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Germylene–sulfoxide as a potential hemilabile ligand: application in coordination chemistry†‡

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We describe here the synthesis of heteroleptic organogermylenes containing a sulfoxide donor function for their application in coordination chemistry. While complexation reaction with [W(cod)(CO)$_4$] and [Mo(nbd)(CO)$_4$] afforded bis(germanium)(II) transition-metal complexes, a bidentate complex coordinated by germanium(II) and the oxygen atom of the sulfinyl group was obtained from [Ru(PPh$_3$)$_3$Cl$_2$].

Introduction

Hemilabile ligands, featuring a combination of strong and weak donor groups, are very useful ligands able to support different metal oxidation states and binding modes, and therefore they have become essential tools in transition-metal catalysis.[1] In this context the search for new combinations of strong and weak donors is of prime interest. Since the first isolation of stable germylenes and stannylenes by Lappert and coworkers,[2] the investigation of the transition-metal chemistry of these metallylenes, heavier analogues of carbenes, has attracted considerable interest.[3] Thus, it has been demonstrated that germylene ligands exhibit relatively high binding energies to transition metals and are very strong donors.[4–6] Particularly, amidinatogermylenes are currently very well-known germanium(II) species and their use as ligands in transition-metal complexes has already been extensively studied.[7] However, the use of transition-metal germylene complexes in catalysis remains sporadic, with only a few recent reports on reduction,[8] hydrocyanation[9] of ketones, or the Sonogashira cross-coupling reaction (Fig. 1).[10] Moreover, to the best of our knowledge, no germylene-based hemilabile ligand has been described in catalysis.

In order to develop new hemilabile ligands combining a strong σ-donating germylene center associated with a weak donor group, we have envisioned the chloroamidinato germanium(II) compounds as suitable precursors to introduce a weak donor group. Among the various possible chemical groups, and in addition to our description of bis-sulfonyl pincer-ligand germylenes and stannylenes to stabilize transition metals,[11] our interest was on the use of the sulfoxide function.[12] Indeed sulfoxide derivatives offer different advantages: a weak coordination of the transition metal either by the sulfur- or oxygen-atom, a stereogenic sulfur center potentially useful in asymmetric catalysis, and the easy formation of an α-sulfinyl carbanion.

We report herein the synthesis of mixed germylene–sulfoxide ligands, from the chloroamidinato germanium(II) derivative and α-sulfinyl carbanions, and the related tungsten(0), molybdenum(0) and ruthenium(II) complexes.

Results and discussion

First of all it is important to take into account the compatibility of germylene and sulfoxide functions. Indeed, Satgé *et al.* reported in 1987 the oxidation of a germylene–chromium complex by dimethylsulfoxide leading to the formation of the

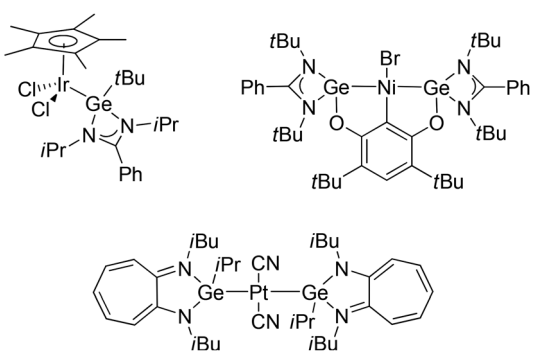

Fig. 1 Examples of transition-metal germylenes used in catalysis.

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†This article is dedicated to the memory of late Professor Jacques Satgé.

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corresponding transient germanone.[13] However, Nagendran *et al*. described in 2016 the use of 2-mercaptopyridine-*N*-oxide as an efficient ligand of stannylenes and germylenes, while *N*-oxides are also known to oxidize low-valent group 14 elements.[14] These two complementary results prompted us to test the reaction of lithium carbanions derived from methyl-arylsulfoxides with chloroamidinato germylene (Scheme 1). Heteroleptic germylene [iPrNC(*t*Bu)NiPr]GeCl was prepared by the well-established transmetalation reaction between lithium amidinate and Cl_2Ge·dioxane,[6] and the α-sulfinyl carbanions were obtained by the deprotonation reaction of the corresponding sulfoxides by lithium diisopropylamide (LDA) at −80 °C in diethyl ether.

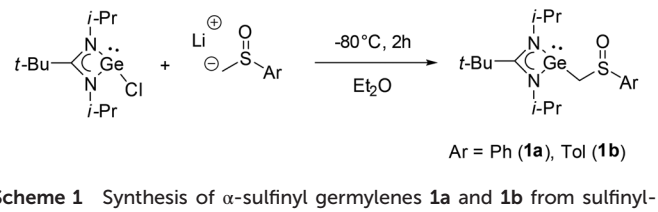
Before the salt metathesis of the α-sulfinyl carbanion on chloroamidinato germylene, it was important to remove the residual diisopropylamine generated during the deprotonation reaction. Indeed, without this precaution, only unidentified by-products were formed. Diisopropylamine was removed under reduced pressure, and the solid α-sulfinyl carbanion was resolubilized in diethyl ether and reacted at −80 °C on chlorogermylene. α-Sulfinyl germylenes **1a** and **1b** were obtained as air-sensitive oils at room temperature in 72% and 82% yields, respectively. Both compounds are perfectly stable in the solid-state at low temperature (−24 °C), under an inert atmosphere, but all attempts to crystallize them have failed. They have been fully characterized by NMR spectroscopy, and the ^{1}H NMR spectra exhibit a characteristic AB signal for Ge-CH_2-SO protons due to the presence of the sulfoxide stereogenic center (δ = 2.74 ppm, $^2J_{HH}$ = 13.8 Hz for **1a** and **1b**). The chemical shift of this signal is in the same range of the starting material methyl-arylsulfoxide. This result can be explained by the close electronegativity of germanium and hydrogen. Moreover, the presence of the sulfoxide stereogenic centre has a significant influence on the iPr group of the amidate entity: while the CH_3 protons of the starting material [iPrNC(*t*Bu)NiPr]GeCl appear as two doublets (δ = 1.20 and 1.24 ppm, $^3J_{HH}$ = 6.4 Hz), α-sulfinyl germylenes **1a** and **1b** show four different doublets between 1.11 and 1.18 ppm ($^3J_{HH}$ = 6.3 Hz for **1a** and **1b**). The ^{13}C NMR spectrum exhibits a characteristic signal for Ge-*C*H_2-SO (δ = 61.5 and 61.9 ppm for **1a** and **1b** respectively). Again, the presence of the sulfoxide stereogenic centre induces a loss of symmetry of the iPr groups by comparison with the starting material [iPrNC(*t*Bu)NiPr]GeCl with two different signals at 47.6 and 47.7 ppm for *C*H and four distinct signals for CH_3 between 24.3 and 27.0 ppm (see Experimental in the ESI†).

In order to test the ability of these new α-sulfinyl germylenes to coordinate transition metals, the reaction of **1b** with [W(cod)(CO)$_4$] (cod = 1,5-cyclooctadiene) and [Mo(nbd)(CO)$_4$] (nbd = 2,5-norbornadiene) was first examined (Scheme 2). Displacement of the ligand (cod or nbd) by two germanium(II) species **1b** occurred easily in THF solution, and complexes **2a** and **2b** were isolated as pale yellow powders in 78% and 84% yields, respectively, stable for weeks at room temperature under an inert atmosphere.

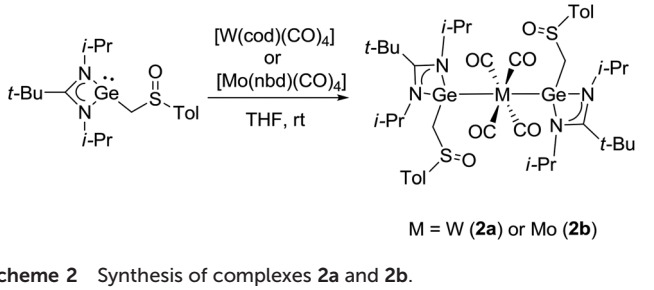
Analytically pure yellow crystals of **2a** and **2b** were obtained from THF solutions at low temperature. The ^{1}H NMR spectrum exhibits a downfield shift of the AB signal for Ge-CH_2-SO protons ($\Delta\delta \approx +0.4$ ppm). However, it is noteworthy that in the ^{13}C NMR spectrum there is only one carbonyl resonance (208 ppm for **2a** and 216 ppm for **2b**). Furthermore, the presence of a band in the IR spectra (1021 cm^{-1} for **2a** and 1015 cm^{-1} for **2b**) indicates a non-coordinated sulfoxide. In addition, a strong band (1938 cm^{-1} for **2a** and 1905 cm^{-1} for **2b**) suggests a "*trans*" octahedral geometry of the W and Mo complexes. An X-ray structure study confirmed the "*trans*" orientation of the two germanium fragments in both cases without any coordination of the sulfinyl groups (Fig. 2).

The germanium atom adopts a distorted tetrahedral geometry, and the transition metals W and Mo are octahedrally coordinated with almost linear Ge–M–Ge bond angles (180° for both **2a** and **2b**) and M–Ge bond lengths (2.519(1) Å and 2.526 (1) Å for **2a** and **2b**) very similar to those in the closely related W and Mo germylene complexes.[5] It is noteworthy that only the **2a**(***R***,**S****) and **2b**(***R***,**S****) diastereomers were characterized by X-ray diffraction analysis, while α-sulfinyl germylene was used in a racemic form. Moreover no diastereomeric differentiation was observed by ^{1}H and ^{13}C NMR spectroscopy, probably due to the wide distance separating the two sulfinyl stereogenic centers. It is important to note that the use of one equivalent of [W(cod)(CO)$_4$] or [Mo(nbd)(CO)$_4$] does not allow the corresponding Ge,O-chelated complexes, **2a** and **2b**, to be isolated in all cases.

In order to exploit the potential of **1a** as a bidentate ligand, its coordination ability towards [Ru(PPh$_3$)$_3$Cl$_2$] was investigated (Scheme 3). Indeed ruthenium shows ability to be coordinated either by the sulfur atom or by the oxygen atom of a sulfinyl group. Displacement of one PPh$_3$ by the α-sulfinyl germylene species **1a** occurred easily in THF solution at room temperature leading to the formation of complex **3a**. Nonetheless it



Scheme 1 Synthesis of α-sulfinyl germylenes **1a** and **1b** from sulfinyl-carbanions.



Scheme 2 Synthesis of complexes **2a** and **2b**.

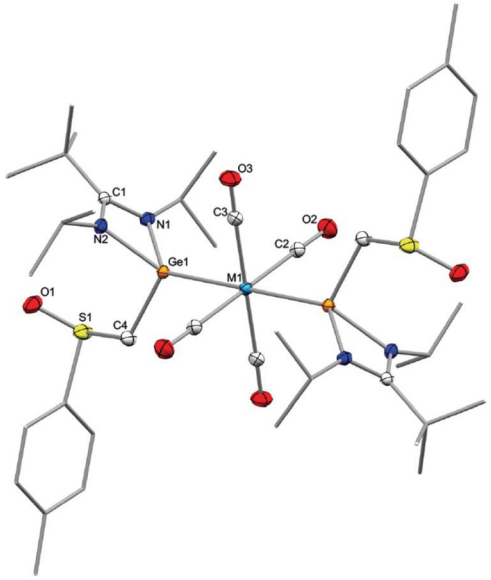


Fig. 2 Molecular structures of **2a** (M1 = W) and **2b** (M1 = Mo). Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond distances [Å] and bond angles [°] for **2a**: Ge1–N1 1.951(2); Ge1–N2 1.961(2); Ge1–C4 2.002(2); C1–N1 1.344(3); C1–N2 1.335(3); Ge1–W1 2.519(1); N1–Ge1–N2 66.61(7); N1–Ge–C4 101.18(8); N2–Ge1–C4 102.18(9); N1–Ge1–W1 132.68(5); N2–Ge1–W1 127.82(5); C4–Ge–W1 115.30(6). Selected bond distances [Å] and bond angles [°] for **2b**: Ge1–N1 1.955(4); Ge1–N2 1.964(4); Ge1–C4 2.008(4); C1–N1 1.343(5); C1–N2 1.338(5); Ge1–Mo1 2.526(1); N1–Ge1–N2 66.47(15); N1–Ge–C4 100.89(17); N2–Ge1–C4 101.79(17); N1–Ge1–Mo1 133.06(11); N2–Ge1–Mo1 128.14(11); C4–Ge1–Mo1 115.26(13).

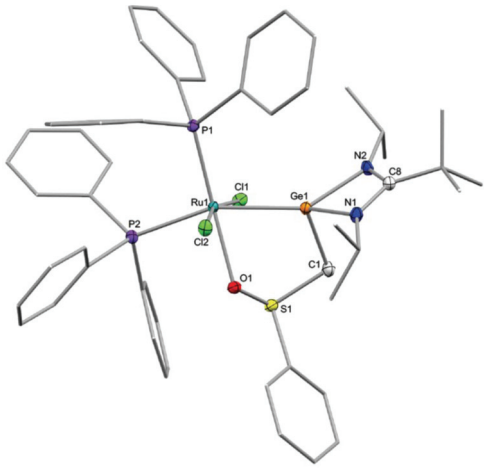
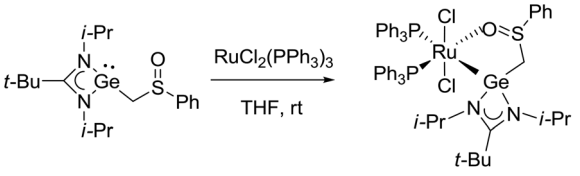


Fig. 3 Molecular structure of **3a**. Hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and bond angles [°]: Ge1–N1 1.979(4); Ge1–N2 1.951(4); Ge1–C1 2.050(5); Ge1–Ru1 2.443(1); S1–O1 1.530(3); S1–C1 1.797(5); Ru1–P1 2.266(1); Ru1–P2 2.383(1); Ru1–Cl1 2.441(1); Ru1–Cl2 2.399(1); Ru1–O1 2.185(3); N1–Ge1–N2 66.13(16); N1–Ge–C1 97.96(19); N2–Ge1–C1 96.38(17); N1–Ge1–Ru1 137.58(11); N2–Ge1–Ru1 143.65(12); Ge1–Ru1–P1 102.77(3); Ge1–Ru1–P2 156.45 (4); G1e–Ru1–O1 75.06(8); Ge1–Ru1–Cl1 78.87(3); Ge1–Ru1–Cl2 89.61 (3); P1–Ru1–O1 170.10(9); P2–Ru1–O1 84.15(9).

was not possible to separate totally complex **3a** from free PPh_3, and in the best case we have obtained **3a** containing still 10% of residual PPh_3 after washing with diethyl ether.

The ^{31}P NMR spectrum exhibits two broad signals at 24 and 55 ppm corresponding to two non-equivalent PPh_3 ligands. Furthermore a strong band in the IR spectrum at 934 cm^{-1} indicates a coordination of ruthenium to the sulfinyl group. Single crystals of **3a**, suitable for X-ray diffraction analysis, were obtained from a saturated solution of THF at −24 °C. The X-ray diffraction analysis confirmed the coordination of ruthenium by the germanium and the oxygen atom of the sulfinyl group *via* the formation of a five-membered ring, validating the bidentate characteristic of the α-sulfinyl germylene ligands **1** (Fig. 3). The ruthenium atom adopts a distorted octahedral geometry. The interatomic Ru–Ge distance (2.443(1) Å) is in the range of values obtained for previously cited germylene–ruthenium complexes.[8,15,16] The two chlorine atoms occupying the axial positions but also the two PPh_3 ligands in the *cis* position present a large deviation to the ideal octahedral angle [Cl1–Ru1–Cl2, 165.53(4)°, P1–Ru1–P2, 99.56(4)° and P1–Ru1–Ge1, 102.77(3)°] which is probably due to the steric hindrance generated from the bulky phosphine ligands and the five membered Ru(II)-metallacycle.

It is noteworthy that the geometry of this structure is especially close to the X-ray structure of $[Ru(PPh_3)_3Cl_2{\cdot}PPh_3]$ described by Grushin *et al.* in 2014 where one PPh_3 was found in the lattice without a hydrogen bond, π-stacking or coordination to the metal center,[17] reinforcing the hypothesis of the potential hemilabile nature of the germylene–sulfoxide ligand.



Scheme 3 Synthesis of complex **3a**.

Conclusions

In conclusion, we have synthesized the first heteroleptic organogermylenes containing a sulfoxide donor function to demonstrate the cohabitation of these two separate entities and to elaborate a new combination of strong and weak donors in potentially hemilabile ligands. The coordination chemistry of these new ligands has been studied, and the corresponding "*trans*" bis(germanium)–W(0) and –Mo(0) complexes have been isolated and fully characterized. Of particular interest is that with $[Ru(PPh_3)_3Cl_2]$, the germylene–sulfoxide ligand acts as a bidentate ligand leading to an original Ru(II)-metallacycle, *via* the coordination of germanium(II) and the oxygen atom of the sulfinyl group.

We are currently investigating the application of these new mixed germylene–sulfoxide ligands in enantioselective catalysis by considering the stereogenic characteristic of the sulfoxide.

Experimental

General procedures

All manipulations with air-sensitive products were performed under a dry and oxygen-free atmosphere by using a Fisher-Porter reactor, a standard Schlenk-line and glovebox techniques. Solvents were purified with an MBraun SBS-800 purification system. [iPrNC(*t*Bu)NiPr]GeCl was prepared according to the literature procedures.[6] All reagents were obtained from commercial suppliers unless otherwise stated.

Characterization

NMR spectra were recorded with the following spectrometers: 1H, Bruker Avance II 300 (300.18 MHz); 13C, Bruker Avance II 300 (75.48 MHz) at 298 K.

Mass spectra were measured on a MicroMass Maldi micro MX in an anthracene matrix (ratio product/matrix: 1/100).

Melting points were measured with a capillary electrothermal apparatus.

Single-crystal X-ray data were collected at low temperature (193(2) K) on a Bruker-AXS APEX II Quazar diffractometer equipped with a 30 W air-cooled microfocus source (**3a**) or on a Bruker-AXS PHOTON100 D8 VENTURE diffractometer (**2a** and **2b**), using MoKα radiation (λ = 0.71037 Å). The structures were solved by direct methods (SHELXS-97)[18] or by the direct intrinsic phasing method (SHELXT)[19] and refined by the full-matrix least-squares method on F^2.[20] All non-H atoms were refined with anisotropic displacement parameters.

Synthesis of (1a). LDA (53.4 mg, 0.5 mmol, 1.04 eq.) in diethyl ether (2 mL) was added dropwise to a solution of phenylmethylsulfoxide (70 mg, 0.5 mmol, 1.04 eq.) in diethyl ether (2 mL) at −78 °C. The solution was stirred for 1 hour at the same temperature (−78 °C). Then the solution was allowed to warm up at room temperature and stirred for an additional period of 45 min. Finally, the solvent was removed under reduced pressure in order to obtain a white solid. The resulting solid was dissolved in diethyl ether (2 mL) and added dropwise to a solution of [iPrNC(*t*Bu)NiPr]GeCl (138.7 mg, 0.48 mmol, 1 eq.) in diethyl ether (2.5 mL) at −78 °C. The mixture was stirred for 2.5 hours at −78 °C. Then the solution was filtered at the same temperature (−78 °C). Finally, the solvent was removed under reduced pressure to afford **1a** as a sticky oil (102 mg) in 72% yield. ^{1}H NMR (300.18 MHz, THF-d_8, 25 °C): δ 1.11 (d, $^3J_{HH}$ = 6.3 Hz, 3H, CH(C$\boldsymbol{H}_3$)$_2$); 1.14 (d, $^3J_{HH}$ = 6.3 Hz, 3H, CH(C$\boldsymbol{H}_3$)$_2$); 1.16 (d, $^3J_{HH}$ = 6.3 Hz, 3H, CH(C$\boldsymbol{H}_3$)$_2$); 1.18 (d, $^3J_{HH}$ = 6.3 Hz, 3H, CH(C$\boldsymbol{H}_3$)$_2$); 1.38 (s, 9H, C(C$\boldsymbol{H}_3$)$_3$); 2.69 (d, 1H, $^2J_{HH}$ = 13.8 Hz, GeC$\boldsymbol{H}_2$SO); 2.76 (d, 1H, $^2J_{HH}$ = 13.8 Hz, GeC$\boldsymbol{H}_2$SO); 4.31 (sept., $^3J_{HH}$ = 6.3 Hz, 2H, C$\boldsymbol{H}$(CH$_3$)$_2$); 7.36–7.47 (m, 3H, C$\boldsymbol{H}_{Ar}$); 7.65–7.70 (m, 2H, C$\boldsymbol{H}_{Ar}$). ^{13}C{^{1}H} NMR (75.48 MHz, THF-d_8, 25 °C): δ 24.3 (CH(C$\boldsymbol{H}_3$)$_2$); 24.5 (CH(C$\boldsymbol{H}_3$)$_2$); 26.9 (CH(C$\boldsymbol{H}_3$)$_2$); 29.3 (C(C$\boldsymbol{H}_3$)$_3$); 40.7(C(CH$_3$)$_3$); 47.6 (C$\boldsymbol{H}$(CH$_3$)$_2$); 47.7 (C$\boldsymbol{H}$(CH$_3$)$_2$); 61.5 (GeC$\boldsymbol{H}_2$SO); 124.4 ($\boldsymbol{C}_{Ar}$); 129.2 ($\boldsymbol{C}_{Ar}$); 129.9 ($\boldsymbol{C}_{Ar}$); 151.5 ($\boldsymbol{C}_{Ar/q}$); 171.9 (N–$\boldsymbol{C}$–N).

Synthesis of (1b). LDA (77 mg, 0.72 mmol, 1.1 eq.) in diethyl ether (2.5 mL) was added dropwise to a solution of *p*-tolylmethylsulfoxide (110 mg, 0.72 mmol, 1.1 eq.) in diethyl ether (2.5 mL) at −78 °C. The solution was stirred for 1 hour at the same temperature (−78 °C). Then the solution was allowed to warm up at room temperature and stirred for an additional period of 45 min. Finally, the solvent was removed under reduced pressure in order to obtain a white solid. The resulting solid was dissolved in diethyl ether (5 mL) and added dropwise to a solution of [iPrNC(*t*Bu)NiPr]GeCl (189 mg, 0.65 mmol, 1 eq.) in diethyl ether (5 mL) at −78 °C. The mixture was stirred for 2.5 hours at −78 °C. Then, the solution was filtered at the same temperature (−78 °C) and concentrated until it attains 1 mL of solution. The product was extracted with pentane (2 × 5 mL) and the solvents were removed in order to afford a sticky oil (220 mg) in 82% yield. The compound is stable and storable at −24 °C under an inert atmosphere of argon. ^{1}H NMR (300.18 MHz, THF-d_8, 25 °C): δ 1.11 (d, $^3J_{HH}$ = 6.3 Hz, 3H, CH(C$\boldsymbol{H}_3$)$_2$); 1.15 (d, $^3J_{HH}$ = 6.3 Hz, 6H, CH(C$\boldsymbol{H}_3$)$_2$); 1.16 (d, $^3J_{HH}$ = 6.3 Hz, 3H, CH(C$\boldsymbol{H}_3$)$_2$); 1.38 (s, 9H, C(C$\boldsymbol{H}_3$)$_3$); 2.36 (s, 3H, *p*-C$\boldsymbol{H}_3$); 2.69 (d, 1H, $^2J_{HH}$ = 13.8 Hz, GeC$\boldsymbol{H}_2$SO); 2.76 (d, 1H, $^2J_{HH}$ = 13.8 Hz, GeC$\boldsymbol{H}_2$SO); 4.31 (sept., $^3J_{HH}$ = 6.3 Hz, 2H, C$\boldsymbol{H}$(CH$_3$)$_2$); 7.26 (d, 2H, $^3J_{HH}$ = 8.2 Hz, C$\boldsymbol{H}_{Ar}$); 7.54 (m, 2H, $^3J_{HH}$ = 8.2 Hz, C$\boldsymbol{H}_{Ar}$). ^{13}C{^{1}H} NMR (75.48 MHz, THF-d_8, 25 °C): δ 21.1 (*p*-$\boldsymbol{C}$H$_3$); 24.3 (CH(C$\boldsymbol{H}_3$)$_2$); 24.5 (CH(C$\boldsymbol{H}_3$)$_2$); 26.9 (CH(C$\boldsymbol{H}_3$)$_2$); 27.0 (CH(C$\boldsymbol{H}_3$)$_2$); 29.4 (C(C$\boldsymbol{H}_3$)$_3$); 40.7 ($\boldsymbol{C}$(CH$_3$)$_3$); 47.6 ($\boldsymbol{C}$H(CH$_3$)$_2$); 47.7 ($\boldsymbol{C}$H(CH$_3$)$_2$); 61.9 (Ge$\boldsymbol{C}$H$_2$SO); 124.3 ($\boldsymbol{C}_{Ar}$); 129.8 ($\boldsymbol{C}_{Ar}$); 139.8 ($\boldsymbol{C}_{Ar/q}$); 148.6 ($\boldsymbol{C}_{Ar/q}$); 171.8 (N–$\boldsymbol{C}$–N). IR (Nujol, cm^{-1}): 1493 (med) (C=C$_{arene}$), 1017 (med) (SO).

Synthesis of (2a). Germylene–sulfoxide **1b** (135 mg, 0.330 mmol, 1 eq.) was dissolved in THF (5 mL). The solution was then added to tetracarbonyl(1,5-cyclooctadiene)tungsten (0) (101 mg, 0.165 mmol, 0.5 eq.) in THF (2 mL). The mixture was stirred for 15 hours at room temperature, then filtered and the solvent was removed under reduced pressure. Finally, the solid was washed with pentane (2 × 3 mL) to obtain a pale yellow solid (143 mg) in 78% yield. Crystallization from THF at 6 °C gave pale yellow crystals suitable for the X-ray study. M.p.: 117 °C (decomposition); ^{1}H NMR (300.18 MHz, C$_6$D$_6$, 25 °C): δ 1.29 (s, 18H, C(C$\boldsymbol{H}_3$)$_3$); 1.45 (d, $^3J_{HH}$ = 6.3 Hz, 6H, CH(C$\boldsymbol{H}_3$)$_2$); 1.48 (d, $^3J_{HH}$ = 6.3 Hz, 6H, CH(C$\boldsymbol{H}_3$)$_2$); 1.57 (d, $^3J_{HH}$ = 6.3 Hz, 12H, CH(C$\boldsymbol{H}_3$)$_2$); 1.99 (s, 6H, *p*-C$\boldsymbol{H}_3$); 2.94 (d, 2H, $^2J_{HH}$ = 13.8 Hz, GeC$\boldsymbol{H}_2$SO); 3.35 (d, 2H, $^2J_{HH}$ = 13.8 Hz, GeC$\boldsymbol{H}_2$SO); 4.34 (sept., $^3J_{HH}$ = 6.3 Hz, 2H, C$\boldsymbol{H}$(CH$_3$)$_2$); 4.43 (sept., $^3J_{HH}$ = 6.3 Hz, 2H, C$\boldsymbol{H}$(CH$_3$)$_2$); 6.88 (d, 4H, $^3J_{HH}$ = 8.2 Hz, C$\boldsymbol{H}_{Ar}$); 7.51 (d, 4H, $^3J_{HH}$ = 8.2 Hz, C$\boldsymbol{H}_{Ar}$). ^{13}C{^{1}H} NMR (75.48 MHz, C$_6$D$_6$, 25 °C): δ 21.1 (*p*-$\boldsymbol{C}$H$_3$); 23.2 (CH(C$\boldsymbol{H}_3$)$_2$); 23.3 (CH(C$\boldsymbol{H}_3$)$_2$); 26.0 (CH(C$\boldsymbol{H}_3$)$_2$); 26.2 (CH(C$\boldsymbol{H}_3$)$_2$); 29.3 (C(C$\boldsymbol{H}_3$)$_3$); 39.8 ($\boldsymbol{C}$(CH$_3$)$_3$); 47.8 ($\boldsymbol{C}$H(CH$_3$)$_2$); 47.9 ($\boldsymbol{C}$H(CH$_3$)$_2$); 59.6 (Ge$\boldsymbol{C}$H$_2$SO); 123.7 (C$_{Ar}$); 129.9 (C$_{Ar}$); 139.7 (C$_{Ar/q}$); 148.2 (C$_{Ar/q}$); 175.2 (N–$\boldsymbol{C}$–N); 208.0 ($\boldsymbol{C}$O). MS *m*/*z* (%): 1002 ([M − (CO)$_4$]$^+$). IR (Nujol, cm^{-1}): 2035 (s) (CO), 1996 (s) (CO), 1938 (s) (CO), 1021 (med) (SO).

Synthesis of (2b). Germylene–sulfoxide **1b** (150 mg, 0.367 mmol, 1 eq.) was dissolved in THF (5 mL). The solution was then added to (bicyclo[2.2.1]hepta-2,5-diene)tetracarbonylmolybdenum(0) (55 mg, 0.184 mmol, 0.5 eq.) in THF (2 mL) at room temperature. The mixture was stirred for 15 hours at room temperature, then filtered and the solvent was removed under reduced pressure. Finally, the solid was washed with pentane

(2 × 3 mL) to obtain a pale yellow solid (159 mg) in 84% yield. Crystallization from THF at 6 °C gave yellow crystals suitable for the X-ray study. M.p.: 103 °C; ^{1}H NMR (300.18 MHz, C_6D_6, 25 °C): δ 1.28 (s, 18H, C(C$\boldsymbol{H}_3$)$_3$); 1.46 (d, $^{3}J_{HH}$ = 6.3 Hz, 12H, CH(C$\boldsymbol{H}_3$)$_2$); 1.56 (d, $^{3}J_{HH}$ = 6.3 Hz, 6H, CH(C$\boldsymbol{H}_3$)$_2$); 1.58 (d, $^{3}J_{HH}$ = 6.3 Hz, 6H, CH(C$\boldsymbol{H}_3$)$_2$); 1.99 (s, 6H, *p*-C$\boldsymbol{H}_3$); 2.90 (d, 2H, $^{2}J_{HH}$ = 13.8 Hz, GeC$\boldsymbol{H}_2$SO); 3.35 (d, 2H, $^{2}J_{HH}$ = 13.8 Hz, GeC$\boldsymbol{H}_2$SO); 4.27 (sept., $^{3}J_{HH}$ = 6.3 Hz, 2H, C$\boldsymbol{H}$(CH$_3$)$_2$); 4.37 (sept., $^{3}J_{HH}$ = 6.3 Hz, 2H, C$\boldsymbol{H}$(CH$_3$)$_2$); 6.88 (d, 4H, $^{3}J_{HH}$ = 8.2 Hz, C$\boldsymbol{H}_{Ar}$); 7.53 (d, 4H, $^{3}J_{HH}$ = 8.2 Hz, C$\boldsymbol{H}_{Ar}$). ^{13}C{^{1}H} NMR (75.48 MHz, C_6D_6, 25 °C): δ 21.1 (*p*-C$\boldsymbol{H}_3$); 23.2 (CH(C$\boldsymbol{H}_3$)$_2$); 23.4 (CH(C$\boldsymbol{H}_3$)$_2$); 26.2 (CH(C$\boldsymbol{H}_3$)$_2$); 26.4 (CH(C$\boldsymbol{H}_3$)$_2$); 29.3 (C(C$\boldsymbol{H}_3$)$_3$); 39.8 (C(CH$_3$)$_3$); 47.9 (C$\boldsymbol{H}$(CH$_3$)$_2$); 50.0 (C$\boldsymbol{H}$(CH$_3$)$_2$); 59.8 (GeCH$_2$SO); 123.7 (C_{Ar}); 129.9 (C_{Ar}); 139.7 ($C_{Ar/q}$); 148.4 ($C_{Ar/q}$); 174.8 (N–C–N); 216.5 (CO). IR (Nujol, cm^{-1}): 2021 (s) (CO), 1999 (s) (CO), 1905 (s) (CO), 1015 (med) (SO). MS *m*/*z* (%): 1026 ([M^{+}]).

Synthesis of (3a). Germylene–sulfoxide **1a** (151 mg, 0.38 mmol, 1eq.) with tris(triphenylphosphine)ruthenium(II) dichloride (364 mg, 0.38 mmol, 1eq.) in THF (5 mL) was stirred for 15 hours at room temperature. Then, the mixture was filtered and the solvent was removed under reduced pressure in order to obtain a red solid. Finally, the resulting solid was washed with diethyl ether (3 × 5 mL) to afford a red solid (240 mg). M.p.: 145 °C (decomposition); ^{1}H NMR (300.18 MHz, C_6D_6): δ 0.78 (d, $^{3}J_{HH}$ = 6.3 Hz, 3H, CH(C$\boldsymbol{H}_3$)$_2$); 0.88 (d, $^{3}J_{HH}$ = 6.3 Hz, 3H, CH(C$\boldsymbol{H}_3$)$_2$); 0.94 (s, 9H, C(C$\boldsymbol{H}_3$)$_3$); 1.09 (d, $^{3}J_{HH}$ = 6.3 Hz, 3H, CH(C$\boldsymbol{H}_3$)$_2$); 1.35 (d, $^{3}J_{HH}$ = 6.3 Hz, 3H, CH(C$\boldsymbol{H}_3$)$_2$); 2.86 (d, 1H, $^{2}J_{HH}$ = 13.8 Hz, GeC$\boldsymbol{H}_2$SO); 3.61 (d, 1H, $^{2}J_{HH}$ = 13.8 Hz, GeC$\boldsymbol{H}_2$SO); 3.69 (sept., $^{3}J_{HH}$ = 6.3 Hz, 2H, C$\boldsymbol{H}$(CH$_3$)$_2$); 6.90 (m, 3H, C$\boldsymbol{H}_{Ar(sulfoxide)}$); 7.09 (m, 19H, C$\boldsymbol{H}_{Ar(phosphine)}$); 7.45 (m, 2H, C$\boldsymbol{H}_{Ar(sulfoxide)}$); 7.93 (m, 11H, C$\boldsymbol{H}_{Ar(phosphine)}$). ^{13}C{^{1}H} NMR (75.48 MHz, C_6D_6): δ 24.0 (CH(C$\boldsymbol{H}_3$)$_2$); 24.8 (CH(C$\boldsymbol{H}_3$)$_2$); 25.0 (CH(C$\boldsymbol{H}_3$)$_2$); 25.5 (CH(C$\boldsymbol{H}_3$)$_2$); 29.2 (C(C$\boldsymbol{H}_3$)$_3$); 38.9 (C(CH$_3$)$_3$); 47.5 (C$\boldsymbol{H}$(CH$_3$)$_2$); 47.9 (C$\boldsymbol{H}$(CH$_3$)$_2$); 49.2 (GeCH$_2$SO); 125.8 ($C_{Ar(sulfoxide)}$); 127.0 ($^{3}J_{PC}$ = 9.0 Hz, $C_{Ar(phosphine)}$); 128.7 ($C_{Ar(phosphine)}$); 128.9 ($C_{Ar(sulfoxide)}$); 125.8 ($C_{Ar(sulfoxide)}$); 134.2 ($^{2}J_{PC}$ = 19.6 Hz, $C_{Ar(phosphine)}$); 138.0 ($^{1}J_{PC}$ = 12.2 Hz, $C_{Ar/q(phosphine)}$); 144.2 ($C_{Ar/q(sulfoxide)}$); 175.5 (N–C–N). ^{31}P NMR (121.49 MHz, C_6D_6): δ 24.5 (br, Ru-P$\boldsymbol{P}$Ph$_3$); 55.5 (br, Ru-$\boldsymbol{P}$Ph$_3$). MS *m*/*z* (%): 830 (M − PPh$_3$), 795 (M − (PPh$_3$ + Cl)), 760 (M − (PPh$_3$ + Cl + Cl)). IR (Nujol, cm^{-1}): 934 (med) (SO).

Conflicts of interest

There are no conflicts to declare.

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