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Mariana Lozano González,[a,b] Laura Bousquet,[a] Sophie Hameury,[a] Cecilio Alvarez Toledano,[b] Nathalie Saffon-Merceron,[c] Vicenç Branchadell,[d] Eddy Maerten*,[a] and Antoine Baceiredo*,[a]

Abstract: A new carbon(0) complex **2** with two different L ligands, a phosphine and a sulfoxide, was synthesized and fully characterized. This new type of carbone exhibits excellent coordination ability, in contrast to the related phosphine/sulfide-supported carbon(0) complexes. Several organometallic complexes were isolated and, of special interest, the ν_{av}(CO) value of Rh(I)-dicarbonyl complex indicates that **2** has a donor capability superior to classical NHCs.

The discovery of the first stable carbenes almost 30 years ago[1] has initiated intensive research leading to a deeper understanding of physical and chemical properties of these divalent species.[2] As a consequence, stable carbenes rapidly became essential as synthetic tools,[3] organocatalysts,[4] and efficient ligands for transition-metal homogeneous catalysis.[5] As represented by N-heterocyclic carbenes (NHCs) **I**, the catalytic activity of the corresponding NHC-metal-complexes relies mainly on the electronic properties of **I** as strong electron-donating auxiliary ligands. The related divalent carbon(0) **II** species (also named carbones), bearing two lone pairs on the central carbon atom, discovered by Ramirez in the 60s,[6] were considered as such only very recently. Indeed, Frenking et al. have suggested that, based on their electronic structure and chemical behavior, these molecules are best described as a carbon atom in the oxidation state zero stabilized by two L-ligands.[7] This vision has shed new light on this family of compounds encouraging the development of new carbon(0) complexes by combining various types of L-ligands.[8] It is well established that carbon(0) complexes such as cyclic carbodiphosphoranes (CDP) **III**, cyclic bent allenes **IV** and carbodicarbenes **V** present a powerful electron-donating ability, which is far stronger than that of classical NHCs **I**.[9] Therefore, carbon(0) species have been used as ligands for the preparation of metal complexes[10] showing interesting catalytic activities.[11-14] Although the robustness of the corresponding organometallics complexes still deserves improvement, their catalytic efficiency often surpass that observed with the related NHC-metal catalysts. Of particular interest, Stephen recently took advantage of the presence of the second lone pair at the central carbon atom to stabilize electron-deficient organometallic complexes thus obtaining high activities for hydrogenation reactions.[15] Alcarazo used the four electron-donor ability of carbodiphosphoranes **II** (L = PR_3) to stabilize the highly reactive dihydroborenium ion (BH_2^+).[16] Finally, Ong evidenced an unexpected π-accepting ability of carbodicarbenes **V** resulting in an ambiphilic-type reactivity, allowing the activation of small molecules.[17]

As a part of our program to design, synthesize and develop new carbon(0) complexes, we report here the synthesis and the characterization of a new phosphine/sulfoxide-supported carbon(0) complex **2** and its ability to act as an efficient ligand for the preparation of transition metal complexes.

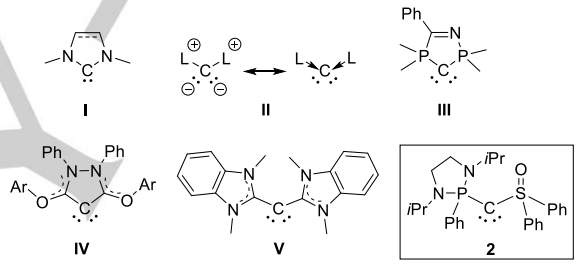
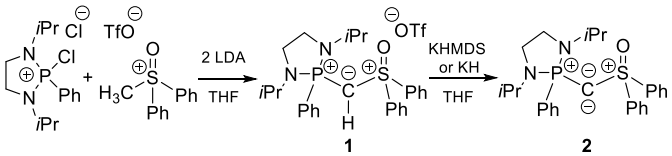


Figure 1. Carbenes and carbon(0) complexes (for a better readability, formal charges were omitted in **III**, **IV**, **V** and **2**.

The phosphine/sulfoxide carbon(0) complex **2** was prepared in two steps from the corresponding chlorophosphonium and methyldiphenylsulfoxonium salts in presence of 2 equivalents of a non-nucleophilic strong base (LDA) (Scheme 1).[18] In a second step, the deprotonation of salt **1** was performed in THF solution at RT, either with potassium hydride (KH) or potassium hexamethyldisilazane (KHMDS) leading to the selective formation of **2**, which was isolated in 69 % overall yield.



Scheme 1. Synthesis of ylide **1** and phosphine/sulfoxide carbon(0) complex **2**.

In the ^{31}P NMR spectrum, **2** displays a signal shifted to higher field (29.0 ppm) compared to **1** (45.0 ppm). The central carbon of **2** exhibits a doublet signal at δ = 31.2 ppm ($^1J_{PC}$ = 84.8 Hz) with a large coupling constant in agreement with a direct P-C connectivity. The structures of both **1** and **2** were confirmed by

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X-Ray diffraction analysis (Figures 2 and 3).[19] The P1-C1 bond length [1.6563(13) Å] in **2** is significantly shorter than in **1** [1.7190(15) Å] and the value remains slightly longer than those reported for CDPs (1.584 - 1.648 Å).[20] The S1-C1 bond length also undergoes significant shortening upon deprotonation [from 1.6539(15) Å in **1** to 1.5929(14) Å in **2**], this value is the shortest S-C bond length reported to date in the sulfur-stabilized carbone series (1.602 – 1.713 Å).[8c,h,21] The S1-O1, S1-C16, and S1-C22 bond lengths get slightly longer ($\Delta_{S\text{-}X}$max = + 0.02 Å). These data clearly indicate the delocalization of p_π-lone pair at the carbon center toward sulfoxide ligand. Similarly to the case of carbodiphosphoranes,[7a] the P-C-S angle remains almost unchanged between the precursor **1** and carbone **2** [120.98(9)° vs 120.74(8)° respectively], and this value is in the range of those observed for iminosulfane/phosphine- or bis(iminosulfane)-carbones.[8a,h]

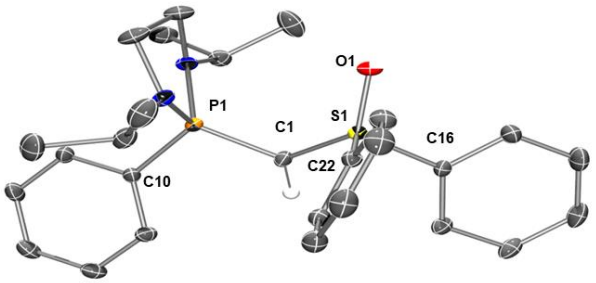


Figure 2. Molecular structure of **1**. Thermal ellipsoids represent 30 % probability. H atoms (except on C1) and counterion (TfO^-) were omitted for clarity. Selected bond lengths [Å] and angles [°]: S1-C1 1.6539(15), P1-C1 1.7190(15), S1-C16 1.7764(15), S1-C22 1.7771(16), P1-C10 1.7888(16), S1-O1 1.4531(12), S1-C1-P1 120.98(9).

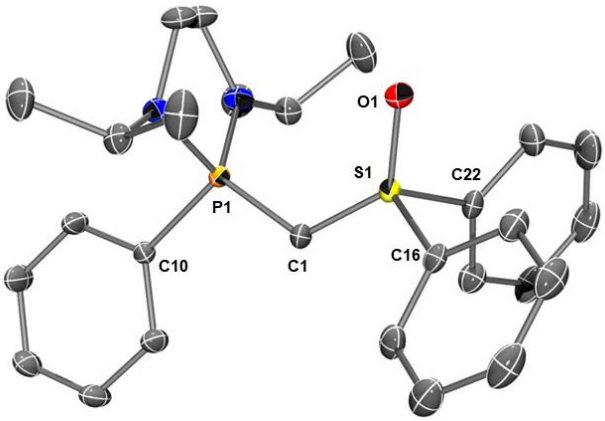


Figure 3. Molecular structure of **2**. Thermal ellipsoids represent 30 % probability. H atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: S1-C1 1.5929(14), P1-C1 1.6563(13), S1-C16 1.7995(14), S1-C22 1.7956(14), P1-C10 1.8083(13), S1-O1 1.4676(10), S1-C1-P1 120.74(8).

To gain more insight into the electronic structures of **1** and **2**, DFT calculation were performed at the M06-2X/6-31G(d) level of theory. The optimized geometries are consistent with the experimental X-Ray data (See Sup. Info for complete comparison). The variation of Wiberg bond indices ongoing from **1** to **2** (for P1-C1: +0.266, C1-S1: +0.241 and S1-O1: -0.089) correlates with the measurement obtained from the X-Ray data (for ΔP1-C1: -0.0627 Å, ΔC1-S1: -0.0610 Å and ΔS1-O1: +0.0145 Å). [22] The central carbon atom in **2** bears a large negative charge (-1.388) similarly to iminosulfane/phosphine-carbone (-1.38).[8h] The two highest occupied molecular orbitals (HOMO-1 $n_{\sigma C}$, HOMO $n_{\pi C}$) correspond to the two lone pairs at the central carbon in **2** (Figure 4). The HOMO-1, the in-plane σ-lone pair, is partially deformed towards the sulfur atom of sulfoxide ligand, suggesting a negative hyperconjugaison $n_{\sigma C}$ / $\sigma^*_{(S\text{-}C\text{ or }S\text{-}O)}$.

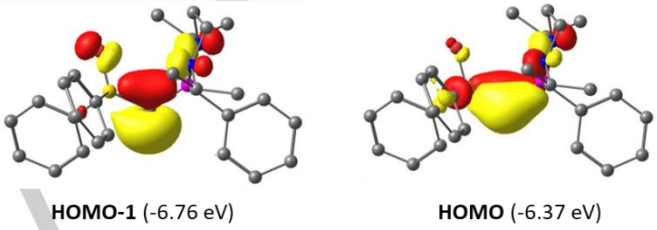
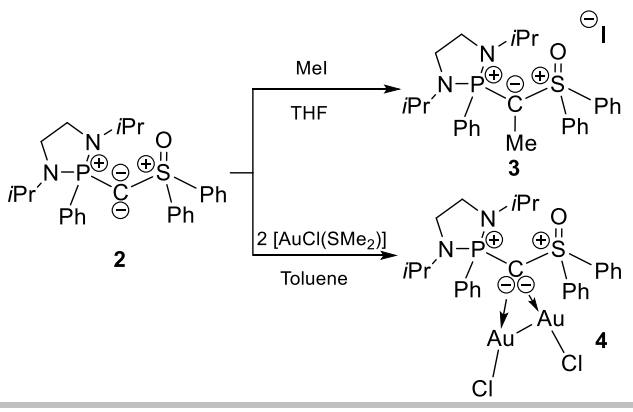


Figure 4. Calculated frontier orbitals of **2** at the M06-2X/6-31G(d) level of theory.

The nucleophilic character of **2** was experimentally confirmed by an immediate reaction with methyl iodide, giving raise to the corresponding C-methylated salt **3**. The ^{31}P NMR spectrum indicates a selective reaction with a unique signal at δ = 51.9 ppm. The methylation was confirmed by the presence of two characteristic doublets at δ = 1.72 ppm (J_{PH} = 12.5 Hz) and at δ = 16.4 (d, J_{CP} = 9.3 Hz) in the ^1H and ^{13}C NMR spectra respectively. Compound **3** was isolated in crystalline form and its structure was confirmed by X-Ray diffraction analysis (See Supporting Information). The molecular structure of **3** shows a significantly elongated S1-C1 bond [1.6717(16) Å] relative to that of **2** [1.5929(14) Å], which is in good agreement with the loss of one of the two lone pairs at the central carbon atom upon C-methylation.



Scheme 2. Methylation and complexation of **2**.

The potential usefulness of phosphine/sulfoxide-carbone **2** as ligand for transition metals was demonstrated by selective reaction with two equivalents of [AuCl(SMe$_2$)] affording cleanly the neutral *gem*-aurated complex **4**, in good yield (68 %). Similarly to carbodisphosphoranes and carbodicarbenes,[8b,23] the formation of complex **4** demonstrates the ability of **2** to act as a four-electron donor ligand. In the ^{31}P NMR spectrum **4** displays a singlet signal at δ = 41.2 ppm, while the central carbon atom appears as a doublet at δ = 35.8 ppm (J_{CP} = 47.5 Hz) in ^{13}C NMR spectrum. Complex **4** has been isolated as colorless crystals from a concentrated dichloromethane solution, and its structure was unambiguously confirmed by X-Ray diffraction analysis (Figure 5).

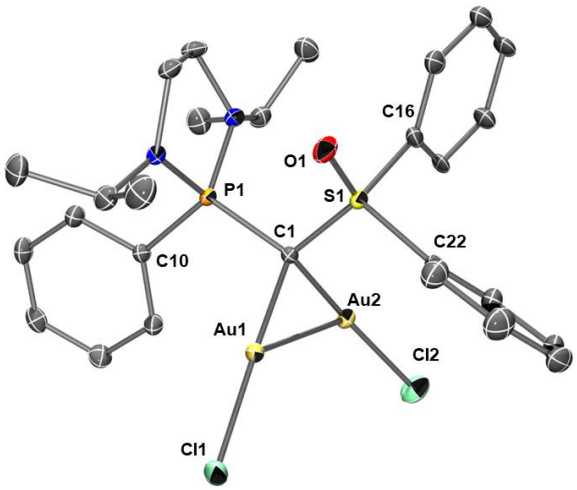
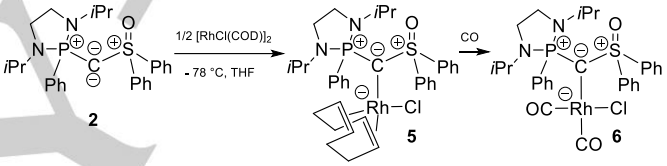


Figure 5. Molecular structure of **4**. Thermal ellipsoids represent 30 % probability. H and disordered atoms and solvent molecule (dichloromethane) were omitted for clarity. Selected bond lengths [Å] and angles [°]: S1-C1 1.737(4), P1-C1 1.781(4), C1-Au1 2.071(4), C1-Au2 2.056(4), P1-C10 1.805(4), S1-C16 1.819(7), S1-C22 1.786(4), O1-S1 1.447(3), Au1-Au2 3.018(1), Au1-Cl1 2.287(1), Au2-Cl2 2.289(1), S1-C1-P1 110.2(2), P1-C1-Au1 109.92(19), Au1-C1-Au2 93.99(15), C1-Au1-Au2 42.81(11), Au1-Au2-C1 43.20(11), C1-Au1-Cl1 176.22(11), C1-Au2-Cl2 172.52(11).

The C-Au bond lengths [2.056(4) and 2.071(4) Å] are shorter than those observed in the related carbodisphosphorane- and carbodicarbene-diaurated complexes (2.074, 2.078 Å and 2.080, 2.103 Å respectively). The aurophilic interaction is classical with Au1-Au2 distance of 3.018(1) Å, which is in the range of other *gem*-diaurated carbones (2.952 - 3.143 Å).[8b, 8h, 18c, 20] Finally, the P1-C1 [1.781(4) Å] and the S1-C1 [1.737(4) Å] bonds lengths are significantly longer than in **1**, typical for single bonds (P-C : 1.79 - 1.82 Å and S-C : 1.73 – 1.75 Å)[24] confirming that the two lone pairs are involved in the formation of complex **4**.

One established method for measuring the electron-donor ability of ligands is based on the carbonyl stretching frequencies of *cis*-[RhCl(CO)$_2$L] complexes.[25] Therefore, phosphine/sulfoxide-carbone **2** was reacted with 0.5 equiv. of [RhCl(COD)]$_2$, leading to the clean formation of rhodium(I) complex **5** as indicated by a doublet at δ = 42.6 ppm (d, J_{PRh} = 2.7 Hz) in the ^{31}P spectrum. In the ^{13}C NMR spectrum, the central carbon atom appears at δ = 16.3 ppm as a doublet of doublet (J_{CP} = 56.7 Hz, J_{CRh} = 37.5 Hz). Complex **5** is stable in solution at low temperature, but decomposes slowly at RT. The corresponding Rh(I) dicarbonyl complex **6** was prepared by bubbling carbon monoxide gas through a THF solution of **5** at -78 °C (Scheme 3). The formation of **6** was indicated by a color change from yellow to brown-red. The ^{31}P spectrum indicates a new doublet at δ = 43.3 ppm (J_{PRh} = 2.3 Hz) and in the ^{13}C NMR spectrum, the signal corresponding to the central carbon atom is relatively deshielded at δ = 20.8 ppm (J_{CP} = 66.6 Hz, J_{CRh} = 33.0 Hz) compared to **5**.[26] The molecular structures of both complexes **5** and **6** were confirmed by X-ray diffraction analysis (Figures 6 and 7). In both complexes, P1-C1 [1.7070(14) Å (**5**) and 1.709(2) Å (**6**)] and S1-C1 [1.6400(14) Å (**5**) and 1.654(2) Å (**6**)] bond lengths are very similar to those observed in **1** and **3**, meaning that only one lone pair of the central carbon atom interacts with the Rh center.



Scheme 3. Formation of Rh(I) complexes **5** and **6**.

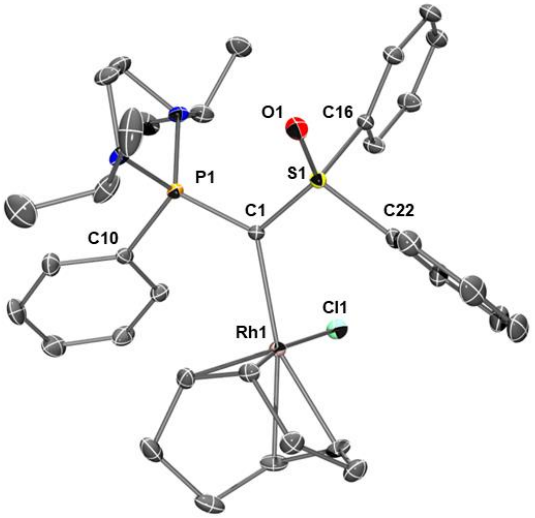


Figure 6. Molecular structure of **5**. Thermal ellipsoids represent 30 % probability. H atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: S1-C1 1.6400(14), P1-C1 1.7070(14), C1-Rh1 2.1757(13), P1-C10 1.8144(14), S1-C16 1.7996(15), S1-C22 1.7928(15), O1-S1 1.4650(11), Rh1-Cl1 2.4503(4), S1-C1-P1 114.36(8), P1-C1-Rh1 125.80(7), Rh1-C1-S1 118.60(7).

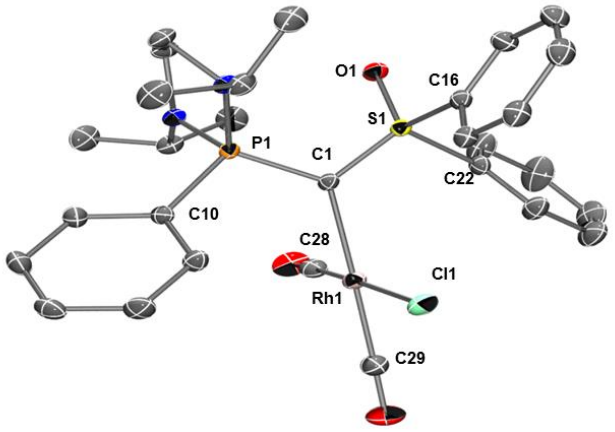


Figure 7. Molecular structure of **6**. Thermal ellipsoids represent 30 % probability. H and disordered atoms and solvent (C_6D_6) were omitted for clarity. Selected bond lengths [Å] and angles [°]: S1-C1 1.654(2), P1-C1 1.709(2), C1-Rh1 2.165(2), P1-C10 1.806(2), S1-C16 1.794(2), S1-C22 1.788(2), O1-S1 1.460(2), Rh1-Cl1 2.400(1), Rh1-C28 1.824(3), Rh1-C29 1.874(3), S1-C1-P1 113.63°(12), S1-C1-Rh1 119.82(11), Rh1-C1-P1 125.02(11), C1-Rh1-Cl1 94.46(6), Cl1-Rh1-C29 85.06(8), C29-Rh1-C28 90.60(11), C28-Rh1-C1 89.95(9).

The IR spectrum of **6** shows the characteristic CO-stretching frequencies with an average value of 2016 cm^{-1}, which is in the range of those observed for cyclic or acyclic bent allenes (2018 and 2014 cm^{-1} respectively).[5b, 9b, 9c, 27] Therefore, phosphine/sulfoxide carbone **2** appears to be stronger electron-donating ligand than classical NHCs (2060 – 2036 cm^{-1}) but weaker compared to cyclic carbodiphosphoranes (2001 cm^{-1}) (Figure 8).[9a, 28]

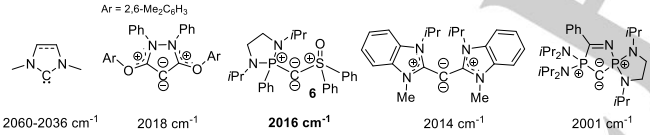


Figure 8. Comparison of ν_{av}(CO) stretching frequencies of *cis*-[RhCl(CO)$_2$L] complexes.

In summary, we have successfully synthesized and characterized an original phosphine/sulfoxide-carbone **2** easily obtained from the corresponding cationic salt. As expected, the introduction of the sulfoxide ligand dramatically enhances the stability of this new carbon(0) complex. In comparison with previous phosphine/sulfide-carbone model, **2** exhibits an excellent coordination ability and thus allowed the stabilization and characterization of several organometallic complexes [Au(I), Rh(I)]. The carbone character of **2** was demonstrated by the isolation of neutral *gem*-aurated complex **4**, establishing the ability of ligand **2** to act as a four-electron donor. Moreover, the electron-donating character of **2** is much stronger than that of NHCs and we can expect that the corresponding transition-metal complexes could exhibit interesting catalytic activities. Efforts are currently underway to extend the diversity of organometallic complexes and in order to test their catalytic activities.

Acknowledgements

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Keywords: carbon(0) complexes • phosphine • sulfoxide • ligand • σ-donor

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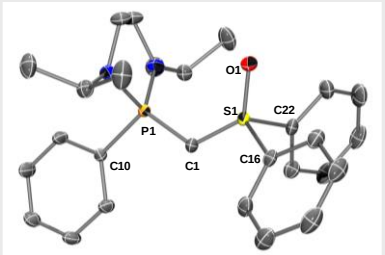
Layout 1:

COMMUNICATION

A stable phosphine/sulfoxide carbone was isolated and fully characterized by NMR spectroscopy and by X-Ray crystallography. This species exhibits excellent coordination ability and the corresponding Rh(I)-dicarbonyl complex indicates a strong nucleophilic character, in clear agreement with theoretical calculations.



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Phosphine/Sulfoxide-Supported Carbon(0) Complex