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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}2Sn] (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 $[C(PPh_2E)_2]^{2-}$ (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] lanthanide[6] and actinide[7] carbene complexes $[L_nM=C(PPh_2E)_2]$ (L = ligand).[8] They can be easily prepared by the simple salt elimination of geminal dianions $[C(PPh_2E)_2]^{2-}$ with metal halides or by the double deprotonation of the parent ligand $[CH_2(PPh_2E)_2]$ 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

$[M(Cl_2)\{C(PPh_2NSiMe_3)_2\}]$ (M = Ti, Hf, Zr) by the reaction of $[Li_2C(PPh_2NSiMe_3)_2]$ with MCl_4.[5a,c] Their reactivity were also been reported.[9] Similar compounds, $[Zr(Cp)_2\{C(PPh_2S)_2\}]$, $[Zr(Cl)_2(THF)\{C(PPh_2S)_2\}]_2$ and $[Zr(Cl)_2(py)\{C(PPh_2S)_2\}]$,[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 $[L_nM=C(PPh_2E)_2]$ 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 $C(PPh_2S)_2^{2-}$ was replaced by the trimethylsilyl substituent, the negative charge at the $C_{methandiide}$ atom in the palladium carbene intermediate $[(PPh_3)_2Pd\{C(PPh_2S)(SiMe_3)\}]$ 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 $[(PPh_3)_2Pd\{SC(PPh_2)(SiMe_3)\}]$.[10] Furthermore, when the trimethylsilyl substituent in $C(PPh_2S)(SiMe_3)^{2-}$ was replaced by a triphenylsilyl substituent, a mixture of $[(PPh_3)_2Pd\{C(PPh_2S)(SiPh_3)\}]$ and $[(PPh_3)_2Pd\{SC(PPh_2)(SiPh_3)\}]$ 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 $Li_2[C(PPh_2S)(SiMe_3)]$ is stable and the negative

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charges at the $C_{methandiide}$ atom can be sufficiently stabilized by both $SiMe_3$ and PPh_2S 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 $[U\{C(PPh_2S)_2\}_2(THF)_2]$ decomposes upon heating in pyridine (py) to form $[U\{C(PPh_2S)_2\}\{SC(PPh_2S)_2\}(py)]$ 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 $[\{\mu-1,3-C_6H_4(PhPS)_2C\}Sn]_2$ by the double deprotonation of $[1,3-C_6H_4(PhPS)_2CH_2]$ with $Sn\{N(SiMe_3)_2\}_2$.[4i] Its reactivity illustrated that the $C_{methandiide}$ atom bearing a negative charge can react with various Lewis acids such as $AlCl_3$ and $GaCl_3$.[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 $[1,3-C_6H_4(PhPS)_2CH_2]$ to react with group 4 metals. In this paper, we report that the M=$C_{methandiide}$ double bonds (M = Hf, Zr) supported by $1,3-C_6H_4(PhPS)_2C^{2-}$ are unstable, which lead to intermolecular sulphur transfer. The mechanism is in contrast to the intramolecular sulphur transfer reaction using the $\{(PPh_2S)(SiMe_3)C\}^{2-}$ ligand, which is proposed by Gessner and her co-workers.[10]

Results and Discussion

Synthesis of $[1,3-C_6H_4(PhPS)_2C(S)]_2M$ (M = Hf, Zr). The reaction of $[LCH_2]$ [**1**, L = $1,3-C_6H_4(PhPS)_2$] and $M(NMe_2)_4$ (M = Hf, Zr) in toluene cannot occur at room temperature. In contrast, when the temperature was warmed to 110 ^{o}C, a mixture of group 4 metal complexes $[\{LC(S)\}_2M]$ [M = Hf (**2**), Zr (**3**), Scheme 1] and $[1,3-C_6H_4(PhPS)(PhP)CH_2]^{4j}$ was afforded, which was confirmed by ^{31}P and ^{1}H 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 $^{31}P\{^1H\}$ NMR [doublet, δ -6.86, 64.62 ppm ($J_{P-P'}$ = 26.5 Hz)] and ^{1}H NMR spectra [doublet of doublets, δ 3.05 ppm ($^2J_{P-H}$ = 13.4, $^2J_{P'-H}$ = 19.5 Hz)] show the presence of $[1,3-C_6H_4(PhPS)(PhP)CH_2]$ 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 [LCH_2] to form **2** and **3**, respectively and the byproducts are $[1,3-C_6H_4(PhPS)(PhP)CH_2]$. Such intermolecular sulphur transfer reaction was also observed in the reaction of the tin(II) 1,3-benzodi(thiophosphinoyl)methandiide $[\{\mu-1,3-C_6H_4(PhPS)_2C\}Sn]_2$ with $ZnEt_2$ to afford a mixture of $[\{\{1,3-C_6H_4(PhPS)_2CSnEt_2\}(\mu-ZnS)]_2$, $SnEt_4$ and $[1,3-C_6H_4(PhPS)(PhP)CH_2]$.[4j]
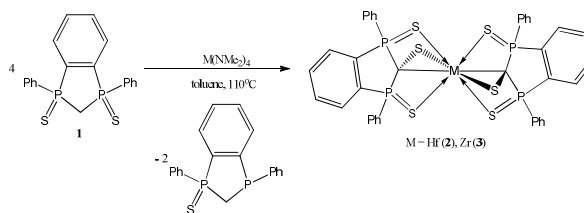
Scheme 1. Synthesis of **2** and **3**

Compounds **2** and **3** are highly insoluble in THF and $CHCl_3$ and slightly soluble in MeCN only. The ^{13}C NMR spectra could not be obtained owing to very poor solubility in any NMR solvents. The ^{1}H NMR spectra display resonances for the phenyl protons. The $^{31}P\{^1H\}$ 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]
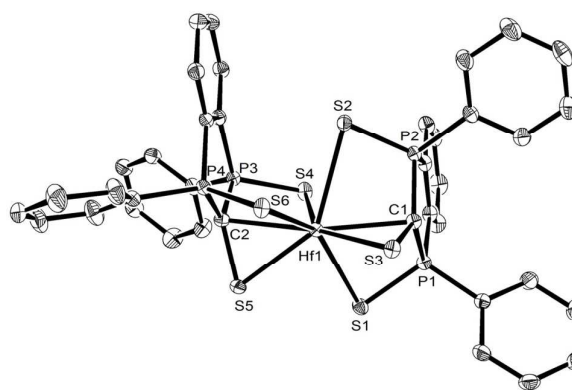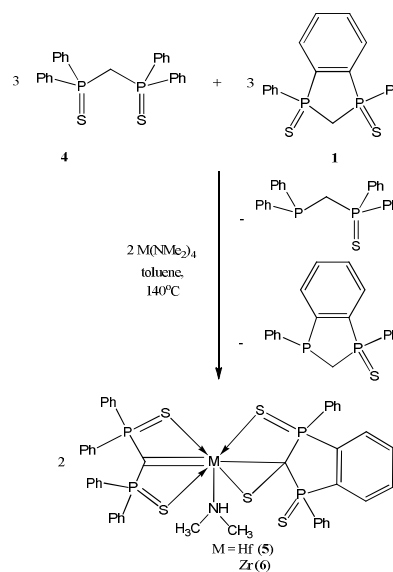

Figure 1. Molecular structure of **2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Hf1-C2 2.4282(18), Hf1-C1 2.4374(18), S3-C1 1.7657(18), S5-C2 1.7607(19), Hf1-S1 2.6764(5), Hf1-S2 2.7712(5), Hf1-S3 2.4919(4), 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 $\{1,3-C_6H_4(PhPS)_2CS\}^{2-}$ coordinating to the metal centres, which display a distorted dodecahedral geometry (**2**: Figure 1; **3**: Figure S1, see the Supporting Information). Although similar ligands $\{EC(PPh_2E)_2\}^{2-}$ (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 $[HC(PPh_2NSiMe_3)_2HfCl_2(NHp-tolyl)]$ (2.437(6) Å) and zirconium methanide complex $[(PPh_2NSiMe_3)C\{C(Ncy-hexyl)_2\}ZrCl_2]$ (2.467(4) Å),[9] respectively. They are significantly longer than the hafnium $[(Cy_2PNSiMe_3)_2CHfCl_2]$ (2.162(6) Å) and zirconium carbene complexes $[(Ph_2PNSiMe_3)_2CZrCl_2]$ (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 [Cp$_2$Zr(SiMe$_3$)(S$_2$CNEt$_2$)] (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(SPPh$_2$)$_2$CS]$_2$ (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-C$_6$H$_4$(PhPS)$_2$C(S)}M(NHMe$_2$){C(PPh$_2$S)$_2$}] (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-C$_6$H$_4$(PhPS)$_2$C}$^{2-}$ ligand. We then further extended our study to investigate whether a C=M=C skeleton can be supported by both {1,3-C$_6$H$_4$(PhPS)$_2$C}$^{2-}$ and {(Ph$_2$PS)$_2$C}$^{2-}$ ligands. The latter is well-known for stabilizing a C$_{methandiide}$=M bond. The reaction of **1**, **4** and M(NMe$_2$)$_4$ in refluxing toluene gave a mixture of [{LC(S)}M(NHMe$_2$){C(PPh$_2$S)$_2$}] [M = Hf (**5**), Zr (**6**)], [1,3-C$_6$H$_4$(PhPS)(PhP)CH$_2$], [CH$_2$(PPh$_2$S)(PPh$_2$)][19] and unidentified products (Scheme 2), which was confirmed by ^{31}P 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-C$_6$H$_4$(PhPS)(PhP)CH$_2$], [CH$_2$(PPh$_2$S)(PPh$_2$)] and unidentified products. Although the mechanisms are unknown as yet, the reactions appear to proceed through the deprotonation of **1** and **4** with M(NMe$_2$)$_4$ to form NHMe$_2$ and [LC=M=C(PPh$_2$S)$_2$], which further undergo intermolecular sulphur-transfer reactions with another molecules of **1** and **4** to form [{LC(S)}M(NHMe$_2$){C(PPh$_2$S)$_2$}] (**5**: M = Hf; **6**: M = Zr), [CH$_2$(PPh$_2$S)(PPh$_2$)] and [1,3-C$_6$H$_4$(PhPS)(PhP)CH$_2$]. Compounds **5** and **6** are first compounds comprising both tridentate dianionic thioketone ligand "1,3-C$_6$H$_4$(PhPS)$_2$CS^{2-} " and geminal dianion "(Ph$_2$PS)$_2$C^{2-}" bonded to the meter center. In addition, a NHMe$_2$ 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 ^{1}H NMR spectra display resonances for the phenyl protons (**5**: δ 7.06 - 8.41; **6**: 7.07 - 8.45 ppm) and NHMe$_2$ [**5**: δ 4.68 (sept, $^3J_{H-H}$ = 5.89 Hz); **6**: 4.99 ppm (sept, $^3J_{H-H}$ = 5.95 Hz)]. The ^{31}P NMR spectra of **5** and **6** display two doublets for "1,3-C$_6$H$_4$(PhPS)$_2$CS^{2-}" (**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 "(Ph$_2$PS)$_2$C^{2-}" (**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**
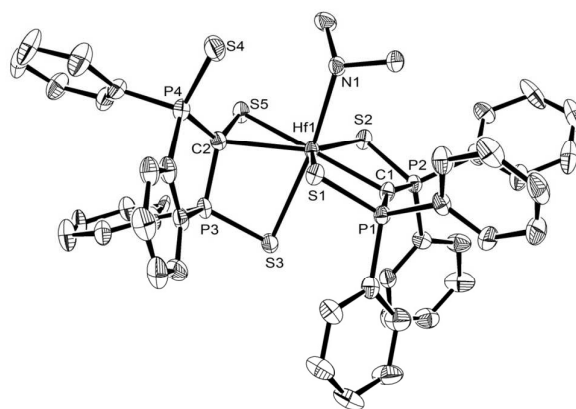
Figure 2. Molecular structure of **5** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Hf1-C1 2.218(5), Hf1-C2 2.407(5), Hf1-S1 2.6165(14), Hf1-S2 2.6024(14), Hf1-S3 2.6875(14), Hf1-S5 2.5149(13), 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-C$_6$H$_4$(PhPS)$_2$CS^{2-}" and geminal dianions "(Ph$_2$PS)$_2$C^{2-}" are tridentate bonded to the metal centers. One of the thiophosphinoyl substituents in "1,3-C$_6$H$_4$(PhPS)$_2$CS^{2-} " 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

the C$_{methandiide}$ 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$_{methandiide}$ 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-C$_6$H$_4$(PhPS)$_2$CS^{2-}" 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 [(PPh$_2$S)(PPh$_2$NSiMe$_3$)CM(NMe$_2$)$_2$] (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-C$_6$H$_4$(PhPS)$_2$CS}$_2$Sn]. In order to illustrate the feasibility of intermolecular sulphur transfer at the C$_{methandiide}$ atom, [{μ-1,3-C$_6$H$_4$(PhPS)$_2$C}Sn]$_2$ (**7**) was reacted with two equivalents of elemental sulphur in CH$_2$Cl$_2$ at ambient temperature to give [{1,3-C$_6$H$_4$(PhPS)$_2$CS}$_2$Sn] (**8**, Scheme 3). The reaction proceeds through the nucleophilic attack of the C$_{methandiide}$ 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 ^{13}C and ^{119}Sn NMR spectra could not be obtained owing to very poor solubility in any NMR solvents. Its ^{31}P NMR spectrum shows a singlet at δ 54.1 ppm.
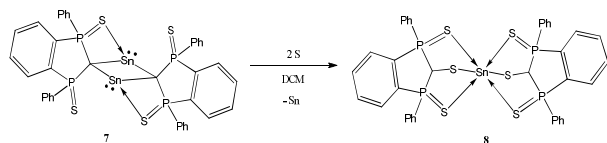

Scheme 3. Synthesis of **8**
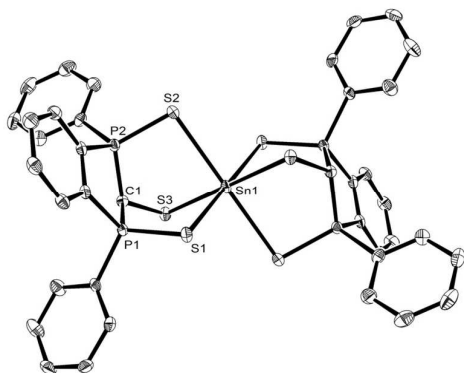
Figure 3. Molecular structure of **8** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn1-S1 2.7045(6), Sn1-S2 2.7390(6), Sn1-S3 2.4818(6), C1-P1 1.749(2), C1-P2 1.755(2), P1-S1 2.0146(9), 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 thioketone 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(SiMe$_3$)$_2$}$_3$C$_6$H$_2$, 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(PPh$_2$S)(PPh$_2$NSiMe$_3$)] (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$_{methandiide}$ double bond supported by the {1,3-C$_6$H$_4$(PhPS)$_2$C}$^{2-}$ ligand, which leads to intermolecular sulfur transfer reaction. In addition, the formation of **5** and **6** demonstrates that the M=C$_{methandiide}$ double bond supported by the {1,3-C$_6$H$_4$(PhPS)$_2$C}$^{2-}$ ligand is more prone to accept sulphur atom than that by the {(Ph$_2$PS)$_2$C}$^{2-}$ 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 CH$_2$Cl$_2$ were dried and distilled over CaH$_2$ 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 ^{1}H, ^{13}C, ^{31}P NMR spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts δ are relative to external references SiMe$_4$ for ^{1}H and ^{13}C and 85% H$_3$PO$_4$ for [31]P. 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-C$_6$H$_4$(PhPS)$_2$C(S)}$_2$Hf] (2). Toluene (20 mL) was added to a mixture of Hf(NMe$_2$)$_4$ (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 C$_{38}$H$_{28}$P$_4$S$_6$Hf: C 46.63; H 2.88. Found: C 46.58; H 2.87. ^{1}H NMR (395.9 MHz, MeCN/C$_6$D$_6$, 24.0 °C): δ 6.62 - 7.68 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}P{^{1}H} NMR (160.3 MHz, MeCN/C$_6$D$_6$, 24.6 °C): δ 54.61 ppm.

[{1,3-C$_6$H$_4$(PhPS)$_2$C(S)}$_2$Zr] (**3**). Toluene (20 mL) was added to a mixture of Zr(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 C$_{38}$H$_{28}$P$_4$S$_6$Zr: C 51.19; H 3.16. Found: C 51.02; H 3.06. ^{1}H NMR (395.9 MHz, MeCN/C$_6$D$_6$, 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}P{^{1}H} NMR (160.3 MHz, MeCN/C$_6$D$_6$, 24.6 °C): δ 55.15 ppm.

[{1,3-C$_6$H$_4$(PhPS)$_2$C(S)}Hf(NHMe$_2$){C(PPh$_2$S)$_2$}] (**5**). Toluene (20 mL) was added to a mixture of Hf(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 C$_{46}$H$_{41}$HfNP$_4$S$_5$: C 51.63; H 3.86; N 1.31. Found: C 51.33; H 3.52; N 1.27. ^{1}H NMR (395.9 MHz, CDCl$_3$, 22.7 °C): δ 2.42 (d, 3H, $^2J_{H\text{-}H}$=6.34 Hz, NH(CH_3)$_2$), 2.83 (d, 3H, $^2J_{H\text{-}H}$=6.34 Hz, NH(CH_3)$_2$), 4.68 (sept, 1H, $^3J_{H\text{-}H}$=5.89 Hz, NH(CH$_3$)$_2$), 7.06 - 8.41ppm (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}P{^{1}H} NMR (161.7 MHz, CDCl$_3$, 24.2 °C): δ 23.91 (s), 24.93 (s), 42.32 (d, $^1J_{P\text{-}C}$= 91.03 Hz), 46.70 ppm (d, $^1J_{P\text{-}C}$= 91.03 Hz).

[{1,3-C$_6$H$_4$(PhPS)$_2$C(S)}Zr(NHMe$_2$){C(PPh$_2$S)$_2$}] (**6**). Toluene (20 mL) was added to a mixture of Zr(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 C$_{46}$H$_{41}$NP$_4$S$_5$Zr: C 56.22; H 4.21; N 1.42. Found: C 56.01; H 3.84; N 1.25. ^{1}H NMR (395.9 MHz, C$_6$D$_6$/MeCN, 22.7 °C): δ 2.29 (d, 3H, $^2J_{H\text{-}H}$=5.95 Hz, NH(CH_3)$_2$), 2.58 (d, 3H, $^2J_{H\text{-}H}$=5.95 Hz, NH(CH_3)$_2$), 4.99 (sept, 1H, $^3J_{H\text{-}H}$=5.95 Hz, NH(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}P{^{1}H} NMR (161.7 MHz, C$_6$D$_6$/MeCN, 24.2 °C): δ 25.62 (d, $^2J_{P'\text{-}P}$ = 8.67 Hz), 27.87 (d, $^2J_{P'\text{-}P}$ = 8.67 Hz), 43.58 (d, $^2J_{P'\text{-}P}$ = 95.4 Hz), 47.22 ppm (d, $^2J_{P'\text{-}P}$ = 95.4 Hz).

[{1,3-C$_6$H$_4$(PhPS)$_2$CS}$_2$Sn] (**8**). S$_8$ (0.31g, 1.2 mmol) was added to a suspension of **7** (0.58 g, 0.6 mmol) in CH$_2$Cl$_2$ (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 C$_{38}$H$_{28}$P$_4$S$_6$Sn: C 49.66; H 3.07. Found: C 49.42; H 2.93. ^{1}H NMR (395.9 MHz, C$_6$D$_6$/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}P{^{1}H} NMR (161.7 MHz, C$_6$D$_6$/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 isotopic 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

Acknowledgements

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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-C$_6$H$_4$(PhPS)$_2$C(S)$^{2-}$]

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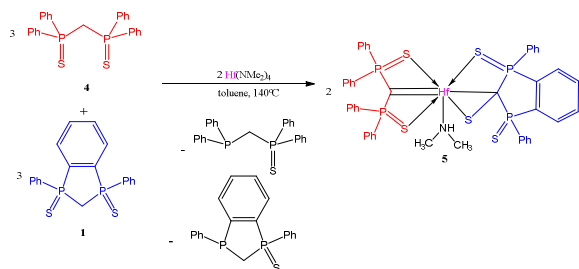
The reaction illustrates that the metal centre and ligand substituents are crucial for the stabilization of a C$_{\text{methandiide}}$=Hf bond.