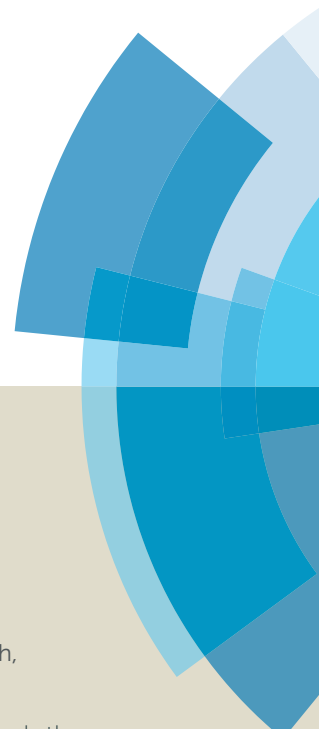


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ARTICLE

Instability of Metal 1,3-Benzodi(thiophosphinoyl)methandiide Complexes: Formation of Hafnium, Tin and Zirconium Complexes of 1,3-Benzodi(thiophosphinoyl)thioketone Dianionic Ligand [1,3-C₆H₄(PhPS)₂CS]²⁻

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The reaction of [LCH₂] (**1**, L = 1,3-C₆H₄(PhPS)₂) and M(NMe₂)₄ (M = Hf, Zr) in toluene at 110 °C afforded a mixture of group 4 metal complexes [(LC(S))₂M] [M = Hf (**2**), Zr (**3**)] and [1,3-C₆H₄(PhPS)(PhP)CH₂]. The reactions appear to proceed through the formation of metal bis(carbene) complexes, [LC=M=CL], which then undergo an intermolecular sulphur transfer reaction with the P=S bond of [LCH₂] to form **2** and **3** and the byproducts are [1,3-C₆H₄(PhPS)(PhP)CH₂], respectively. In addition, the reaction of **1**, [CH₂(PPh₂S)₂] (**4**) and M(NMe₂)₄ in refluxing toluene gave a mixture of [(LC(S))M(NHMe₂){C(PPh₂S)₂}] [M = Hf (**5**), Zr (**6**)], [1,3-C₆H₄(PhPS)(PhP)CH₂] and [CH₂(PPh₂S)(PPh₂)]. Moreover, the intermolecular sulfur transfer reaction is evidenced by the reaction of the tin(II) 1,3-benzodi(thiophosphinoyl)methandiide complex [{μ-1,3-C₆H₄(PhPS)₂C}Sn]₂ (**7**) with two equivalents of elemental sulfur in CH₂Cl₂ at ambient temperature to give [{1,3-C₆H₄(PhPS)₂CS}Sn] (**8**). Compounds **2**, **3**, **5**, **6**, and **8** were characterized by NMR spectroscopy and X-ray crystallography.

Introduction

Transition-metal carbene complexes have attracted much attention due to their application in organic transformation in which the nature of carbenes greatly depends on the electronic properties of substituents bound to the C_{carbene} atoms.¹ For example, Fischer carbenes comprising electronegative heteroatom substituents are electrophilic while Schrock carbenes containing hydrogen, alkyl, or aryl substituents are nucleophilic.² Besides these two spectacular carbene classes, in recent years, geminal dianions [C(PPh₂E)₂]²⁻ (E = NSiMe₃ or S), which were pioneered by research groups of Cavell, Stephan and Le Floch,^{3,5e} bearing two iminophosphoranyl or thiophosphinoyl substituents were utilized for the synthesis of main-group element,⁴ transition metal,⁵ lanthanide⁶ and actinide⁷ carbene complexes [L_nM=C(PPh₂E)₂] (L = ligand).⁸ They can be easily prepared by the simple salt elimination of geminal dianions [C(PPh₂E)₂]²⁻ with metal halides or by the double deprotonation of the parent ligand [CH₂(PPh₂E)₂] with metal alkyls or amides. Among these examples, group 4 metal derivatives were well experimentally and theoretically studied. Cavell et al. reported a series of group 4 carbene complexes

[M(Cl)₂{C(PPh₂NSiMe₃)₂}] (M = Ti, Hf, Zr) by the reaction of [Li₂C(PPh₂NSiMe₃)₂] with MCl₄.^{5a,c} Their reactivity were also been reported.⁹ Similar compounds, [Zr(Cp)₂{C(PPh₂S)₂}], [Zr(Cl)₂(THF){C(PPh₂S)₂}]₂ and [Zr(Cl)₂(py){C(PPh₂S)₂}]₂,^{5g} were also reported by Le Floch et al.. X-ray crystallography and theoretical studies show that the σ and π electrons of the M=C_{methandiide} double bond in [L_nM=C(PPh₂E)₂] are mainly donated from the C_{methandiide} atom to the metal centre. This unique electronic property results in different reactivity compared with Fischer and Schrock carbene complexes.

Recently, Gessner et al. showed that when one of the thiophosphinoyl substituents in C(PPh₂S)₂²⁻ was replaced by the trimethylsilyl substituent, the negative charge at the C_{methandiide} atom in the palladium carbene intermediate [(PPh₃)₂Pd{C(PPh₂S)(SiMe₃)}] cannot be sufficiently stabilized, which resulted in the intramolecular transfer of the sulphur atom from the thiophosphinoyl substituent to the carbenic carbon atom to form the palladium thioketone complex [(PPh₃)₂Pd{SC(PPh₂)(SiMe₃)}].¹⁰ Furthermore, when the trimethylsilyl substituent in C(PPh₂S)(SiMe₃)²⁻ was replaced by a triphenylsilyl substituent, a mixture of [(PPh₃)₂Pd{C(PPh₂S)(SiPh₃)}] and [(PPh₃)₂Pd{SC(PPh₂)(SiPh₃)}] was isolated. These results illustrate that the steric and electronic effects of ligand substituents are crucial for the stabilization of metal bis(phosphonium)methandiide complexes. However, So and Mézailles et al. report that the geminal dianion Li₂[C(PPh₂S)(SiMe₃)] is stable and the negative

^a Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371 Singapore. Electronic Supplementary Information (ESI) available: Figures S1 and S2 giving the molecular structures of compounds **3** and **6**. Table S1 giving selected X-ray crystallographic data of compounds **2**, **3**, **5**, **6**, and **8**. See DOI: 10.1039/x0xx00000x

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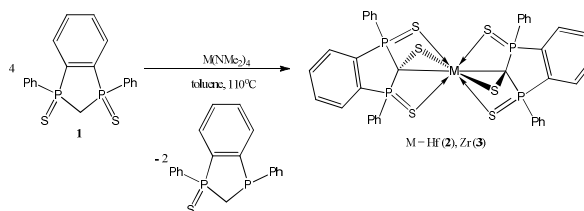
charges at the C_{methandiide} atom can be sufficiently stabilized by both SiMe₃ and PPh₂S substituents.¹¹

We anticipate that metal centres also affect the stability of metal bis(phosphonium)methandiide complexes. This can also be evidenced by a recent example reported by Mézailles et al. that the uranium carbene complex [U{C(PPh₂S)₂}(THF)₂] decomposes upon heating in pyridine (py) to form [U{C(PPh₂S)₂}{SC(PPh₂S)₂}(py)] in which a sulfur atom is added to the U=C bond.^{6e}

Our research group has been involving in the preparation of main-group carbene complexes using geminal dianions. We prepared the tin(II) 1,3-benzodi(thiophosphinoyl)methandiide [{μ-1,3-C₆H₄(PhPS)₂C}Sn]₂ by the double deprotonation of [1,3-C₆H₄(PhPS)₂CH₂] with Sn{N(SiMe₃)₂}₂.⁴ⁱ Its reactivity illustrated that the C_{methandiide} atom bearing a negative charge can react with various Lewis acids such as AlCl₃ and GaCl₃.^{4j} No sulphur-transfer reaction was observed. In order to understand whether the metal center can affect the stability of a M-C_{methandiide} bond and results in a sulfur transfer reaction, we used [1,3-C₆H₄(PhPS)₂CH₂] to react with group 4 metals. In this paper, we report that the M=C_{methandiide} double bonds (M = Hf, Zr) supported by 1,3-C₆H₄(PhPS)₂C²⁻ are unstable, which lead to intermolecular sulphur transfer. The mechanism is in contrast to the intramolecular sulphur transfer reaction using the {(PPh₂S)(SiMe₃)C}²⁻ ligand, which is proposed by Gessner and her co-workers.¹⁰

Results and Discussion

Synthesis of [1,3-C₆H₄(PhPS)₂C(S)]₂M (M = Hf, Zr). The reaction of [LCH₂] [1, L = 1,3-C₆H₄(PhPS)₂] and M(NMe₂)₄ (M = Hf, Zr) in toluene cannot occur at room temperature. In contrast, when the temperature was warmed to 110 °C, a mixture of group 4 metal complexes [{LC(S)}₂M] [M = Hf (2), Zr (3), Scheme 1] and [1,3-C₆H₄(PhPS)(PhP)CH₂]^{4j} was afforded, which was confirmed by ³¹P and ¹H NMR spectroscopy. The reaction mixture was filtered and the filtrate was concentrated to afford [{LC(S)}₂M] [M = Hf (2), Zr (3)] as highly air- and moisture-sensitive yellow crystalline solids. The mother liquor was then filtered out and its ³¹P{¹H} NMR [doublet, δ -6.86, 64.62 ppm (*J*_{P-P'} = 26.5 Hz)] and ¹H NMR spectra [doublet of doublets, δ 3.05 ppm (²*J*_{P-H} = 13.4, ²*J*_{P'-H} = 19.5 Hz)] show the presence of [1,3-C₆H₄(PhPS)(PhP)CH₂] only. The reactions appear to proceed through the formation of metal bis(carbene) complexes, [LC=M=CL], which then undergo an intermolecular sulphur transfer reaction with the P=S bond of [LCH₂] to form 2 and 3, respectively and the byproducts are [1,3-C₆H₄(PhPS)(PhP)CH₂]. Such intermolecular sulphur transfer reaction was also observed in the reaction of the tin(II) 1,3-benzodi(thiophosphinoyl)methandiide [{μ-1,3-C₆H₄(PhPS)₂C}Sn]₂ with ZnEt₂ to afford a mixture of [{1,3-C₆H₄(PhPS)₂C}SnEt₂](μ-ZnS)₂, SnEt₄ and [1,3-C₆H₄(PhPS)(PhP)CH₂].^{4j}



Scheme 1. Synthesis of 2 and 3

Compounds 2 and 3 are highly insoluble in THF and CHCl₃ and slightly soluble in MeCN only. The ¹³C NMR spectra could not be obtained owing to very poor solubility in any NMR solvents. The ¹H NMR spectra display resonances for the phenyl protons. The ³¹P{¹H} NMR spectra of 2 and 3 display a singlet (2: δ 54.6, 3: 55.2 ppm) for the equivalent P nuclei, which are shifted downfield in comparison with that of 1 (δ 45.80 ppm).⁴ⁱ

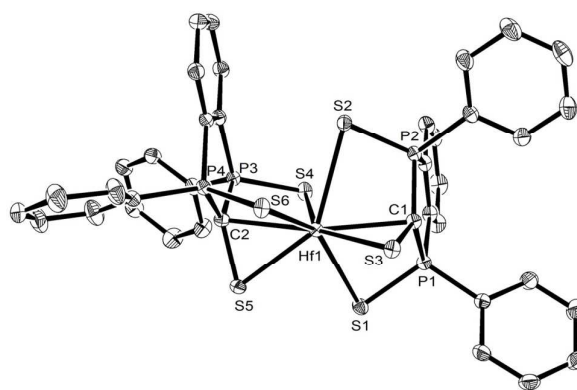


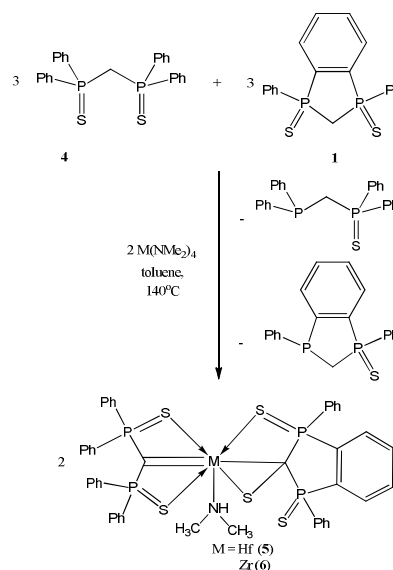
Figure 1. Molecular structure of 2 with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Hf1-C2 2.4282(18), Hf1-C1 2.4374(18), S3-C1 1.7657(18), S5-C2 1.7607(19), Hf1-S1 2.6764(5), Hf1-S2 2.7712(5), Hf1-S3 2.4919(4), Hf1-S4 2.7039(5), Hf1-S5 2.5020(5), Hf1-S6 2.7030(4), C1-P1 1.7386(18), C1-P2 1.7381(19), C2-P3 1.7420(19), C2-P4 1.7335(19), P1-S1 1.9947(7), P2-S2 1.9977(6), P3-S4 2.0017(6), P4-S6 1.9936(6), P1-C1-P2 115.26(10), P1-C1-Hf1 95.98(8), P2-C1-Hf1 95.44(8), C1-P1-S1 104.59(6), C1-P2-S2 107.05(6), P1-S1-Hf1 83.03(2), P2-S2-Hf1 80.09(2), C1-S3-Hf1 67.37(6), S3-C1-Hf1 70.67(6), S3-Hf1-C1 41.96(4).

Compounds 2 and 3 comprise tripodal bis(thiophosphinoyl)thioketone dianionic ligands {1,3-C₆H₄(PhPS)₂C(S)}²⁻ coordinating to the metal centres, which display a distorted dodecahedral geometry (2: Figure 1; 3: Figure S1, see the Supporting Information). Although similar ligands {EC(PPh₂E)₂}²⁻ (E = S, Se) were reported by Chivers et al.,¹² their group 4 metal derivatives were still unknown. The thiolate atoms [2: S(3/5); 3: S(1/4) atoms] are bridged between the methanide and metal atoms. The M-C bonds (2: average 2.433; 3: 2.439 Å) are comparable with the hafnium [HC(PPh₂NSiMe₃)₂HfCl₂(NH_p-tolyl)] (2.437(6) Å) and zirconium methanide complex [(PPh₂NSiMe₃)C{C(Ncy-hexyl)₂}ZrCl₂] (2.467(4) Å),⁹ respectively. They are significantly longer than the hafnium [(C₂PNSiMe₃)₂CHfCl₂] (2.162(6) Å) and zirconium carbene complexes [(Ph₂PNSiMe₃)₂CZrCl₂] (2.190(8) Å), respectively.^{5a,c} These indicate that the M-C bonds in 2 and 3 are single bonds. The M-S_{thiolate} bonds (2: average 2.497; 3: 2.519 Å) are comparable with those in [Cp*₂M(SPh)₂] (M = Hf:

2.502(1) Å; Zr: average 2.522 Å).¹³ The PS→M bonds (**2**: average 2.714; **3**: 2.741 Å) are comparable to the S→Zr dative bond in the zirconium dithiocarboxylate complex [Cp₂Zr(SiMe₃)(S₂CNEt₂)] (Zr-S: 2.713(1) Å).¹⁴ Moreover, comparing the bond lengths of the ligand skeletons in **2** and **3** [P-C: average 1.738 (**2**), 1.743 Å (**3**); P-S: average 1.997 (**2**), 1.997 Å (**3**); C-S: average 1.763 (**2**), 1.762 Å (**3**)] with those of the thioketone dianionic ligand [(tmeda)Li(SPPH₂)₂CS]₂ (P-C: average 1.757, P-S: average 2.001, C-S: 1.736(3) Å),¹⁵ it is suggested that there is an electron delocalization along the ligand backbones.

Synthesis of [(1,3-C₆H₄(PhPS)₂CS)(S))M(NHMe₂){C(PPh₂S)₂}] (M = Hf, Zr). The abovementioned results illustrate that the nature of a metal centre can affect the stability of a M=C bond supported by the {1,3-C₆H₄(PhPS)₂C}²⁻ ligand. We then further extended our study to investigate whether a C=M=C skeleton can be supported by both {1,3-C₆H₄(PhPS)₂C}²⁻ and {(Ph₂PS)₂C}²⁻ ligands. The latter is well-known for stabilizing a C_{methandiide}=M bond. The reaction of **1**, **4** and M(NMe₂)₄ in refluxing toluene gave a mixture of [(LC(S))M(NHMe₂){C(PPh₂S)₂}] [M = Hf (**5**), Zr (**6**)], [1,3-C₆H₄(PhPS)(PhP)CH₂], [CH₂(PPh₂S)(PPh₂)₂]¹⁹ and unidentified products (Scheme 2), which was confirmed by ³¹P NMR spectroscopy. The reaction mixtures were filtered and the filtrates were concentrated to afford **5** and **6** as air- and moisture-sensitive yellow crystalline solids, respectively. The NMR spectra of the mother liquors show the presence of [1,3-C₆H₄(PhPS)(PhP)CH₂], [CH₂(PPh₂S)(PPh₂)₂] and unidentified products. Although the mechanisms are unknown as yet, the reactions appear to proceed through the deprotonation of **1** and **4** with M(NMe₂)₄ to form NHMe₂ and [LC=M=C(PPh₂S)₂], which further undergo intermolecular sulphur-transfer reactions with another molecules of **1** and **4** to form [(LC(S))M(NHMe₂){C(PPh₂S)₂}] (**5**: M = Hf; **6**: M = Zr), [CH₂(PPh₂S)(PPh₂)₂] and [1,3-C₆H₄(PhPS)(PhP)CH₂]. Compounds **5** and **6** are first compounds comprising both tridentate dianionic thioketone ligand “1,3-C₆H₄(PhPS)₂CS²⁻” and geminal dianion “(Ph₂PS)₂C²⁻” bonded to the meter center. In addition, a NHMe₂ moiety is coordinated to the metal center in **5** and **6**. These results illustrate that the steric and electronic effects of ligand are crucial for the stabilization of metal bis(phosphonium)methandiide complexes.

Compounds **5** and **6** were isolated as air- and moisture-sensitive yellow crystalline solids which show poor solubility in any organic solvents, such as THF, DME, MeCN. The ¹H NMR spectra display resonances for the phenyl protons (**5**: δ 7.06 – 8.41; **6**: 7.07 – 8.45 ppm) and NHMe₂ [**5**: δ 4.68 (sept, ³J_{H-H} = 5.89 Hz); **6**: 4.99 ppm (sept, ³J_{H-H} = 5.95 Hz)]. The ³¹P NMR spectra of **5** and **6** display two doublets for “1,3-C₆H₄(PhPS)₂CS²⁻” (**5**: δ 42.3 and 46.7 ppm, ²J_{P-P} = 91.0 Hz; **6**: δ 43.58 and 47.22 ppm, ²J_{P-P} = 95.4 Hz), which are upfield shifted compared with those of **2** and **3**. In addition, their spectra show signals for “(Ph₂PS)₂C²⁻” (**5**: δ 23.9, 24.9; **6**: 25.6, 27.9 ppm), which are comparable with those of group 4 bis(phosphonium)-stabilized carbene complexes.^{5g}



Scheme 2. Synthesis of **5** and **6**

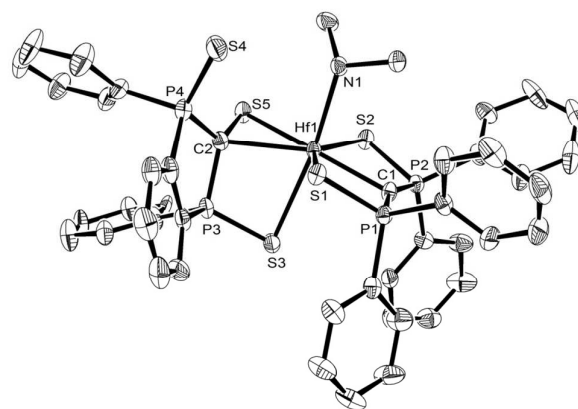


Figure 2. Molecular structure of **5** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Hf1-C1 2.218(5), Hf1-C2 2.407(5), Hf1-S1 2.6165(14), Hf1-S2 2.6024(14), Hf1-S3 2.6875(14), Hf1-S5 2.5149(13), Hf1-N1 2.341(4), P1-S1 2.0400(19), P2-S2 2.0440(19), P3-S3 1.994(2), P4-S4 1.955(2), C2-S5 1.783(5), C1-P1 1.680(5), C1-P2 1.657(5), C2-P3 1.764(5), C2-P4 1.757(6), C1-Hf1-C2 153.55(19), P2-C1-P1 156.0(3), P4-C2-P3 110.8(3), C2-S5-Hf1 65.55(16), P3-C2-S5 116.9(3), P4-C2-S5 126.8(4).

The molecular structures of **5** and **6** are shown in Figures 2 and S2, respectively. The dianionic thioketone ligands “1,3-C₆H₄(PhPS)₂CS²⁻” and geminal dianions “(Ph₂PS)₂C²⁻” are tridentate bonded to the metal centers. One of the thiophosphinoyl substituents in “1,3-C₆H₄(PhPS)₂CS²⁻” is uncoordinated. The C1-M bonds (**5**: 2.218(5); **6**: 2.2243(15) Å) are comparable with those in the zirconium (2.180(3) – 2.251(2) Å) and hafnium bis(phosphonium)-stabilized carbene complexes (2.162(6) Å), respectively.^{5c,g} Moreover, the P-C_{methandiide} bonds (**5**: average 1.669; **6**: 1.668 Å) are shorter than those in the parent ligand **4** (P-C: 1.820(3), 1.831(3) Å),⁴ⁱ which are due to the electrostatic interaction within the P⁺-C⁻-P⁺ skeletons resulting from the substantial negative charge on

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the C_{methanide} atoms. Furthermore, due to negative hyperconjugation effects, the elongation of the P-S (P1-S1, P2-S2) bonds (**5**: average 2.042; **6**: 2.039 Å) are also observed compared with those in **4**.⁴ⁱ Similar shortening of the P-C_{methanide} bonds and lengthening of the P-S bonds can be found in the group 4 metal bis(phosphonium)-stabilized carbene complexes.^{5g} The M-C_{methanide} and M-S_{thiolate} bonds (**5**: Hf1-C2: 2.407(5), Hf1-S5: 2.5149(13); **6**: Zr1-C26: 2.4126(15), Zr1-S5: 2.5275(4) Å), together with the bonding of the "1,3-C₆H₄(PhPS)₂CS²⁻" ligands in **5** and **6**, are comparable with those in **2** and **3**, respectively. The M-N bonds (**5**: 2.341(4); **6**: 2.3766(13) Å) are longer than the M-N_{amido} bonds in [(PPh₂S)(PPh₂NSiMe₃)CM(NMe₂)₂] (Hf-N_{amido}: 2.017(2), 2.031(2); Zr-N_{amido}: 2.038(2), 2.028(2) Å), which indicate that they are N→M dative bonds.²⁰

Synthesis of [(1,3-C₆H₄(PhPS)₂CS)₂Sn]. In order to illustrate the feasibility of intermolecular sulphur transfer at the C_{methanide} atom, [(μ-1,3-C₆H₄(PhPS)₂C)Sn]₂ (**7**) was reacted with two equivalents of elemental sulphur in CH₂Cl₂ at ambient temperature to give [(1,3-C₆H₄(PhPS)₂CS)₂Sn] (**8**, Scheme 3). The reaction proceeds through the nucleophilic attack of the C_{methanide} atoms in **7** to the sulphur atoms, followed by the elimination of elemental tin to form **8**. It was isolated as a dark red crystalline solid. It is only slightly soluble in MeCN. The ¹³C and ¹¹⁹Sn NMR spectra could not be obtained owing to very poor solubility in any NMR solvents. Its ³¹P NMR spectrum shows a singlet at δ 54.1 ppm.

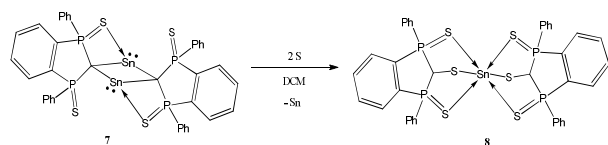
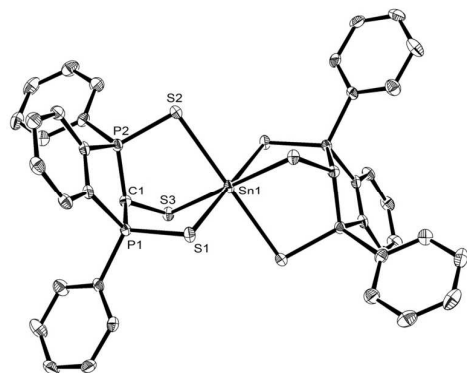
Scheme 3. Synthesis of **8**

Figure 3. Molecular structure of **8** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn1-S1 2.7045(6), Sn1-S2 2.7390(6), Sn1-S3 2.4818(6), C1-P1 1.749(2), C1-P2 1.755(2), P1-S1 2.0146(9), P2-S2 2.0183(9), S3-Sn1-S3A 180.0, C1-S3-Sn1 95.15(8), P1-C1-P2 106.08(12), P1-C1-S3 115.51(13), P2-C1-S3 117.03(13).

The molecular structure of **8** shows that the dianionic thioether ligand is tridentate coordinated to the Sn atom, which adopts an octahedral geometry. The Sn1-S3 bond

(2.4818(6) Å) is slightly longer than that in [Sn(SPh)₄] (2.379(4), 2.401(4) Å)¹⁶ and [(Tbt)(Mes)Sn(μ-S)]₂ (Tbt = 2,4,6-{CH(SiMe₃)₂}₃C₆H₂, 2.434(3), 2.432(3) Å),¹⁷ but it is shorter than the dative Sn1-S1 (2.7045(6) Å) and Sn1-S2 bonds (2.7390(6) Å). This indicates that the Sn1-S3 bond is a single bond. In addition, the C1-S3 bond (1.742(2) Å) is comparable with that in **2** and **3**. Moreover, the C1 atom adopts a trigonal pyramidal geometry and the Sn1...C1 distance (3.158(2) Å) is longer than the Sn-C_{methanide} bond in [SnCH(PPh₂S)(PPh₂NSiMe₃)] (2.384(4) Å).¹⁸ These indicate that the negative charge is presented at the C1 atom. It is stabilized by the delocalization along the ligand backbone, which is indicated by the shortening of the C-P bonds (1.749(2), 1.755(2) Å) and the lengthening of the P-S bonds (2.0146(9), 2.0183(9) Å) compared with **1**.⁴ⁱ

Conclusions

The formation of **2** and **3** shows that the metal centres and ligand substituents can affect the stability of a M=C_{methanide} double bond supported by the {1,3-C₆H₄(PhPS)₂C}²⁻ ligand, which leads to intermolecular sulfur transfer reaction. In addition, the formation of **5** and **6** demonstrates that the M=C_{methanide} double bond supported by the {1,3-C₆H₄(PhPS)₂C}²⁻ ligand is more prone to accept sulphur atom than that by the {(Ph₂PS)₂C}²⁻ ligand. The intermolecular sulfur transfer reaction is evidenced by the reaction of **7** with two equivalents of elemental sulphur to form **8**.

Experimental

General procedure. All manipulations were carried out under an inert atmosphere of argon gas by standard Schlenk techniques. MeCN and CH₂Cl₂ were dried and distilled over CaH₂ prior to use. Toluene was dried and distilled over Na/K alloy prior to use. **1** and **7** were prepared as described in the literatures.⁴ⁱ The ¹H, ¹³C, ³¹P NMR spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts δ are relative to external references SiMe₄ for ¹H and ¹³C and 85% H₃PO₄ for ³¹P. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

[(1,3-C₆H₄(PhPS)₂C(S))₂Hf] (**2**). Toluene (20 mL) was added to a mixture of Hf(NMe₂)₄ (0.36 g, 1.0 mmol) and **1** (1.48 g, 4.0 mmol) at ambient temperature. The resulting yellow solution was heated at 110 °C in a sealed flask overnight. After filtration and concentration of the filtrate (approx. 8 mL), **2** was afforded as yellow crystals. Yield: 0.30 g (30.7 %). Mp: 275 °C (dec.). Anal. Calcd for C₃₈H₂₈P₄S₂Hf: C 46.63; H 2.88. Found: C 46.58; H 2.87. ¹H NMR (395.9 MHz, MeCN/C₆D₆, 24.0 °C): δ 6.62 – 7.68 ppm (m, 28H, Ph). The ¹³C NMR spectrum could not be obtained owing to poor solubility in any NMR solvents. In

addition, the ^{31}P NMR spectroscopy was performed overnight. $^{31}\text{P}\{^1\text{H}\}$ NMR (160.3 MHz, MeCN/ C_6D_6 , 24.6 °C): δ 54.61 ppm.

$[\{1,3\text{-C}_6\text{H}_4(\text{PhPS})_2\text{C}(\text{S})\}_2\text{Zr}]$ (**3**). Toluene (20 mL) was added to a mixture of $\text{Zr}(\text{NMe}_2)_4$ (0.27 g, 1.0 mmol) and **1** (1.48 g, 4.0 mmol) at ambient temperature. The resulting orange solution was heated at 110 °C in a sealed flask overnight. After filtration and concentration of the filtrate (approx. 8 mL), **3** was afforded as yellow crystals. Yield: 0.38 g (42.6 %). Mp: 238 °C (dec.). Anal. Calcd for $\text{C}_{38}\text{H}_{28}\text{P}_4\text{S}_6\text{Zr}$: C 51.19; H 3.16. Found: C 51.02; H 3.06. ^1H NMR (395.9 MHz, MeCN/ C_6D_6 , 25.9 °C): δ 6.63 - 7.55 ppm (m, 28H, Ph). The ^{13}C NMR spectrum could not be obtained owing to poor solubility in any NMR solvents. In addition, the ^{31}P NMR spectroscopy was performed overnight. $^{31}\text{P}\{^1\text{H}\}$ NMR (160.3 MHz, MeCN/ C_6D_6 , 24.6 °C): δ 55.15 ppm.

$[\{1,3\text{-C}_6\text{H}_4(\text{PhPS})_2\text{C}(\text{S})\}\text{Hf}(\text{NHMe}_2)\{\text{C}(\text{PPh}_2\text{S})_2\}]$ (**5**). Toluene (20 mL) was added to a mixture of $\text{Hf}(\text{NMe}_2)_4$ (0.36 g, 1.0 mmol), **1** (0.56 g, 1.5 mmol) and **4** (0.68 g, 1.5 mmol) at ambient temperature. The resulting yellow solution was heated at 140 °C in a sealed flask overnight. After filtration and concentration of the filtrate (approx. 8 mL), **5** was afforded as yellow crystals. Yield: 0.44 g (41.2 %). Mp: 276 °C (dec.). Anal. Calcd for $\text{C}_{46}\text{H}_{41}\text{HfNP}_4\text{S}_5$: C 51.63; H 3.86; N 1.31. Found: C 51.33; H 3.52; N 1.27. ^1H NMR (395.9 MHz, CDCl_3 , 22.7 °C): δ 2.42 (d, 3H, $^2J_{\text{H-H}}=6.34$ Hz, $\text{NH}(\text{CH}_3)_2$), 2.83 (d, 3H, $^2J_{\text{H-H}}=6.34$ Hz, $\text{NH}(\text{CH}_3)_2$), 4.68 (sept, 1H, $^3J_{\text{H-H}}=5.89$ Hz, $\text{NH}(\text{CH}_3)_2$), 7.06 - 8.41 ppm (m, 34H, Ph). The ^{13}C NMR spectra could not be obtained owing to poor solubility in any NMR solvents. In addition, the ^{31}P spectroscopy was performed overnight. $^{31}\text{P}\{^1\text{H}\}$ NMR (161.7 MHz, CDCl_3 , 24.2 °C): δ 23.91 (s), 24.93 (s), 42.32 (d, $^1J_{\text{P-C}}=91.03$ Hz), 46.70 ppm (d, $^1J_{\text{P-C}}=91.03$ Hz).

$[\{1,3\text{-C}_6\text{H}_4(\text{PhPS})_2\text{C}(\text{S})\}\text{Zr}(\text{NHMe}_2)\{\text{C}(\text{PPh}_2\text{S})_2\}]$ (**6**). Toluene (20 mL) was added to a mixture of $\text{Zr}(\text{NMe}_2)_4$ (0.27 g, 1.0 mmol) and **1** (0.56 g, 1.5 mmol) and **4** (0.68 g, 1.5 mmol) at ambient temperature. The resulting orange solution was heated at 140 °C in a sealed flask overnight. After filtration and concentration of the filtrate (approx. 8 mL), **6** was afforded as yellow crystals. Yield: 0.36 g (36.7 %). Mp: 256 °C (dec.). Anal. Calcd for $\text{C}_{46}\text{H}_{41}\text{NP}_4\text{S}_5\text{Zr}$: C 56.22; H 4.21; N 1.42. Found: C 56.01; H 3.84; N 1.25. ^1H NMR (395.9 MHz, $\text{C}_6\text{D}_6/\text{MeCN}$, 22.7 °C): δ 2.29 (d, 3H, $^2J_{\text{H-H}}=5.95$ Hz, $\text{NH}(\text{CH}_3)_2$), 2.58 (d, 3H, $^2J_{\text{H-H}}=5.95$ Hz, $\text{NH}(\text{CH}_3)_2$), 4.99 (sept, 1H, $^3J_{\text{H-H}}=5.95$ Hz, $\text{NH}(\text{CH}_3)_2$), 7.07 - 8.45 ppm (m, 34H, Ph). The ^{13}C NMR spectrum could not be obtained owing to poor solubility in any NMR solvents. In addition, the ^{31}P spectroscopy was performed overnight. $^{31}\text{P}\{^1\text{H}\}$ NMR (161.7 MHz, $\text{C}_6\text{D}_6/\text{MeCN}$, 24.2 °C): δ 25.62 (d, $^2J_{\text{P-P}}=8.67$ Hz), 27.87 (d, $^2J_{\text{P-P}}=8.67$ Hz), 43.58 (d, $^2J_{\text{P-P}}=95.4$ Hz), 47.22 ppm (d, $^2J_{\text{P-P}}=95.4$ Hz).

$[\{1,3\text{-C}_6\text{H}_4(\text{PhPS})_2\text{CS}\}_2\text{Sn}]$ (**8**). S_8 (0.31g, 1.2 mmol) was added to a suspension of **7** (0.58 g, 0.6 mmol) in CH_2Cl_2 (20 mL) at room temperature. The resulting mixture was stirred overnight and black precipitate was observed. After filtration and concentration of the filtrate (approx. 5 mL), **8** was afforded as dark red crystals. Yield: 0.23 g (41.7 %). Mp: 267 °C (dec.).

Anal. Calcd for $\text{C}_{38}\text{H}_{28}\text{P}_4\text{S}_6\text{Sn}$: C 49.66; H 3.07. Found: C 49.42; H 2.93. ^1H NMR (395.9 MHz, $\text{C}_6\text{D}_6/\text{MeCN}$, 22.7 °C): δ 6.94 - 6.97 (m, 2H, Ph), 7.04 - 7.07 (m, 5H, Ph), 7.23 - 7.29 (m, 5H, Ph), 7.36 - 7.43 (m, 8H, Ph), 7.54 - 7.56 (m, 4H, Ph), 7.67 - 7.72 ppm (m, 4H, Ph). The ^{13}C NMR spectrum could not be obtained owing to poor solubility in any NMR solvents. In addition, the ^{31}P spectroscopy was performed overnight. $^{31}\text{P}\{^1\text{H}\}$ NMR (161.7 MHz, $\text{C}_6\text{D}_6/\text{MeCN}$, 24.2 °C): δ 54.11 ppm.

X-ray data collection and structural refinement: Intensity data for compounds **2**, **3**, **5**, **6** and **8** were collected by using a Bruker APEX II diffractometer. Reflections were measured at 103(2) K. The structures were solved by direct-phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on F^2 .²¹ All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculation. CCDC-1056394 (**2**), CCDC-1056395 (**3**), CCDC-1056396 (**5**), CCDC-1056397 (**6**), CCDC-1056398 (**8**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif

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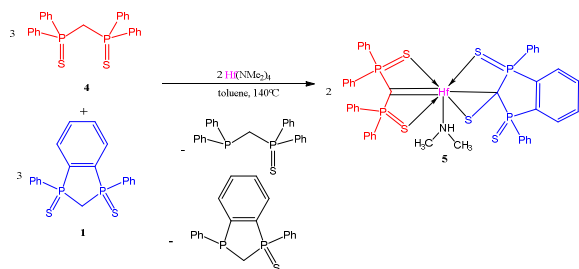
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Instability of Metal 1,3-Benzodi(thiophosphinoyl)methandiide Complexes: Formation of Hafnium, Tin and Zirconium Complexes of 1,3-Benzodi(thiophosphinoyl)thioketone Dianionic Ligand [1,3-C₆H₄(PhPS)₂C(S)²⁻]

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Graphical Abstract for the content page:



The reaction illustrates that the metal centre and ligand substituents are crucial for the stabilization of a C_{methandiide}=Hf bond.