Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2023

ELECTRONIC SUPPORTING INFORMATION

Tuneable Tetrel Bonds between Tin and Heavy Pnictogens

Sachin Liyanage,[a] Jeffrey S. Ovens,[a] Steve Scheiner,[*b] and David L. Bryce[*a]

a. Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, Ontario, K1N6N5, Canada.

b. Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300, USA.

* Authors to whom correspondence may be addressed: dbryce@uottawa.ca; steve.scheiner@usu.edu

Table of Contents

1. Single Crystal X-Ray Diffraction

Crystallographic data for cocrystal **1** were collected from a single crystal mounted on a MiTeGen MicroMount using parabar oil. Data were collected on a Bruker Kappa ApexII single crystal diffractometer equipped with a sealed tube Mo K$\boldsymbol{\alpha}$ source ($\boldsymbol{\lambda} = 0.71073$ Å), a TRIUMPH monochromator, and an ApexII CCD detector. The crystal was held at 200 K using a dry compressed air cooling system. Raw data collection and processing were performed with the Apex3 software package from Bruker.[1] Initial unit cell parameters were determined from 36 data frames from select $\boldsymbol{\omega}$ scans. Semi-empirical absorption corrections based on equivalent reflections were applied.[2] Systematic absences in the diffraction data-set and unit-cell parameters were consistent with the assigned space group. The initial structural solutions were determined using ShelxT direct methods,[3] and refined with full-matrix least-squares procedures based on $\boldsymbol{F^2}$ using ShelXL and ShelXle.[4] Hydrogen atoms were placed geometrically and refined using a riding model. The structure was deposited with the Cambridge Structural Database, entry 2266467.

2. DFT Calculations

The DFT approach was used to perform quantum chemical calculations within the framework of the Gaussian 16[5] program, applying the M06-2X functional[6] and the polarized triple-ζ def2-TZVP basis set. Geometries were fully optimized and confirmed as true minima by the lack of any imaginary vibrational frequencies. The interaction energy E_{int} of each complex was evaluated as the difference between the energy of the full dimer and the sum of the energies of the individual components, each in the geometry they adopt within the dimer, then corrected for basis set superposition error by the counterpoise procedure.[7] Atoms in

Molecules (AIM) bond paths and their associated critical points were identified with the aid of the AIMAll program,[8] and measures of charge transfer were assessed within the NBO formalism as contained in the Gaussian set of programs.

A set of calculations using coordinates from the X-ray crystal structure of **1** was carried out to assess the potential role of π-π interactions. The phenyl rings on the Sn are largely perpendicular to those on P, thus mitigating most π-π attractions. There is only one pair of rings that adopt a nearly parallel orientation. An NBO treatment of this complex finds only a combined second-order perturbation energy E(2) of 0.46 kcal/mol for this pair, far lower than the 11.89 kcal/mol associated with the Sn··P tetrel bond; the density of the critical point along the AIM π··π bond path is only 0.0053 au, as compared to 0.0113 for the Sn··P path. It is reasonable to assert then that the π··π interaction makes only a minor contribution to the total binding between these two triphenyl moieties.

3. Crystal Packing

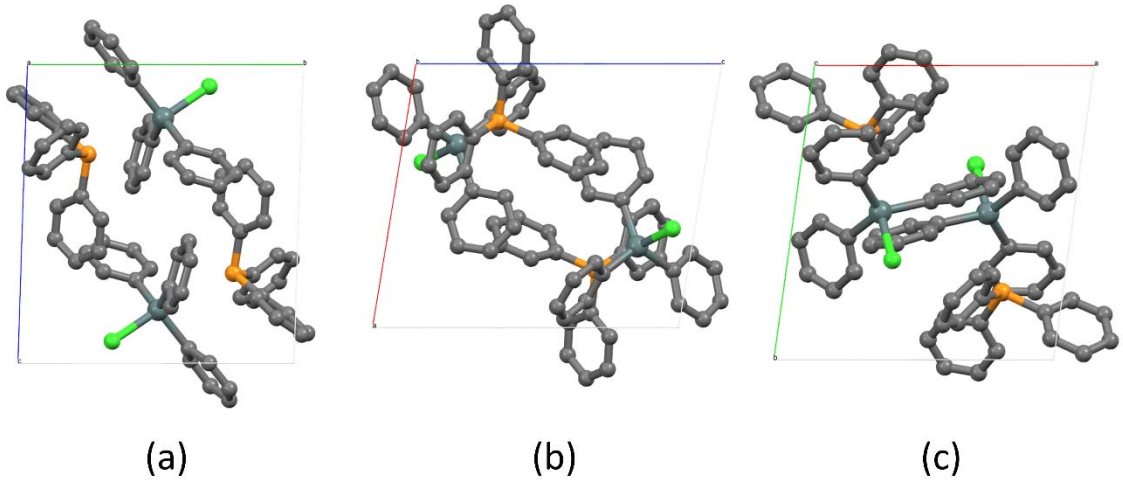

Figure S1. View of cocrystal **1** along the (a) a, (b) b, and (c) c unit cell axes.

4. CSD Survey

Table S1. CSD search results for Sn···P contacts between 2.50 and 4.00 Å.

CCDC refcode	CIF number	Sn-P distance / Å	type
USUFOG	2038373	2.988	organometallic sandwich; possible TB
		2.992	molecule; possible intramolecular TB
PUYVAJ	1975272	3.001	molecule; possible intramolecular TB
XARHUT	127416	3.020	molecule; possible intramolecular TB; two P with one Sn
UMEGUR	2025725	3.058	molecule; possible intramolecular TB
XAPCEW	143976	3.064	molecule; possible intramolecular TB
MOVJAI	170812	3.086	molecule; possible intramolecular TB; two P with one Sn
		3.091	molecule; possible intramolecular TB
NUVGET	1995876	3.136	molecule; possible intramolecular TB
LEHKIS	1204971	3.139	molecule; possible intramolecular TB
ZOLBAF	992228	3.141	molecule; possible intramolecular TB
QIFWAD	161249	3.188	cluster with pendant arms; possible intramolecular TB
		3.191	molecule; possible intramolecular TB
YERBUT	623248	3.228	molecule; possible intramolecular TB
ZOLFUD	985249	3.247	molecule; possible intramolecular TB
XANMEI	2041511	3.249	molecule; possible intramolecular TB
ZOKZEG	992224	3.251	molecule; possible intramolecular TB
YICNOP	928769	3.285	molecule; possible intramolecular TB
TIZFAM	1856313	3.308	molecule; possible intramolecular TB
ILEDIM	207947	3.310	molecule; possible intramolecular TB
TILNOR	1270939	3.348	organometallic sandwich; possible TB
		3.353	molecule; possible intramolecular TB; two P with one Sn
ZOLQOI	985248	3.362	molecule; possible intramolecular TB
TOCHUO	1272982	3.369	molecule; possible intramolecular TB
PEHFOB	2152292	3.487	molecule; possible intramolecular TB
FOWDAZ	1909930	3.533	molecule; possible intramolecular TB; two P with one Sn
		3.536	molecule; possible intramolecular TB
RAQHAW	2097501	3.555	molecule; possible intramolecular TB
USUFAS	2038370	3.566	organometallic sandwich; possible TB
PUCQIP	1022565	3.608	molecule; possible intramolecular TB
FOWCUS	1909929	3.692	molecule; possible intramolecular TB
TIDVAD	1270841	3.760	molecule; possible intramolecular TB
RAQHEA	2097502	3.763	molecule; possible intramolecular TB
KOJMII	1896344	3.785	molecule; possible intramolecular TB
		3.843	molecule; possible intramolecular TB
		3.867	molecule; possible intramolecular TB; two P with one Sn
GUXTUP01	1057381	3.875	molecule; possible intramolecular TB
FOWCOM	1909928	3.917	molecule; possible intramolecular TB
MOVJEM	170813	2.605	molecule; unlikely to be TB
		4.041	molecule; unlikely to be TB
MOVJUC	170816	2.930	molecule; example with TB geometry but very short
MOVKAJ	170817	3.415	molecule; Sn-O-P over two bonds
XOWSEI	680524	3.290	molecule; Sn-N-P over two bonds
		3.247	molecule; Sn-N-P over two bonds

MOVJIQ	170814	2.686	molecule; example with TB geometry but very short
QIWTAT	947192	3.553	molecule; unlikely to be TB
ROBKUP	694941	3.748	molecule; unlikely to be TB
		3.767	molecule; unlikely to be TB
		4.089	molecule; unlikely to be TB
		4.126	molecule; unlikely to be TB
NUVFUI	1995874	3.476	molecule; unlikely to be TB
HAPLUF	1172232	3.912	molecule; Sn-O-P over two bonds
MOVKIR	170819	3.438	molecule; Sn-O-P over two bonds
QIWSUM	947191	2.727	molecule; covalent bond?
BUXWEW	1117734	3.885	molecule; Sn-O-P over two bonds
		3.642	molecule; Sn-O-P over two bonds
FACHAT	1151284	3.516	molecule; Sn-O-P over two bonds
		3.386	molecule; Sn-O-P over two bonds
FOJVUV	1158717	3.824	molecule; Sn-O-P over two bonds
		3.611	molecule; Sn-O-P over two bonds
ACAWAC	171551	3.453	framework; Sn-O-P over two bonds
		3.416	framework; Sn-O-P over two bonds
		3.830	framework; Sn-O-P over two bonds
		3.620	framework; Sn-O-P over two bonds

5. References

[1] APEX Software Suite v 2010 Bruker AXS Inc. Madison Wisconsin USA, 2010.

[2] R. H. Blessing, *Acta Crystallogr. Sect. A* 1995, **51**, 33.

[3] G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112.

[4] C. B. Hübschle, G. M. Sheldrick,and B. Dittrich, J. Appl. Crystallogr., 2011, **44**, 1281.

[5] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, et al. Gaussian 16 Rev. C.01, Wallingford, CT, 2016.

[6] Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215.

[7] S. F. Boy and F. Bernardi, *Mol. Phys.* 1970, **19**, 553.

[8] T. A. Keith, AIMAll, TK Gristmill Software: Overland Park KS, 2013.