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# Phosphine/sulfoxide-carbone, a ligand with a flexible bonding mode for early to late transition metals†

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In recent years, carbones have emerged as a new exciting class of carbon-based ligands. We report here a series of organometallic complexes demonstrating the versatility in coordination mode of phosphine/sulfoxide carbone **1**. Indeed, **1** is able to chelate both early and late transition metals, in a mono- or bidentate fashion depending on the oxyphilic character of metal center thanks to the presence of the sulfoxide moiety. All complexes have been fully characterized by X-ray diffraction analysis and by NMR spectroscopy (except hafnium complex because of its extreme insolubility). It is noteworthy that silver(I) and zirconium(IV) complexes are efficient transmetalating reagents toward copper(I) complexes.

## Introduction

The discovery of the first stable carbenes more than 30 years ago[1] shed light on divalent carbon chemistry.[2] Since then, carbon-based ligands have undergone considerable development to the point of becoming essential tools in homogeneous transition metal catalysis.[3] Carbenes naturally occupy a prominent place, but bis-ylides, also named "carbones", have recently been attracting a great attention of many research groups.[4] Indeed, these species **I** initially described by Ramirez in 1961,[5] present a peculiar electronic environment with a divalent carbon atom bearing two lone pairs (Fig. 1).[6] The central carbon being extremely electron-rich, they can be used as NHCs alternative as ligand, their electron-donating ability was even shown to be superior.[7] Thanks to the presence of the two lone pairs on the central carbon atom, they are excellent ligands for the synthesis of a wide range of transition metal complexes. It has been shown that carbones **I–IV** (Fig. 1) can act as either two- or four-electron-donors[8,9] and give access to homo- and hetero-bimetallic complexes.[10,11] Nevertheless, their use in catalysis remains scarce when compared to NHCs[12] probably due to the different electronic situation of central carbon atom. Indeed, NHCs are known to bind tightly to metal centers thanks to a strong C–metal bond with some π-back donation from the metal to the vacant orbital of carbon center.[13] In the case of carbones, without an empty orbital available at the carbon center, the stabilization effect of π-back donation is not possible. Thus, we have shown that a carbone ligand **V**,[14] featuring aminophosphine and sulfide moieties, despite a strong nucleophilic character could not lead to stable organometallic complexes. In contrast, the introduction of a sulfoxide moiety instead of sulfide dramatically alters the coordination behavior and with carbone **1** several stable organometallic complexes have been prepared.[15] Indeed, the presence of sulfoxide function allows a better stabilization of one of the two lone pairs at the carbon center as indicated by a shorten C–S bond length.[15a] Therefore, as a part of our studies
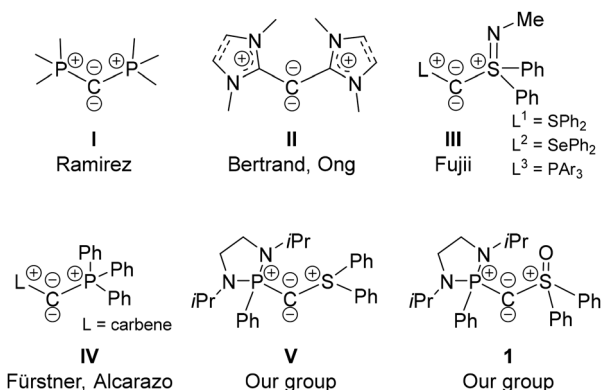
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†Electronic supplementary information (ESI) available. CCDC 2366566–2366571. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d4dt03372h



Fig. 1 Selected examples of carbones.

on low valent species,[16] we have decided to evaluate in depth the ligand efficiency of phosphine/sulfoxide carbone **1** towards various metallic centers.

## Results and discussion

We have initiated our study with group 11 metals taking into account preliminary results obtained with gold(I) precursors. Indeed, we have previously established than **1** could act as a four electrons donor ligand towards gold and *gem*-aurated dinuclear complex **VI** was selectively formed by reaction of **1** with 2 equivalents of [AuCl(SMe₂)] (Scheme 1, left).[15a] The use of 0.5 equivalent of metal precursor with respect to the ligand allowed the selective formation of the cationic bis-ligated Au(I) complex **2**, which was isolated as a white powder in 80% yield (Scheme 1, right).[17] In the ³¹P NMR spectrum, **2** displays a singlet signal at $\delta$ = 42.3 ppm, while the central carbon atom appears as a doublet at $\delta$ = 40.7 ppm ($^1J_{CP}$ = 80.3 Hz) in the ¹³C NMR spectrum.

Single crystals of **2** were grown from a saturated dichloromethane/diethyl ether solution at 4 °C and the structure has been established by X-ray diffraction analysis (80% yield, Fig. 2). Complex **2** adopts a nearly linear geometry with a C1–Au1–C28 angle of 177.4°. Both C1 and C28 are in a quasi-planar planar environment ($\sum° $ = 357.5° and 355.7° respectively), the P–C and S–C bond lengths are longer than those in **1** but shorter than those in **VI**, indicating that only one lone pair is involved in the Au–C bond whereas the second one is delocalized towards phosphorus and sulfur atoms (Table 1). The Au1–C1 and Au1–C28 bond lengths of 2.043(2) and 2.051(2) Å are in the range of the previously observed values for carbone–Au complexes (2.01–2.08 Å)[7d,10a,b,12a] and slightly longer than those observed in the case of NHC ligated cationic gold(I) complexes (1.95–2.02 Å).[18]

Using the same methodology **1** reacts with 0.5 equivalent of [AgOTf] leading to the cationic silver(I) complex **3** in 90% yield (Scheme 2).

In the ³¹P NMR spectrum, complex **3** shows a characteristic doublet signal at $\delta$ = 41.4 ppm ($^2J_{AgP}$ = 5.9 Hz), which confirms unambiguously the coordination of the ligand to the silver atom. Moreover, in the ¹³C NMR spectrum, the central carbon atom appears as two sets of doublets of doublets at $\delta$ =
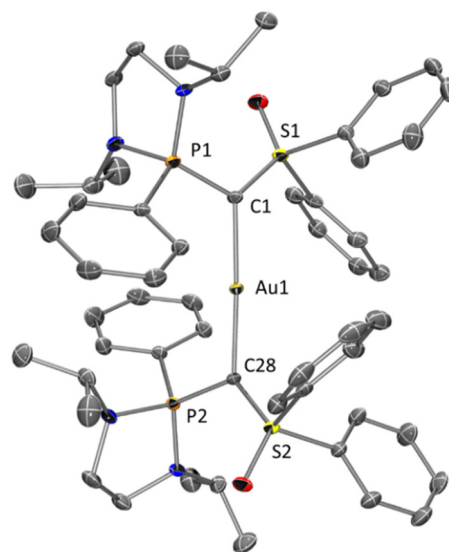


**Fig. 2** Molecular structure of **2**. Thermal ellipsoids represent 30% probability. H, disordered atoms, solvent molecule (dichloromethane) and counter ion (Cl⁻) were omitted for clarity. Selected bond lengths [Å] and angles [°]: Au1–C1 2.043(2), Au1–C28 2.051(2), P1–C1 1.706(3), P2–C28 1.698(3), S1–C1 1.649(3), S2–C28 1.644(2), C1–Au1–C28 177.41(11), S1–C1–P1 116.26(15), S2–C28–P2 117.44(15), P1–C1–Au1 120.40(14), P2–C28–Au1 115.87(13), S1–C1–Au1 120.86(14), S2–C28–Au1 122.37(14).

**Table 1** Selected geometrical parameters for **1**, **2** and **VI** (distances in [Å], angles in [°])

|  | **1** | **2** | **VI** |
|---|---|---|---|
| P–C | 1.656(2) | 1.706(3) 1.698(3) | 1.781(4) |
| S–C | 1.593(1) | 1.649(3) 1.644(2) | 1.737(4) |
| P–C–S | 120.7(1) | 116.3(1) 117.4(2) | 110.2(2) |
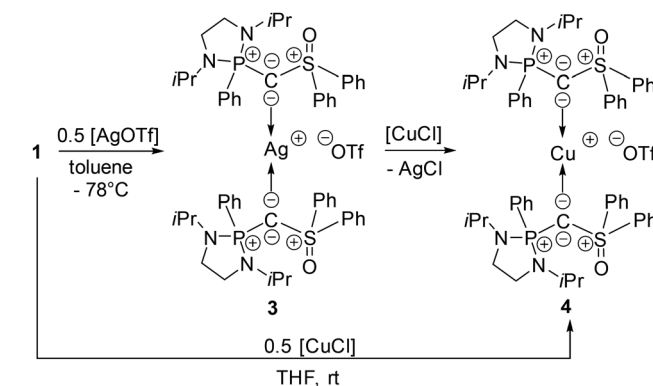


**Scheme 2** Formation of cationic silver complex **3** and transmetalation reaction with CuCl affording copper complex **4**.
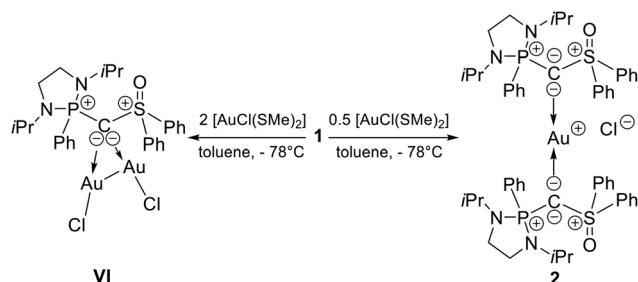


**Scheme 1** Reactivity of **1** with [AuCl(SMe₂)].

30.9 ppm and $\delta$ = 30.7 ppm. Indeed, in addition to the classical $^1J_{CP}$ coupling, $^1J_{CAg}$ coupling with both ¹⁰⁷/¹⁰⁹Ag isotopes are observed ($^1J_{CAg}$ = 137.8 Hz, $^1J_{CAg}$ = 140.7 Hz, $^1J_{CP}$ = 60.0

Hz).[19] The identification of the respective coupling constants was ensured by a $^{13}C\{^1H;^{31}P\}$ spectrum (see ESI†).

Similarly to NHC–Ag(I) complexes,[20] silver complex **3** is an excellent transmetalation agent toward copper (Scheme 2). The addition of copper chloride to **3** in $CD_2Cl_2$, monitored by $^{31}P$ NMR spectroscopy, lead to a complete conversion in 16 h, as indicated by a new singlet signal at $\delta = 44.0$ ppm corresponding to the new cationic complex **4**. In the $^{13}C$ NMR spectrum, the central carbon is slightly downfield shifted at $\delta = 31.2$ ppm and the silver–carbon coupling constants have disappeared. Noteworthy, complex **4** can also be directly obtained from the direct reaction between carbone **1** and 0.5 equivalent of [CuCl] (77% yield).

The molecular structures of **3** and **4** were confirmed by X-ray diffraction analysis (Fig. 3). As complex **2**, both cationic complexes **3** and **4** display an almost perfect linear geometry with a C1–Ag1–C2 angle of 179.3° for **3** and a C1–Cu1–C2 angle of 178.3° for **4** respectively. Again, for both complexes, the P1–C1, P2–C2, S1–C1 and S2–C2 distances are longer than in **1** indicating that each ligand acts as a two-electron donor. Those values together with C1–Ag1 and C2–Ag1 bond lengths (2.110(3) and 2.114(3) respectively) in **3** are in good agreement with those reported by Fujii for analogous silver complexes coordinated by iminosulfide/phosphine- and iminosulfide/sulfide-carbones.[8f,10d–f]

Selected bond lengths [Å] and angles [°] for **4**: Cu1–C2 1.919(2), Cu1–C1 1.918(2), P1–C1 1.702(2), P2–C2 1.706(2), S1–C1 1.638(2), S2–C2 1.641(2), C1–Cu1–C2 178.34(9), S1–C1–P1 114.70(11), S2–C2–P2 114.49(11), S1–C1–Cu1 121.66(11), S2–C2–Cu1 121.44(11), P1–C1–Cu1 119.31(10), P2–C2–Cu1 118.16(11).

In addition to carbophilic metals from group 11, the coordination behavior of **1** toward oxophilic metals was also studied.

In this context, group 4 metals were chosen to favor the coordination of the sulfoxide to the metal center. Our study was initiated with the reactivity of **1** toward titanium precursor $[TiCl_4(THF)_2]$ with the aim of synthesizing complex **5** in which **1** could act as a (C,O)-chelating ligand (Scheme 3). Surprisingly, instead of complex **5**, product **6** was formed, resulting from the chlorination of the central carbon of **1** and reduction of the sulfoxonium moiety into the corresponding sulfonium.[21]

The molecular structure of **6** was confirmed by X-ray diffraction analysis (Fig. 4). Monitoring the reaction by $^{31}P$ NMR spectroscopy, chlorinated compound **6** was formed with 90% selectivity together with 10% hydrolysis product. Product **6** can also be obtained by reacting $C_2Cl_6$ with phosphine/sulfide-carbone **7** (Scheme 3).

The formation of **6** was assigned to the high reactivity of $[TiCl_4]$ and its tendency to form titanium oxide, which for-
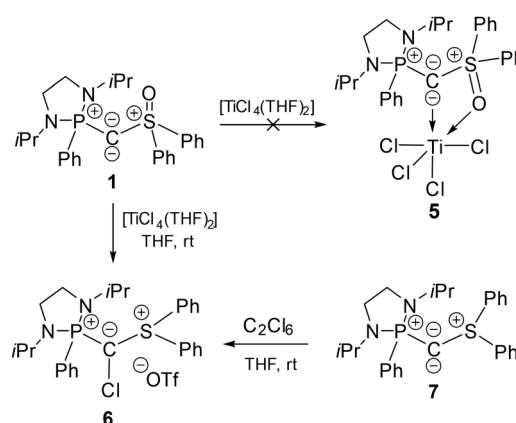
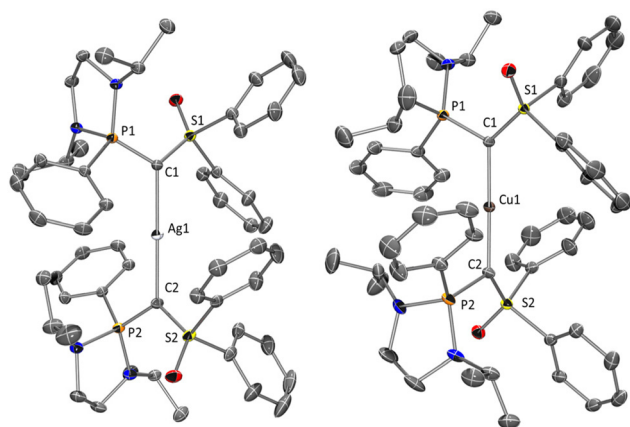**Scheme 3**  Reactivity of **1** with titanium(IV) precursor.

**Fig. 3**  Molecular structures of **3** and **4**. Thermal ellipsoids represent 30% probability. H atoms, solvent (THF) and a triflate molecule (as counter ion) were omitted for clarity in **3**. H atoms and a triflate molecule (as counter ion) were omitted for clarity in **4**. Selected bond lengths [Å] and angles [°] for **3**: Ag1–C2 2.110(3), Ag1–C1 2.114(3), P1–C1 1.695(3), P2–C2 1.694(3), S1–C1 1.636(3), S2–C2 1.634(3), C1–Ag1–C2 179.31(11), S1–C1–P1 115.58(16), S2–C2–P2 116.42(18), S1–C1–Ag1 118.59(15), S2–C2–Ag1 119.01(16), P1–C1–Ag1 120.38(16), P2–C2–Ag1 122.65(15).
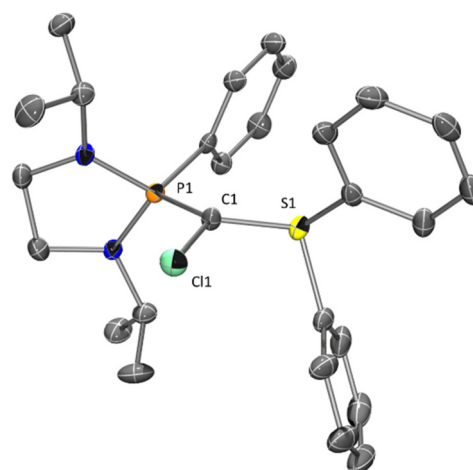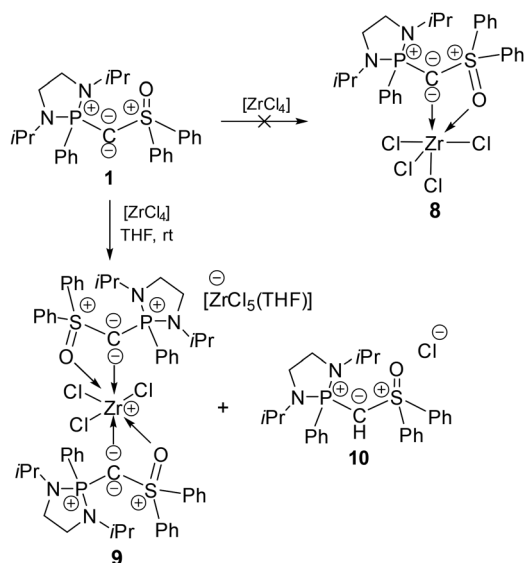
**Fig. 4**  Molecular structure of **6**. Thermal ellipsoids represent 30% probability. H atoms and a triflate molecule (as counter ion) were omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.710(3), S1–C1 1.684(3), Cl1–C1 1.748(3), P1–C1–S1 120.3(2), P1–C1–Cl1 118.0(2), S1–C1–Cl1 119.0(2).

mation was confirmed by XRD analysis. With less reactive titanium precursors, such as [Ti(Cp)$_2$Cl$_2$] or [Ti(Cp)$_2$(Me)$_2$], no reaction was observed. In contrast, **1** reacts with [ZrCl$_4$] affording a new cationic complex **9** (90% selectivity) together with 10% of phosphonium/sulfoxonium salts **10** (Scheme 4). Colorless crystals of **9**, suitable for X-ray diffraction analysis, were obtained from a saturated THF solution (Fig. 5).

Instead of the expected carbone–ZrCl$_4$ complex **8**, a cationic complex **9** featuring two carbone ligands was observed (Scheme 4). Indeed, even though the overall stoichiometry of the reaction was respected, two carbone ligands act as (C,O)-bidentate hybrid ligand chelating a single [ZrCl$_3$]$^+$ moiety. The

electroneutrality of the complex is ensured by [ZrCl$_5$(THF)]$^-$ anion resulting from a halide abstraction thus allowing the formation of the cationic counterpart.

Zr$^{IV}$ ions feature a coordination number of seven with two (C,O)-chelating carbones and three terminal chlorido ligands (pentagonal bipyramid), more classically observed with group 5 metals.[22] The two carbones and a chlorido group constitute a quasi-planar pentagonal environment. The P–C and C–Zr bond lengths differ quite significantly for the two carbones (~0.04 Å and ~0.05 Å respectively, see Fig. 5). The apical positions are occupied by the last two chlorido groups, with typical Zr–Cl bonds lengths of 2.491(3) and 2.453(4) Å, slightly longer than the one in the pentagonal plan [2.442(4) Å]. If the P–C bond lengths in complex **9** are extremely similar to those described in the complexes **2**, **3** or **4** (less than 1% variation), the S–C bond lengths are significantly shortened upon coordination of the sulfoxonium to the metal center (respectively 1.619 Å and 1.602 Å in **9** compared to 1.634–1.649 Å observed in **2**, **3** or **4**). The characterization by NMR spectroscopy in solution suffers from large signals that arise from fluxional behavior (see ESI†).[23] Nevertheless, a large signal can be observed in the $^{31}$P NMR spectrum at $\delta$ = 42.7 ppm, in the same range of previous complexes.

Zirconium complexes being known to be efficient transmetalation agents,[24] transfer of carbones from Zr to Cu was tested. Pleasingly, complex **9** smoothly reacts with [CuCl] at room temperature to afford quantitatively copper complex **4** (Scheme 5).

A heavier analogue of complex **9** was obtained by reacting **1** with [HfCl$_4$] (Scheme 6). The formation of cationic complex **11**
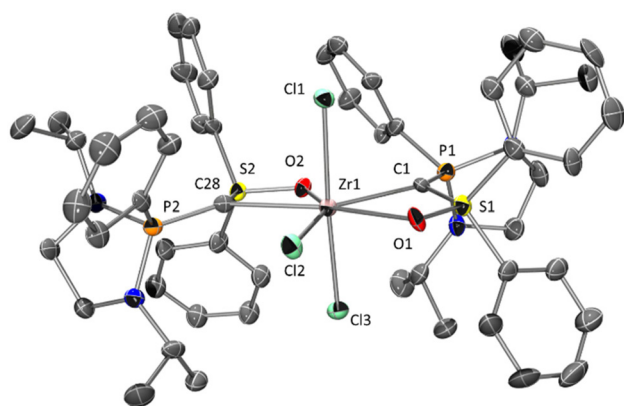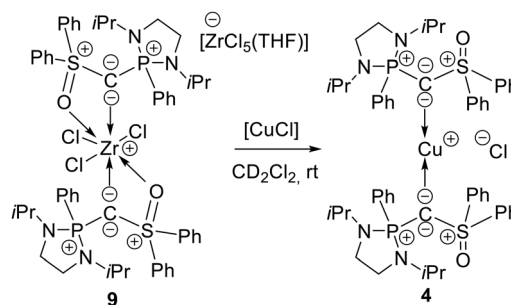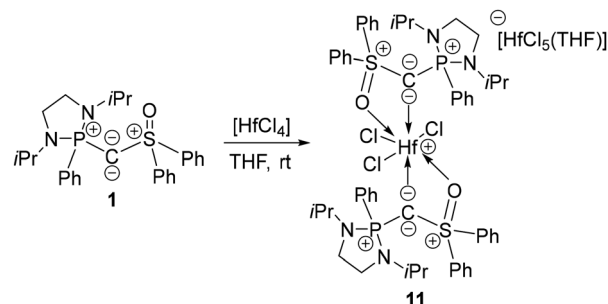


**Scheme 4** Reactivity toward zirconium(IV).



**Fig. 5** Molecular structure of **9**. Thermal ellipsoids represent 30% probability. H atoms, disordered atoms, anion (ZrCl$_5^-$) and solvent molecules (THF) were omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.689(15), P2–C28 1.726(13), S1–C1 1.619(14), S2–C28 1.602(12), Zr1–C1 2.438(13), Zr1–O1 2.295(9), Zr1–C28 2.383(12), Zr1–O2 2.244(8), Zr1–Cl1 2.491(3), Zr1–Cl2 2.446(4), Zr1–Cl3 2.453(4), S1–C1–P1 126.4 (8), S2–C28–P2 124.2(7) S1–C1–Zr1 91.6(6), S2–C28–Zr1 92.3(5), P1–C1–Zr1 140.2(7), P2–C28–Zr1 141.4(6).



**Scheme 5** Carbones transfer from Zr complex **9** to Cu complex **4**.



**Scheme 6** Reactivity of **1** with hafnium(IV) chloride.

was evidenced by X-Ray diffraction analysis. The ligand coordination mode and complex geometry are strictly identical to complex **9** (see ESI† for X-Ray data). Unfortunately, no NMR characterization could be performed because of an extreme insolubility of **11** in all common organic solvent.

## Conclusions

A series of group 4 and 11 complexes coordinated by phosphine/sulfoxide-carbone **1** were successfully synthesized in good yields under mild conditions. The X-ray diffraction analyses of all the synthesized complexes have contributed to the elucidation of the solid-state coordination modes. For group 11, new cationic complexes were obtained when reacted with half an equivalent of the metal. A bimetallic complex could be obtained in the case of gold, when **1** was reacted with 2 equivalents of metal. For group 4 complexes, carbone **1** acts as a bidentate (C,O)-chelating ligand which are the first examples of such coordination mode. Silver and zirconium complexes **3** and **9** are excellent transmetallation agents toward copper(ı) complexes. Taking in account the easy access of carbone **1**, the mild conditions used to obtain the described complexes and their relative stability, their use in catalytic transformations should extend the scope of carbones as ligand.

## Experimental

### General procedure

All manipulations were performed under an inert atmosphere of argon by using standard Schlenk techniques. Dry and oxygen-free solvents were used. $^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded on Brucker Avance 500 or Avance 300 spectrometers. $^1$H NMR and $^{13}$C NMR chemical shifts are reported in parts per million (ppm) relative to $Me_4Si$ as external standard. $^{31}$P NMR downfield chemical are expressed in ppm relative to 85% $H_3PO_4$. $^{19}$F-chemical shifts were reported in ppm relative to $C_FCl_3$ as an external standard. Mass spectra were recorded on Hewlett Packard 5989A spectrometer. Powder X-Ray diffraction data were recorded at room temperature on a Rigaku MiniFlex600 ($\theta$–2$\theta$) diffractometer with Cu $K_{\alpha 1}, K_{\alpha 2}$ radiation ($\lambda$ = 1.54059, 1.54442 Å). Data collection was performed over the angular range 5° < 2$\theta$ < 90° with a step size of 0.02°. All commercially available reagents were used without further purification otherwise noted. Ylide **1-HOTf**[15a] and **7-HOTf**[14a] were prepared following previously reported procedures.

### Synthetic procedures

**Synthesis of gold(ı) complex 2.** Both solid **1-HOTf** (200 mg, 0.325 mmol, 1 eq.) and KH (39 mg, 0.98 mmol, 3 eq.) were charged in a Schlenk, and THF (2 mL) was added at room temperature. The reaction mixture was stirred overnight at room temperature. The volatiles were removed under reduced pressure, and the carbone **1** was extracted with pentane (3 × 5 mL). The pentane was removed under reduced pressure then

carbone **1** was dissolved in toluene (3 mL), added to a solution of $[AuCl(SMe)_2]$ (48 mg, 0.16 mmol, $\frac{1}{2}$ eq.) in toluene (1 mL) at −78 °C. The reaction mixture was slowly warmed up to room temperature and stirred overnight. A white precipitate corresponding to the desired product formed overnight. The precipitate was isolated by filtration and the residue was washed with toluene (2 × 3 mL). The white powder was then washed with pentane (2 × 3 mL) and dried under reduced pressure. Gold(ı) complex **2** was isolated as a white powder in 80% yield (150 mg, 0.129 mmol). Crystals suitable for X-Ray diffraction analysis were obtained from a $CH_2Cl_2$/diethyl ether solution at 4 °C.

$^{31}$P{$^1$H} NMR ($CD_2Cl_2$, 298 K, 202 MHz) $\delta$ = 42.3 (s). $^1$H NMR ($CD_2Cl_2$, 298 K, 500 MHz) $\delta$ = 7.88–7.80 (m, 8H, C$H_{Ph}$), 7.72–7.64 (m, 8H, C$H_{Ph}$), 7.61–7.53 (m, 10H, C$H_{Ph}$), 7.41–7.36 (m, 4H, C$H_{Ph}$), 3.01–2.82 (m, 12H, C$H_{2bridge}$ & C$H_{iPr}$), 0.37 (d, $J_{HH}$ = 6.6 Hz, 12H, C$H_{3iPr}$), 0.34 (d, $J_{HH}$ = 6.6 Hz, 12H, C$H_{3iPr}$). $^{13}$C NMR ($CD_2Cl_2$, 298 K, 126 MHz) $\delta$ = 147.6 (d, $J_{CP}$ = 6.3 Hz, S$C_{ipso}$), 133.9 (d, $J_{CP}$ = 130.0 Hz, P$C_{ipso}$), 132.9 (s, C$H_{Ph}$), 132.8 (d, $J_{CP}$ = 2.9 Hz, C$H_{Ph}$), 132.5 (d, $J_{CP}$ = 10.1 Hz, C$H_{Ph}$), 129.4 (s, C$H_{Ph}$), 128.9 (d, $J_{CP}$ = 13.2 Hz, C$H_{Ph}$), 127.6 (s, C$H_{Ph}$), 44.9 (d, $J_{CP}$ = 5.3 Hz, C$H_{iPr}$), 40.7 (d, $J_{CP}$ = 80.3 Hz, P$CS$), 38.5 (d, $J_{CP}$ = 7.2 Hz, C$H_{2bridge}$), 19.5 (2 overlapping broad doublets, C$H_{3iPr}$). HRMS (ES+): $m/z$ [M]+ calculated for $C_{54}H_{66}O_2N_4P_2S_2Au$ = 1125.3762, found = 1125.3793.

**Synthesis of silver complex 3.** Both solid **1-HOTf** (500 mg, 0.813 mmol, 1 eq.) and KH (97 mg, 2.4 mmol, 3 eq.) were charged in a Schlenk, and THF (6 mL) was added at room temperature. The reaction mixture was stirred overnight at room temperature. The volatiles were removed under reduced pressure, and the carbone **1** was extracted with toluene (3 × 3 mL). The toluene solution of **1** was concentrated (3 mL) and was added to a cold solution of [AgOTf] (104 mg, 0.404 mmol, $\frac{1}{2}$ eq.) in toluene (2 mL) at −78 °C. The reaction mixture was slowly warmed up to room temperature and stirred overnight. A white precipitate corresponding to the desired product formed overnight. The precipitate was isolated by filtration and the residue was washed with pentane (2 × 4 mL) then dried under reduced pressure. Complex **3** was isolated as a white powder in 90% yield (430 mg, 0.363 mmol). Suitable crystals for X-ray diffraction analysis were obtained upon cooling a boiling saturated THF solution to room temperature.

$^{31}$P{$^1$H} NMR ($CD_2Cl_2$, 298 K, 121 MHz) $\delta$ = 41.4 (d, $J_{AgP}$ = 5.9 Hz). $^1$H NMR ($CD_2Cl_2$, 298 K, 300 MHz) $\delta$ = 7.89 (d, $J_{HH}$ = 7.3 Hz, 8H, C$H_{Ph}$), 7.74–7.54 (m, 18H, C$H_{Ph}$), 7.46–7.36 (m, 4H, C$H_{Ph}$), 3.06–2.70 (m, 12H, C$H_{2bridge}$ & C$H_{iPr}$), 0.38 (d, $J_{HH}$ = 6.3 Hz, 24H, C$H_{3iPr}$). $^{13}$C NMR ($CD_2Cl_2$, 298 K, 75 MHz) $\delta$ = 148.9 (d, $J_{CP}$ = 8.2 Hz, S$C_{ipso}$), 148.8 (d, $J_{CP}$ = 8.3 Hz, S$C_{ipso}$), 134.9 (d, $J_{CP}$ = 130.0 Hz, P$C_{ipso}$), 132.9 (d, $J_{CP}$ = 3.0 Hz, C$H_{Ph}$), 132.8 (s, C$H_{Ph}$), 132.3 (d, $J_{CP}$ = 9.7 Hz, C$H_{Ph}$), 129.7 (s, C$H_{Ph}$), 129.3 (d, $J_{CP}$ = 13.1 Hz, C$H_{Ph}$), 127.3 (s, C$H_{Ph}$), 121.7 (q, $J_{CF}$ = 321.6 Hz, $CF_3$), 45.1 (d, $J_{CP}$ = 5.2 Hz, C$H_{iPr}$), 38.6 (d, $J_{CP}$ = 6.9 Hz, C$H_{2bridge}$), 30.8 (ddd, $J_{CAg}$ = 137.9 Hz, $J_{CAg}$ = 138.1 Hz, $J_{CP}$ = 60.0 Hz, P$CS$), 19.8 (d, $J_{CP}$ = 4.6 Hz, C$H_{3iPr}$), 19.6 (d, $J_{CP}$ = 3.0 Hz, C$H_{3iPr}$). $^{19}$F{$^1$H} NMR ($CD_2Cl_2$, 298 K, 282 MHz): $\delta$ = −78.7 (s).

**Synthesis of copper complex 4.** *Method A*: both solid ylide **1-HOTf** (200 mg, 0.325 mmol, 1 eq.) and KHMDS (65 mg,

0.33 mmol, 1 eq.) were charged in a Schlenk, and THF (2 mL) was added at room temperature. The reaction mixture was stirred for 2 h at room temperature. The solution of carbone **1** was cannulated to a suspension of [CuCl] (16 mg, 0.16 mmol, $\frac{1}{2}$ eq.) in THF (3 mL). The reaction mixture was stirred overnight at room temperature. A white precipitate corresponding to the desired product formed overnight. The solvent was removed under reduced pressure and the desired product was extracted with dichloromethane (3 × 2 mL). The solvent was evaporated under reduced pressure and the resulting white solid was washed with $Et_2O$ (4 × 2 mL). The desired compound was then dried under reduced pressure and complex **4** was isolated as a white powder in 77% yield (140 mg, 0.122 mmol). Suitable crystals for X-ray diffraction analysis were grown from a saturated THF solution. *Method B*: both solid [CuCl] (15 mg, 0.15 mmol, 1 eq.) and silver complex **3** (180 mg, 0.151 mmol, 1 eq.) were charged in a J. Young NMR tube, and $CD_2Cl_2$ (0.6 mL) was added at room temperature. The reaction was monitored by $^1H$ and $^{31}P$ NMR and was finished after 16 h. A grey precipitated corresponding to AgCl formed and was filtered off to afford the desired copper complex **4** quantitatively. *Method C*: [CuCl] (15 mg, 0.15 mmol, 1 eq.) and zirconium complex **9** (219 mg, 0.15 mmol, 1 eq.) were charged in a J. Young NMR tube, and $CD_2Cl_2$ (0.6 mL) was added at room temperature. Full conversion was confirmed by $^1H$ and $^{31}P$ NMR after 16 h as well as the formation of a grey precipitate corresponding to AgCl. The salt was filtered off to afford the desired copper complex **4** quantitatively.

$^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 298 K, 121 MHz) $\delta$ = 44.0 (s). $^1H$ NMR ($CD_2Cl_2$, 298 K, 300 MHz) $\delta$ = 7.89 (d, $J_{HH}$ = 7.4 Hz, 8H, $CH_{Ph}$), 7.77–7.58 (m, 18H, $CH_{Ph}$), 7.50–7.40 (m, 4H, $CH_{Ph}$), 3.05–2.70 (m, 12H, $CH_{2bridge}$ & $CH_{iPr}$), 0.37 (d, $J_{HH}$ = 6.5 Hz, 12H, $CH_{3iPr}$) 0.33 (d, $J_{HH}$ = 6.5 Hz, 12H, $CH_{3iPr}$). $^{13}C$ NMR ($CD_2Cl_2$, 298 K, 75 MHz) $\delta$ = 147.7 (d, $J_{CP}$ = 7.7 Hz, $SC_{ipso}$), 134.8 (d, $J_{CP}$ = 127.5 Hz, $PC_{ipso}$), 133.0 (d, $J_{CP}$ = 3.1 Hz, $CH_{Ph}$), 132.9 (s, $CH_{Ph}$), 132.2 (d, $J_{CP}$ = 10.0 Hz, $CH_{Ph}$), 129.6 (s, $CH_{Ph}$), 129.3 (d, $J_{CP}$ = 13.0 Hz, $CH_{Ph}$), 127.4 (s, $CH_{Ph}$), 121.6 (q, $J_{CF}$ = 321.5 Hz, $CF_3$), 44.9 (d, $J_{CP}$ = 5.6 Hz, $CH_{iPr}$), 38.6 (d, $J_{CP}$ = 7.1 Hz, $CH_{2bridge}$), 31.2 (d, $J_{CP}$ = 64.5 Hz, $PCS$), 19.8 (d, $J_{CP}$ = 4.8 Hz, $CH_{3iPr}$), 19.6 (d, $J_{CP}$ = 3.0 Hz, $CH_{3iPr}$). $^{19}F\{^1H\}$ NMR ($CD_2Cl_2$, 298 K, 282 MHz): $\delta$ = −78.7 (s). Elemental analysis for **4** calculated for $C_{55}H_{66}CuF_3N_4O_5P_2S_3$: C: 57.86; H: 5.83; N: 4.91. Found: C: 57.12; H: 5.84; N: 4.82.

**Synthesis of chlorinated ylide 6.** *Method A*: both solid **1-HOTf** (50 mg, 0.081 mmol, 1 eq.) and KHMDS (16 mg, 0.081 mmol, 1 eq.) were charged in a Schlenk, and THF (3 mL) was added at room temperature. The reaction mixture was stirred for 45 min at room temperature. The reaction mixture is added to [TiCl$_4$] at room temperature (15 mg, 0.081 mmol, 1 eq.). After 1 h 30, the solvent was removed under reduced pressure. The desired product was extracted with $CH_2Cl_2$ (3 × 2 mL). The solvent was evaporated under reduced pressure and the resulting white solid was washed with pentane (3 × 2 mL). The desired compound was then dried under reduced pressure and **6** was isolated as a white powder in 85% yield (35.7 mg, 68.9 mmol). *Method B*: both solid phosphonium–

sulfonium ylide **7-HOTF** (200 mg, 0.334 mmol, 1 eq.) and KHMDS (67.0 mg, 0.334 mmol, 1 eq.) were charged in a Schlenk, and THF (3 mL) was added at room temperature. The reaction mixture was stirred for 45 min at room temperature. The reaction mixture is cooled down to −80 °C then added to $C_2Cl_6$ (83 mg, 0.35 mmol, 1.05 eq.). The reaction mixture was slowly warmed up to room temperature then stirred overnight. The solvent was removed under reduced pressure and the residue was washed with $Et_2O$ (3 × 3 mL). The desired product was extracted with chloroform (3 × 2 mL). The solvent was evaporated under reduced pressure and the resulting white solid was washed with pentane (3 × 2 mL). The desired compound was then dried under reduced pressure and **6** was isolated as a white powder in 80% yield (138 mg, 0.267 mmol). Recrystallization was performed from a saturated THF/pentane solution.

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K, 121 MHz) $\delta$ = 49.8 (s). $^1H$ NMR ($CDCl_3$, 298 K, 300 MHz) $\delta$ = 7.83–7.69 (m, 3H, $CH_{Ph}$), 7.68–7.52 (m, 12H, $CH_{Ph}$), 3.45–3.33 (dsept, $J_{HH}$ = 6.6 Hz, $J_{PH}$ = 9.0 Hz, 2H, $CH_{iPr}$), 3.45–3.33 (m, $CH_2$, 2H), 3.29–3.17 (m, $CH_2$, 2H), 1.03 (d, $J_{HH}$ = 6.6 Hz, 6H, $CH_{3iPr}$), 0.98 (d, $J_{HH}$ = 6.6 Hz, 6H, $CH_{3iPr}$). $^{13}C$ NMR ($CDCl_3$, 298 K, 75 MHz) $\delta$ = 135.0 (d, $J_{CP}$ = 3.0 Hz, $CH_{Ph}$), 133.1 (s, $CH_{Ph}$), 132.5 (d, $J_{CP}$ = 10.4 Hz, $CH_{Ph}$), 130.8 (s, $CH_{Ph}$), 130.5 (d, $J_{CP}$ = 3.8 Hz, $SC_{ipso}$), 130.3 (d, $J_{CP}$ = 13.4 Hz, $CH_{Ph}$), 129.1 (s, $CH_{Ph}$), 123.7 (d, $J_{CP}$ = 128.3 Hz, $PC_{ipso}$), 121.1 (q, $J_{CF}$ = 321.1 Hz, $CF_3$), 45.5 (d, $J_{CP}$ = 5.6 Hz, $CH_{iPr}$), 38.9 (d, $J_{CP}$ = 9.8 Hz, $CH_2$), 37.5 (d, $J_{CP}$ = 158.0 Hz, $PCS$), 20.6 (d, $J_{CP}$ = 4.8 Hz, $CH_{3iPr}$), 20.2 (d, $J_{CP}$ = 3.1 Hz, $CH_{3iPr}$).

**Synthesis of zirconium complex 9.** Both solid **1-HOTf** (50 mg, 0.081 mmol, 1 eq.) and KHMDS (16 mg, 0.081 mmol, 1 eq.) were charged in a Schlenk, and THF (3 mL) was added at room temperature. The reaction mixture was stirred for 45 min at room temperature. The reaction mixture is added to [ZrCl$_4$] (19 mg, 0.081 mmol, 1 eq.) at room temperature. The reaction mixture was stirred for 45 min at room temperature. The solvent was removed under reduced pressure and the desired product was extracted with $CH_2Cl_2$ (3 × 2 mL). No isolated yield could be calculated because the desired product was systematically contaminated by about 10% of **10** (NMR). Suitable crystals for X-ray diffraction analysis were grown from a saturated THF solution.

$^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 298 K, 121 MHz) $\delta$ = 42.7 (broad s). $^1H$ NMR ($CD_2Cl_2$, 298 K, 300 MHz) $\delta$ = 8.40–7.90 (m, 5H, $CH_{Ph}$), 7.86–7.51 (m, 7H, $CH_{Ph}$), 7.49–7.05 (m, 2H, $CH_{Ph}$), 4.60–4.38 (coord THF), 3.95–3.41 (m, 4H, $CH_{iPr}$ + THF), 3.24–2.73 (m, $CH_2$, 4H), 2.11–1.63 (m, coord. THF + THF, 4H), 0.73–0.28 (m, 6H, $CH_{3iPr}$), 0.20 (d, $J_{HH}$ = 6.2 Hz, 6H, $CH_{3iPr}$). $^{13}C$ NMR ($CD_2Cl_2$, 298 K, 75 MHz) $\delta$ = 140.9 (broad s, $CH_{Ph}$), 135.3 (s, $CH_{Ph}$), 133.1 (d, $J_{CP}$ = 3.0 Hz, $CH_{Ph}$), 132.0 (d, $J_{CP}$ = 128.4 Hz $PC_{ipso}$), 130.9 (s, $CH_{Ph}$), 130.0 (s, $CH_{Ph}$), 128.6 (s, $CH_{Ph}$), 128.5 (overlapping d, $J_{CP}$ could not be calculated, $CH_{Ph}$), 76.7 (s, $CH_2$-coord THF), 68.5 (s, $CH_2$-THF), 45.2 (broad s, $CH_{iPr}$), 38.9 (d, $J_{CP}$ = 7.9 Hz, $CH_{2bridge}$), 26.1 (s, $CH_2$-THF), 20.5 (d, $J_{CP}$ = 5.6 Hz, $CH_{3iPr}$), 18.9 (broad s, $CH_{3iPr}$). The signal for the central carbon was not observed in this analysis but was detected in another sample [$\delta$ = 33.1 (d, $J_{CP}$ = 135.1 Hz, $PCS$)].

**Hafnium complex 11.** Both solid **1-HOTf** (50 mg, 0.081 mmol, 1 eq.) and KHMDS (16 mg, 0.081 mmol, 1 eq.) were charged in a Schlenk, and THF (3 mL) was added at room temperature. The reaction mixture was stirred for 45 min at room temperature. The reaction mixture is added to [HfCl$_4$] (26 mg, 0.081 mmol, 1 eq.) at room temperature. After few minutes, large amount crystals appeared in the solution. The structure of **11** was confirmed by X-Ray diffraction analysis. Unfortunately, the ionic hafnium complex presents an extremely poor solubility in all organic solvent preventing its characterization by NMR spectroscopy. **11** was isolated in 30% yield (19 mg, 0.04 mmol).

### Crystallography

The data of the structures for **2**, **3**, **4**, **6**, **9** and **11** were collected at 193 K on a Bruker-AXS APEX II CCD Quazar diffractometer equipped with a 30 W air-cooled microfocus source (**3**, **6**, **9** and **11**), or on a Brucker-AXS D8-Venture diffractometer equipped with a CMOS Area detector (**2** and **4**) with MoKα radiation (wavelength = 0.71073 Å) by using phi- and omega-scans. The data were integrated with SAINT, and an empirical absorption correction with SADABS was applied.[25] The structures were solved using an intrinsic phasing method (ShelXT)[26] and refined using the least-squares method on $F^2$ (ShelXL-2014).[27] All non-H atoms were treated anisotropically. All H atoms attached to C atoms were fixed geometrically and treated as riding on their parent atoms with C–H = 0.95 Å (aromatic), 0.98 Å (CH$_3$), 0.99 Å (CH$_2$) or 1.0 Å (CH) with $U_{iso}$(H) = $1.2U_{eq}$(CH, CH$_2$) or $U_{iso}$(H) = $1.5U_{eq}$(CH$_3$).

Most of the structures were found to be strongly disordered, especially the solvent molecules and the counter anions. Several restraints (SAME, SADI, SIMU, DELU, RIGU, ISOR) and equal $xyz$ and $U_{ij}$ constraints EXYZ and EADP (for **11**) were applied to refine some moieties of the molecules and to avoid the collapse of the structures during the least-squares refinement by the large anisotropic displacement parameters. Some bond lengths were restrained with DFIX and DANG to suitable target values (**9** and **11**).

## Author contributions

Conceptualization: E.M., S.H.; investigation: S.H. except the synthesis of **2** which was performed by L.B.; validation: E.M.; data curation: E.M.; X-ray structural studies: N. S. M.; supervision: E.M., D.M.; writing—original draft preparation: S.H., E. M.; writing—review and editing: all authors.; All authors have read and agreed to the published version of the manuscript.

## Data availability

Additional data supporting this article have been included as part of the ESI† (additional experimental information, NMR spectra and crystallographic data).

CCDC 2366566–2366571 (**2**, **3**, **4**, **6**, **9**, **11**) contain the supplementary crystallographic data for this paper.†

## Conflicts of interest

There are no conflicts to declare.

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