View Article Online

Dalton Transactions

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: B. Wei, W. Zhang and Z. Xi, *Dalton Trans.*, 2018, DOI: 10.1039/C8DT01046C.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/dalton

YAL SOCIETY CHEMISTRY

Dalton Transactions

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Well-Defined Styryl and Biphenyl Calcium Complexes from Dilithio Compounds and Calcium Iodide: Synthesis, Structure and Reactivity toward Nitrous Oxide

Baosheng Wei,^a Wen-Xiong Zhang*^a and Zhenfeng Xi*^{a,b}

Efficient synthesis and structure elucidation of carbon–calcium σ-bonded compounds are of remarkable interest and importance in organometallic chemistry of the heavier s-block metals. In this paper, we report that styryl and biphenyl calcium complexes with well-defined structures can be facilely obtained via metathesis reaction between their corresponding dilithio compound and calcium iodide. Single-crystal X-ray structural analysis of these calcium complexes revealed their unique iodide-bridged or dicalcium-bridged structures. Their reactivity toward nitrous oxide was disclosed.

Introduction

Calcium, a heavier s-block element with global abundance, easy availability and low toxicity, has attracted much interest in both organometallic and synthetic chemistry.¹ However, in contrast to the prosperity of Grignard reagents in modern organometallic chemistry,² advances in the synthesis and characterization of Ca-based organometallic compounds still infrequent,³ irrespective of the abundant remain cyclopentadienyl π -bonded calcium complexes. Actually, many efforts toward C-Ca σ-bonded compounds have been in vain because of synthetic setbacks mainly caused by their inherent instability,⁴ although an enumerable set of alkyl,⁵ alkynyl,⁶ aryl⁷ and alkenyl⁸ calcium compounds were synthesized by virtue of certain strategies. Among the limited synthetic pathways, salt metathesis reaction has proven to be a powerful strategy, which allowed the efficient synthesis of many calcium compounds including the important bis[tris(trimethylsilyl)methyl]calcium,5c dibenzylcalcium5d and bis(allyl)calcium⁹ complexes. Recently, Anwander reported the successful isolation of dimethylcalcium species applying the metathesis reaction between methyllithium and calcium bis(trimethylsilyl)amide.¹⁰ Very recently, we investigated the metathesis reaction between 1,4-dilithio-1,3-butadienes and CaI₂, leading to the isolation of a series of novel butadienylcalcium-based heavy Grignard reagents.8b

compounds and our continued interest in organocalcium chemistry,^{8b,11} we would further explore the metathesis reaction between dilithio compounds and CaI_2 in this work by expanding the scope of dilithio compounds. Here we report the synthesis of two kinds of calcium complexes based on styryl and biphenyl skeletons, respectively, from the reaction between their corresponding dilithio compound and CaI₂. Single-crystal X-ray structural analysis of these complexes revealed their unique structures. The iodide-bridged styryltricalcium complex should be formed from a styryldicalcium complex via an observed Schlenk equilibrium with the elimination of calcium iodide. The dicalcium-bridged biphenylcalcium compound was first generated as a formal dimeric calciafluorene complex en route to a trimeric analogue after ligand redistribution. Finally, the reactivity of these calcium complexes toward nitrous oxide was investigated.

Considering the ongoing demand for σ -bonded calcium

Results and discussion

Westerhausen and co-workers made major contributions to the synthesis and structure elucidation of aryl and alkenyl calcium halides.^{3c} Based on our previous study,^{8b} we envisaged that the mixed alkenyl/aryl calcium bonds might be simultaneously formed when styryldilithium compound **1** was applied in the metathesis reaction with CaI₂. At the outset, we commenced the reaction of **1** with 1.0 equiv of CaI₂ in THF, in an attempt to determine the moiety that calcium might take priority to bond with. However, ¹H NMR analysis of this reaction in *d*⁸-THF showed that **1** could not react completely. An orange crystalline compound **2** was isolated from the reaction as the sole product. Further experiments demonstrated that compound **2** was always the preferred product in the reaction between **1** and CaI₂, regardless of the amount (0.5–3.0 equiv) of CaI₂ used. As shown in Scheme 1, the reaction of **1** with 2.0 equiv of CaI₂ in

^a Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China. E-mail: zfxi@pku.edu.cn; wx_zhang@pku.edu.cn
^b State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic

^a State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry (SIOC), Chinese Academy of Sciences, Shanghai 200032, China †Electronic Supplementary Information (ESI) available: Materials including experimental procedures, NMR spectra of all new compounds and X-ray data for 2, 5, 6, CCDC 1823281, 1823282 and 1823283. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

DOI: 10.1039/C8DT01046C Journal Name

ARTICLE

THF at room temperature proceeded smoothly and afforded a clear orange solution within 10 min. When THF was removed and Et_2O was added, white precipitate would appear. Crystallization of the reaction residue in Et_2O/THF (20:1) mixed solvent at -28°C yielded compound **2** in relatively high yield.

The NMR spectra of **2** in d^8 -THF showed single set of peaks assignable to the styryl skeleton, which probably indicated a symmetrical structure of **2**. Single-crystal X-ray analysis of **2** revealed an iodide-bridged monomeric structure (Fig. 1), in which three calcium centers are simultaneously bridged by an iodide and two styryl skeletons. One calcium atom lies in between two styryl skeletons. The formed dicalcium bridges in the structure of **2** are analogous to those in our previous reported 2,3-dimethyl-1,4-bis(trimethylsilyl)-substituted butadienyl/dicalcium complexes.^{8b} The lengths of alkenyl/aryl C–Ca bonds and Ca–I bonds in the structure of **2** are comparable to those in the reported structures.⁸



Scheme 1 Synthesis of styryltricalcium complex 2 and possible mechanism.



Fig. 1 ORTEP drawing of **2** with 20% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond length (Å) and bond angle (°): Ca1–C1 2.546(7), Ca1–C4 2.552(7), Ca2–C1 2.681(7), Ca2–C4 2.589(7), Ca2–C13 2.622(7), Ca2–C16 2.574(7), Ca3–C13 2.559(7), Ca3–C16 2.575(7), Ca1–I1 3.1803(14), Ca2–I1 3.3053(14), Ca3–I1 3.1981(14), Ca3–I2 3.0922(15), Ca1–Ca2 3.4640(18), Ca2–-Ca3 3.509(2); C1–Ca1–C4 70.3(2), C1–Ca2–C4 67.6(2), C13–Ca2–C16 68.0(2), C13–Ca3–C16 68.9(2), Ca1–I1–Ca2 64.53(3), Ca2–I1–Ca3 65.28(4), Ca1–I1–Ca3 129.77(4), I1–Ca3–I2 92.84(4).

The structure of **2** prompted us to investigate the mechanism for its formation. As given in Scheme 1, we envisioned that compound **2** might be generated from a putative styryldicalcium complex **3** via the well-known Schlenk equilibrium with the elimination of CaI_2 .¹² To gain some mechanistic evidence, the THF solution obtained from **1** and 2.0 equiv of CaI_2 was monitored by ¹H NMR analysis, which revealed a clean set of peaks that was different from that of **2**. When the pure **2** was reacted with 1.0 equiv of CaI_2 in THF, a new compound showing the same set of peaks as above in ¹H NMR spectrum was observed. These experiments might indicate the involvement of **3** in the reaction toward **2** (Scheme 1). However, all attempts to isolate **3** failed due to its remarkable lability in THF, as evidenced by the unclean NMR spectrum after a long-time preservation of **3** in THF at -28°C.

The structure of dilithio compound may have a decisive effect on the product structure. When biphenyl-2,2'-dilithium compound **4** was treated with CaI₂ in THF, regardless of the amount (0.5–2.0 equiv) of CaI₂ used, a yellow crystalline compound **5** was always isolated from the THF solution at -28°C. As shown in Scheme 2, the reaction of **4** with 1.0 equiv of CaI₂ in THF at room temperature could afford compound **5** in a quantitative yield as determined by ¹H NMR analysis and in 88% isolated yield after crystallization in THF.



Scheme 2 Synthesis of biphenylcalcium complexes 5 and 6.



Fig. 2 ORTEP drawing of **5** with 20% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond length (Å) and bond angle (°): Ca1–C2 2.6698(18), Ca1–C8 2.6502(19), Ca1–C14 2.5072(19), Ca1–C20 2.6494(17), Ca2–C2 2.5845(17), Ca2–C8 2.6593(18), Ca2–C20 2.6036(18), C1–C2 1.423(2), C1–C7 1.507(2), C7–C8 1.420(3), C13–C14 1.422(3), C13–C19

Published on 03 May 2018. Downloaded by National University of Kaohsiung on 05/05/2018 07:17:03.

Journal Name

1.503(3), C19–C20 1.425(3), Ca1---Ca2 3.1355(5); C2–Ca1–C8 65.44(6), C2–Ca2–C8 66.50(6), C14–Ca1–C20 70.56(6).

Compound **5** was structurally characterized to be a dicalcium-bridged biphenylcalcium complex, which can also be interpreted as a formal dimeric calciafluorene complex. The short distance between Ca1 and Ca2 (3.1355(5) Å) indicates a weak Ca---Ca interaction.¹³ The lengths of aryl C–Ca bonds are in the range from 2.5072(19) Å (Ca1–C14) to 2.6698(18) Å (Ca1–C2), which are close to those of the reported structures.⁷ In comparison to the structure of **2**, the less steric hindrance around the biphenyl dianion should favor the formation of the calciafluorene structure other than an iodide-bridged structure.

When compound **5** was stirred in toluene at room temperature for 12 h followed by crystallization in toluene/THF (10:1) mixed solvent at -28° C, another yellow crystalline compound **6** was isolated in 59% yield and characterized by Xray structural analysis. Understandably, **6** can be directly obtained from **4** via a one-pot procedure as shown in Scheme 2. The structure of **6** shown in Fig. 3 can be regarded as a trimeric analogue of complex **5**. The loss of a THF molecule in **5** might have caused the change from **5** to **6**. In the structure of **6**, three Ca centers are nearly located at three vertices of a regular triangle. Together with three bridging biphenyl dianions, a void was thus formed in the centroid of the structure, which might find further application. It should also be noted that other analogous compounds with more than three Ca centers were not observed.



Fig. 3 ORTEP drawing of 6 with 20% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond length (Å) and bond angle (°): Ca1–C2 2.586(4), Ca1–C8 2.613(4), Ca1–C14 2.586(4), Ca1–C20 2.581(4), Ca2–C22 2.602(4), Ca2–C8 2.609(4), Ca2–C26 2.591(4), Ca2–C32 2.605(4), Ca3–C14 2.589(4), Ca3–C20 2.594(4), Ca3–C26 2.593(4), Ca3–C32 2.591(4), C1–C2 1.434(6), C1–C7 1.509(6), C7–C8 1.419(6), C13–C14 1.422(6), C13–C19 1.519(6), C19–C20 1.427(6), C25–C26 1.429(6), C25–C31 1.515(6), C31–C32 1.433(6), Ca1–-Ca2 3.4581(11), Ca1–-Ca3 3.4644(12), Ca2–-Ca3 3.4429(12); C2–Ca1–C8 66.95(14), C2–Ca2–C8 66.76(14), C14–Ca1–C20 67.26(14), C14–Ca3–C20 67.03(14), C26–Ca2–C32 67.06(13), C26–Ca3–C32 67.23(13).

Inspired by the early report that phenylcalcium iodide could react with nitrous oxide to provide azobenzene,¹⁴ we explored the reactivity of these styryl and biphenyl calcium compounds with nitrous oxide in search for some N-containing compounds. As indicated in Scheme 3, when **2** or **3** was stirred in THF bubbling

with a N₂O balloon for 0.5 h, the redox reaction should have occurred but no product was obtained in a preparative yield. Whereas compound **5** or **6** can react relatively cleanly with N₂O at 0°C, providing the benzo[c]cinnoline **8** in moderate yield. This reaction should proceed via the double nucleophilic attack of N₂O by biphenyl dianion followed by elimination of calcium oxide. The appropriate reductivity and nucleophilicity of biphenyl dianion should be beneficial to this reaction. This novel synthetic method toward benzo[c]cinnoline would expand the utilization of N₂O in Ntransfer reactions in synthesis.^{14c}



Scheme 3 Reaction of calcium complexes with nitrous oxide.

Conclusion

In summary, we have synthesized styryl and biphenyl calcium complexes via metathesis reaction between their corresponding dilithio compound and CaI₂. Their well-defined structures were demonstrated by single-crystal X-ray analysis, revealing unique structural characteristics and bonding modes. Schlenk equilibrium and ligand redistribution were found to be key processes. The reactivity of these calcium complexes toward nitrous oxide was investigated.

Experimental section

General experimental details

All reactions were carried out under a slightly positive pressure of dry and oxygen-free argon atmosphere by using standard Schlenk line techniques or under an argon atmosphere in a Mikrouna Super (1220/750) Glovebox. The argon in the glovebox was constantly circulated through a copper/molecular sieve catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O2/H2O Combi-Analyzer to ensure both were always below 1 ppm. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvents were purified by the Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in the glovebox. Organometallic samples for NMR analysis were prepared in the glovebox using J. Young valve NMR tubes (Wilmad 528-JY). ¹H and ¹³C NMR spectra were recorded on a Bruker 400 MHz spectrometer (FT, 400 MHz for ¹H; 100 MHz for ¹³C) at 30°C. Chemical shifts were reported in units (ppm) by assigning one resonance of d^8 -THF in the ¹H NMR spectrum as 3.58 ppm, in the ¹³C NMR spectrum as 67.57 ppm. Dilithio compounds 1 and 4 were synthesized by the reported procedures.¹⁵ Calcium complexes 2 and 5 are too sensitive to be characterized by elemental analysis.

DOI: 10.1039/C8DT01046C

ARTICLE

Synthetic procedures

General procedure for synthesis of styryltricalcium complex 2. In a 50 mL flask, the dilithio compound 1 (101 mg, 0.5 mmol) was added to the slurry of CaI₂ (294 mg, 1.0 mmol) in THF (5 mL). The solution was stirred at room temperature for about 10 min until a clear orange solution was afforded. The solvent was removed under reduced pressure. A mixed Et₂O/THF (20:1) solvent (5 mL) was added and a white turbid solution was obtained. After filtration, the saturated solution was stored at -28°C with exposure to hexane vapor for 3 days, producing single crystals of 2 suitable for X-ray analysis. Compound 2 was isolated in 72% yield as an orange solid (0.18 mmol, 212 mg). ¹H NMR (400 MHz, d^{δ} -THF) δ 0.08 (s, 18H, SiMe₃), 1.76-1.79 (m, 24H, β-CH₂ in THF), 2.38 (s, 6H, Me), 3.60-3.63 (m, 24H, α-CH₂ in THF), 6.66-6.69 (m, 2H, CH), 6.80 (td, J = 7.6 Hz, 2.0 Hz, 2H, CH), 7.38 (d, J = 8.0 Hz, 2H, CH), 7.91 $(dd, J = 6.4 Hz, 1.2 Hz, 2H, CH); {}^{13}C NMR (100 MHz, d^{8}-THF)$ δ 4.1, 26.5, 27.0, 68.4, 121.9, 122.5, 124.7, 143.1, 156.8, 157.5, 188.8, 202.5.

NMR determination of intermediate 3. In a 50 mL flask, the dilithio compound 1 (10 mg, 0.05 mmol) was added to the slurry of CaI₂ (30 mg, 0.10 mmol) in d^8 -THF (0.5 mL). The solution was stirred at room temperature for about 10 min until a clear orange solution was afforded. The solution was quickly transferred into NMR tubes for NMR analysis. The putative intermediate 3 can be detected by the clean set of peaks. ¹H NMR (400 MHz, d^8 -THF) δ 0.31 (s, 9H, SiMe₃), 1.75–1.78 (m, 16H, β-CH₂ in THF), 2.40 (s, 3H, Me), 3.60–3.63 (m, 16H, α-CH₂ in THF), 6.86 (t, *J* = 6.8 Hz, 1H, CH), 7.03 (td, *J* = 7.6 Hz, 1.6 Hz, 1H, CH), 7.53 (d, *J* = 8.0 Hz, 1H, CH), 8.00 (dd, *J* = 6.4 Hz, 0.8 Hz, 1H, CH); ¹³C NMR (100 MHz, d^8 -THF) δ 4.2, 26.4, 26.7, 68.4, 124.2, 125.1, 127.8, 142.5, 156.2, 164.4, 186.4, 210.0.

General procedure for synthesis of biphenylcalcium complex **5.** In a 50 mL flask, the dilithio compound **4** (85 mg, 0.5 mmol) was added to the slurry of CaI₂ (147 mg, 0.5 mmol) in THF (5 mL). The solution was stirred at room temperature for about 10 min until a clear yellow solution was afforded. The solvent was partly removed under reduced pressure. The saturated THF solution was stored at -28°C with exposure to hexane vapor for 3 days, producing single crystals of **5** suitable for X-ray analysis. Compound **5** could be isolated in 88% yield as a yellow solid (0.22 mmol, 164 mg). ¹H NMR (400 MHz, d^8 -THF) δ 1.76–1.79 (m, 20H, β -CH₂ in THF), 3.60–3.63 (m, 20H, α -CH₂ in THF), 6.81-6.85 (m, 4H, CH), 6.94 (td, J = 7.6 Hz, 1.6 Hz, 4H, CH), 7.53 (d, J = 7.6 Hz, 4H, CH), 8.08 (dd, J = 6.8 Hz, 1.6 Hz, 4H, CH); ¹³C NMR (100 MHz, d^8 -THF) δ 26.5, 68.4, 123.0, 123.7, 125.4, 142.5, 159.9, 191.3.

The reaction of **4** (8 mg, 0.05 mmol) with 1.0 equiv of CaI₂ (15 mg, 0.05 mmol) in d^8 -THF at room temperature was monitored by ¹H NMR analysis, which demonstrated that compound **5** was *in situ* generated in a quantitative yield.

General procedure for synthesis of biphenylylcalcium complex 6. In a 50 mL flask, the dilithio compound 4 (85 mg, 0.5 mmol) was added to the slurry of CaI_2 (147 mg, 0.5 mmol) in THF (5 mL). The solution was stirred at room temperature for about 10 min until a clear yellow solution was afforded. The solvent was removed under reduced pressure. Toluene (10 mL) was added and the reaction solution was stirred at room temperature for 12 h. After filtration, the solvent was partly removed and a small amount of THF was added. The saturated toluene/THF (10:1) solution was stored at -28°C with exposure to hexane vapor for 3 days, producing single crystals of **6** suitable for X-ray analysis. Compound **6** was isolated in 59% yield as a yellow solid (0.10 mmol, 99 mg). ¹H NMR (400 MHz, *d*⁸-THF) δ 1.76–1.80 (m, 24H, β -CH₂ in THF), 3.60–3.63 (m, 24H, α -CH₂ in THF), 6.87 (t, *J* = 6.8 Hz, 6H, CH), 7.12 (t, *J* = 7.2 Hz, 6H, CH), 7.96 (dd, *J* = 6.8 Hz, 1.6 Hz, 12H, CH); ¹³C NMR (100 MHz, *d*⁸-THF) δ 26.5, 68.4, 124.2, 127.0, 143.9, 156.6, 176.0. Anal. Calcd for C₆₀H₇₂Ca₃O₆: C, 71.4; H, 7.19; Found: C, 71.0; H, 6.98.

Reaction of calcium complexes with nitrous oxide. To the THF solution (5 mL) of **2**, **3**, **5** and **6** (0.5 mmol), respectively, in a 50 mL Schlenk tube at -40°C or 0°C, N₂O was bubbled with a balloon for 0.5 h, all affording a dark red solution. The reaction solution was quenched with NaHCO₃ aqueous solution. The aqueous layer of the solution was extracted with CH₂Cl₂ for three times and the combined organic layer was washed with brine. Solvent was evaporated and the residue was purified by column chromatography using CH₂Cl₂ as eluent to give product **8**. ¹H NMR (400 MHz, CDCl₃) δ 7.86-7.90 (m, 4H, CH), 8.51-8.55 (m, 2H, CH), 8.71-8.75 (m, 2H, CH); ¹³C NMR (100 MHz, CDCl₃) δ 120.8, 121.3, 129.1, 131.2, 131.4, 145.2. The isolated benzo[c]cinnoline was compared with NMR spectra of an authentic sample.¹⁶

X-ray crystallography

Single crystals of 2 suitable for X-ray analysis were grown in mixed Et₂O/THF (20:1) solvent at -28°C for 3 days. Single crystals of 5 suitable for X-ray analysis were grown in THF at -28°C with exposure to hexane vapor for 3 days. Single crystals of 6 suitable for X-ray analysis were grown in toluene/THF (10:1) at -28°C with exposure to hexane vapor for 3 days. Data collections for them were performed at 180 K or 130 K on a XtaLAB Pro: Kappa single diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). Using Olex2¹⁷, the structures were solved with Superflip¹⁸ solution program using Charge Flipping or ShelXS-9719 solution program using Direct Methods and refined with the ShelXL²⁰ refinement package using Least Squares minimization. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the fullmatrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. A very large solvent accessible void in 2 was squeezed by using Platon.²¹ In all of the structures, the commands DELU, SIMU and ISOR were applied to mostly restrain the disorders of coordinated THF molecules. In the structure of 6, the command AFIX 66 was applied to constrain one benzene ring. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1823281 (2), CCDC-1823282 (5), CCDC-1823283 (6). Copies of these data can be

View Article Online DOI: 10.1039/C8DT01046C ARTICLE

obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

This work was supported by the Natural Science Foundation of China (nos. 21690061, 21725201).

Notes and references

- (a) T. P. Hanusa, Coord. Chem. Rev., 2000, 210, 329; (b) M. Westerhausen, Z. Anorg. Allg. Chem., 2009, 635, 13; (c) S. Harder, Chem. Rev., 2010, 110, 3852; (d) S. Harder (Ed.), Alkaline-Earth Metal Compounds, Topics in Organometallic Chemistry, Springer: Berlin, 2013, Vol. 45; (e) A. S. S. Wilson, M. S. Hill, M. F. Mahon, C. Dinoi and L. Maron, Science, 2017, 358, 1168.
- 2 (a) F. Bickelhaupt, J. Organomet. Chem., 1994, 475, 1; (b) H. G. Richey (Ed.), Grignard Reagents: New Developments, Wiley-VCH, Weinheim, 2000; (c) P. Knochel, W. Dohle, N. Gommermann, F. F. Kneisel, F. Kopp, T. Korn, I. Sapountzis and V. A. Vu, Angew. Chem., Int. Ed., 2003, 42, 4302; (d) Z. Rappoport and I. Marek (Eds.), The Chemistry of Organomagnesium Compounds, Patai Series, Wiley, Chichester, UK, 2008; (e) R. E. Mulvey and S. D. Robertson, Top. Organomet. Chem., 2013, 45, 103.
- 3 (a) M. Westerhausen, Angew. Chem., Int. Ed., 2001, 40, 2975; (b) J. D. Smith, Angew. Chem., Int. Ed., 2009, 48, 6597; (c) M. Westerhausen, A. Koch, H. Görls and S. Krieck, Chem. Eur. J., 2017, 23, 1456.
- 4 (a) J. Langer, M. Köhler, R. Fischer, F. Dündar, H. Görls and M. Westerhausen, *Organometallics*, 2012, 31, 6172; (b) M. Köhler, J. Langer, H. Görls and M. Westerhausen, *Organometallics*, 2014, 33, 6381.
- 5 For examples of alkylcalcium compounds, see: (a) F. G. N. Cloke, P. B. Hitchcock, M. F. Lappert, G. A. Lawless and B. Royo, J. Chem. Soc., Chem. Commun., 1991, 724; (b) K. Mashima, H. Sugiyama, N. Kanehisa, Y. Kai, H. Yasuda and A. Nakamura, J. Am. Chem. Soc., 1994, 116, 6977; (c) C. Eaborn, S. A. Hawkes, P. B. Hitchcock and J. D. Smith, Chem. Commun., 1997, 1961; (d) S. Harder, S. Müller and E. Hübner, Organometallics, 2004, 23, 178; (e) M. R. Crimmin, A. G. M. Barrett, M. S. Hill, D. J. MacDougall, M. F. Mahon and P. A. Procopiou, Chem. Eur. J., 2008, 14, 11292; (f) O. Michel, H. Kaneko, H. Tsurugi, K. Yamamoto, K. W. Törnroos, R. Anwander and K. Mashima, Eur. J. Inorg. Chem., 2012, 998; (g) M. Köhler, A. Koch, H. Görls and M. Westerhausen, Organometallics, 2016, 35, 242.
- 6 For reports of alkynylcalcium compounds, see: (a) D. J. Burkey and T. P. Hanusa, *Organometallics*, 1996, 15, 4971;
 (b) D. C. Green, U. Englich and K. Ruhlandt-Senge, *Angew. Chem., Int. Ed.*, 1999, 38, 354;
 (c) A. G. Avent, M. R. Crimmin, M. S. Hill and P. B. Hitchcock, *Organometallics*, 2005, 24, 1184.
- For examples of arylcalcium compounds, see: (a) S.-O. Hauber, F. Lissner, G. B. Deacon and M. Niemeyer, Angew. Chem., Int. Ed., 2005, 44, 5871; (b) M. Westerhausen, M. Gärtner, R. Fischer and J. Langer, Angew. Chem., Int. Ed., 2007, 46, 1950; (c) M. Westerhausen, J. Langer, S. Kriech, R. Fischer, H. Görls and M. Köhler, Top. Organomet. Chem., 2013, 45, 29.

- 8 For reports of alkenylcalcium compounds, see: (a) M. Köhler, H. Görls, J. Langer and M. Westerhausen, *Chem. Eur. J.*, 2014, **20**, 5237; (b) B. Wei, L. Liu, W.-X. Zhang and Z. Xi, *Angew. Chem., Int. Ed.*, 2017, **56**, 9188.
- 9 (a) M. J. Harvey, T. P. Hanusa and V. G. Young, Jr., Angew. Chem., Int. Ed., 1999, 38, 217; (b) P. Jochmann, T. Dols, L. Perrin, L. Maron, T. P. Spaniol and J. Okuda, Angew. Chem., Int. Ed., 2009, 48, 5715.
- 10 B. M. Wolf, C. Stuhl, C. Maichle-Mössmer and R. Anwander, J. Am. Chem. Soc., 2018, 140, 2373.
- (a) H. Li, X.-Y. Wang, B. Wei, L. Xu, W.-X. Zhang, J. Pei and Z. Xi, *Nat. Commun.*, 2014, 5, 4508; (b) B. Wei, H. Li, W.-X. Zhang and Z. Xi, *Organometallics*, 2015, 34, 1339; (c) B. Wei, H. Li, W.-X. Zhang and Z. Xi, *Organometallics*, 2016, 35, 1458.
- 12 (a) R. Fischer, M. Gärtner, H. Görls, L. Yu, M. Reiher and M. Westerhausen, *Angew. Chem., Int. Ed.*, 2007, 46, 1618; (b) J. Langer, S. Krieck, H. Görls and M. Westerhausen, *Angew. Chem., Int. Ed.*, 2009, 48, 5741.
- 13 For calculated values of Ca-Ca bond lengths, see: (a) M. Westerhausen, M. Gärtner, R. Fischer, J. Langer, L. Yu and M. Reiher, *Chem. Eur. J.*, 2007, **13**, 6292; (b) H. Li, H. Feng, Y. Xie and H. F. Schaefer III, *Chem. Eur. J.*, 2016, **22**, 15019.
- 14 (a) R. Meier and K. Rappold, Angew. Chem., 1953, 65, 560;
 (b) M. Hays and T. P. Hanusa, Tetrahedron Lett., 1995, 36, 2435;
 (c) K. Severin, Chem. Soc. Rev., 2015, 44, 6375.
- (a) L. Liu, W.-X. Zhang, C. Wang, C. Y. Wang and Z. Xi, Angew. Chem., Int. Ed., 2009, 48, 8111; (b) E. H. Braye, W. Hübel and I. Caplier, J. Am. Chem. Soc., 1961, 83, 4406; (c) B. Wei, H. Li, J. Yin, W.-X. Zhang and Z. Xi, J. Org. Chem., 2015, 80, 8758.
- 16 S. Wada, M. Urano and H. Suzuki, J. Org. Chem., 2002, 67, 8254.
- 17 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program., *J. Appl. Cryst.*, 2009, **42**, 339.
- (a) L. Palatinus and G. Chapuis, J. Appl. Cryst., 2007, 40, 786;
 (b) L. Palatinus, S. J. Prathapa and S. van Smaalen, J. Appl. Cryst., 2012, 45, 575.
- 19 G. M. Sheldrick, Acta Cryst., 2008, A64, 112.
- 20 G. M. Sheldrick, Acta Cryst., 2015, C71, 3.
- 21 A. L. Spek, Acta Cryst., 2009, D65, 148.

TOC:



This journal is C The Royal Society of Chemistry 20xx