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London Dispersion Effects on the Stability of Heavy Tetrel Molecules

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Abstract: London dispersion (LD) interactions, which stem from long-range electron correlations arising from instantaneously induced dipoles can occur between neighboring atoms or molecules, for example, between H atoms within ligand C–H groups. These interactions are currently of interest as a new method of stabilizing long bonds and species with unusual oxidation states. They can also limit reactivity by installing LD enhanced groups into organic frameworks or ligand substituents. Here, we address the most recent advances in the design of LD enhanced ligands, the sterically counterintuitive structures that can be generated and the consequences that these interactions can have on the structures and reactivity of sterically crowded heavy group 14 species.

1. Introduction

London dispersion (LD) effects,[1,2] which arise from attractions involving instantaneously induced dipoles between neighboring atoms, are usually relatively weak, particularly for light atoms such as hydrogen.[3,4] This has unfortunately led to their importance often being discounted or ignored when considering molecular geometry, stability, and reactivity. Nonetheless, it is worth noting that although individual C–H···HC interactions in organic groups are generally weak (ca. 1 kcal mol^{-1}, depending on the nature of the system),[3] if numerous C–H···H–C interactions are present, a cumulative LD energy equaling several tens of kcal mol^{-1} may be generated.[5–8] These effects in larger systems can therefore play a critical role in various aspects of molecular behavior. Some key examples have been presented by the groups of Schreiner and Grimme. For example, Schreiner et al. have employed LD effects to stabilize long C–C bonds,[9,10] form highly ordered 2D lattices,[8] and also have experimentally determined LD interactions between certain ligand systems in the gas-phase and in solution.[11–19] In a key advance, Grimme et al. developed low-cost density functional theory (DFT) calculations with dispersion corrections,[20–26] making it possible to quantify LD interactions and specifically, extract important thermochemical information in molecular systems. This contribution has proven to be extremely beneficial and has allowed the rationalization of several reactivity profiles[27,28] and counterintuitive structures. For example, we have shown[29,30] (Figure 1) that LD energies exert important effects on the stability of distannenes in solution.[31]

Here, we focus on the effects of LD interactions of hydrocarbon ligands in molecules containing the heavier group 14 elements tin and lead,[28,31–38] in a wider context though it is worth noting that LD energies play important roles in a wide range of fields in chemistry, including catalysis,[39] inorganic synthesis,[40] crystal growth,[41] photochemistry,[42] regioselectivity.[43] Specifically, we address the relationship between LD effects in certain ligands (termed dispersion energy donor or DED ligands)[22] on the energies of molecular processes, such as stability, dimer-trimer equilibria, and monomer-dimer dissociation. Though, we also note that many examples of DED ligands have been used to stabilize species that include silicon[44–46] and germanium,[47,48] and their effects have been the subject of post-hoc rationalizations of LD effects. This has proven useful in understanding molecular structures and reactivity.

2. Discussion

Our initial studies involved terphenyl chalcogenolate derivatives of the formula M(ChAr)$_2$ (M=Si, Ge, Sn, or Pb; Ch = chalcogen, S or Se; Ar = bulky terphenyl, Figure 2)[47] which showed that the divalent complexes displayed a pattern of decreasing interli-

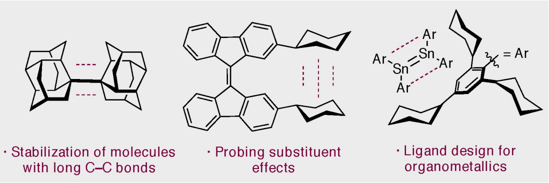

Figure 1. Illustrations of LD interactions (magenta dashed lines) that have been investigated in studies where LD effects play a crucial part in the properties of molecular structures or reactivities.[9,13,31]

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gand angles (most below 90°) with increasing substituent size. This fortuitous discovery led to the view that the principal causes that led to the sub-90° bond angles to afford the sterically counterintuitive structures were rationalized through the effects of intramolecular LD interactions.

These are generated between the bulky chalcogenolate ligand substituents across the molecules and contribute to an overall stabilizing effect (Figure 2, right).

The concept of LD effects contributing substantially to molecular structure was further highlighted by the isolation and X-ray crystallographic analysis of various terphenyl-stabilized diplumbynes.[36] The diplumbynes were initially synthesized during attempts to isolate a stable lead(II) hydride, which we proposed was formed in situ but subsequently decomposed to the diplumbyne under ambient conditions.[33] It was later shown that these diplumbynes could also be accessed by the reduction of the parent Pb(II) halide. It should be noted that very few lead(II) hydride complexes have been isolated or detected, (see reports from Liu and Wesemann)[49,50] and LD effects likely play a role in their stabilization.[51]

Certainly, for the diplumbynes, interligand dispersion interactions between each of Pb(II) fragments play a crucial role in their stability. This was confirmed from a study in which the synthesis of five different terphenyl-substituted diplumbynes (Figure 3), combined with dispersion-corrected DFT calculations (at the B3LYP/def2-TZVPP/TPSS-D3(BJ)-ATM/def2-TZVP level of theory) suggested that none of the five complexes is stable without the DED properties of the terphenyl ligands.[36] In fact, all are unstable to dissociation via Pb–Pb bond cleavage in the

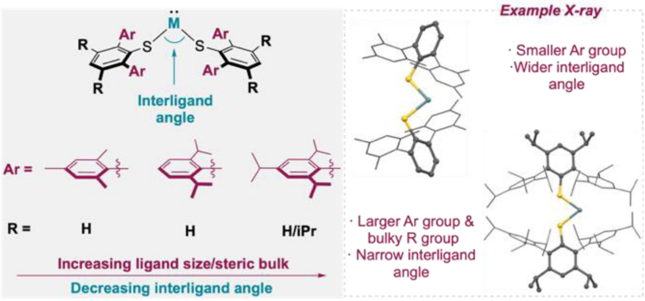


Figure 2. Example of counterintuitive sterics induced at the central atom by LD interactions in terphenyl thiolate group 14 complexes. Left: Schematic of different Ar groups used. Right: X-ray analysis on the least bulky thiolate (upper left) and the bulkiest thiolate (lower right). Green = Group 14 atom, yellow = sulfur, grey = carbon. Aryl groups shown in wireframe format and hydrogen atoms are not shown.[47]

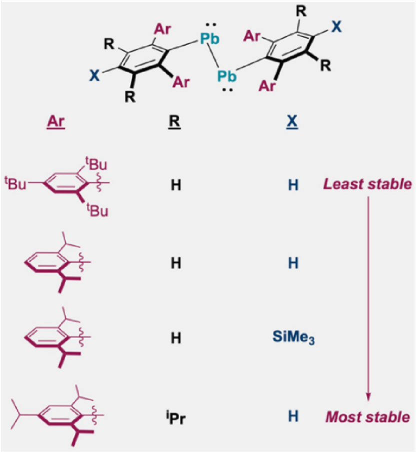


Figure 3. Examples of the terphenyl-stabilized diplumbyne complexes with varying aryl substituents that were used to investigate the relationship between DED properties and diplumbyne stability in solution.[36]

Kristian L. Mears received his M.Sci. (2017) and then his Ph.D. (2021) from University College London in the field of precursor design and synthesis with Professor Claire Carmalt and Dr Caroline Knapp. During this time, he was supported by an RSC travel grant to work with Professor Philip Power (2020) on the synthesis of low-coordinate mixed-metal complexes at the University of California, Davis. He returned to the Power laboratory as a postdoctoral research associate in 2021, investigating London dispersion effects in organometallic systems and the synthesis of low-valent main-group complexes.

Philip P. Power received his B.A. degree from Trinity College Dublin in 1974 and his D.Phil. degree, under the direction of M. F. Lappert, from the University of Sussex in 1977. After postdoctoral studies with R. H. Holm at Stanford, he joined the faculty at the University of California, Davis, where he is currently a distinguished professor of chemistry. His main research interests involve the structural chemistry of organoalkali metal and organocopper compounds, low-coordinate transition-metal chemistry, multiple bonding in main-group chemistry, and the development of new ligands that feature London dispersion interactions for the stabilization of low coordination numbers, unusual oxidation states, and multiple bonding in both transition-metal and heavier main-group compounds. He is a recipient of fellowships from the A. P. Sloan and Alexander von Humboldt foundations and is a member of the Royal Society. In addition, he has been a faculty research lecturer at the University of Iowa (1993), a visiting professor at the University of Auckland, New Zealand (1993), a Reilly lecturer at the University of Notre Dame (1995), a recipient of the Esther and David Parkin Visiting Professorship (2013), and the Global Chair (2018) at the University of Bath.

absence of LD stabilization (with calculated negative values of ΔG_{diss} ranging from -14.5 kcal mol^{-1} to -34.0 kcal mol^{-1}).

When the calculations were repeated with the inclusion of a dispersion correction, the ΔG_{diss} values become positive, meaning that dissociation is no longer thermodynamically favored. The new ΔG_{diss} values ranged between $+24.3$ to $+51.0$ kcal mol^{-1} with D3 and D4 corrections applied (the DFT approximation models for London dispersion interactions developed by Grimme and coworkers).[26,52]

Dispersion energies are clearly important, although they are just one part of the overall bonding interaction that we wish to highlight in this review. We direct readers to works that discuss the other important aspects of bonding in heavier main group systems, including charge-shift bonding, lone-pair effects, and second-order Jahn-Teller (SOJT) distortions.[53–59]

We have since focused on developing ligands with more effective DED properties, for example, those that contain rigid, multicyclic frameworks and high numbers of C–H moieties that can be directed towards each other through-space to generate LD stabilization.

This led us to investigate the 2,4,6-tricyclohexylphenyl ligand. This ligand can be synthesized relatively easily,[60] but had only been employed previously in the nickel complex [Ni(Br)(bipy)(2,4,6-Cy_3-C_6H_2)], bipy = 2,2′-bipyridine.[61] By synthesizing the lithium salt Li(2,4,6-Cy_3-C_6H_2) and reacting two equivalents of this species with $SnCl_2$, the generation of a solution-stable distannene of the formula $\{Sn(2,4,6\text{-}Cy_3\text{-}C_6H_2)_2\}_2$ (Figure 4) was achieved.[31] Unlike almost all distannenes, this species does not dissociate to stannylenes in solution. It remains a distannene, even when the solution is heated, indicated by its ^{119}Sn NMR signal ($\delta = +361.3$ ppm), and is the second instance of a distannene to behave in this manner.[62] The only other example of a solution-stable distannene was reported in 2006 by Sekiguchi, Apeloig and coworkers who synthesized the complex $[Sn\{SiMe(^tBu_2)\}_2]_2$ that had a ^{119}Sn NMR signal of $\delta = +630.7$ ppm (Figure 4).[63] This complex displays a Sn=Sn bond length of 2.6679(8) Å while the DED-substituted distannene $\{Sn(2,4,6\text{-}Cy_3\text{-}C_6H_2)_2\}_2$ has a longer Sn=Sn bond length of 2.7011(7) Å.

While initial comparisons of the bond lengths in these two complexes showed that Sn=Sn distance in $[Sn\{SiMe(^tBu_2)\}_2]_2$ was shorter, the tin atoms in this complex are essentially planar-coordinated. Moreover, the Si–Sn-Si planes have a torsion angle of ca. 45° between them, and the shorter Sn=Sn bond can be attributed, at least in part, to the presence of a covalent σ bond and a 'twisted' π bond between two triplet state tin units. In contrast, the distannene $\{Sn(2,4,6\text{-}Cy_3\text{-}C_6H_2)_2\}_2$ has the more common trans-pyramidal structure, which is believed to be consistent with weak Sn=Sn bonding. The unusually strong interaction between its $\{Sn(2,4,6\text{-}Cy_3\text{-}C_6H_2)_2\}$ units must therefore originate from other factors. Indeed, computational studies indicated that when dispersion effects are excluded, the monomeric stannylene $\{:Sn(2,4,6\text{-}Cy_3\text{-}C_6H_2)_2\}$ is favored. The monomer to dimer association was calculated indicating a Gibbs free energy of dimerization (ΔG_{dimer}) of $+31.9$ kcal mol^{-1}. When LD effects are included in the calculations using Grimme's accurate D4 correction (at the BLYP–D4/def2-QZVP//r2SCAN-3c level of theory), the monomer to dimer association ΔG_{dimer} became thermodynamically favored with a value of -6.1 kcal mol^{-1}. The importance of the LD contribution to the overall bonding energy is further supported by energy decomposition analysis (EDA) which showed that there is a comparatively small orbital energy (E_{orb}) component. In comparison, the interaction to dispersion energy (E_{int} and E_{disp} respectively) ratio amounted to 1.0. Essentially, neglecting the dispersion component results in a slightly repulsive interaction energy of $+0.3$ kcal mol^{-1}, which underlines the crucial role of LD effects in this system. The distannene $\{Sn(2,4,6\text{-}Cy_3\text{-}C_6H_2)_2\}$ showed no reactivity toward unsaturated organic substrates such as phenylacetylene or ethylene under a variety of conditions (high temperatures, various solvents etc.), further indicating its LD generated stability. In contrast, Sekiguchi's distannene was shown to form the 4-membered [2+2] cycloaddition product when added to phenylacetylene.

For comparison, the reaction of tin(II) chloride with the lithium salt of the 2,4,6-triphenylphenyl analogue $-2,4,6\text{-}Ph_3\text{-}C_6H_2$) was carried out, which yielded the monomeric stannylene complex $\{:Sn(2,4,6\text{-}Ph_3\text{-}C_6H_2)_2\}$ (Figure 5). The isolation of this monomer was an important aspect of this study, since the triphenylphenyl ligand $2,4,6\text{-}Ph_3\text{-}C_6H_2$) is less bulky than its tricyclohexylphenyl analogue, and yet it did not afford a solution- or solid-state distannene that is stable. Results where sterically counterintuitive structures are observed are often indicative of the presence dispersion effects, as well as high stabilities of compounds despite lengthened bonds, a lack of

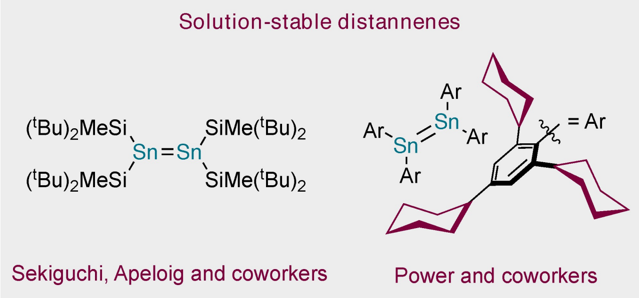


Figure 4. Solution stable distannenes. Left: Sekiguchi, Apeloig and coworkers' $[Sn\{SiMe(^tBu_2)\}_2]_2$. Right: Power and coworkers' $\{Sn(C_6H_2\text{-}2,4,6\text{-}Cy_3)_2\}_2$.[31,64]

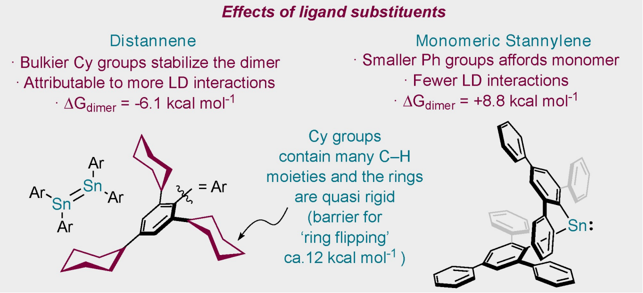


Figure 5. Overview of the effects of -C_6H_2-2,4,6-Cy_3 and -C_6H_2-2,4,6-Ph_3 ligands on distannene and stannylene formation respectively.[31]

expected correlations of various structural parameters, isolability of electronically disfavored molecules and an apparent mutual attraction of rigid multicyclic groups within molecules.[3] Computational analysis revealed that in this case the formation of the monomeric stannylene is favored over the distannene, even when the dispersion correction is applied to the calculation (monomer to dimer association was calculated to be disfavored, with a $\Delta G_{dimer} = +8.8$ kcal mol^{-1}).

These results indicated that it is possible to design and synthesize new ligands specifically to install DED properties. This led to the synthesis of the new ligand ($-2,4,6$-Cyp$_3$-C$_6$H$_2$, Cyp = cyclopentyl), which has one fewer CH$_2$ unit per alkyl substituent than 2,4,6-Cy$_3$-C$_6$H$_2$). With this synthesis, we aimed to compare the strength of the DED enhancement of the Cyp substituents with those of the Cy that afforded the solution stable distannene. Following a similar procedure as described for the synthesis of $\{Sn(2,4,6\text{-}Cy_3\text{-}C_6H_2)_2\}_2$, two equivalents of the lithium salt of the Cyp derivative $\{(Et_2O)Li(2,4,6\text{-}Cyp_3\text{-}C_6H_2)\}_2$ were reacted with tin(II) chloride. This afforded only a trace amount of the distannene $\{Sn(2,4,6\text{-}Cyp_3\text{-}C_6H_2)_2\}_2$, but a good yield of the cyclotristannane $\{Sn(2,4,6\text{-}Cyp_3\text{-}C_6H_2)_2\}_3$ (Scheme 1).

Co-crystallization of the dimer with the trimer proved sufficient for single crystal X-ray analysis, but the low solubility of the dimer in hydrocarbon solvents made it difficult to isolate a large amount of the dimer for full spectroscopic characterization. However, ^{119}Sn NMR spectroscopy showed the trimer had an upfield signal at $\delta = -343.3$ ppm at ambient temperature, with no other signals present. This implied that at ambient temperature, conversion of the trimer into the dimer does not occur (at least in sufficient quantities to be detected by NMR spectroscopy). Variable temperature ^{119}Sn NMR spectroscopy showed that on heating a solution of the trimer in toluene-d$_8$, the signal for the trimer diminished in intensity and a new signal appeared at $\delta = +417.5$ ppm, which was assigned to the distannene dimer (supporting computational studies predicted a $\delta_{calc.} = +505.9$ ppm for the dimer). This new signal intensified as the temperature was increased further, consistent with the formation of greater quantities of the dimer in solution. For context, the analogous cyclohexyl-derivative distannene $\{Sn(2,4,6\text{-}Cy_3\text{-}C_6H_2)_2\}_2$ has a ^{119}Sn NMR signal of $\delta = +361.3$ ppm. In addition, Masamune and coworkers synthesized the cyclotristannane $\{Sn(2,4,6\text{-}{}^iPr_3\text{-}C_6H_2)_2\}_3$ and the distannene $\{Sn(2,4,6\text{-}{}^iPr_3\text{-}C_6H_2)_2\}_2$ which displayed ^{119}Sn NMR signals at $\delta = -378.9$ ppm and $+427.0$ ppm respectively.[65]

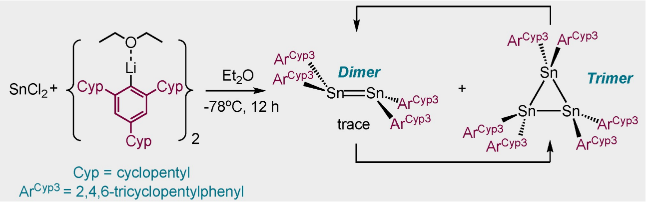
No other signal was detected in the chemical shift range $+1200$ to $+3000$ ppm (cf. ^{119}Sn NMR signal of Lappert's stannylene monomer $[:Sn\{CH(SiMe_3)_2\}_2]$ appears at $\delta = +2328.0$ ppm).[66] Cooling the solution of the dimer back to 300 K resulted in the disappearance of the signal at $\delta = +427.0$ ppm and the reappearance of the signal (the trimer) at $\delta = -343.3$ ppm, implying a reversable mechanism from the conversion of the trimer to the dimer (scheme 2).

A signal attributable to the monomeric $\{:Sn(C_6H_2\text{-}2,4,6\text{-}Cyp_3)_2\}$ was not observed in these studies. The ^{119}Sn NMR signals of monomeric diorganostannylenes fall within the range $\delta = +723.0$ to $+2328.0$ ppm, which was in agreement with the calculated ^{119}Sn signal for the monomer $\{:Sn(2,4,6\text{-}Cyp_3\text{-}C_6H_2)_2\}$ at $\delta_{calc} = +2313.0$ ppm. ^{1}H DOSY NMR experiments on the trimer carried out at 373 K, further confirmed that the trimer is fully converted into the dimer, with only one species (the trimer) being observed.

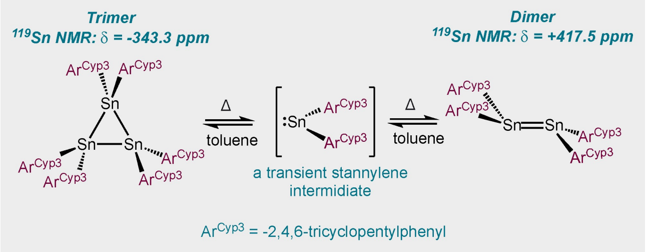
In comparison to the triisopropylphenyl substituted system, the cyclotristannane $\{Sn(2,4,6\text{-}{}^iPr_3\text{-}C_6H_2)_2\}_3$ was reported to dissociate into the distannene $\{Sn(2,4,6\text{-}{}^iPr_3\text{-}C_6H_2)_2\}_2$ and the monomeric stannylene $\{:Sn(2,4,6\text{-}{}^iPr_3\text{-}C_6H_2)_2\}$ ($\delta = +1420.0$ ppm)[67] on heating, which was determined through the detection of each species in the ^{119}Sn NMR spectrum, although no thermodynamic data had been reported for this process.

In this latest study,[28] we measured the energy values of the trimer-dimer equilibrium by using VT multinuclear NMR spectroscopy for both our new DED-ligand derivative of a cyclotristannane, $\{Sn(2,4,6\text{-}Cyp_3\text{-}C_6H_2)_2\}_3$ and $\{Sn(2,4,6\text{-}{}^iPr_3\text{-}C_6H_2)_2\}_3$ as a comparison. This publication thus reported previously unknown dissociative Sn(trimer-dimer) equilibrium energy data, in addition to the effects of London dispersion on the corresponding free energies determined.

Van't Hoff analysis of the VT ^{1}H NMR data for the new DED-ligand derivative $\{Sn(2,4,6\text{-}Cyp_3\text{-}C_6H_2)_2\}_3$ yielded a dissociation from the trimer-to-dimer enthalpy, $\Delta H_{(trimer\text{-}dimer)} = +35.1$ kcal mol^{-1} and a free energy, $\Delta G_{(trimer\text{-}dimer)} = +2.7$ kcal mol^{-1} at 300 K, (with a corresponding $\Delta S_{(trimer\text{-}dimer)} = +0.1$ kcal mol^{-1} K^{-1}). In addition, EDA (B3LYP-D4/def2-TZVP level of theory) revealed a high LD interaction energy contribution of $E_{disp} = -85.6$ kcal mol^{-1} which partially compensated the strong Pauli repulsive interaction of $+447.7$ kcal mol^{-1}. The large dispersion-to-interaction energy ratio ($E_{disp} = -85.6$ kcal mol^{-1})/($E_{int} = -91.8$ kcal mol^{-1}) $= 0.9$ further indicated the importance



Scheme 1. Synthetic route to the cyclotristannane $\{Sn(2,4,6\text{-}Cyp_3\text{-}C_6H_2)_2\}_3$ and trace quantities of the distannene $\{Sn(2,4,6\text{-}Cyp_3\text{-}C_6H_2)_2\}_2$.[28] Reproduced from Ref. [28] Copyright (2023), with permission from Wiley-VCH.



Scheme 2. Proposed interconversion mechanism between the trimer $\{Sn(2,4,6\text{-}Cyp_3\text{-}C_6H_2)_2\}_3$ and dimer $\{Sn(2,4,6\text{-}Cyp_3\text{-}C_6H_2)_2\}_2$, with the suppression of a monomeric stannylene intermediate.[28] Reproduced from Ref. [28] Copyright (2023), with permission from Wiley-VCH.

of dispersion in stabilizing the cyclotristannane $\{Sn(2,4,6\text{-}Cyp_3\text{-}C_6H_2)_2\}_3$. However, at higher temperatures (above 70 °C), the conversion to the distannene $\{Sn(2,4,6\text{-}Cyp_3\text{-}C_6H_2)_2\}_2$ becomes slightly exergonic, with a corresponding free energy of $\Delta G_{(trimer\text{-}dimer)} = -0.2\ kcal\,mol^{-1}$.

In comparison to Masamune's cyclotristannane $\{Sn(2,4,6\text{-}{}^iPr_3\text{-}C_6H_2)_2\}_3$, the free energy of conversion from the trimer to the dimer was calculated to be exergonic even at room temperature, with a corresponding free energy of $\Delta G_{(trimer\text{-}dimer)} = -5.1\ kcal\ mol^{-1}$. This suggested that the new DED enhanced $2,4,6\text{-}Cyp_3\text{-}C_6H_2$ ligand, despite being sterically similar to that of $2,4,6\text{-}{}^iPr_3\text{-}C_6H_2$, displayed much greater stabilization of the cyclotristannane system due to higher LD interactions.

3. Conclusion

While London dispersion interactions remain underappreciated in their ability to affect the stability of organometallic systems, particularly relating to complex structure and reactivity, we are now seeing more studies where DED enhancement is being used to illuminate the relationship underpinning steric protection and non-covalent attractive energy stabilization.

Common rigid and semi-rigid, cyclic frameworks (-Cyp, -Cy, -norbornyl, -adamantyl) have been recognized for their enhanced DED properties and are being designed into inorganic and organometallic ligand frameworks.[43] This concept highlights the main feature of these groups that facilitate their enhanced DED properties is the high number of rigidly directional C–H moieties which they contain. Ligands that contain these organic groups, or other ligands that feature many through-space C···H and H···H close-contacts in a constrained manner may be expected to result in enhanced LD interactions. The studies presented are complemented by the growing number of computational analyses focused on dispersion interactions in sterically crowded compounds. We anticipate that the number of isolable inorganic and organometallic complexes will be greatly expanded with further research on DED ligand installation.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: ligand synthesis · London dispersion · tetrels

[1] F. London, *Trans. Faraday Soc.* **1937**, *33*, 8b–26.
[2] F. London, *Z. Phys.* **1930**, *63*, 245–279.
[3] D. J. Liptrot, P. P. Power, *Nat. Chem. Rev.* **2017**, *1*, 1–12.
[4] J. P. Wagner, P. R. Schreiner, *Angew. Chem. Int. Ed.* **2015**, *54*, 12274–12296.
[5] S. Rösel, C. Balestrieri, P. R. Schreiner, *Chem. Sci.* **2016**, *8*, 405–410.
[6] E. Solel, M. Ruth, P. R. Schreiner, *J. Am. Chem. Soc.* **2021**, *143*, 20837–20848.
[7] J. M. Schümann, L. Ochmann, J. Becker, A. Altun, I. Harden, G. Bistoni, P. R. Schreiner, *J. Am. Chem. Soc.* **2023**, *145*, 2093–2097.
[8] D. Ebeling, M. Šekutor, M. Stiefermann, J. Tschakert, J. E. P. Dahl, R. M. K. Carlson, A. Schirmeisen, P. R. Schreiner, *ACS Nano* **2017**, *11*, 9459–9466.
[9] P. R. Schreiner, L. V. Chernish, P. A. Gunchenko, E. Y. Tikhonchuk, H. Hausmann, M. Serafin, S. Schlecht, J. E. P. Dahl, R. M. K. Carlson, A. A. Fokin, *Nature* **2011**, *477*, 308–311.
[10] A. A. Fokin, L. V. Chernish, P. A. Gunchenko, E. Y. Tikhonchuk, H. Hausmann, M. Serafin, J. E. P. Dahl, R. M. K. Carlson, P. R. Schreiner, *J. Am. Chem. Soc.* **2012**, *134*, 13641–13650.
[11] S. Rösel, J. Becker, W. D. Allen, P. R. Schreiner, *J. Am. Chem. Soc.* **2018**, *140*, 14421–14432.
[12] L. Rummel, M. H. J. Domanski, H. Hausmann, J. Becker, P. R. Schreiner, *Angew. Chem. Int. Ed.* **2022**, *61*, e202204393.
[13] F. M. Wilming, B. Marazzi, P. P. Debes, J. Becker, P. R. Schreiner, *J. Org. Chem.* **2023**, *88*, 1024–1035.
[14] J. M. Schümann, J. P. Wagner, A. K. Eckhardt, H. Quanz, P. R. Schreiner, *J. Am. Chem. Soc.* **2021**, *143*, 41–45.
[15] D. Maué, P. H. Strebert, D. Bernhard, S. Rösel, P. R. Schreiner, M. Gerhards, *Angew. Chem. Int. Ed.* **2021**, *60*, 11305–11309.
[16] H. F. König, L. Rummel, H. Hausmann, J. Becker, J. M. Schümann, P. R. Schreiner, *J. Org. Chem.* **2022**, *87*, 4670–4679.
[17] S. Schwan, A. J. Achazi, F. Ziese, P. R. Schreiner, K. Volz, S. Dehnen, S. Sanna, D. Mollenhauer, *J. Comput. Chem.* **2023**, *44*, 843–856.
[18] S. Rösel, H. Quanz, C. Logemann, J. Becker, E. Mossou, L. Cañadillas-Delgado, E. Caldeweyher, S. Grimme, P. R. Schreiner, *J. Am. Chem. Soc.* **2017**, *139*, 7428–7431.
[19] A. A. Fokin, T. S. Zhuk, S. Blomeyer, C. Pérez, L. V. Chernish, A. E. Pashenko, J. Antony, Y. V. Vishnevskiy, R. J. F. Berger, S. Grimme, C. Logemann, M. Schnell, N. W. Mitzel, P. R. Schreiner, *J. Am. Chem. Soc.* **2017**, *139*, 16696–16707.
[20] S. Grimme, *WIREs Comput. Mol. Sci.* **2011**, *1*, 211–228.
[21] S. Grimme, *J. Comput. Chem.* **2004**, *25*, 1463–1473.
[22] S. Grimme, R. Huenerbein, S. Ehrlich, S. Grimme, R. Huenerbein, S. Ehrlich, *ChemPhysChem* **2011**, *12*, 1258–1261.
[23] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.
[24] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
[25] M. Bursch, E. Caldeweyher, A. Hansen, H. Neugebauer, S. Ehlert, S. Grimme, *Acc. Chem. Res.* **2019**, *52*, 258–266.
[26] E. Caldeweyher, S. Ehlert, A. Hansen, H. Neugebauer, S. Spicher, C. Bannwarth, S. Grimme, *J. Chem. Phys.* **2019**, *150*, 154122.
[27] K. L. Mears, C. R. Stennett, E. K. Taskinen, C. E. Knapp, C. J. Carmalt, H. M. Tuononen, P. P. Power, *J. Am. Chem. Soc.* **2020**, *142*, 19874–19878.
[28] W. Zou, M. Bursch, K. L. Mears, C. Stennett, P. Yu, J. Fettinger, S. Grimme, P. P. Power, *Angew. Chem. Int. Ed.* **2023**, e202301919.
[29] K. L. Mears, M. A. Kutzleb, C. R. Stennett, J. C. Fettinger, D. C. Kaseman, P. Yu, P. Vasko, P. P. Power, *Chem. Commun.* **2022**, *58*, 9910–9913.
[30] K. L. Mears, C. R. Stennett, J. C. Fettinger, P. Vasko, P. P. Power, *Angew. Chem. Int. Ed.* **2022**, *61*, e202201318.
[31] C. R. Stennett, M. Bursch, J. C. Fettinger, S. Grimme, P. P. Power, *J. Am. Chem. Soc.* **2021**, *143*, 21478–21483.
[32] L. Pu, B. Twamley, P. P. Power, *J. Am. Chem. Soc.* **2000**, *122*, 3524–3525.
[33] J. D. Queen, J. C. Fettinger, P. P. Power, *Chem. Commun.* **2019**, *55*, 10285–10287.
[34] J. D. Guo, D. J. Liptrot, S. Nagase, P. P. Power, *Chem. Sci.* **2015**, *6*, 6235–6244.
[35] B. D. Rekken, T. M. Brown, M. M. Olmstead, J. C. Fettinger, P. P. Power, *Inorg. Chem.* **2013**, *52*, 3054–3062.
[36] J. D. Queen, M. Bursch, J. Seibert, L. R. Maurer, B. D. Ellis, J. C. Fettinger, S. Grimme, P. P. Power, *J. Am. Chem. Soc.* **2019**, *141*, 14370–14383.
[37] Y. Peng, R. C. Fischer, W. A. Merrill, J. Fischer, L. Pu, B. D. Ellis, J. C. Fettinger, R. H. Herber, P. P. Power, *Chem. Sci.* **2010**, *1*, 461–468.

[38] L. Rummel, J. M. Schümann, P. R. Schreiner, *Chem. Eur. J.* **2021**, *27*, 13699–13702.
[39] N. I. Saper, A. Ohgi, D. W. Small, K. Semba, Y. Nakao, J. F. Hartwig, *Nat. Chem.* **2020**, *12*, 276–283.
[40] A. M. Borys, L. A. Malaspina, S. Grabowsky, E. Hevia, *Angew. Chem. Int. Ed.* **2022**, *61*, 10.1002/anie.202209797.
[41] R. Chakrabarti, P. G. Vekilov, *Cryst. Growth Des.* **2020**, *20*, 7429–7438.
[42] A. Fabrizio, C. Corminboeuf, *J. Phys. Chem. Lett.* **2018**, *9*, 464–470.
[43] T. Ikawa, Y. Yamamoto, A. Heguri, Y. Fukumoto, T. Murakami, A. Takagi, Y. Masuda, K. Yahata, H. Aoyama, Y. Shigeta, H. Tokiwa, S. Akai, *J. Am. Chem. Soc.* **2021**, *143*, 10853–10859.
[44] A. Sekiguchi, R. Kinjo, M. Ichinohe, *Science (1979)* **2004**, *305*, 1755–1757.
[45] V. Y. Lee, A. Sekiguchi, in *Organometallic Compounds of Low-Coordinate Si, Ge, Sn and Pb: From Phantom Species to Stable Compounds*, John Wiley and Sons, **2010**.
[46] B. D. Rekken, T. M. Brown, J. C. Fettinger, H. M. Tuononen, P. P. Power, *J. Am. Chem. Soc.* **2012**, *134*, 6504–6507.
[47] B. D. Rekken, T. M. Brown, J. C. Fettinger, F. Lips, H. M. Tuononen, R. H. Herber, P. P. Power, *J. Am. Chem. Soc.* **2013**, *135*, 10134–10148.
[48] M. L. McCrea-Hendrick, M. Bursch, K. L. Gullett, L. R. Maurer, J. C. Fettinger, S. Grimme, P. P. Power, *Organometallics* **2018**, *37*, 2075–2085.
[49] S. Wang, K. Y. Liu, H. J. Li, W. C. Lee, S. L. Huang, W. C. Wu, F. K. Shi, Y. S. Cheng, I. C. Lu, H. J. Liu, *Inorg. Chem.* **2022**, *61*, 13096–13103.
[50] J. Schneider, C. P. Sindlinger, K. Eichele, H. Schubert, L. Wesemann, *J. Am. Chem. Soc.* **2017**, *139*, 6542–6545.
[51] K. L. Mears, P. P. Power, *Acc. Chem. Res.* **2022**, *55*, 1337–1348.
[52] E. Caldeweyher, J. M. Mewes, S. Ehlert, S. Grimme, *Phys. Chem. Chem. Phys.* **2020**, *22*, 8499–8512.
[53] P. P. Power, *Chem. Rev.* **1999**, *99*, 3463–3503.
[54] R. C. Fischer, P. P. Power, *Chem. Rev.* **2010**, *110*, 3877–3923.
[55] G. Sini, P. Maitre, P. C. Hiberty, S. S. Shaik, *J. Mol. Struct.* **1991**, *229*, 163–188.
[56] H. B. Wedler, P. Wendelboe, P. P. Power, *Organometallics* **2018**, *37*, 2929–2936.
[57] H. B. Wedler, P. Wendelboe, D. J. Tantillo, P. P. Power, *Dalton Trans.* **2020**, *49*, 5175–5182.
[58] E. Rivard, P. P. Power, *Dalton Trans.* **2008**, 4336–4343.
[59] Y. Cornaton, J.-P. Djukic, *Acc. Chem. Res.* **2021**, *54,* 3828–3840
[60] L. Salvi, N. R. Davis, S. Z. Ali, S. L. Buchwald, *Org. Lett.* **2012**, *14*, 170–173.
[61] I. F. Sakhapov, Z. N. Gafurov, V. M. Babaev, I. K. Rizvanov, A. B. Dobrynin, D. B. Krivolapov, K. R. Khayarov, O. G. Sinyashin, D. G. Yakhvarov, *Mendeleev Commun.* **2016**, *26*, 131–133.
[62] D. E. Goldberg, D. H. Harris, M. F. Lappert, K. M. Thomas, *J. Chem. Soc. Chem. Commun.* **1976**, *7*, 261–262.
[63] V. Y. Lee, T. Fukawa, M. Nakamoto, A. Sekiguchi, B. L. Tumanskii, M. Karni, Y. Apeloig, *J. Am. Chem. Soc.* **2006**, *128*, 11643–11651.
[64] A. Sekiguchi, T. Fukawa, V. Y. Lee, M. Nakamoto, *J. Am. Chem. Soc.* **2003**, *125*, 9250–9251.
[65] S. Masamune, L. R. Sita, *J. Am. Chem. Soc.* **1985**, *107*, 6390–6391.
[66] K. W. Zilm, G. A. Lawless, R. M. Merrill, J. M. Millar, G. G. Webb, *J. Am. Chem. Soc.* **1987**, *109*, 7236–7238.
[67] M. Weidenbruch, A. Schafer, H. Kilian, S. Pohl, W. Saak, H. Marsmann, M. Weidenbruch, A. Schafer, H. Kilian, S. Pohl, W. Saak, H. Marsmann, *Chem. Ber.* **1992**, *125*, 563–566.

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