A Platinum Open Access Journal
for Organic Chemistry

Paper

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Arkivoc **2023**, part v, 21-29

Synthesis and structure of *N*-acetyliminosulfane-stabilized carbone $C(SPh_2NC(O)Me)_2$

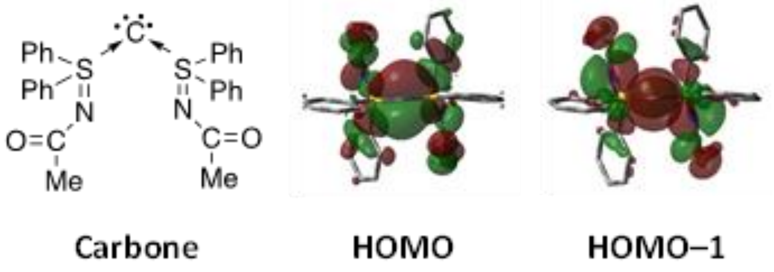
Keiko Noguchi, Yuuta Suzuki, Michiaki Umeda, and Takayoshi Fujii*

Department of Applied Molecular Chemistry, College of Industrial technology, Nihon University, Izumi-cho, Narashino, Chiba 275-8575, Japan
Email: fujii.takayoshi@nihon-u.ac.jp

Received 09-22-2022 **Accepted Manuscript** 11-03-2022 **Published on line** 11-09-2022

Abstract

N-acetyliminosulfane-stabilized carbone bis(acetyliminosulfane)carbon(0) $C(SPh_2NC(O)Me)_2$ has been successfully synthesized by deprotonation of the corresponding salt $[HC(SPh_2NC(O)Me)_2]ClO_4$. The molecular structures of $[HC(SPh_2NC(O)Me)_2]ClO_4$ and $C(SPh_2NC(O)Me)_2$ were characterized using ^1H- and ^{13}C-NMR and X-ray crystallographic analyses. Density functional theory calculations revealed that the electronic structure of $C(SPh_2NC(O)Me)_2$ has two lone pairs of electrons at the central carbon atom. The first and second proton affinities (PAs) of $C(SPh_2NC(O)Me)_2$ (PA(1): 271.3 kcal mol^{-1}; PA(2): 181.2 kcal mol^{-1}) are smaller than those of (methyliminosulfane)carbone(0) $C(SPh_2NMe)_2$ (PA(1): 278.8 kcal mol^{-1}; PA(2): 182.2 kcal mol^{-1}). $C(SPh_2NC(O)Me)_2$ was also compared with previously prepared sulfur-stabilized carbones.



Keywords: Carbones, density functional calculations, donor–acceptor interaction, electronic structure, iminosulfane

DOI: https://doi.org/10.24820/ark.5550190.p011.890

Introduction

Many functional organic compounds that enrich our lives, such as pharmaceuticals, agrochemicals, and polymers, are synthesized by catalytic reactions.[1, 2] Therefore, new catalysts with higher activity and higher efficiency should be developed. The reactivity of a metal complex catalyst depends on the ligand bound to the central metal, thus, a new ligand can be expected to alter the reactivity of a catalyst using it.[2, 3]

Recently, divalent carbon(0) species, known as carbones (CL_2), have been proposed as new ligands for catalytic reactions.[4–6] Carbones are recognized as a class of compounds that bear unique bonding and electron-donating characteristics at the central carbon.[7–9] Carbones consist of two strong electron-donating ligands (L) coordinated to a central zero-valent carbon atom, which maintains four valence electrons in σ- and π-type lone pair (LP) orbitals. Therefore, they are frequently described as general-type carbon complexes ($L\rightarrow C\leftarrow L$). The central carbon is stabilized by two strongly electron-donating ligands, such as phosphane, sulfane, or carbene ligands.[4, 6, 10–15] Various substituent groups can be introduced onto these ligands to control their function.[4, 15–19]

Recently, we investigated the syntheses, structures, and reactivities of carbones CL^1_2 (**A**), CL^1L^2 (**B**), CL^1L^3 (**C**), CL^1L^4 (**D**), and CL^2_2 (**E**) (Figure 1), stabilized by methyliminosulfane (L^1), sulfane (L^2), selenane (L^3), and phospane (L^4), and suggested that the electron-donating ability of the central carbon in these carbones can be tuned by replacing L^1 with L^2, L^3, or L^4 ligands.[14, 15, 20–24] Herein, we report the synthesis, crystal, and electronic structure of *N*-acetyliminosulfane-stabilized carbone **3**, and compare **3** to previously reported *N*-methyliminosulfane-stabilized carbones **A**.

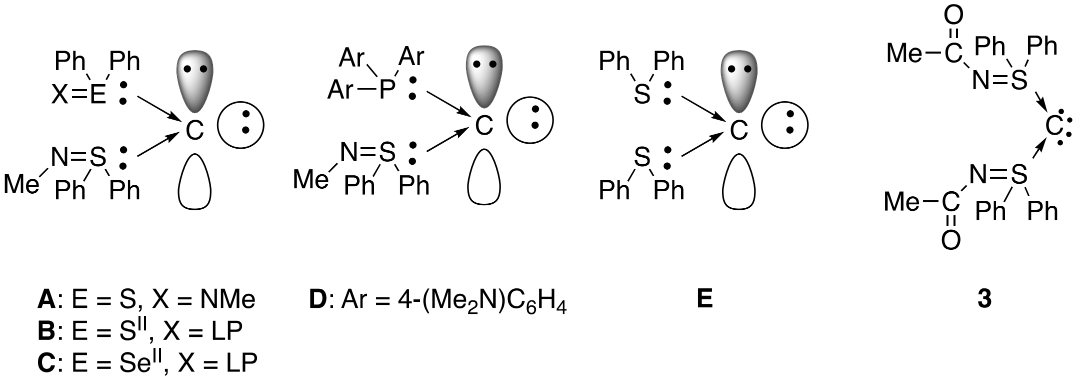
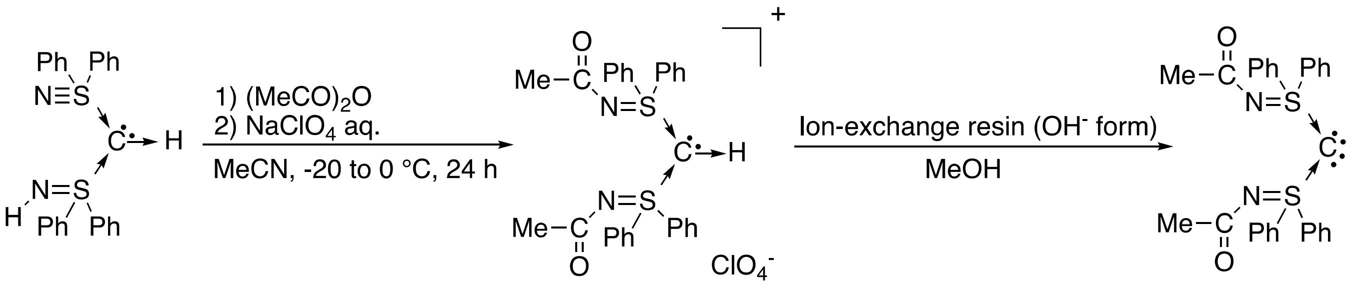


Figure 1. Molecular structures of **A**–**E** and **3**.

Results and Discussion

In our previous study, the key intermediate **1** was synthesized from the reaction of fluorodiphenyl-λ^6-sulfanenitrile with α-lithiated methyl diphenyl-λ^6-sulfanenitrile.[12] The reaction of **1** with two equivalents of acetic anhydride in THF at –20 °C afforded the corresponding monoprotonated salt **2** in 87% yield (Scheme 1). The desired carobone **3** was prepared in essentially quantitative yield by passing a methanolic solution of **2** through an ion-exchange resin column (IRA-410, OH^- form). The formation of **2** and **3** was confirmed by ^1H and ^{13}C NMR spectroscopy and elemental analysis. The ^1H and ^{13}C NMR spectroscopy results revealed four equivalent phenyl, two equivalent acetyl groups, and a central carbon atom. The ^{13}C NMR signal for the central carbon atom of **3** (δ = 29.6 ppm) was shifted to a higher field relative to that of **A** (δ = 39.7 ppm).[12]



1 **2** **3**

Scheme 1. Synthesis of **3**.

The molecular structures of **2** and **3** were determined using X-ray crystallographic analysis (Figure 2). Selected bond lengths and angles of **2** and **3** are listed in Table 1, together with the data for bis(methyliminosulfane)carbon(0) **A**.

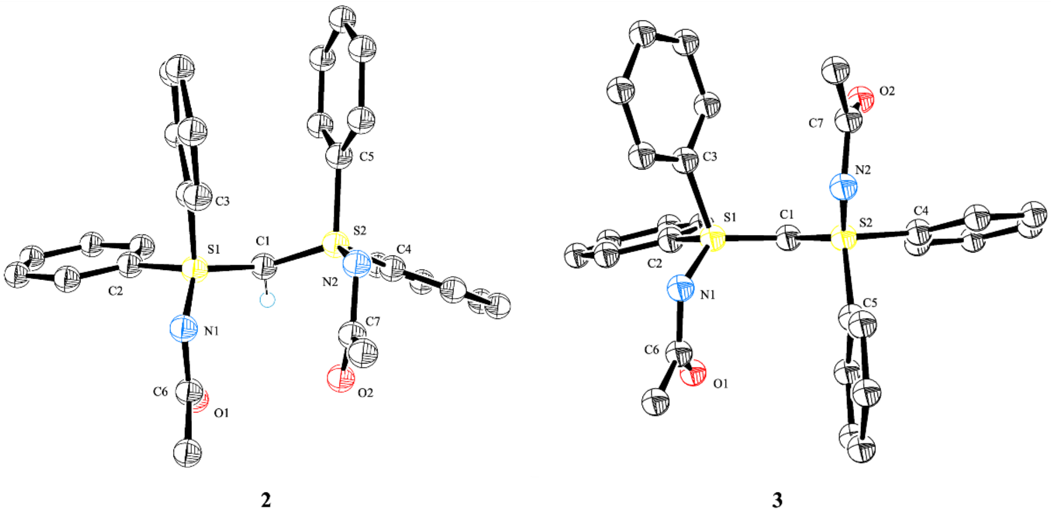


Figure 2. Molecular structure of **2** and **3**. Ellipsoids are shown at 50% probability. Hydrogen atoms (except for that on C_{center}) and ClO_4^- anions are omitted for clarity.

The crystal structure of bis(acetyliminosulfane)carbon(0) **3** exhibits the following characteristic properties : The S1-C2 and S2-C4 bonds lie in the S1-C1-S2 plane, and the π-faces of the two phenyl groups are orientated in the same direction. Notably, the S1-C3 and S2-C5 bonds of **3** favor an anticlinal arrangement at the S1•••S2 axis (C3-S1•••S2-C5: 126.4°) and almost eclipse each S-N bond (C3-S1•••S2-N2: 23.9°; C5-S2•••S1-N1: 23.2°), whereas the corresponding S-C bonds of **2** and **A** adopt a near synclinal eclipsed conformation (torsional angles of C3-S1•••S-C5, **2**: –30.7°; **A**: –30.7°[12]). The average central S-C1 bond distance in **3** is 1.626(2) Å, which is significantly shorter than that of **2** (av. S-C1: 1.694(2) Å), and slightly shorter than that of **A** (av. S-C1: 1.636(3) Å[12]). The mean S-N bond distance (1.592(1) Å) in **3** is longer than that in **A** (1.552(9) Å[12]). However, the C-N (mean: 1.374(2) Å) and C-O (mean: 1.224(2) Å) distances in **3** are comparable to the standard lengths of C-N bonds (1.38 Å) and C-O bonds (1.21 Å).[25] The S1-C1-S2 bond angle (115.2(1)°) of **3** is very similar to that of monoprotonated salt **2** (116.3(1)°). This trend is similar to that observed for bis(methyliminosulfane)carbon(0) **A**,[12] but is different from the trend for **B**–**D**.[15, 20, 23]

Table 1. Selected bond lengths (Å) and angles (°) of **2**, **3** and **A**

	2[a]	**3**[a]	**A**[b]
S1–N1	1.5766(16)	1.5948(13)	1.553(10)
S1–C1	1.696(2)	1.6278(15)	1.635(4)
S1–C2	1.7751(19)	1.7824(15)	1.802(4)
S1–C3	1.762(2)	1.7933(14)	1.801(2)
S2–N2	1.5669(16)	1.5895(13)	1.550(8)
S2–C1	1.6912(19)	1.6248(15)	1.636(2)
S2–C4	1.7762(19)	1.7836(14)	1.808(4)
S2–C5	1.7733(19)	1.7986(15)	1.799(4)
N1–C6	1.383(3)	1.3750(18)	1.464(4)
N2–C7	1.397(2)	1.373(2)	1.470(5)
C6–O1	1.221(3)	1.2242(19)	–
C7–O2	1.214(2)	1.223(2)	–
N1–S1–C1	120.61(10)	123.76(7)	124.1(2)
N1–S1–C2	112.19(9)	110.90(7)	110.6(3)
N1–S1–C3	103.30(9)	100.78(6)	102.2(2)
C1–S1–C2	105.27(9)	104.43(7)	101.9(3)
C1–S1–C3	108.62(9)	113.10(7)	115.4(1)
C2–S1–C3	106.01(9)	101.98(7)	100.5(1)
N2–S2–C1	122.92(9)	125.08(7)	128.1(2)
N2–S2–C4	113.77(9)	111.14(7)	110.1(3)
N2–S2–C5	102.17(9)	99.72(8)	101.1(3)
C1–S2–C4	102.59(9)	103.59(7)	102.1(1)
C1–S2–C5	108.33(9)	113.71(8)	111.6(1)
C4–S2–C5	106.01(9)	101.44(7)	101.0(3)
S1–C1–S2	116.28(11)	115.19(9)	116.8(2)

[a] Experimental values. [b] Ref. [12].

To gain insight into the electronic structures of **3**, density functional theory (DFT) calculations were performed at the B3PW91/6–311G(d,p) level (Figure 3).[26–30]

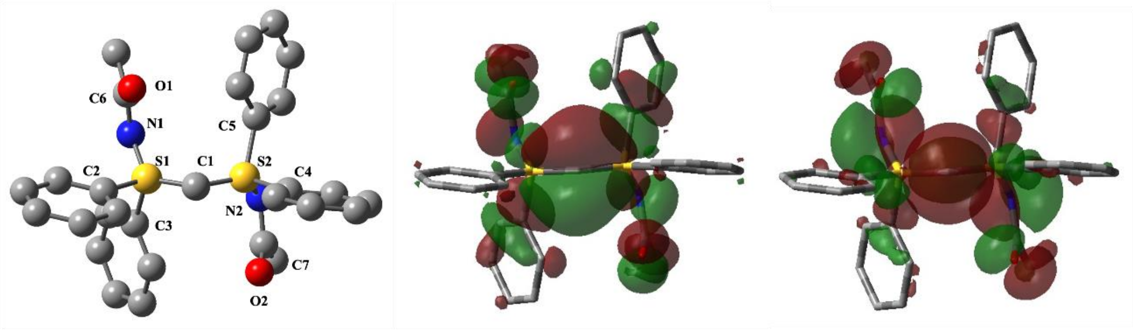


Figure 3. The optimized structure of **3** (left, hydrogen atoms are omitted for clarity) and its HOMO (center) and HOMO–1 (right).

The optimized structure of **3** closely matches that determined using the experimental data. Molecular orbital analysis indicates that the central carbon atom of **3** has two LP orbitals in the HOMO ($n\pi_c$) and HOMO–1 ($n\sigma_C$) (Figure 3). Natural bond orbital (NBO) analysis indicated that the $n\sigma_c$ enhanced the *s* character (45%), indicating a hybridization similar to *sp*, whereas the $n\pi_c$ LP of carbon has 100% *p* character.[31] The central carbon atom of **3** bears a large negative charge (−1.16 e), which is similar to that in **A** (–1.24 e).[12] Both carbon LPs of **3** are stabilized through interactions with σ^*(S-N) and σ^*(S-C_{ph}), as determined by NBO second-order perturbation analysis. In particular, $n\sigma_C$ interacts with two σ^*(S-N; $E_{SN\text{-}total}$: 17.5 kcal mol^{-1}) and four σ^*(S-C; $E_{SC\text{-}total}$: 14.9 kcal mol^{-1}), whereas the stabilization energy for $n\pi_C$ indicates almost no interactions involving the $n\pi_C$ to σ^*(S1-C1) and σ^*(S2-C3), and $n\pi_C$ interacts with σ^*(S1-N1; 14.1 kcal mol^{-1}), σ^*(S1-C2; 19.9 kcal mol^{-1}), σ^*(S2-N2; 14.9 kcal mol^{-1}), and σ^*(S2-C4; 19.9 kcal mol^{-1}). These results indicate that the two acetyliminosulfane ligands decrease the electron density of the two LPs (occupancy of LPs, $n\sigma_C$: 1.73; $n\pi_C$: 1.52).

To verify the carbone character, we calculated the first and second proton affinities[32, 33] (PA(1) and PA(2)) of **3** and compared them with the theoretically predicted values for the PAs of carbones **A**–**E** (Table 2).

Table 2. Calculated energy levels of the HOMO, HOMO-1 and proton affinities (PAs) of **3** and **A**–**E** at B3PW91/6-311G(d,p)

	HOMO (eV)	HOMO-1 (eV)	PA(1) (kcal mol^{-1})	PA(2) (kcal mol^{-1})
3	-5.68	-6.03	271.3	181.2
A[23]	-5.26	-5.56	278.8	182.2
B[20]	-5.08	-5.32	288.0	184.4
C[20]	-5.09	-5.36	287.1	187.0
D[15]	-4.58	-4.73	301.6	207.8
E[23]	-4.89	-5.02	297.5	183.7

As expected, the theoretically predicted PA(1) (271.3 kcal mol^{-1}) of bis(acetyliminosulfane)carbon(0) **3** is smaller than that of bis(methyliminosulfane)carbone(0) **A** and is the smallest PA discussed in this study (Table 2). These results suggest that the *N*-acetylated iminosulfane ligand has reduced the electron density at the carbone center of **3**. Therefore, the functionality of the central carbon can be easily controlled by introducing electron-donating or -withdrawing substituents to the nitrogen atom of the iminosulfane ligand. PA(1) is predominantly determined by the energy level of the highest occupied *s* orbital of neutral carbone **3**, whereas PA(2) is predominantly determined by the highest occupied *p* orbital of monoprotonated **2**.

Conclusions

In conclusion, we successfully prepared the *N*-acetyliminosulfane-stabilized carbone **3** by the deprotonation of the corresponding protonated salt **2** with Amberlite/OH$^-$ form. In addition, the molecular structures of **2** and **3** were determined using X-ray crystallographic analysis. Furthermore, DFT calculations for **3** revealed that the two LPs at the central carbon atom are efficiently stabilized by an n–σπ* interaction with adjacent acetyliminosulfane ligands, and the PA value of **3** is the lowest value among **A**–**E**. These results suggested that the electronic properties of the central carbon in the carbones can be tuned by choosing appropriate substituents.

Experimental Section

General considerations. Unless otherwise specified, reactions were performed under a dry argon atmosphere. The reagents were purchased from commercial suppliers and used after further purification. ^{1}H and ^{13}C{^{1}H} NMR spectroscopies were recorded using a Bruker Avance 500 MHz spectrometer. The ^{1}H and ^{3}C{^{1}H} NMR chemical shifts (δ) in $CDCl_3$ are given in ppm relative to $Si(CH_3)_4$ and the coupling constants (*J*) are expressed in Hz. Compound **1** was prepared according to the literature procedure.[12]

2: Acetic anhydride (0.19 mL, 2.0 mmol) was added dropwise at –20 °C to a solution of **1** (170 mg, 0.41 mmol) in acetonitrile (10 mL) and the mixture stirred for 24 h. The solution of **2** was evaporated under reduced pressure, and the residue was added to an aqueous solution of sodium perchlorate (0.244 g, 2.0 mmol). The white solid obtained was filtered off and washed with water and diethyl ether. The residue was recrystallized from hot-methanol/diethyl ether to afford monoprotonated salt **2** (206 mg, 84%) as a white solid. M.p. 189–190 °C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.31 (s, 6H), 5.62 (s, 1H), 7.52–7.66 (m, 12H), 8.08–8.15 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ= 26.9, 40.1, 128.7, 130.9, 131.4, 135.5, 179.9 ppm; elemental analysis calcd (%) for $C_{29}H_{27}ClN_2O_6S_2$: C 58.14, H 4.54, N 4.68; found: C 57.77, H 4.51, N 4.71.

3: A solution of **2** (120 mg, 0.20 mmol) in methanol was passed through a column of Amberlite IRA-410 ion-exchange resin (strong base, OH$^-$ form) and the eluate was evaporated to afford **3** as a white powder (98 mg, 98%). M.p.: 218–220 °C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.49 (s, 6H), 7.40–7.50 (m, 12H), 8.12–8.24 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ= 26.2, 29.6, 127.4, 129.3, 131.7, 142.4, 178.6 ppm; elemental analysis calcd (%) for $C_{29}H_{26}N_2O_2S_2$: C 69.85, H 5.26, N 5.62; found: C 69.66, H 5.25, N 5.57.

CCDC 2207010 (**3**), and 2207011 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/structures/.

Computational section. The geometries of **3** were optimized at the B3PW91/6-311G* level of theory.[26-28] The resulting structures were characterized as stationary points on the potential energy surface by evaluating their vibrational frequencies at the same level of theory. All calculations were performed using the Gaussian09 suite of quantum chemical programs.[29] Natural bond order and charge analyses were performed at the B3PW91/6-311G* level of theory using the NBO 3.1 program.[30]

Acknowledgements

This work was partially supported by a Grants-in-Aid for Scientific Research (C) (No. 19K05424 and 22K05072) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. We thank Prof. Dr. Toshiaki Yoshimura at Toyama University for the helpful discussions. We also thank Mr. Wangjie Pan and Miss. Hitomi Shimohara for their experimental assistance.

Supplementary Material

Supplementary materials (Crystallographic data of **2** and **3** and Cartesian coordinates and NBO second-order perturbation analysis results of **3** associated with this article are provided.

References

1. Devendar, P.; Qu, R. -Y.; Kang, W. -M.; He, B.; Yang, G. -F. *J. Agric. Food Chem.* **2018**, *66*, 8914–8934. https://doi.org/10.1021/acs.jafc.8b03792
2. Furst, M. R. L.; Goff, R. L.; Quinzer, D.; Mecking, S.; Botting, C. H.; Cole-Hamilton, D. J. *Green Chem*. **2012**, *14*, 472–477. https://doi.org/10.1039/C1GC16094J
3. Hansen, E. C.; Pedro, D. J.; Wotal, A. C.; Nelson, N. J.; Caron, S.; Weix, D. J. *Nat. Chem*. **2016**, *8*, 1126–1130. https://doi.org/10.1038/nchem.2587
4. Corberán, R.; Marrot, S.; Dellus, N.; Saffon-Merceron, N.; Kato, T.; Peris, E.; Baceiredo, A. *Organometallics* **2009**, *28*, 326–330. https://doi.org/10.1021/om8008958
5. El-Hellani, A.; Bour, C.; Gandon, V. *Adv. Synth. Catal.* **2011**, *353*, 1865– 1870. https://doi.org/10.1002/adsc.201100287
6. Hsu, Y.; Shen, J.; Lin, B.; Chen, W.; Chan, Y.; Ching, W.; Yap, G.; Hsu, C.; Ong, T. *Angew. Chem. Int. Ed.* **2015**, *54*, 2420–2424; *Angew. Chem*. **2015**, *127*, 2450–2454. https://doi.org/10.1002/ange.201406481
7. Tonner, R.; Frenking, G. *Chem. Eur. J.* **2008**, *14*, 3260–3272. https://doi.org/10.1002/chem.200701390
8. Tonner, R.; Frenking, G. *Chem. Eur. J.* **2008**, *14*, 3273–3289. https://doi.org/10.1002/chem.200701392
9. Frenking, G. *Angew. Chem. Int. Ed*. **2014**, *53*, 6040–6046; *Angew. Chem*. **2014**, *126*, 6152–6158. https://doi.org/10.1002/anie.201311022
10. Kneusels, N.-J.; Münzer, J.; Flosdorf, K.; Jiang, D.; Neumüller, B.; Zhao, A.; Eichhöfer, A.; Frenking, G.; Kuzu, I. *Dalton Trans.* **2020**, *49*, 2537-2546. https://doi.org/10.1039/C9DT04725E
11. Liu, Z.; Mckay, A. I.; Zhao, L.; Forsyth, C. M.; Jevtović, V.; Petković, M.; Frenking, G.; Vidović, D. *J. Am. Chem. Soc*. **2022**, *144*, 7357-7365. https://doi.org/10.1021/jacs.2c00936

12. Fujii, T.; Ikeda, T.; Suzuki, T.; Yoshimura, T. *Angew. Chem. Int. Ed*. **2002**, *41*, 2576 – 2578; *Angew. Chem.* **2002**, *114*, 2688–2690.
https://doi.org/10.1002/1521-3757(20020715)114:14<2688::AID-ANGE2688>3.0.CO;2-R
13. Pascual, S.; Asay, M.; Illa, O. Kato, T.; Bertrand, G.; Saffon-Merceron, N.; Branchadell, V.; Baceiredo, A. *Angew. Chem. Int. Ed*. **2007**, *46*, 9078–9080; *Angew. Chem*. **2007**, *119*, 9236–9238.
https://doi.org/10.1002/ange.200704071
14. Dellus, N.; Kato, T.; Bagán, X.; Saffon-Merceron, N.; Branchadell, V.; Baceiredo, A. *Angew. Chem. Int. Ed*. **2010**, *49*, 6798–6801; *Angew. Chem*. **2010**, *122*, 6950–6953.
https://doi.org/10.1002/ange.201002833
15. Morosaki, T.; Wang, W.-W.; Nagase, S.; Fujii, T. *Chem. Eur. J*. **2015**, *21*, 15405–15411.
https://doi.org/10.1002/chem.201502166
16. Tonner, R.; Franking,G. *Angew. Chem. Int. Ed.* **2007**, *46*, 8695–8698; *Angew. Chem*. **2007**, *119*, 8850–8853.
https://doi.org/10.1002/ange.200701632
17. Klen, S.; Tonner, R.; Frenking, G. *Chem. Eur. J.* **2010**, *16*, 10160–10170.
https://doi.org/10.1002/chem.201000174
18. Kaufhold, O.; Hahn, F. *Angew. Chem, Int. Ed*. **2008**, *47*, 4057–4061; *Angew. Chem*. **2008**, *120*, 4122–4126.
https://doi.org/10.1002/ange.200800846
19. Petz, W. *Coord. Chem. Rev*. **2015**, *291*, 1–27.
https://doi.org/10.1016/j.ccr.2015.01.007
20. Morosaki, T.; Suzuki, T.; Wang, W.-W.; Nagase, S.; Fujii, T. *Angew. Chem. Int. Ed.* **2014**, *53*, 9569–9571; *Angew. Chem*. **2014**, *126*, 9723–9725.
https://doi.org/10.1002/ange.201404795
21. Morosaki, T.; Fujii, T. *Phosphorus Sulfur Silicon Relat. Elem*. **2016**, *191*, 159–162.
https://doi.org/10.1080/10426507.2015.1114488
22. Morosaki, T.; Suzuki, T.; Fujii, T. *Organometallics* **2016**, *35*, 2715–2721.
https://doi.org/10.1021/acs.organomet.6b00452
23. Morosaki, T.; Iijima, R.; Suzuki, T.; Wang, W.-W.; Nagase, S.; Fujii, T. *Chem. Eur. J.* **2017**, *23*, 8694–8702.
https://doi.org/10.1002/chem.201700863
24. Morosaki, T.; Fujii, T. *Adv. Organomet. Chem*. **2017**, *68*, 137–196.
https://doi.org/10.1016/bs.adomc.2017.08.002
25. Emsley, J. *The Elements*, third ed., Oxford University Press, Oxford, UK, **1998**.
https://doi.org/10.1103/PhysRevA.38.3098
26. Becke, A. D. *Phys. Rev.* **1988**, A *38*, 3098–3100.
https://doi.org/10.1103/PhysRevA.38.3098
27. Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648–5652.
https://doi.org/10.1063/1.464913
28. Perdew, Y. P.; Wang, Y. *Phys. Rev*. **1996**, B *45*, 13244–13249.
https://doi.org/10.1103/PhysRevB.45.13244
29. Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.;

Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmenn, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2010**.

30. NBO 6.0. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, **2013**.
31. Takagi, N.; Tonner, R.; Frenking, G. *Chem. Eur. J*. **2012**, *18*, 1772–1780. https://doi.org/10.1002/chem.201100494
32. Tonner, R.; Heydenrych, G.; Frenking, G. *ChemPhysChem*. **2008**, *9*, 1474–1481. https://doi.org/10.1002/cphc.200800208
33. Klein, S.; Tonner, R.; Frenking, G. *Chem. Eur. J*. **2010**, *16*, 10160–10170. https://doi.org/10.1002/chem.201000174