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Thulium Alkylidene Complexes: Synthesis, X-ray Structures, and Reactivity

Thibault Cantat, Florian Jaroschik, Louis Ricard, Pascal Le Floch, François Nief,* and Nicolas Mézailles*

Laboratoire "Hétéroéléments et Coordination", UMR CNRS 7653 (DCPH), Département de Chimie, Ecole Polytechnique, 91128 Palaiseau Cédex, France

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*Summary: The first thulium alkylidene complexes (**2** and **5**) were synthesized using a stable dianionic ligand as carbene precursor and were characterized by X-ray diffraction analysis. These complexes were shown to involve metal−carbon double-bond character by their reactivity toward benzophenone. A solid-state dimorphism revealed the participation of a π-overlap between the carbon and the thulium centers in the stabilization of the homoleptic complex **5**.*

Introduction

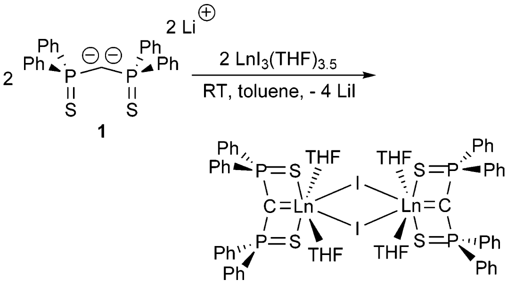
Transition-metal complexes involving a metal−carbon double bond have been widely investigated via both experimental and theoretical studies.[1] In contrast, very few examples of complexes bearing a carbene ligand have been reported in the lanthanide series so far.[2,3] In lanthanide chemistry, bonding is essentially electrostatic in nature.[4] Therefore, in a lanthanide carbene complex, the stabilization of the carbenic center cannot be provided by π-back-donation from the metal fragment[5] and has thus to be ensured by the substituents at the carbon atom. As a result, most of the reported lanthanide carbene complexes feature a neutral stable N-heterocyclic carbene and can be considered as Lewis base adducts.[6]

To date, only two structurally characterized lanthanide carbene complexes which are not neutral carbene adducts have been isolated, using two different approaches.[3,7] For instance, Cavell and co-workers obtained a samarium carbene complex by double deprotonation of a bis(iminophosphorane)methylene ligand in the coordination sphere of the metal center.[7] On the other hand, we used the stable bis(thiophosphinoyl)methanediide dianion (**1**) to generate samarium mono- and bis(alkylidene) complexes. These compounds showed reactivity similar to that of Schrock-type carbene complexes, which allowed us to establish the lanthanide−carbon double-bond character.[3] On the basis of this similarity, and in order to mark the difference with neutral carbene adducts, the terminology "alkylidene complex" is adopted here, as suggested by Giesbrecht and Gordon.[2]

Herein, we extend our strategy to access the first thulium alkylidene complexes, as examples of late-lanthanide alkylidene complexes, and report on their reactivity toward ketones. Evidence for the existence of a π-overlap between the carbenic fragment and the thulium center is also presented, corroborated by a low-temperature solid-state dimorphism.

Results and Discussion

Reaction of 1 equiv of dianion **1**, whose synthesis has recently been reported by some of us,[8] with 1 equiv of $TmI_3(THF)_{3.5}$ under argon led to the formation of the thulium alkylidene complex **2** (eq 1), within a few minutes at room temperature.



(1)

2 : Ln=Tm
3 : Ln=Sm see ref. 3

This complex was isolated as a white solid in 78% yield, after removal of the lithium salts. This reaction shows the versatility of our approach for the synthesis of both early- and late-lanthanide alkylidene complexes. As expected, the complex is paramagnetic and could not be characterized by NMR. X-ray-quality crystals were obtained by diffusion of hexanes into a toluene solution of the complex. As shown in the ORTEP plot

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* To whom correspondence should be addressed. Tel: +33 1 69 33 40 79. Fax: +33 1 69 33 39 90. E-mail: mezaille@poly.polytechnique.fr (N.M.).

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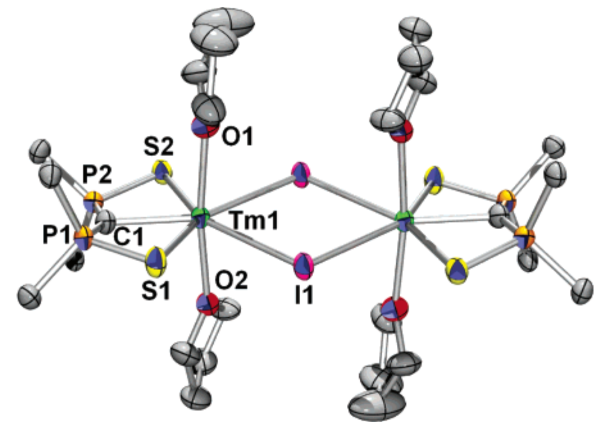


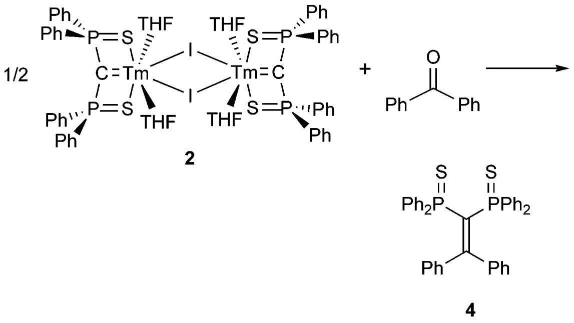
Figure 1. ORTEP plot of one molecule of **2** (ellipsoids set at 50% probability). The phenyl rings are omitted for clarity (only ipso carbon atoms are shown). Selected bond lengths (Å) and angles (deg): Tm1−C1 = 2.325(5), Tm1−S1 = 2.822(1), Tm1−S2 = 2.777(1), Tm1−I1 = 3.1575(4), Tm1−O1 = 2.307(3), Tm1−O2 = 2.323(3), P1−C1 = 1.661(5), P2−C1 = 1.653(5), P1−S1 = 2.024(2), P2−S2 = 2.030(2), P1−C1−P2 = 150.8(3), P1−C1−Tm1 = 104.6(2), Tm1−C1−P2 = 104.0(2).

(Figure 1), **2** crystallizes as a C_2-symmetric iodine-bridged dimer with two molecules of THF bound to the thulium center.[9]

Two molecules of **2** crystallize in the asymmetric unit and possess very similar features. In particular, very short bond distances between the carbon atom and the thulium center are observed (2.325(5) and 2.323(4) Å), proving a strong interaction. Indeed, these bond distances are considerably shorter than Tm−η^1-C bond distances by over 0.1 Å (2.438 Å (av)).[10] Short P−C bond distances are measured (1.66 Å (av)), which very likely result from negative hyperconjugation from carbon to phosphorus σ*-orbitals. Most relevant to our discussion (vide infra) are the sums of the angles at the carbon atoms in complex **2**, which are 357.8 and 359.4° in the two cocrystallized molecules, respectively. The planarity at these carbon centers shows the donation of both lone pairs from the dianionic fragment to the metal center.

As can be seen in Figure 1, complex **2** is the analogue of the previously reported Sm complex **3** and constitutes an example of a late-lanthanide alkylidene complex.[3] The bond shortenings observed for the Tm−C, Tm−S, and Tm−I bonds are in agreement with the well-known lanthanide contraction. In contrast, no change in bond lengths or angles is observed for the alkylidene fragment. The electronic natures of the metal−carbon bonds seem therefore to be similar for early- and late-lanthanide centers.

We previously showed that the nucleophilic nature of the Sm═C double bond could be determined in analogy to Schrock-type carbenes via its reaction with ketones. When 1/2 equiv of **2** was reacted with 1 equiv of benzophenone, immediate and complete transformation into the expected alkene **4** was observed (eq 2); this product could not be obtained by reacting the dianion **1** itself with benzophenone.[3] This result establishes the carbenic nature of the Ln═C bond and its nucleophilic character, where Ln is a late-lanthanide element such as Tm.



(2)

To conclude, ligand **1** is an efficient Lewis base, able to stabilize the thulium(III) center after displacement of two iodide ligands. This synthesis, together with the structural parameters (planarity at the carbenic atom, short Tm═C bond), indicates that the carbon center behaves as a four-electron X_2-type ligand in complex **2**.

For the lanthanide series the f orbitals are strongly contracted and cannot participate in bonding interactions.[5] Moreover, trivalent lanthanides (and most divalent ones) have d^0 configurations; thus, no π-back-donation is possible. Therefore, in lanthanide carbene complexes, the stability of the carbenic center cannot be provided by the metal fragment and has thus to be ensured by the substituents at the carbon atom. Due to the lanthanide−carbon bond polarity ($X_C = 2.5$ vs $X_{Ln} < 1.2$), two cases will therefore be discussed, depending on their ability to stabilize the metal-free carbene fragment (Chart 1).

First, the carbene ligand could behave as a two-electron donor ligand and should therefore be stabilized in its free form as a neutral singlet carbene (Chart 1, case A). This formally corresponds to the well-known transition-metal Fischer carbene complexes, in which the stability of the carbene center is partly provided by π-donor substituents so that little back-donation is required from the metal. Thus, little or no double-bond character is found between the metal and the carbene fragment. This case has clearly been illustrated by the isolation of some lanthanide complexes bearing an N-heterocyclic carbene ligand.[6] Similarly to the analogous transition-metal complexes, this ligand was found to behave as a two-electron-donor L-type ligand and lanthanide−carbon bond lengths corresponded to single bonds. We should note that no reactivity studies of these complexes have been reported so far to extend their analogy to Fischer-type carbene complexes.

On the other hand, in transition-metal Schrock-type carbene complexes, the carbenic moiety is a nonstabilized alkylidene ligand whose stabilization is mainly brought about by the metal fragment and leads to short metal−carbon bond distances. These

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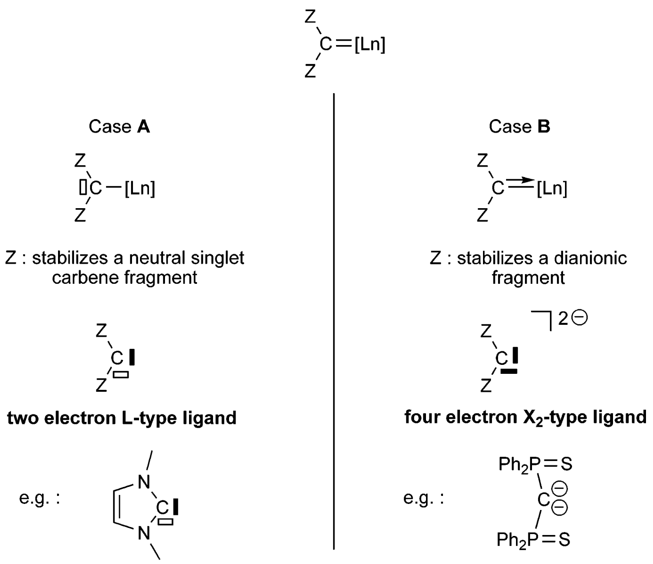
(9) Crystal data for **2**: $C_{66}H_{72}I_2O_4P_4S_4Tm_2$; $M_r = 1865.15$; monoclinic; $a = 19.7560(10)$ Å, $b = 20.6800(10)$ Å, $c = 18.3020(10)$ Å; $\beta = 95.8700(10)°$; $V = 7438.1(7)$ Å^3; $T = 150.0(1)$ K; space group $P2_1/c$; $Z = 4$; $\mu = 3.444$ cm^{-1}; 39 234 reflections measured, 21 652 unique reflections, 14 676 used reflections, criterion $I > 2\sigma(I)$; $R_{int} = 0.0398$; wR2 = 0.1347. Crystal data for **5a**: $C_{50}H_{40}P_4S_4Tm,C_{16}H_{32}LiO_4$; $M_r = 1357.23$; triclinic; $a = 14.8860(10)$ Å, $b = 20.6060(10)$ Å, $c = 22.2730(10)$ Å; $\alpha = 74.5200(10)°$, $\beta = 95.8700(10)°$, $\gamma = 76.4200(10)°$; $V = 6348.4(6)$ Å^3; $T = 150.0(1)$ K; space group $P\bar{1}$; $Z = 4$; $\mu = 1.676$ cm^{-1}; 25 834 reflections measured, 25 834 unique reflections, 19 424 used reflections, criterion $I > 2\sigma(I)$; $R_{int} = 0.0295$; wR2 = 0.2227. Crystal data for **5b**: $C_{50}H_{40}P_4S_4Tm$, $C_{16}H_{32}LiO_4$; $M_r = 1357.23$; monoclinic; $a = 26.4430(10)$ Å, $b = 14.6880(10)$ Å, $c = 17.0920(10)$ Å; $\beta = 98.6800(10)°$; $V = 6562.4(6)$ Å^3; $T = 150.0(1)$ K; space group $C2/c$; $Z = 4$; $\mu = 1.622$ cm^{-1}; 15 640 reflections measured, 9548 unique reflections, 7651 used reflections, criterion $I > 2\sigma(I)$; $R_{int} = 0.0194$; wR2 = 0.1075. Crystal data for **7**: $C_{80}H_{68}LiO_3P_4S_4Tm$; $M_r = 1505.37$; monoclinic; $a = 20.0750(10)$ Å, $b = 11.6070(10)$ Å, $c = 29.6480(10)$ Å; $\beta = 108.3510(10)°$; $V = 6557.0(7)$ Å^3; $T = 150.0(1)$ K; space group $C2/c$; $Z = 4$; $\mu = 1.631$ cm^{-1}; 14 568 reflections measured, 9350 unique reflections, 8599 used reflections, criterion $I > 2\sigma(I)$; $R_{int} = 0.0210$; wR2 = 0.1276. CCDC-277615 (**2**), CCDC-277616 (**5a**), CCDC-277617 (**5b**), and CCDC-286081 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax (+44) 1223-336-033; email deposit@ccdc.cam.ac.uk).

(10) A search performed on the Cambridge Structural Database afforded four thulium complexes containing η^1-carbon ligands. We found an average Tm−C bond length of 2.438 Å (median 2.425 Å).

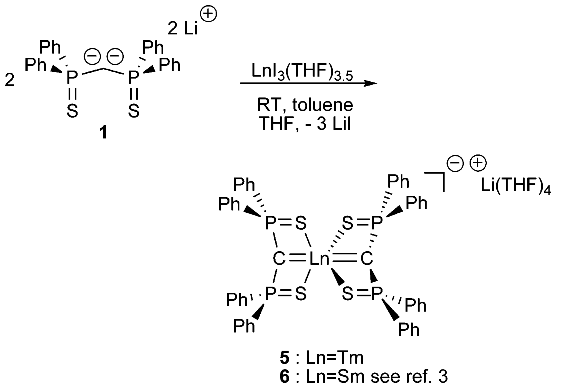
Chart 1



complexes usually exhibit a strong double-bond character. This situation cannot be directly transposed to the lanthanide complexes, since the metal is not able to stabilize the carbenic center by back-donation. The stability must thus be ensured by the substituents at the carbon atom. This leads to a second case, where the stable form of the metal-free carbene fragment is a dianionic ligand which behaves as a four-electron X_2-type ligand (Chart 1, case B). Complexes **2** and **3**, which result from the coordination of a dianionic ligand stabilized by electron-withdrawing substituents, illustrate this second class of lanthanide carbene complexes, namely alkylidene complexes. Their reactivity toward benzophenone together with short lanthanide−carbon bond distances support the analogy to transition-metal Schrock-type carbene complexes.

As our approach for the synthesis of mono(alkylidene) complexes had proven to be viable for early and late lanthanides, we then attempted the stabilization of the thulium(III) center by two dianionic fragments.

Addition of 2 equiv of dianion **1** to $TmI_3(THF)_{3.5}$ led to the formation of the first homoleptic thulium bis(alkylidene) complex, **5** (eq 3), which is an analogue of the samarium complex **6**. Crystals of the anionic complex **5** were grown by diffusing hexanes into a solution of the complex in a toluene/diethyl ether mixture, at room temperature.[9] These crystals exhibited a phase transition near 177 K, which allowed us to obtain two significantly different structures at 150 K (**5a**, two molecules in unit cell) and 230 K (**5b**, one molecule in unit cell).[11]



(3)

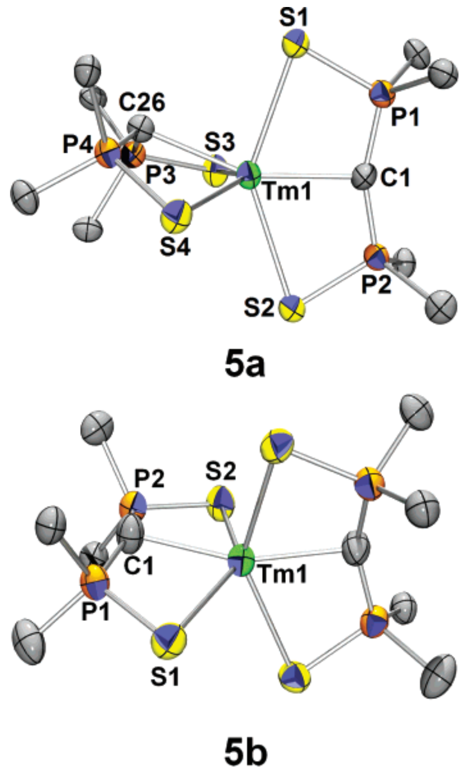
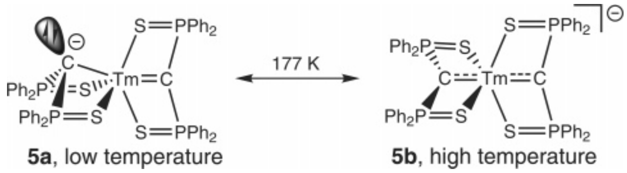


Figure 2. ORTEP plots of the anions corresponding to **5a** (only one of the two anions crystallized in the unit cell is shown) and **5b** (ellipsoids set at 50% probability). The phenyl rings and cocrystallized lithium are omitted for clarity. Selected bond lengths (Å) and angles (deg): for **5a**, Tm1−C26 = 2.423(9), Tm1−C = 2.378(9), Tm1−S1 = 2.751(2), Tm1−S2 = 2.788(2), Tm1−S3 = 2.754(2), Tm1−S4 = 2.747(2), P1−C1 = 1.657(9), P2−C1 = 1.647(9), P3−C26 = 1.673(9), P4−C26 = 1.655(9), P1−C1−P2 = 158.0(6), P1−C1−Tm1 = 101.3(4), P2−C1−Tm1 = 100.6(4), P3−C26−P4 = 134.6(6), P3−C26−Tm1 = 96.1(4), P4−C26−Tm1 = 97.7(4); for **5b**, Tm1−C1 = 2.368(3), Tm1−S1 = 2.7655(7), Tm1−S2 = 2.7618(7), P1−C1 = 1.652(3), P2−C1 = 1.647(3), P1−C1−P2 = 151.1(2), P1−C1−Tm1 = 100.1(1), P2−C1−Tm1 = 100.7(1).

Scheme 1



As shown in the ORTEP plot (Figure 2) of the low-temperature form **5a**, the two carbenic moieties are geometrically different. In one fragment, the carbon C26 is tetrahedral with Σ(angles) = 332° (av). The corresponding Tm1−C26 bond distance of 2.42 Å (av) falls in the range of Tm−C single bonds. In the second carbenic fragment, the geometry at the carbon atom is strictly planar (Σ(angles) = 360° (av)) and a shorter Tm1−C1 bond distance of 2.38 Å (av) is measured (however, this distance is longer than in **2**). These geometrical parameters are in favor of a double-bond character for the C1=Tm1 bond. Therefore, as shown in Scheme 1, in this structure, a strongly localized electron distribution is observed. The overall charge is mainly located on the tetrahedral C26 atom, which clearly exhibits a significant sp^3 character. While the C26 carbon center

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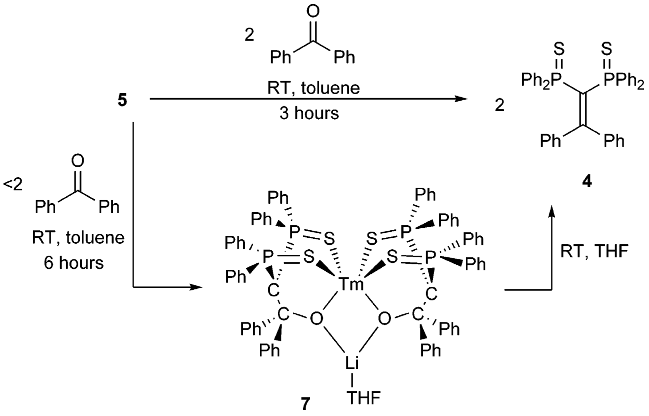
(11) This irreversible transition cracks the crystals. A usable sample was obtained by slowly ramping through the transition temperature.

Scheme 2



behaves as a two-electron X-type ligand, the C1 center donates four electrons to stabilize the thulium(III) center.

At 230 K, another structure was observed for complex **5**.[12] In this form (**5b**), the two carbenic moieties are identical (related by a C_2 axis). The P−C and P═S bonds as well as the Tm−S bonds are not perturbed by this modification of geometry (**5a** to **5b**) (Figure 2). Moreover, the Tm1−C1 bond distance of 2.368(3) Å is the average between double (2.32 Å in **2**) and single bonds (Tm1−C26: 2.42 Å in form **5a**) and is similar to the Tm1−C1 bond length in **5a** (2.38 Å). Most interestingly, the geometry at both carbon atoms is here nearly planar (Σ(angles) = 351.9°) and suggests the coordination of formally two four-electron-donor ligands. Taken together, these data can be attributed to a delocalization of the anionic charge over the two carbon and the thulium atoms, as shown on Scheme 1, thereby indicating that a π-overlap develops between these three atoms. Indeed, Gordon and co-workers recently showed that empty lanthanide d orbitals are involved in the stabilization of lanthanide imido complexes via π-donation from the imido ligand to the metal fragment.[13] In the same way we propose that the two alkylidene fragments interact via both σ- and π-donation with the thulium center in form **5b**.

The solid-state dimorphism of **5** emphasizes the different electronic effects involved in the stabilization of this class of lanthanide alkylidene complexes. First the additional charge involved in **5** can be centered at the carbon atom (low-temperature form **5a**). This geometry is in complete agreement with the ability of the bis(thiophosphinoyl)methylene ligand to accommodate a dianionic center. More surprisingly, complex **5b** (which was observed at higher temperature) reveals that to a certain extent the metal center is also able to participate in stabilizing this extra charge via its delocalization on the C−Tm−C backbone using the empty d orbitals on the thulium center.

To examine the electronic nature of the Tm═C bonds in complex **5**, the reactivity of **5** toward benzophenone was tested (Scheme 2). Addition of 2 equiv of benzophenone to **5** resulted in the complete formation of the expected alkene **4** within a few hours. In the presence of a substoichiometric amount of ketone, the reaction appeared to be much slower and crystals of the intermediate complex **7** were obtained (which rearranged into **4** upon dissolution in THF) from the crude mixture. Complex **7** is an open form of metallaoxetane. This reactivity confirms the carbenic nature of complex **5** and generalizes the mechanism proposed for the reaction between nucleophilic lanthanide alkylidene complexes and ketones.[3]

Conclusion

In conclusion, the use of a stable dianionic ligand (**1**) as precursor has proved successful to access the first thulium alkylidene complexes (**2** and **5**) as examples of late-lanthanide alkylidene complexes. This illustrates the versatility of our approach to access new lanthanide alkylidene complexes, which should thus be available across the whole lanthanide series. The nucleophilicity of these new complexes has been demonstrated by their reaction toward benzophenone which takes place via the formation of an open metallaoxetane. A dimorphism in the solid state revealed that π-overlap could develop between the carbon center and the metal, in complex **5**. This π-donation from the dianionic ligand orbitals to the lanthanide empty d orbitals accounts for the short thulium−carbon bonds and planarity at the carbene centers and confirms the nature of the Ln═C double bonds, in these complexes. Future investigations, including theoretical studies, are currently in progress to rationalize and quantify these new findings.

Experimental Section

All reactions were carried out in an argon-filled glovebox or on a vacuum line. Solvents were distilled and degassed prior to use. Elemental analyses were performed by the “Service d’analyses de l’Université de Dijon”, at Dijon, France.

Synthesis of 2. To $TmI_3(THF)_{3.5}$ (325 mg, 0.40 mmol) was added a solution of **1** in toluene (3.0 mL, 0.40 mmol), and this mixture was stirred for 30 min at room temperature. LiI salt was removed by centrifugation, and diethyl ether (5 mL) was condensed onto the solution. A white precipitate of **2** was collected after 24 h in 78% yield (276 mg, 0.31 mmol). Anal. Calcd for $C_{66}H_{72}I_2O_4P_4S_4$-Tm_2: C, 44.71; H, 4.09. Found: C, 44.83; H, 4.16.

Synthesis of 4. Benzophenone (10 mg, 0.06 mmol) and thulium carbene **2** (50 mg, 0.06 mmol) were reacted in toluene (5 mL) for 1 h, upon which a white precipitate formed. After centrifugation the precipitate was removed and the solution evaporated, giving the product as a pale yellow solid in 94% yield (0.034 g, 0.056 mmol). Selected data: ^{1}H NMR (300 MHz, toluene-d_8, 25 °C, TMS) δ 8.2 (br s, 4 H; ortho aryl), 7.1−6.7 ppm (m, 16 H; meta + para aryl); ^{31}P NMR (121.5 MHz, toluene-d_8, 25 °C, H_3PO_4) δ 40.1 ppm (s); ^{13}C NMR (75 MHz, toluene-d_8, 25 °C, TMS) δ 177.5 (d, ^2J(C,P) = 2.3 Hz, C═CPh_2), 142.7 (d, ^1J(C,P) = 11.5 Hz, C═CPh_2), 132.2−125.6 ppm (phenyl).

Synthesis of 5. Two equivalents of **1** in toluene (3.0 mL, 0.40 mmol) was added to $TmI_3(THF)_{3.5}$ (163 mg, 0.20 mmol) at room temperature. Elimination of the LiI salt by centrifugation and evaporation of the solvent yielded a yellow solid, which was purified by washing with a THF (0.5 mL)−diethyl ether (10 mL) mixture. Pure product **5** was obtained in 81% yield (218 mg, 0.16 mmol). Anal. Calcd for $C_{66}H_{72}LiO_4P_4S_4Tm$: C, 58.40; H, 5.35. Found: C, 58.63; H, 5.29.

Acknowledgment. We thank the CNRS and the Ecole Polytechnique for financial support.

Supporting Information Available: CIF files giving crystallographic data for **2**, **5a**, **5b**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] The structural differences between **5a** and **5b** may arise from packing effects. Therefore, the origin of the dimorphism and the difference in energy between the two forms **5a** and **5b** is not discussed.

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