



Account / Revue

New anionic and dianionic polydentate systems featuring ancillary phosphinosulfides as ligands in coordination chemistry and catalysis

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Received 24 August 2006; accepted after revision 23 October 2006

Available online 18 December 2006

Abstract

This article provides an overview of the chemistry of monoanionic S–P–S and dianionic S–C–S ligands featuring two phosphosulfide ligands as pendant groups. These new pincer-type structures are easily assembled from phosphinines and the bis-sulfide derivative of the bis(diphenylphosphino)methane, respectively. Monoanionic S–P–S pincer ligands easily coordinate group 10 and group 9 metal fragments through displacement reactions. Palladium(II) complexes of S–P–S ligands efficiently catalyze cross-coupling processes, allowing the formation of boronic esters and biphenyl derivatives. Rh(I) complexes of S–P–S ligands react in a regioselective way with small molecules (O₂, SO₂, CS₂, MeI) to afford the corresponding Rh(I) or Rh(III) derivatives. S–C–S dianionic ligands, which are readily obtained through a bis-metallation at the central carbon atom of Ph₂P(=S)CH₂P(=S)Ph₂, react with Pd(II) and Ru(II) precursors to afford new carbene complexes. Samarium and thulium alkylidene complexes of these S–C–S dianionic ligands were synthesized in a similar way. Reaction of the lanthanide derivatives with ketones or aldehydes yields olefinic derivatives through a ‘Wittig-like’ process. *To cite this M. Doux et al., C. R. Chimie 10 (2007).* © 2006 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

Résumé

Dans cet article est présentée notre contribution à la chimie de ligands « pinceurs » anionique S–P–S et dianionique S–C–S, possédant tous deux des bras sulfure de phosphine. Ces nouveaux types de ligands pinceurs sont obtenus simplement, respectivement à partir de phosphinines et du dérivé bis sulfure du ligand commercial bis(diphenylphosphino)methane. Le ligand pinceur S–P–S monoanionique a pu être coordonné à de nombreux centres métalliques (U(IV) à Cu(I)). Les complexes de palladium(II) de ce ligand se sont montrés efficaces dans des processus de couplage croisé permettant la formation d’esters boroniques et de dérivés biphenyles. Un complexe de Rh(I) incorporant le ligand S–P–S réagit de manière régiosélective avec de « petites » molécules (O₂, SO₂, CS₂, MeI) pour conduire aux dérivés de Rh(I) ou Rh(III) correspondants. Le ligand dianionique S–C–S a été obtenu par double déprotonation du carbone central de Ph₂P(=S)CH₂P(=S)Ph₂. La réaction de ce ligand avec des précurseurs de Pd(II) et de Ru(II) a conduit à la formation de nouveaux complexes carbéniques. Des

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complexes alkylidènes de samarium et de thulium ont aussi été synthétisés. La réaction de ces complexes de lanthanides avec des cétones ou aldéhydes a conduit aux dérivés alcènes correspondants par un mécanisme de type « Wittig » **Pour citer cet article** : M. Doux et al., C. R. Chimie 10 (2007).

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Keywords: Phosphinine; Pincer ligands; Transition metals; Lanthanides; DFT calculations

Mots-clés : Phosphinine ; Ligands pinceurs ; Métaux de transition ; Lanthanides ; Calculs DFT

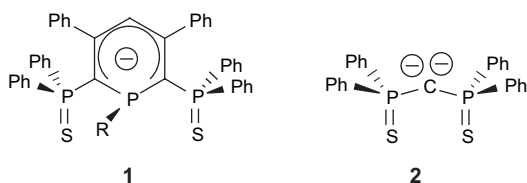
1. Introduction

After seminal report by Shaw in the 1970s, the chemistry of pincer ligands has undergone a rapid development, especially over the last decade [1]. Systems featuring a central carbon ligand and ancillary heteroatomic ligands (O, N, P) have found many applications in coordination chemistry and catalysis, and their chemistry has been extensively reviewed. Comparatively, only a moderate attention has been paid so far to structures featuring sulfur-based ligands as pendent arms and most studies exclusively focused on the chemistry of S–C–S pincer backbones in which the central carbon ligand belongs to a benzene ring, the sulfur ligands being a thioether, a thioketone or a phosphinosulfide [2]. As part of a new program aimed at exploring the use of new polydentate structures featuring ancillary phosphinosulfide ligands in coordination chemistry and catalysis, we recently developed an access to a new class of monoanionic S–P–S **1** and dianionic S–C–S **2** systems (Scheme 1). In this account we summarize our contribution in this area.

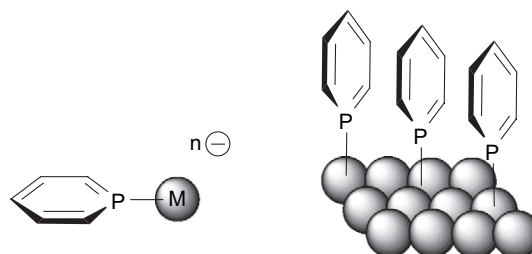
2. Results and discussion

2.1. S–P–S pincer ligands

The discovery of ligands **1** arises from our studies on the chemistry of phosphinines. Over the last few years we showed that these aromatic phosphorus derivatives which behave as powerful electron acceptor ligands could be successfully employed to stabilize electron-



Scheme 1. Monoanionic bis(phosphinosulfide) phosphacyclohexadienyl **1** and dianionic bis(phosphinosulfide) methanediide ligands.

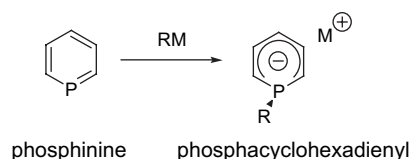


Scheme 2. Stabilization of electron reduced transition metal complexes and metallic nanoparticles with phosphinine ligands.

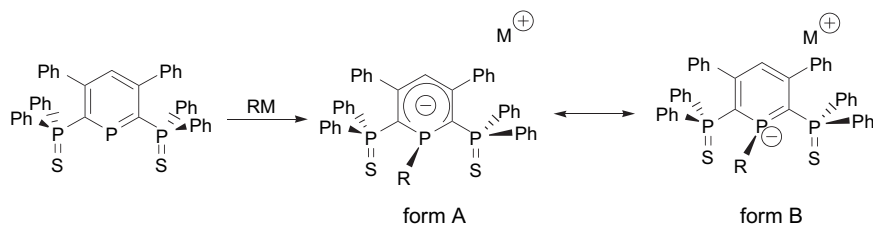
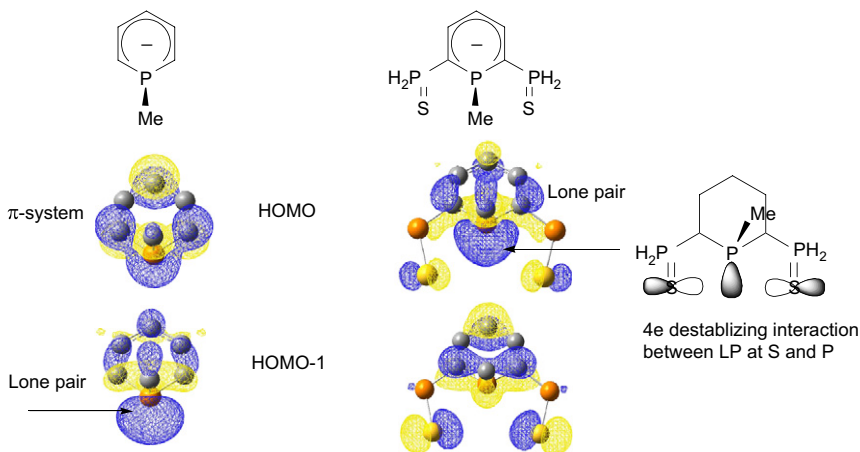
reduced transition metal complexes and metal surfaces [3–6]. Thus for example, we showed that their very specific electronic properties could be employed to significantly modify optical properties of gold nanoparticles (Scheme 2) [7–9].

However, like other low coordinate phosphorus derivatives, these ligands are quite sensitive towards nucleophiles and their use in coordination chemistry and catalysis is essentially limited to processes relying on the use of electron-rich metal fragments [10–14].

This limitation mainly results from the presence of a substantial positive charge at phosphorus which renders the ring sensitive towards nucleophiles. However, this property can be exploited to assemble a new type of anionic ligand featuring a delocalized negative charge (Scheme 3). Some of these phosphacyclohexadienyl ligands have found interesting applications in coordination chemistry in the synthesis of π -complexes. Recently we also showed that Rh(I) complexes of these phosphacyclohexadienyl ligands behave as efficient hydroformylation catalysts [15].



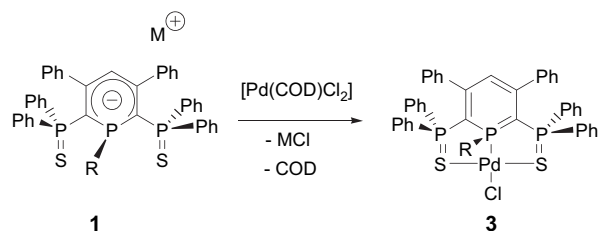
Scheme 3. Reactivity of phosphinines towards nucleophilic reagents.

Scheme 4. Synthesis of dianions **1** and possible mesomeric forms.Scheme 5. Two highest molecular orbitals of phosphacyclohexadienyl and anionic ligands **1** as given by DFT calculations.

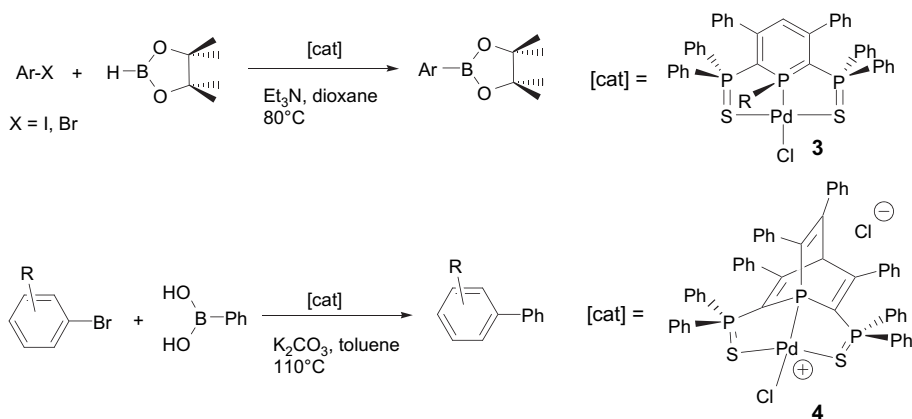
When the ring is substituted by two ancillary phosphinosulfide ligands, the phosphinine ring appeared to be sufficiently reactive to undergo a nucleophilic attack at phosphorus, leading to ligands of type **1** (Scheme 4). Though two mesomeric forms (A and B) can be proposed to rationalize the electronic structure of these ligands, DFT studies unambiguously showed that the negative charge is delocalized over the phosphorus ring (form A).

Contrary to classical phosphacyclohexadienyl anions, anions **1** favor σ coordination through the lone pair at phosphorus over π -coordination through the carbocyclic system. This preference can be rationalized taking into account the electronic perturbation induced by the presence of two sulfur atoms. Indeed, as can be seen in Scheme 5, the HOMO of phosphacyclohexadienyl anions is usually localized over the carbocyclic system, justifying why coordination through the π -system is favored. On the other hand, in S–P–S anionic ligands, the presence of two lone pairs at sulfur induces a four-electron through-space destabilizing interaction with the lone pair at phosphorus. As a consequence, in these pincer ligands, the HOMO is the lone pair at phosphorus.

These new systems, which behave as a 6-electron donor, display a very rich coordination chemistry, whose most-significant aspects will be summarized here. Palladium(II) complexes of ligands **1** are easily available through the reaction of the anion with precursors such as L_2PdCl_2 (L being a 2-electron donor ligand) (Scheme 6) [16]. Palladium chloride complexes such as **3** proved to be particularly robust and could be employed as very efficient catalysts in C–C (Suzuki) and C–B (Suzuki–Miyaura) coupling reactions. Coupling reactions of pinacolborane with iodoarenes yielded the corresponding boronic esters with excellent yields with



Scheme 6. Synthesis of palladium(II) complexes through a displacement process.



Scheme 7. S–P–S palladium(II) complexes and their phosphabarrelene derivatives in catalyzed C–B and C–C bond coupling reactions.

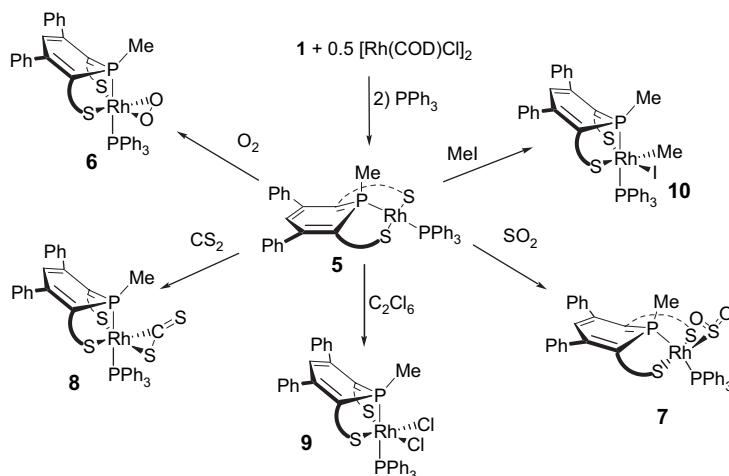
low catalyst loading (TON between 5×10^3 and 10×10^3) [17].

In the course of these studies, we also discovered another possible way to exploit the phosphinine ring in the elaboration of neutral tridentate S–P–S pincer ligands. 2,6-Bis(phosphinosulfide)phosphinines proved to be sufficiently reactive towards electron deficient alkynes to afford phosphabarrelenes such as **4** through a [4 + 2] cycloaddition process. These new S–P–S ligands easily coordinated Pd–Cl fragments and afford very efficient catalyst. Thus complex **4** catalyzes the coupling between Ph-B(OH)₂ and bromoarenes with a TON of 9.5×10^4 (TOF [h⁻¹] = 3958). Additionally the palladium complexes featuring P–S ligands (combination of a phosphinosulfide with a phosphinine anion or a phosphabarrelene) could also be successfully

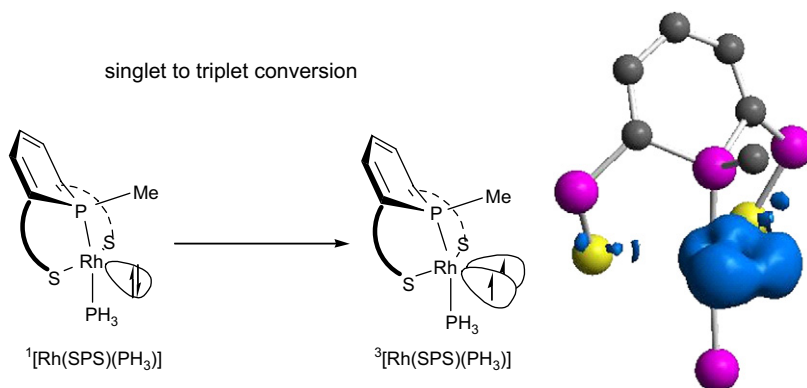
employed in the allylation of primary amines with allylic alcohols [18] (Scheme 7).

Another striking feature of anionic ligands **1** was discovered in exploring the chemistry of Rh(I) complexes. The 16 VE species **5** was synthesized via the reaction of **1** with the classical Rh(I) precursor [Rh(COD)Cl]₂ followed by addition of PPh₃. This complex exhibits a high reactivity towards small molecules such as O₂, CS₂, SO₂, MeI, and C₂Cl₆ [19]. A summary of the reactivity of these complexes is presented in Scheme 8.

As can be seen in Scheme 8, in all cases attack of the substrate occurred with complete regioselectivity on the upper side of the complex. This result was rationalized through DFT calculations on a model reaction with H₂ [20]. It was demonstrated that the overall energy associated with this oxidative addition process results



Scheme 8. Reactivity of complex **5**.

Scheme 9. Singlet to triplet conversion explaining the regioselectivity of attacks in Rh(I) complex **5**.

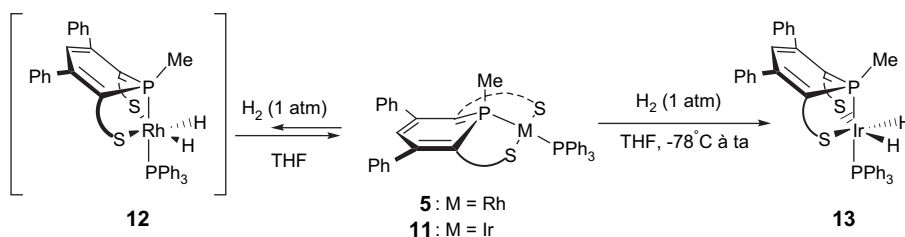
from different factors such as the distortion of the metal fragment, a singlet to triplet conversion, the energy of the dissociation of H_2 and the energy associated with the formation of two new Rh–H bonds. Using a thermodynamic cycle, taking into account these different data, it was shown that preference for the *syn* attack essentially results from the ability of the $[\text{Rh}(\text{SPS})(\text{PPh}_3)]$ fragment to form a triplet state in the appropriate geometry to react with the incoming substrate (Scheme 9). A view of the calculated spin density in the model complex $[\text{Rh}(\text{SPS})(\text{PH}_3)]$ is also presented in Scheme 9 (in the model for SPS, all phenyl groups were replaced by H atoms).

Contrary to the Rh(I) complex for which the reaction is reversible, the Ir(I) counterpart **11** reacts with dihydrogen to form the corresponding dihydride Ir(III) derivative **13** which was structurally characterized (Scheme 10). A view of one molecule of **13** is presented in Fig. 1. A DFT study has shown that the oxidative addition of H_2 onto the Ir derivative **11** is more exothermic ($\Delta G = -36.1$ kcal/mol) than the addition onto the Rh complex ($\Delta G = -14.9$ kcal/mol) which is in equilibrium with the dihydride complex **12**. Though the singlet to triplet conversion requires a weaker activation barrier

in the case of the rhodium complex, the gain in stabilization energy provided by the formation of two strong Ir–H bond (-171.2 kcal/mol) is the determinant factor (-145 kcal/mol for the Rh complex).

Anions of type **1** can also allow the stabilization of paramagnetic Rh(II) complexes [21]. In a first step, the homoleptic Rh(III) complex featuring two SPS ligands was obtained by reacting two equivalents of the anion with the $[\text{RhCl}_3(\text{THT})_3]$ precursor. Interestingly, complex **14** showed a reversible reduction wave by electrochemistry to form the 19 VE Rh(II) complex **15**. The reduction of **14** was then achieved chemically using Zn as a mild reducing agent. Though complex **15** could not be characterized by X-ray techniques, complete EPR and DFT studies were performed. Combination of the calculations and the experimental data allowed us to conclude that the odd electron is localized in an MO which results from the antibonding combination of the metal d_{z^2} AO with two lone pairs at sulfur atoms of different ligands. A view of the SOMO of **15** is presented in Scheme 11.

The chemistry of these SPS anionic derivatives is not limited to group 9 and group 10 metal complexes and various other complexes were synthesized with different

Scheme 10. Reactivity of complexes **5** and **11** towards H_2 .

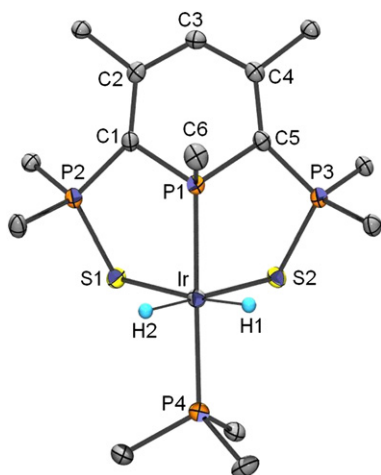
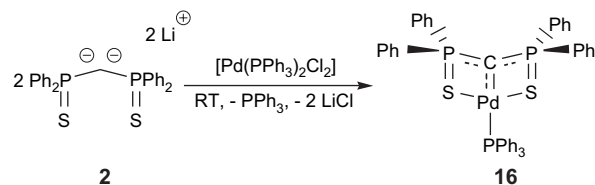


Fig. 1. View of one molecule of complex **13** in the solid state. Copyright American Chemical Society 2006.

transition metals: Au(I), Cu(I), Ni(II), Pt(II), Fe(II), Ru(II), Mn(I) and Re(I) and even actinides such as U(IV) [22,23].

2.2. Dianionic S–C–S pincer ligands

So far, as stated in Section 1, only monoanionic SCS pincer ligands were known. Following a similar strategy that was already employed by Cavell et al. and Ong and Stephan for the synthesis of bis-(iminophosphorane)-methanediide ligands [24,25], sulfide derivatives of

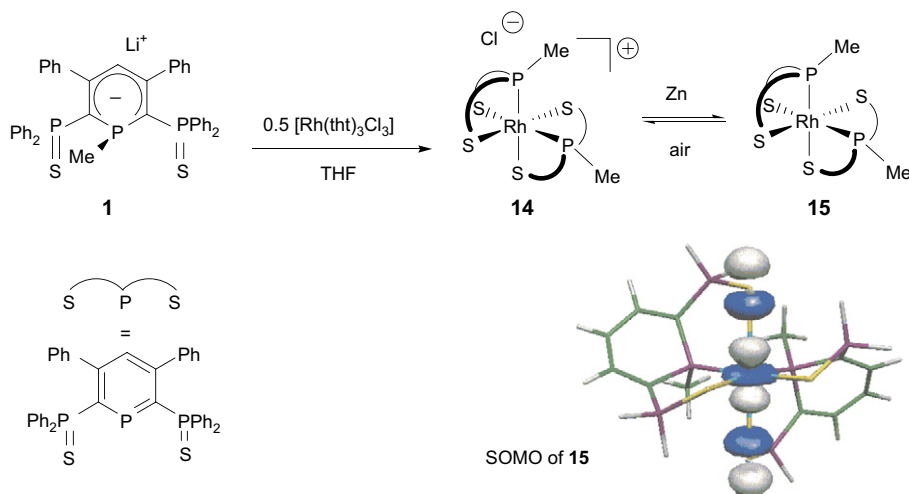


Scheme 12. Synthesis of the palladium complex **16** through reaction of dianion **2** with $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$.

the dppm ligand (dppm = bis(diphenylphosphino)methane) could be easily deprotonated twice to afford the corresponding dianionic ligand **2**. This metallation process easily takes place in toluene at room temperature and yields dianion **2** in quantitative yield as a highly moisture sensitive yellow powder. In the solid state, dianion **2** adopts a dimeric structure which bears some resemblance with that of the bis-(iminophosphorane) analogue.

The most significant feature of these dianions is their reactivity towards transition metals since they can potentially act as precursor of transition metal carbene complexes through ligand displacement reactions. In a first series of experiments we explored the reactivity of **2** towards Pd(II) precursors such as $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ (Scheme 12) [26]. Upon reaction, the two chloride ligands are displaced and the new complex **16** is formed. The X-ray crystal structure of complex **16** is presented in Fig. 2.

As shown, the X-ray structure of complex **16** presents a central tricoordinate carbon atom as expected. Unusual features were found. First, a long Pd–C1



Scheme 11. Synthesis and reduction of the homoleptic Rh(III) complex **14** into the paramagnetic 19 VE complex **15**. A view of the SOMO of **15** is also presented.

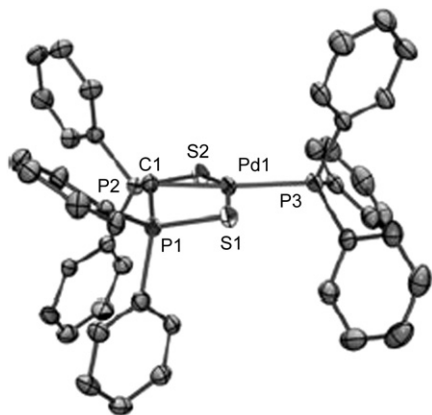
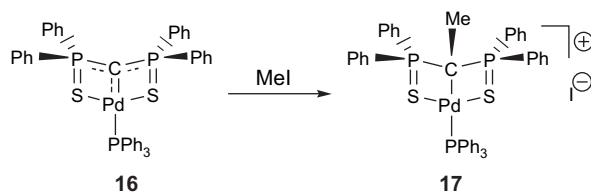


Fig. 2. View of one molecule of complex **16** in the solid state. Copyright Wiley 2004.

bond (2.113(2) Å) ruled out a ‘true’ double bond. Second, the metal center seems to be located in a quasi-perpendicular plane to the carbene fragment (angle of 102.0°). The particular electronic structure of this complex was rationalized through DFT calculations. The HOMO of the complex, which is shown in Scheme 13, consists of a π type antibonding interaction between the n_{σ} orbital of the carbene fragment and the d_{xz} orbital of the metal center. Overall, as both the π bonding and antibonding orbitals are filled, there is no π bonding character between the Pd and C centers, which corroborates the long Pd–C bond.

As can be expected from this electronic situation, complex **16** behaves as a nucleophile and it indeed reacts with strong electrophiles such as MeI to afford the cationic complex **17** which features a single bond between the carbon and palladium centers (Scheme 14).

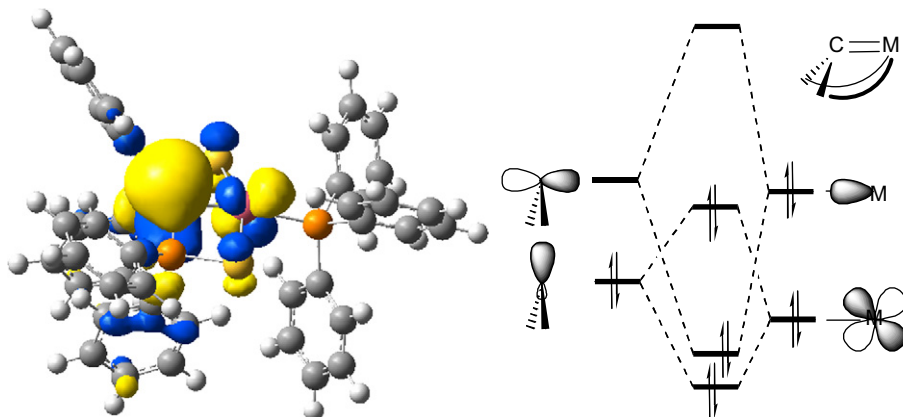


Scheme 14. Reaction of complex **16** with methyl iodide.

Following a similar strategy, Ru(II) complexes such as **18** were also synthesized [27] (Fig. 3). The X-ray structure of **18** showed a more typical coordination of the carbene fragment with the metal center in the plane of the carbene (Scheme 15). However, here again the C–metal bond length appears to be quite long (Ru–C of 2.053(2) Å), suggesting a very weak double-bond character. This hypothesis was confirmed by DFT calculations which indicate a Wiberg bond index of 0.67 for the Ru–C bond. Moreover, the LUMO of this complex is an antibonding π^* orbital between the n_{σ} orbital of the carbene fragment with the d_{xz} orbital of the metal center. Contrary to its Pd(II) counterpart, complex **18** proved to be very robust, neither reacting with nucleophiles nor with electrophiles, even under drastic conditions.

Dianions **2** also proved to be remarkable ligands for lanthanides and, very recently, the strategy employed for the synthesis of Pd(II) and Ru(II) derivatives was successfully extended to the synthesis of rare lanthanide alkylidene complexes (Ln = Sm, Tm) (Scheme 16) [28,29].

The X-ray crystal structures of the iodide bridged dimeric Sm **19** and Tm **20** complexes were recorded. In both structures the geometry at carbon is planar (sum



Scheme 13. HOMO of complex **16** and simplified MO diagram. Copyright Wiley 2004.

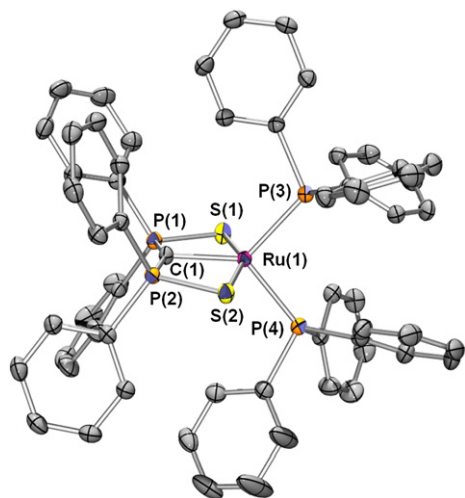
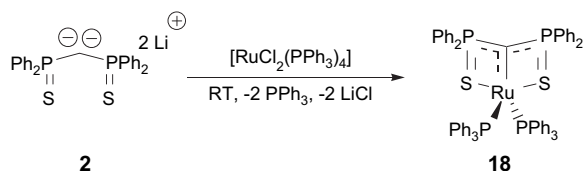
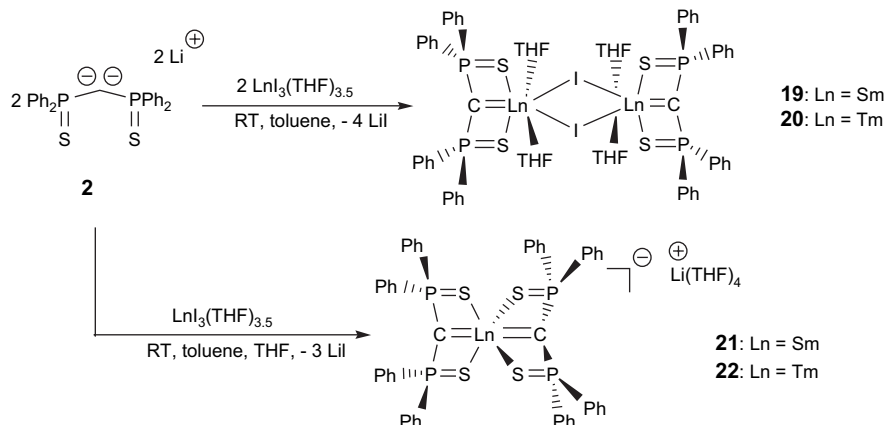


Fig. 3. A view of one molecule of complex **18** in the solid state. Copyright American Chemical Society 2005.

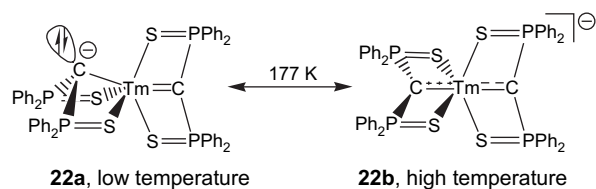


Scheme 15. Synthesis of the Ru(II) complex **18**.

of the angles of $357.8\text{--}359.4^\circ$), showing the donation of both lone pairs of the dianionic fragment to the Ln center. Unexpectedly, the homoleptic complex **22** adopts two different solid-state structures depending on the temperature, and a low-temperature (177 K) phase transition in the crystal was observed. Two significantly



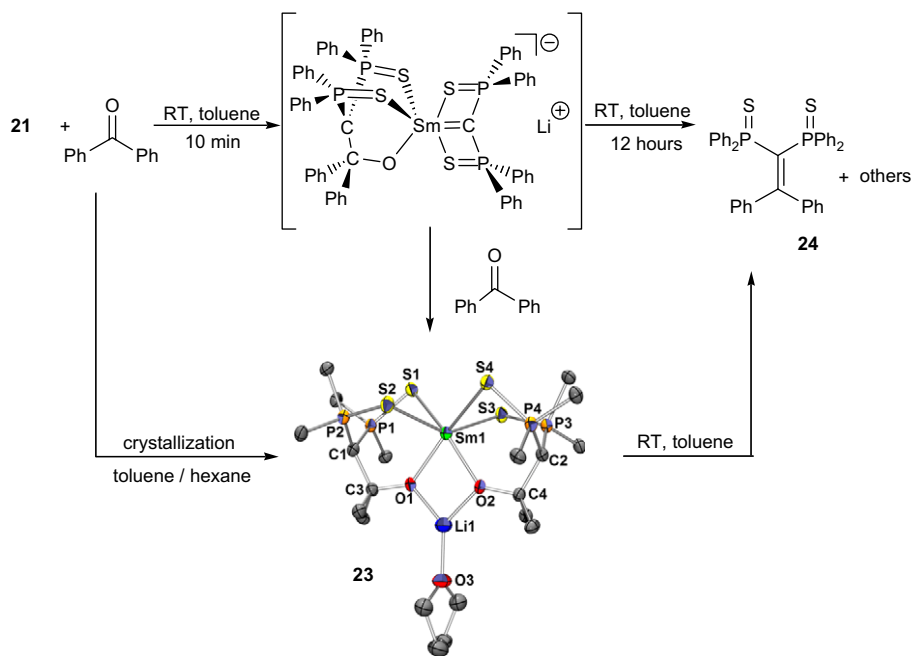
Scheme 16. Syntheses of dimeric **19**, **20** and monomeric homoleptic complexes of Sm and Tm **21** and **22**.



Scheme 17. Phase transition in the solid state for complex **22**.

different structures were thus recorded (at 150 K and 230 K). In the low-temperature form (**22a**), the two carbonic moieties are geometrically different. In one fragment, the carbon is tetrahedral (Σ angles = 332°) and the bond distance of $2.423(9)$ Å falls in the range of single Tm–C bonds. In the other fragment, it is planar and the bond length is shorter ($2.378(9)$ Å). Therefore one can conclude that the overall charge is located on the first carbon atom, which bears a significant sp^3 character, whereas the second carbon center behaves as a four-electron donor. In the higher temperature form (**22b**), the two fragments become identical, the bond distance averages between single and double bond length, and the geometry at the carbon atoms is nearly planar. These data point to a delocalization of the anionic charge over the two carbons and the thulium centers, thereby indicating that a π interaction can develop between these atoms (Scheme 17).

As can be expected, both complexes are highly reactive towards electrophiles. Reaction with ketones and aldehydes is a convenient route to form 1,1-bis(diphenylphosphinosulfide) olefin derivatives through a ‘Wittig-like’ process. Monitoring of the process by ^{31}P NMR spectroscopy attested the presence of several intermediates. Fortunately, one of these intermediates,



Scheme 18. Reaction of the Sm complex **21** with benzophenone. X-ray crystal structure of the samara-oxetane **23** in the solid state. Copyright American Chemical Society 2006.

the open metalla-oxetane complex **23** was isolated and structurally characterized, and one molecule is presented in Scheme 18. Metalla-oxetanes have been proposed as intermediates in the reaction of early transition metal carbene complexes with carbonyl derivatives, but few related species have been isolated so far. In the structure, new C–C and O–Sm bonds are formed, while the Sm–alkylidene bond is cleaved. When redissolved in toluene, this complex evolved to the alkene **24** and samarium oxide derivatives, proving this open metalla-oxetane to be an intermediate in the transformation.

3. Conclusion

Over the last few years, we have been involved in the development of new S–X–S pincer ligands featuring phosphinosulfide pendent arms, and either phosphorus or carbon central donating moiety. The monoanionic ligand **1** was used to stabilize both electron-rich and electron-poor metal centers: from Cu(I), Au(I) to U(IV). In terms of applications in catalysis, some Pd complexes bearing this ligand not only have shown promising activities, but also proved very robust towards moisture and air. Small molecule activation (CS₂, SO₂, C₂Cl₆, MeI...) was achieved with Rh

complex in a regioselective manner, which was corroborated by DFT calculations. Most interestingly, this ligand proved quite flexible, being able to accommodate various geometries at the metal center. Finally, electrochemical studies showed ligand **1** to be comparable with the highly electron donating Cp* ligand.

Dianionic ligand **2** was obtained quantitatively from the bis-sulfide of the commercially available dppm ligand, which opened the way to the synthesis of new carbene complexes of Pd and Ru centers. DFT calculations have allowed describing in depth the peculiar electronic situation found in these complexes. Alkylidene complexes of the Ln centers Sm and Tm have also been synthesized. Reactivity of these complexes towards ketones has led to the isolation of a rare open metalla-oxetane species, often proposed as intermediate in the reaction of alkylidene complexes of early transition metals with ketones. X-ray studies of the Tm complexes have proved a double bond character for the C=Tm bond. Thus, in these complexes, the carbon acts as both a σ and a π donor to the lanthanide center.

Acknowledgements

The authors thank the CNRS and the 'École polytechnique' for supporting these studies. MD thanks

the DGA for a fellowship. IDRIS is gratefully acknowledged for the allowance of computer time (project No. 061616).

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