands show coordination motif B, where two sulfur donors coordinate to one, each, and the third sulfur coordinates to two thallium atoms, resulting in a μ-(κ^2,κ^2) mode. Interestingly, one scorpionate ligand shows a bidentate coordination with a μ-(κ^2,κ) mode, with the third sulfur having a nonbonding Tl−S distance of 3.728(3)

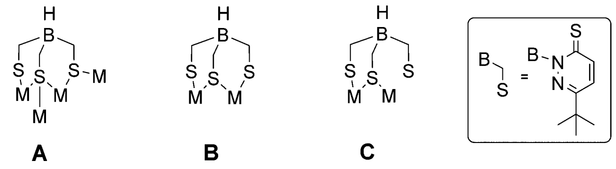


Figure 4. Coordination motifs in the molecular structure of **TlTn**.

Å. The boron−hydrogen atoms, clearly identified by a difference Fourier map, are oriented to two thallium atoms, showing average Tl−H distances of 2.77(4)−3.57(5) Å, Tl−H−Tl bond angles of 73.9(7)−94.2(11)°, and B−H−Tl bond angles of 112(4)−144(4)°.

A similar coordination mode of a scorpionate ligand has been described previously in the molecular structure of Tl[PhB(CH$_2$SR)$_3$] showing a μ-(κ^2,κ)-coordination mode.[33,34] However, the thallium center is only tetrahedrally coordinated because of the sterically more demanding phenyl substituent at boron. Another similar coordination mode, namely, a μ_3-(κ^2,κ,κ), where one sulfur is bridging two thallium atoms and a μ_5-(κ^2,κ^2,κ^2,κ,κ), has already been published, using a thallium salt of the tris(mercaptothiadiazolyl)borate ligand.[35]

In conclusion, the potassium salt, as well as the sodium and thallium salts, of the hydrotris(6-*tert*-butyl-3-thiopyridazinyl)borate ligand **Tn** shows pronounced photoreactivity in protic solvents, forming 2 equiv of **PnH** and 1 equiv of **H$_2$PnH**. The fact that, under exclusion of light, the ligand is stable presents an important finding because protic solvents are often required for solubility reasons in subsequent reactions. Thus, the yield for **KTn** and its copper boratrane complex [Cu{B(Pn)$_3$}Cl] could be improved significantly by excluding light from the reaction. Furthermore, the yet-unknown sodium and thallium salts of the ligand could be synthesized in high yields. The latter revealed an interesting polynuclear array, consisting of eight thallium atoms surrounded by eight **Tn** ligands. The discovery of the photoreactivity of electron-deficient scorpionate ligands is very relevant for their future use and will trigger the development of new electron-deficient scorpionate ligands.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01417.

Full experimental details, HPLC data, and NMR and UV−vis spectra (PDF)
Crystallographic data for CCDC 1401974 (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: nadia.moesch@uni-graz.at.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Fruitful discussions with Prof. Dr. Gescheidt (Institute for Physical and Theoretical Chemistry, Graz University of Technology) and support from NAWI Graz are gratefully acknowledged.

■ REFERENCES

(1) Trofimenko, S. *J. Am. Chem. Soc.* **1966**, *88*, 1842−1844.
(2) Looney, A.; Han, R.; McNeill, K.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 4690−4697.
(3) Looney, A.; Parkin, G.; Alfsasser, R.; Ruf, M.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 92−3.
(4) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943−980.
(5) Trofimenko, S. *Polyhedron* **2004**, *23*, 197−203.
(6) Garner, M.; Reglinski, J.; Cassidy, I.; Spicer, M. D.; Kennedy, A. R. *Chem. Commun.* **1996**, 1975−1976.
(7) Al-Harbi, A.; Sattler, W.; Sattler, A.; Parkin, G. *Chem. Commun.* **2011**, *47*, 3123−3125.
(8) Silva, R. M.; Gwengo, C.; Lindeman, S. V.; Smith, M. D.; Gardinier, J. R. *Inorg. Chem.* **2006**, *45*, 10998−11007.
(9) Silva, R. M.; Gwengo, C.; Lindeman, S. V.; Smith, M. D.; Long, G. F.; Grandjean, F.; Gardinier, J. R. *Inorg. Chem.* **2008**, *47*, 7233−7242.
(10) Ojo, J. F.; Slavin, P. A.; Reglinski, J.; Garner, M.; Spicer, M. D.; Kennedy, R. R.; Teat, S. J. *Inorg. Chim. Acta* **2001**, *313*, 15−20.
(11) Soares, L. F.; Menezes, D. C.; Silva, R. M.; Doriguetto, A. C.; Ellena, J.; Mascarenhas, Y. P.; Castellano, E. E. *Polyhedron* **2004**, *23*, 205−209.
(12) Bailey, P. J.; Lanfranchi, M.; Marchio, L.; Parsons, S. *Inorg. Chem.* **2001**, *40*, 5030−5035.
(13) Imran, M.; Mix, A.; Neumann, B.; Stammler, H.; Monkowius, U.; Bleckenwegner, P.; Mitzel, N. W. *Dalton Trans* **2014**, *43*, 14737−14748.
(14) Dyson, G.; Hamilton, A.; Mitchell, B.; Owen, G. R. *Dalton Trans.* **2009**, *31*, 6120−6126.
(15) Nuss, G.; Saischek, G.; Harum, B. N.; Volpe, M.; Gatterer, K.; Belaj, F.; Mösch-Zanetti, N. C. *Inorg. Chem.* **2011**, *50*, 1991−2001.
(16) Nuss, G.; Saischek, G.; Harum, B. N.; Volpe, M.; Belaj, F.; Mösch-Zanetti, N. C. *Inorg. Chem.* **2011**, *50*, 12632−12640.
(17) Colebatch, A. L.; Hill, A. F.; Shang, R.; Willis, A. C. *Organometallics* **2010**, *29*, 6482−6487.
(18) Abernethy, R. J.; Hill, A. F.; Tshabang, N.; Willis, A. C.; Young, R. D. *Organometallics* **2009**, *28*, 488−492.
(19) Hill, A. F.; Tshabang, N.; Willis, A. C. *Eur. J. Inorg. Chem.* **2007**, *24*, 3781−3785.
(20) Pang, K.; Tanski, J. M.; Parkin, G. *Chem. Commun.* **2008**, 1008−1010.
(21) Al-Harbi, A.; Rong, Y.; Parkin, G. *Dalton Trans.* **2013**, *42*, 11117−11127.
(22) Rajasekharan-Nair, R.; Marckwordt, A.; Lutta, S. T.; Schwalbe, M.; Biernat, A.; Armstrong, D. R.; Watson, A. J. B.; Kennedy, A. R.; Reglinski, J.; Spicer, M. D. *Chem. - Eur. J.* **2013**, *19*, 13561−13568.
(23) Blagg, R. J.; Charmant, J. P. H.; Connelly, N. G.; Haddow, M. F.; Orpen, A. G. *Chem. Commun.* **2006**, 2350−2352.
(24) Kimblin, C.; Bridgewater, B. M.; Churchill, D. G.; Parkin, G. *Chem. Commun.* **1999**, 2301−2302.
(25) Amgoune, A.; Bourissou, D. *Chem. Commun.* **2011**, *47*, 859−871.
(26) Hill, A. F.; Owen, G.; White, A.; Williams, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 2759−2761.
(27) Spicer, M.; Reglinski, J. *Eur. J. Inorg. Chem.* **2009**, *12*, 1553−1574.
(28) Rajasekharan-Nair, R.; Moore, D.; Kennedy, A. R.; Reglinski, J.; Spicer, M. D. *Inorg. Chem.* **2014**, *53*, 10276−10282.
(29) Choi, K. W.; Ahn, D. S.; Lee, S.; Choi, H.; Baeck, K. K.; Heo, S. U.; Baek, S. J.; Choi, Y. S.; Kim, S. K. *ChemPhysChem* **2004**, *5*, 737−739.
(30) Dias, H. V. R.; Jin, W.; Kim, H.-J.; Lu, H.-L. *Inorg. Chem.* **1996**, *35*, 2317−2328.
(31) Dias, H. V. R.; Kim, H.-J. *Organometallics* **1996**, *15*, 5374−5379.
(32) Despagnet-Ayoub, E.; Jacob, K.; Vendier, L.; Etienne, M.; Álvarez, E.; Caballero, A.; Díaz-Requejo, M. M.; Pérez, P. J. *Organometallics* **2008**, *27*, 4779−4787.
(33) Fujita, K.; Rheingold, A. L.; Riordan, C. G. *Dalton Trans.* **2003**, *10*, 2004−2008.
(34) Schebler, P. J.; Riordan, C. G.; Guzei, I. A.; Rheingold, A. L. *Inorg. Chem.* **1998**, *37*, 4754−4755.
(35) Gardinier, J. R.; Silva, R. M.; Gwengo, C.; Lindeman, S. V. *Chem. Commun.* **2007**, *15*, 1524−1526.