# Rhodium (Thiophosphinoyl)(trimethylsilyl)methanide and Bis(thiophosphinoyl)methanide Complexes: S~S vs. C~S Coordination

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Dedicated to the memory of our friend and colleague Pascal Le Floch

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A comparative study of the coordination modes of a (thiophosphinoyl)(trimethylsilyl)methanide  $(1^{-}Li^{+})$  and bis(thiophosphinoyl)methanide  $(2^{-}Li^{+})$  ligand with Rh<sup>I</sup> was carried out. Several complexes were synthesized and characterized. For  $1^{-}Li^{+}$ , C~S coordination is forced, whereas for  $2^{-}Li^{+}$ , S~S

and C~S coordination can be achieved. In one case, a dynamic equilibrium between these two modes of coordination was observed. DFT calculations were carried out to rationalize this phenomenon and the stability of the methanide compounds.

### Introduction

Anionic  $X \sim C \sim X$  (X = heteroatom) ligands play a significant role in coordination chemistry and catalysis. They are typically designed to be tridentate pincer ligands, to provide both a strong electronic donation to the metal center and a controlled steric environment. After a seminal report by Shaw in the 70s, the chemistry of pincer ligands has evolved to maturity.<sup>[1]</sup> The structures that were studied early on,  $[2,6-(LCH_2)_2C_6H_3]^-$  (L~C~L) where L is a two-electron donor and C is an anionic aryl carbon atom, have allowed researchers to uncover the peculiarities of these tridentate ligands. Of the L~C~L ligands, the P~C~P pincers have found the most fruitful uses.<sup>[2]</sup> Pincer ligand complexes with an alkane backbone have attracted much less attention, probably because of the high flexibility of the alkane rings as well as the higher electron-donating ability of the *ipso*  $sp^3$ carbon atom. This increased donation results in enhanced reactivity, which makes the complexes more difficult to manipulate. Most interestingly, the presence of the CH-M moiety in the latter complexes can be used to generate a C=M carbene fragment. Regardless of the nature of the central carbon atom, sp<sup>2</sup> or sp<sup>3</sup>, the tridentate pincer coordination is observed. However, the  $[CH(PPh_2X)_2]^-$  (X = S, NR) anionic species may be found as tridentate,<sup>[3]</sup> bidentate by the coordination of the two X moieties,<sup>[4]</sup> or by X and C (Scheme 1).<sup>[5]</sup>



S~C coordination: late transition metals S~C~S: very few examples, U(VI), Ru(II)

#### Scheme 1.

The parameters that govern the various coordination modes have not been rationalized, yet this versatility might provide controlled hemilability in catalytic processes. Hemilability has not been observed so far with these systems but, in relation to this topic, Milstein et al. have proved the hemilability of the N moiety in anionic N~C~P pincer complexes of Ru, Rh, and Pt.<sup>[6]</sup> In this contribution, we wish to address the rationalization of the coordination in X~C~X' by comparing two ligand systems as well as different coligands on Rh<sup>I</sup> centers. We have chosen two anionic ligand systems, **1**<sup>-</sup>·**Li**<sup>+</sup> and **2**<sup>-</sup>·**Li**<sup>+</sup> (Scheme 2), which are believed to bear some electronic resemblance. For

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**1**<sup>-</sup>**Li**<sup>+</sup>, the S~C bidentate coordination is forced, whereas for **2**<sup>-</sup>**Li**<sup>+</sup>, the three coordination modes can be envisaged. In fact, in **2**<sup>-</sup>**Li**<sup>+</sup>, only very few examples of tridentate coordination are found.<sup>[3f]</sup> Among them, most are reported with Y ≠ H.<sup>[3b,7]</sup> With group 9 metal fragments, only bidentate S~S coordination has been observed,<sup>[4c]</sup> and tridentate coordination was only proposed in a highly reactive Ir<sup>I</sup> fragment, which resulted in CH activation of the phenyl ring of the ligand.<sup>[8]</sup>



Scheme 2. Possible coordination modes for 1-·Li+ and 2-·Li+.

In the first part, we present an experimental and theoretical comparison of the two anions, with the aim to quantify the stabilization of the charge at the carbon atom by the two substituents. In the second part, coordination with several Rh<sup>I</sup> centers was studied, which revealed that switching between S~S and S~C is indeed possible. A dynamic exchange between two S moieties was observed by NMR and rationalized by DFT calculations.

#### **Results and Discussion**

#### Synthesis of the Anions and DFT Calculations

The synthesis of **1** was achieved following a reported procedure by Holmes-Smith et al.<sup>[9,10]</sup> to yield **1** as a white crystalline solid after purification in good yield (84%, Scheme 3).

Compound 1 exhibits a sharp singlet at 37.7 ppm in the <sup>31</sup>P NMR spectrum. Single crystals of 1 were obtained by

slow evaporation of a concentrated solution in  $CH_2Cl_2$ . The X-ray crystal structure of 1 is presented in Figure 1. Bond lengths and angles are all standard.



Figure 1. ORTEP plot (50% thermal ellipsoids) of 1. Hydrogen atoms on the phenyl and trimethylsilyl substituents and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–P(1) 1.795(3), C(1)–Si(1) 1.897(3), P(1)–S(1) 1.962(1), Si(1)–C(15) 1.867(3), S(1)–P(1)–C(1) 114.9(1), P(1)–C(1)–Si(1) 119.8(1).

Deprotonation of 1 with one equivalent of methyllithium in tetrahydrofuran (THF), Et<sub>2</sub>O, or toluene yielded 1<sup>-</sup>·Li<sup>+</sup> as reported by Gessner (Scheme 3).<sup>[11]</sup> Compound 1<sup>-</sup>·Li<sup>+</sup> is characterized by a singlet at 44.5 ppm in the <sup>31</sup>P NMR spectrum in C<sub>6</sub>D<sub>6</sub>. Single crystals of 1<sup>-</sup>·Li<sup>+</sup> suitable for Xray diffraction were obtained by slow diffusion of hexanes into a concentrated solution of the compound in diethyl ether. A view of the structure of 1<sup>-</sup>·Li<sup>+</sup> is presented in Figure 2.

Compound 1<sup>-</sup>·Li<sup>+</sup> crystallizes as a dimer in the solid state. The two units are connected by an S–Li–C bridge. Compared to neutral 1, the anion 1<sup>-</sup>·Li<sup>+</sup> features a significantly elongated P–S distance [2.0263(4) vs. 1.962(1) Å]. Shortened P–C(1) and C(1)–Si bonds [1.701(1) vs. 1.795(3) Å and 1.827(1) vs. 1.897(3) Å, respectively] correlate with the elongation. The monoanion of **2** was also synthesized and studied. The structures of **2** and 2<sup>-</sup>·Li<sup>+</sup> are known and present the related bond shortening (P–C<sub>bridge</sub>) and elongation (P–S).<sup>[12,13]</sup> These geometric changes were investigated by DFT using B3LYP at the 6-31+G\* level of theory on all atoms to compare the two anions. It was of interest to quantify the stabilization of the lone pair at C by the PPh<sub>2</sub>S and SiMe<sub>3</sub> substituents. Our group has already



Scheme 3. Synthesis of 1-·Li+ and 2-·Li+.



Figure 2. ORTEP plot (50% thermal ellipsoids) of  $1^{-}Li^{+}$ . Hydrogen atoms on the phenyl and trimethylsilyl substituents are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–P(1) 1.701(1), C(1)–Si(1) 1.827(1), P(1)–S(1) 2.0263(4), S(1)–Li(1) 2.542(2), C(1)–H(1) 0.95(2), P(1)–C(1)–Si(1) 129.56(7), S(1)–P(1)–C(1) 113.72(4).

reported the synthesis of the dianion derived from bis(diphenylthiophosphanyl)methane 2  $(2^{2-}\cdot Li^+_2)$ ,<sup>[14]</sup> and it was shown that the stability of this compound relies on the stabilization of the negative charges at the central carbon atom by donation into empty vicinal orbitals. Calculations have been made on model compounds derived from the crystal structures of  $1^-\cdot Li^+$  and  $2^-\cdot Li^+$  in which the phenyl rings have been replaced by hydrogen atoms ( $I^-\cdot Li^+$  and  $II^-\cdot Li^+$ , Scheme 4). We have verified that solvent coordination at  $Li^+$  does not significantly change the results, and only the simplified model is presented here. Full details of these calculations are given in the Supporting Information.



Scheme 4. Model compounds used for theoretical calculations.

The structural parameters for the optimized geometries are in excellent agreement with the X-ray data. The elongation of the P–S bond and the shortening of the P–C bond are particularly well reproduced (Table 1).

Table 1. Comparison of the calculated and experimental bond lengths [Å] in 1- $\cdot$ Li<sup>+</sup> and 2- $\cdot$ Li<sup>+</sup>.

Distance	1-•Li+			2-•Li+		
	RX	DFT	$\Delta$	RX	DFT	$\Delta$
P1–C	1.70	1.75	0.05	1.71	1.74	0.03
P2–C	_	_	_	1.71	1.74	0.03
C–Si	1.83	1.86	0.03	_	_	_
P1-S1	2.03	2.05	0.02	1.99	2.02	0.03
P2-S2	_	_	-	1.99	2.02	0.03

Natural bond orbital (NBO) analysis was performed on  $\mathbf{I} \cdot \mathbf{Li}^+$  and  $\mathbf{II} \cdot \mathbf{Li}^+$  with focus on the stabilization of the lone pair at the central carbon atom. This lone pair is almost a pure p orbital in both species (91.3% p in  $\mathbf{I} \cdot \mathbf{Li}^+$  and 99.1% p in  $\mathbf{II} \cdot \mathbf{Li}^+$ ). It is stabilized by negative hyperconjugation

into the two antibonding  $\sigma^*(P-H)$  and the  $\sigma^*(P-S)$  orbitals in **I**-·**L**i<sup>+</sup> and into the two antibonding  $\sigma^*(P-H)$ , the  $\sigma^*(P-S)$ , and the  $\sigma^*(Si-C)$  orbitals in **II**-·**L**i<sup>+</sup>. The results of the stabilization are given in Tables 2 (for **I**-·**L**i<sup>+</sup>) and 3 (for **II**-·**L**i<sup>+</sup>). The resulting interaction energy can be estimated by either deletion of the appropriate off-diagonal elements of the Fock matrix in the NBO basis ( $E_{del}$  energy) or the standard second-order perturbation approach [which affords an E(2) energy]. The magnitude of the donor– acceptor interaction is mainly controlled by i) the energy gap ( $\Delta E_{ij}$ ) between the donor and acceptor orbitals, ii) the corresponding Fock matrix element ( $F_{ij}$ ) and iii) the occupation of the donor orbital ( $n_i$ ). As expected, the NBO analysis indicates that the S–Li and C–Li interactions are essentially electrostatic in nature ( $n_{Wiberg} \approx 0.1$ ,  $q_{Li} > 0.85$ ).

Table 2. Main stabilization of the lone pair at the central carbon atom in  $I^{-}Li^{+}$  [only E(2) > 0.5 kcal/mol are considered].

Donating orbital	Accepting orbitaltype $E(2)$ $\Delta E_{ij}$ kcal/mol(u.a.)		$\Delta E_{ij}$ (u.a.)	$F_{ij}$ (u.a.)	$\Sigma[E(2)]$ kcal/mol	
LP1(C)	σ*(P–S)	8.30	0.32	0.048	19.20	total
LP1(C)	$\sigma^*(P-H)$	10.27	0.41	0.060		31.78
LP1(C)	$\sigma^*(P-H)$	0.63	0.41	0.015		
LP1(C)	$\sigma^*(Si-C)$	1.72	0.47	0.027	12.58	
LP1(C)	σ*(Si–C)	9.96	0.47	0.064		
LP1(C)	σ*(Si–C)	0.90	0.47	0.019		

Table 3. Main stabilization of the lone pair at the central carbon atom in  $\mathbf{H}$ - $\mathbf{Li}^+$  [only E(2) > 0.5 kcal/mol are considered].

Accepting orbital					$\Sigma[E(2)]$	
type	<i>E</i> (2) kcal/mol	$\Delta E_{ij}$ (u.a.)	$F_{ij}$ (u.a.)	kcal/m	nol	
$\sigma^{*}(P-S)$ $\sigma^{*}(P-H)$	10.86	0.31	0.055	20.53	total	
$\sigma^{*}(P-S)$	10.86	0.39	0.055	20.52	41.05	
	Accepting $\sigma^{*}(P-S)$ $\sigma^{*}(P-H)$ $\sigma^{*}(P-S)$ $\sigma^{*}(P-S)$	Accepting orbitaltype $E(2)$ kcal/mol $\sigma^*(P-S)$ 10.86 $\sigma^*(P-H)$ 9.67 $\sigma^*(P-S)$ 10.86	Accepting orbital           type $E(2)$ $\Delta E_{ij}$ kcal/mol         (u.a.) $\sigma^*(P-S)$ 10.86         0.31 $\sigma^*(P-H)$ 9.67         0.39 $\sigma^*(P-S)$ 10.86         0.31 $\sigma^*(P-S)$ 0.67         0.29	Accepting orbital $E(2)$ $\Delta E_{ij}$ $F_{ij}$ (u.a.)           type $E(2)$ $\Delta E_{ij}$ $F_{ij}$ (u.a.) $\sigma^*(P-S)$ 10.86         0.31         0.055 $\sigma^*(P-H)$ 9.67         0.39         0.057 $\sigma^*(P-S)$ 10.86         0.31         0.055	Accepting orbital $\Sigma[E(2)]$ type $E(2)$ $\Delta E_{ij}$ $F_{ij}$ (u.a.)         kcal/m $\sigma^*(P-S)$ 10.86         0.31         0.055         20.53 $\sigma^*(P-H)$ 9.67         0.39         0.057 $\sigma^*(P-S)$ 10.86         0.31         0.055         20.52 $\sigma^*(P-S)$ 10.86         0.31         0.055         20.52 $\sigma^*(P-S)$ $0.66$ 0.32         0.057	

It is obvious that the stabilization brought by the PPh<sub>2</sub>S groups in the two compounds is very similar (19.0 kcal/mol in  $I^-Li^+$  and 20.0 kcal/mol in  $II^-Li^+$ ). The stabilization by the SiMe<sub>3</sub> substituent is 12.0 kcal/mol, which results in a weaker overall stabilization of the lone pair in  $I^-Li^+$ . The geometric changes observed upon deprotonation are therefore readily rationalized. Indeed, the electron donation from C into the antibonding orbitals results in the elongation of the P–S bond and the shortening of the P–C bond in  $II^-Li^+$  and a shortening of the C–Si bond in  $I^-Li^+$ . As a consequence, the stabilization of the lone pair at C in  $I^-Li^+$  appears less efficient, which could in turn result in a better electron transfer to a metal center.

### **Coordination Chemistry**

We then focused our study on the use of the two anions as ligands for  $Rh^{I}$  metal fragments. The addition of two equivalents of  $1 - Li^{+}$  to a solution of one equivalent of



Scheme 5. Synthesis of 3, 4, and 5.

[Rh(COD)Cl]<sub>2</sub> (COD = 1,5-cyclooctadiene) in toluene instantaneously led to a dark solution. The reaction was conveniently followed by <sup>31</sup>P NMR spectroscopy, and completion was reached within 15 min. After elimination of LiCl and evaporation of the solvent, **3** was isolated as a dark orange powder (Scheme 5). Evidence of the coordination of **1**<sup>-</sup>**Li**<sup>+</sup> to the rhodium center was seen by <sup>31</sup>P NMR spectroscopy, where **3** exhibited a doublet at 37.8 ppm (<sup>2</sup>J<sub>PRh</sub> = 15.5 Hz).

Complex **3** was characterized by multinuclear NMR spectroscopy. The alkenic protons of the COD ligand were found as two well separated sets of peaks at  $\delta_{\rm H}$  = 4.68 (2 H) and 4.22 (1 H)–3.99 ppm (1 H), which highlights the very different *trans* effect of the sulfur and CH moieties. The signal that corresponds to the central CH proton is unfortunately masked by the COD ligand. In the <sup>13</sup>C NMR spectrum, the corresponding signal is found at a high field (–2.7 ppm as a doublet of doublets, <sup>1</sup>J<sub>RhC</sub> = 15.5 and <sup>1</sup>J<sub>PC</sub> = 26 Hz). This chemical shift is high-field shifted compared to the starting anion (11.7 ppm). Slow evaporation of a concentrated solution of **3** in CH<sub>2</sub>Cl<sub>2</sub> led to the formation of single crystals suitable for X-ray diffraction. An ORTEP plot of **3** is presented in Figure 3.



Figure 3. ORTEP plot (50% thermal ellipsoids) of **3.** Hydrogen atoms [except H(1)] are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)-P(1) 1.739(6), P(1)-S(1) 2.019(2), C(1)-Si(1) 1.880(5), C(1)-Rh(1) 2.171(6), S(1)-Rh(1) 2.415(2), Rh(1)-C(17) 2.102(5), Rh(1)-C(18) 2.160(6), Rh(1)-C(21) 2.146(6), Rh(1)-C(22) 2.201(6), C(17)-C(18) 1.402(8), C(21)-C(22) 1.38(1), P(1)-C(1)-Si(1) 119.6(3), S(1)-P(1)-C(1) 103.1(2), C(1)-Rh(1)-S(1) 79.8(2), P(1)-C(1)-Rh(1) 89.2(2), S(1)-P(1)-C(1)-Rh(1) 35.1.

Complex 3 features a slightly distorted square-planar geometry at the rhodium center. This geometry is usual for  $ML_4$  complexes with 16 electrons and a d<sup>8</sup> metal center. The Rh–C(H) bond length falls in the range of other reported pincer complexes of rhodium.<sup>[15]</sup> In 3, the P–C(1) distance is longer than that in 1-·Li+ [1.739(6) vs. 1.701(1) Å] as well as the C-Si bond [1.880(5) vs. 1.827(1) Å]. These increases in bond lengths are consistent with the high-field chemical shift of the CH moiety in the <sup>13</sup>C NMR spectrum because they point a higher electron density at C than in the anion itself. These types of complexes are typically used as starting materials for further transformations as the COD ligand can easily be displaced. Thus, the reaction of 3 with carbon monoxide or stoichiometric amounts of 2,6-dimethylphenyl isocyanide was investigated (Scheme 5). Complexes 4 and 5 both exhibit a doublet in the <sup>31</sup>P NMR spectra, shifted downfield compared to **3** (62.1 ppm with  ${}^{2}J_{RhP}$  = 16.6 Hz for **4**, and 51.4 ppm with  ${}^{2}J_{\rm RhP}$  = 12.3 Hz for 5, vs. 37.8 ppm in 3). The <sup>13</sup>C NMR spectrum of 4 (and 5) shows that two inequivalent CO (isocyanide) ligands are present as expected. Most interestingly, the chemical shifts of the CH moieties in 4 and 5 are again found at higher field than in 3: -7.4 ppm ( ${}^{1}J_{RhC} = 12$ ,  ${}^{1}J_{PC} = 21$  Hz) for 4 and -5.0 ppm ( ${}^{1}J_{RhC} = 11.5$ ,  ${}^{1}J_{PC} = 24.7$  Hz) for 5. The bidentate S~C coordination in both complexes was proven by X-ray diffraction analysis. Quite surprisingly, single crystals of 4 were obtained by diffusion of water into a concentrated solution of 4 in acetone, and crystals of 5 were obtained by diffusion of pentane into concentrated solutions of 5 in toluene at -40 °C. Views of 4 and 5 are given in Figures 4 and 5, respectively.



Figure 4. ORTEP plot (50% thermal ellipsoids) of 4. Hydrogen atoms [except H(1)] are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)-P(1) 1.752(3), P(1)-S(1) 2.023(1), C(1)-S(1) 1.883(3), Rh(1)–C(1) 2.149(3), Rh(1)–C(17) 1.888(4), Rh(1)–C(18) 1.847(4), C(17)–O(1) 1.131(5), C(18)–O(2) 1.138(5), Rh(1)–S(1) 2.398(1), P(1)–S(1) 2.023(1), P(1)–C(1)–Si(1) 119.7(2), O(1)–C(17)–Rh(1) 177.4(4), O(2)–C(18)–Rh(1) 177.3(4), C(17)–C(18)–C(1)–S(1) 3.77.



Figure 5. ORTEP plot (50% thermal ellipsoids) of 5. Hydrogen atoms [except H(1)] are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–P(1) 1.749(1), P(1)–S(1) 2.0131(6), C(1)–Si(1) 1.871(2), C(1)–Rh(1) 2.174(1), S(1)–Rh(1) 2.4097(4), C(17)–N(1) 1.167(2), C(26)–N(2) 1.163(2), P(1)–C(1)–Si(1) 118.76(8), S(1)–P(1)–C(1) 103.23(5), C(1)–Rh(1)–S(1) 80.06(4), P(1)–C(1)–Rh(1) 89.21(6), S(1)–C(1)–C(26)–C(17) 2.35.

Both complexes feature expected square planar geometries. The CO bond lengths in **4** [1.131(5) and 1.138(5) Å] are in the range for CO bonds usually reported for carbonyl pincer complexes of Rh<sup>1,[16]</sup> The same applies for the CN bonds in **5**.<sup>[17]</sup> Infrared stretches of the carbonyl groups in **4** were found at 2145 and 2078 cm<sup>-1</sup>, which indicate weak backbonding of the rhodium center. The CN bands in **5** were found at 2117 and 2046 cm<sup>-1</sup>. Interestingly, the coordination of two strongly accepting ligands, such as CO or CNR, did not result in a significant change of the C(H)– Rh bond length in **4** or **5** compared to **3** [2.171(6) in **3**, 2.149(3) in **4**, 2.174(1) Å in **5**]. The same holds for the C–P, P–S, and C–Si bond lengths of **1**<sup>-</sup>. Overall, it appears that the coligands (COD, CNR, or CO) exert a similar influence on **1**<sup>-</sup> coordinated to the Rh center.

We compared the reactivity of  $1 - Li^+$  with  $2 - Li^+$  with the same rhodium precursor. The reaction of two equivalents of  $2 - Li^+$  with one equivalent of  $[Rh(COD)Cl]_2$  led to a doublet at 36.1 ppm ( ${}^2J_{RhP} = 5$  Hz, 6) in the  ${}^{31}P$  NMR spectrum, which indicated coordination to the rhodium center ( $2 - Li^+$  exhibits a singlet at 37.5 ppm) as reported by Dixon et al. (Scheme 6).<sup>[4c]</sup>



A slightly different set of data was obtained for the Xray structure of 6 (Supporting Information). These data confirmed that 2-·Li+ acts as a S~S bidentate ligand. COD was successfully displaced from 6 using 2,6-diphenyl isocyanide. In a first attempt to favor S~C~S tridentate coordination of the Rh center, the reaction of 6 with one equivalent of isocyanide was carried out, which resulted in the conversion of half of 6 into a new complex characterized by a broad singlet at 54.1 ppm in the <sup>31</sup>P NMR spectrum (7), leaving half of 6 unreacted. The addition of a second equivalent of isocyanide to the crude mixture led to the total conversion of 6 into 7 (Scheme 6). This new complex was fully characterized by NMR spectroscopy. The signal for the central CH proton is seen as a triplet of doublets at  $\delta_{\rm H}$  = 2.58 ppm (<sup>2</sup>J<sub>RhH</sub> = 1.5 and <sup>2</sup>J<sub>PH</sub> = 8 Hz). Similarly, the reaction of 6 with carbon monoxide led to the full conversion of 6 into a new complex, 8, characterized by a doublet at 62 ppm ( ${}^{2}J_{RhP}$  = 10 Hz) in the  ${}^{31}P$  NMR spectrum. In 8, the signal for the central CH proton is seen at  $\delta_{\rm H}$  = 2.68 ppm (doublet of triplets,  ${}^2J_{\rm RhH}$  = 1.8 and  ${}^2J_{\rm PH}$  = 8 Hz). Surprisingly, in the <sup>13</sup>C NMR spectra of 7 and 8 only one signal can be seen for the isocyanide ligands at 160.0 ppm ( ${}^{1}J_{RhC}$  = 69 Hz) for CN in 7 and 185.6 ppm  $({}^{1}J_{RhC} = 70 \text{ Hz})$  for CNR in 8. The signal for the PCHP carbon atom in 7 is found at 6.2 ppm as an unresolved multiplet and at 0 ppm in 8. In this case, these chemical shifts are at much higher field than in 2-·Li+ (20 ppm).<sup>[14]</sup> At this point, because of the apparent equivalence of the two isocyanide (or carbonyl) ligands and the two phosphorus moieties by NMR, three cases can be envisaged for the geometry of 7 and 8: a) a pentacoordinate Rh center with tridentate S~C~S coordination, b) a static S~S bidentate coordination as in 6, or c) a fast equilibrium between two  $ML_4$  complexes that feature S~C coordination. An initial answer was provided by the X-ray analysis of single crystals of 7 grown by the slow diffusion of pentane into a concentrated solution of the complex in toluene. A view of 7 is given Figure 6.

In this structure of 7, the central carbon atom is coordinated to the Rh<sup>I</sup> center and one pendant sulfur atom has been decoordinated. This is confirmed by the short Rh– $C_{bridge}$  distance in 7 compared to that in 6 [2.198(3) vs.



#### Scheme 6. Synthesis of 6, 7, and 8.



Figure 6. ORTEP plot (50% thermal ellipsoids) of 7. Hydrogen atoms [except H(1)] are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–P(1) 1.768(3), C(1)–P(2) 1.792(3), Rh(1)–C(1) 2.198(3), Rh(1)–S(1) 2.390(1), P(1)–S(1) 2.014(1), P(2)–S(2) 1.972(1), Rh(1)–C(27) 1.908(4), Rh(1)–C(26) 1.887(4), N(1)–C(26) 1.167(5), N(2)–C(27) 1.160(4), P(1)–C(1)–P(2) 118.7(2), N(2)–C(27)–Rh(1) 177.0(3), N(1)–C(26)–Rh(1) 176.2(3), C(27)–C(26)–C(1)–S(1) 2.27.

3.99 Å]. The coordination of the isocyanide ligand results in a drastic change in the coordination mode of  $2^{-}$  from S~S to S~C. In the solid state, 7 features two nonequivalent phosphorus atoms, which rules out two of our three hypotheses. A variable-temperature (VT) <sup>31</sup>P NMR experiment was carried out to confirm a dynamic exchange between the two S atoms. On cooling the solution from 25 °C, a coalescence of the broad singlet at 54 ppm was observed at ca. -65 °C. At -80 °C, the <sup>31</sup>P NMR spectrum presents a broadened AB system at 76.5 and 56.7 ppm. This process is fully reversible, and increasing the temperature back to 25 °C resulted in the reappearance of the singlet at 54 ppm. From this data, the energy associated with this dynamic phenomenon can be calculated as 8.4 kcal/mol.<sup>[18]</sup> DFT calculations were conducted to give an insight into the mechanism that renders the two phosphane sulfides equivalent at room temperature. Several complexes with different structures (VII-sp<sub>a</sub>, VII-bpt, VII-tp, VII-sp<sub>b</sub>) were envisaged (Scheme 7). The starting geometry of VII-sp was taken directly from the X-ray structure prior to optimization, VIIbpt features a five-coordinate rhodium center with a trigonal bipyramid geometry, and VII-tp features a three-coordinate rhodium center with a trigonal planar geometry. VIIbpt and VII-tp were suspected to be possible intermediates

in the sulfur exchange process, and VII-sp<sub>a</sub> was found to be a minimum on the potential energy surface. Interestingly, when trying to optimize VII-bpt and VII-tp, both structures evolved towards VII-sp<sub>c</sub>, which features a square-planar rhodium center in which the uncoordinated sulfur atom is brought nearer to the metal than in VII-sp<sub>a</sub> (Scheme 7). In fact, it results from a rotation of the PPh<sub>2</sub>PS arm. Energetically, VII-sp<sub>c</sub> is 6.4 kcal/mol above VII-sp<sub>a</sub>. A transition state (TS) that connects VII-sp<sub>c</sub> and its mirror image was sought but could not be found. VII-sp<sub>b</sub> was also optimized and its energy is 7.2 kcal/mol above VII-sp<sub>a</sub>. This difference in energy corroborates the fact that 7 is only found as C~S bidentate.

These data allow us to propose the following mechanism for the fast dynamic process observed by NMR spectroscopy that renders the two thiophosphinoyl moieties equivalent (Scheme 8). From the most stable complex, VIIsp<sub>a</sub>, rotation of the arm results in an increase of the energy to form VII-sp<sub>c</sub>. In this complex, the S–Rh and C–Rh distances are 4.73 and 2.24 Å, respectively. We then propose the reaction to go to VII-sp<sub>b</sub> (the S–Rh and C–Rh distances are 2.51 and 4.20 Å, respectively). The S atom becomes bonded while the C atom decoordinates from the metal center. We have not found a TS that connects these two minima, which can be explained by the apparent very flat potential energy surface. Indeed, experimentally, the overall exchange was measured at 8.4 kcal/mol, which points a TS within 2–3 kcal/mol from VII-sp<sub>c</sub>.



Scheme 8. Proposed mechanism for the equilibrium.

#### Conclusions

We compared two anionic ligand systems that have a "CH–PPh<sub>2</sub>S" fragment in common. These ligands differ only in the remaining substituent at the carbon atom. DFT calculations showed that the stabilization of the lone pair provided by two thiophosphinoyl fragments is more efficient than the stabilization by one thiophosphinoyl and a



L = CNR, R = 2,6-dimethylphenyl

Scheme 7. Starting structures for the theoretical calculations.

SiMe<sub>3</sub> fragment. The coordination of  $1 - Li^+$  to Rh<sup>I</sup> resulted in the expected bidentate C~S coordination with little influence of the coligands on the geometric parameters of the complex. The coordination of  $2^- \cdot Li^+$  to Rh<sup>I</sup> resulted in both C~S and S~S coordination, which shows that the coordination mode can be tuned by the coligands. In the C~S bonded structure, VT NMR experiments proved a low-energy pathway that equilibrated the two PPh<sub>2</sub>S moieties. DFT calculations showed the energies of the associated complexes to be very similar and the S~S coordinated complex was within 7.2 kcal/mol. This switch in coordination could provide "inside tuning" of the electronic properties of a metal center during a catalytic process.

## **Experimental Section**

**General Procedures:** All reactions were performed under an inert atmosphere of argon or nitrogen by using Schlenk and glovebox techniques and dry, deoxygenated solvents. Solvents were dried using a MBRAUN SPS-800 system. NMR spectra were recorded with a Bruker AC-300 SY spectrometer operating at 300.0 MHz for <sup>1</sup>H, 75.5 MHz for <sup>13</sup>C, and 121.5 MHz for <sup>31</sup>P. Solvent peaks are used as internal references relative to Me<sub>4</sub>Si for <sup>1</sup>H and <sup>13</sup>C chemical shifts; <sup>31</sup>P chemical shifts are relative to a 85% H<sub>3</sub>PO<sub>4</sub> external reference. The following abbreviations are used: s singlet, br. s broad singlet, d doublet, dd doublet of doublets, t triplet, td triplet of doublets, m multiplet. [Rh(COD)Cl]<sub>2</sub> was prepared according to a literature procedure.<sup>[19]</sup> All other reagents and chemicals were obtained commercially and used as received.

Synthesis of 1: Compound 1 was prepared according to a slight modification of ref.<sup>[7]</sup> To a solution of diphenylphosphane (2.22 mL, 12.8 mmol) in THF (30 mL) was added butyllithium (1.6 m in hexanes, 8 mL, 12.8 mmol) at -78 °C. The solution turned instantly red and was left to warm to room temperature. Chloromethyltrimethylsilane (1.8 mL, 12.8 mmol) was added at 0 °C, and the solution was warmed to room temperature and stirred for 1 h. The <sup>31</sup>P NMR spectrum showed the formation of the desired phosphane. S<sub>8</sub> (410.5 mg, 1.6 mmol) was then added, and the solution was left to stir at 60 °C for 4 h. Solvents were evaporated and hexanes (20 mL) were added. After heating at reflux for 15 min and filtration followed by evaporation of the solvent, 1 was isolated as a white crystalline solid (3.3 g, 10.8 mmol, 84%).  ${}^{31}P{}^{1}H$  NMR  $(C_6D_6)$ :  $\delta = 37.7$  (s) ppm. <sup>1</sup>H NMR  $(C_6D_6)$ :  $\delta = 7.78-7.88$  (m, 4 H, phenyl), 7.0 (m, 6 H, phenyl), 1.70 (d,  ${}^{2}J_{PH} = 16$  Hz, CH<sub>2</sub>), 0.06 [s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 136.6 (d, <sup>1</sup>J<sub>PC</sub> = 80 Hz, C phenyl), 130.5 (d,  ${}^{2}J_{PC}$  = 10.7 Hz, CH phenyl), 130.1 (d,  ${}^{2}J_{PC}$  = 3.6 Hz, CH phenyl), 127.8 (d,  ${}^{2}J_{PC}$  = 12.3 Hz, CH phenyl), 21 (d,  ${}^{1}J_{PC}$  = 47.6 Hz, CH<sub>2</sub>), 0.02 [d,  ${}^{2}J_{PC}$  = 3.3 Hz, Si(CH<sub>3</sub>)<sub>3</sub>] ppm.

**Synthesis of 1<sup>--</sup>Li<sup>+</sup>:** To a solution of **1** (121.8 mg, 0.04 mmol) in toluene at -78 °C was added methyllithium (1.6 M in Et<sub>2</sub>O, 0.25 mL, 0.04 mmol). The solution was left to warm to room temperature and rapidly turned yellow. The reaction was complete after 1 h of stirring. Compound 1<sup>--</sup>Li<sup>+</sup> was typically not isolated but used directly as prepared. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 44.5 (s) ppm. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 8.12 (m, 4 H, *o*-phenyl), 7.08–7.19 (m, 6 H, *m*-phenyl + *p*-phenyl), 0.50 [d, <sup>2</sup>J<sub>PH</sub> = 9 Hz, 1 H, PCHSi(CH<sub>3</sub>)<sub>3</sub>], 0.00 [s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 138.6 (br. s, C-*ipso*), 131.9 (d, <sup>2</sup>J<sub>PC</sub> = 11.6 Hz, *o*-phenyl), 130.1 (br. s, *p*-phenyl), 127.6 (d, <sup>3</sup>J<sub>PC</sub> = 12.4 Hz, *m*-phenyl), 11.7 [d, <sup>1</sup>J<sub>PC</sub> = 60 Hz, PCHSi(CH<sub>3</sub>)<sub>3</sub>], 2.2 [d, <sup>3</sup>J<sub>PC</sub> = 2 Hz, Si(CH<sub>3</sub>)<sub>3</sub>] ppm.



Synthesis of 3: To a solution of 1-Li<sup>+</sup> (0.1 mmol/mL in toluene, 5 mL, 0.5 mmol) in toluene (1 mL) was added a solution of [Rh(COD)Cl]<sub>2</sub> (123.3 mg, 0.25 mmol) in toluene (1 mL). The solution immediately turned orange and was left to stir for 15 min. After centrifugation and evaporation of the solvent, 3 was isolated as a dark orange powder (231.5 mg, 90%). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 37.8 (d,  $J_{RhP}$  = 15.5 Hz) ppm. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.90 (m, 2 H, 2CH-ortho PPh<sub>2</sub>), 7.70 (m, 2 H, 2CH-ortho PPh<sub>2</sub>), 7.06 (m, 3 H, 2CH-meta + CH-para PPh<sub>2</sub>), 6.98 (m, 3 H, 2CH-meta + CH-para PPh<sub>2</sub>), 4.68 (m, 2 H, 2CH COD), 4.22 (m, 1 H, CH COD), 3.99 (m, 1 H, CH COD), 1.37–2.44 (m, 9 H, 4CH<sub>2</sub> COD + PCHSiMe<sub>3</sub>), 0.26 [s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub> ppm.] <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 140.7 (dd, J = 1.2, J = 46.5 Hz, C of phenyl); 139.3 (d, J = 81 Hz, C of phenyl); 84.6 (d, J = 8.8 Hz, CH of COD), 83.2 (d, J = 8.8 Hz, CH of COD), 77.4 (d, J = 14 Hz, CH of COD), 70.9 (d, J = 14 Hz, CH of COD), 32.3 (s, CH<sub>2</sub> of COD), 30.2 (s, CH<sub>2</sub> of COD), 29.1 (s, CH<sub>2</sub> of COD), 27.8 (s, CH<sub>2</sub> of COD), 2.9 [d,  $J_{\rm PC}$  = 4.8 Hz, PCHSi(CH<sub>3</sub>)<sub>3</sub>], -2.7 (dd,  $J_{RhC}$  = 15.5,  $J_{PC}$  = 26 Hz, PCSi) ppm. C24H32PRhSSi (514.54): calcd. C 56.02, H 6.27; found C 55.84, H 6.23.

**Synthesis of 4:** To a solution of **3** (41.2 mg, 0.08 mmol) in toluene (3 mL) was added carbon monoxide with a balloon for 5 min. The solution turned immediately orange then brown. The solvents were evaporated under vacuum to yield **4** as a brown powder (30 mg, 81%). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 62.1$  (d,  $J_{RhP} = 16.6$  Hz) ppm. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 7.92-7.82$  (m, 2 H), 7.74–7.66 (m, 2 H), 7.61–7.46 (m, 6 H), 0.76 (dd,  $J_{RhH} = 1.3$ ,  $J_{PH} = 7.5$  Hz, 1 H, PCHSi), 0.00 [s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 187.3$  (d,  $J_{RhC} = 78$  Hz, CO), 186.1 (d,  $J_{RhC} = 61$  Hz, CO), 137.9 (d,  $J_{PC} = 55$  Hz,  $C_{ipso}$ ), 136.6 (d,  $J_{PC} = 78$  Hz,  $C_{ipso}$ ), 131.9 (d,  $J_{PC} = 11.8$  Hz, C), 130.0 (d,  $J_{PC} = 12.2$  Hz, C), 128.6 (d,  $J_{PC} = 12.6$  Hz, C), 128.5 (d,  $J_{PC} = 12.0$  Hz, C), 30 [br. s, Si(CH<sub>3</sub>)<sub>3</sub>], -7.4 (dd,  $J_{RhC} = 12$ ,  $J_{PC} = 21$  Hz, PCHSi) ppm. HRMS (EI): calcd. for C<sub>18</sub>H<sub>20</sub>O<sub>2</sub>PRhSSi [M]<sup>+</sup> 461.9746; found 461.9753.

Synthesis of 5: To a solution of 3 (123.6 mg, 0.24 mmol) in toluene (3 mL) was added 2,6-dimethylphenyl isocyanide (63 mg, 0.48 mmol) under nitrogen. The solution turned instantly red. After stirring for 15 min, the solvent was evaporated under vacuum. Petroleum ether (5 mL) was added under nitrogen, which caused the precipitation of a yellow solid. The solid was isolated by centrifugation and washed twice with petroleum ether (3 mL) to yield 5 (149 mg, 93%). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 51.4 (d,  $J_{PRh}$  = 12.3 Hz) ppm. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 8.36–8.27 (m, 2 H), 7.82–7.73 (m, 2 H), 2.32 (s, 6 H, CH<sub>3</sub> isocyanide), 2.09 (s, 6 H, CH<sub>3</sub> isocyanide), 0.75 (dd,  $J_{RhH} = 1.1$ ,  $J_{PH} = 7.3$  Hz 1 H, PCHSi), 0.38 [s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 161.7 (d,  $J_{RhC}$  = 78 Hz, CN), 161.3 (d,  $J_{RhC}$  = 60 Hz, CN), 143.5 (d,  $J_{RhC}$  = 48 Hz,  $C_{qat}P$ ), 142.3 (d,  $J_{RhC}$  = 79.8 Hz,  $C_{qat}P$ ), 134.1 (s,  $C_{phenyl}N$ ), 133.8 (s,  $C_{phenyl}N$ ), 21.4 (s, CH<sub>3</sub> isocyanide), 21.1 (s, CH<sub>3</sub> isocyanide), 6.7 [d,  $J_{RhC}$  = 4.5 Hz, Si(CH<sub>3</sub>)<sub>3</sub>], -5.0 (dd,  $J_{RhC}$  = 11.5,  $J_{PC}$  = 24.7, PCHSi) ppm. HRMS (EI): calcd. for C<sub>34</sub>H<sub>38</sub>N<sub>2</sub>PRhSSi [M]<sup>+</sup> 668.1318; found 668.1315.

Synthesis of 6: To a solution of dppmS2 (143.4 mg, 0.32 mmol) in toluene (4 mL) was added methyllithium (1.6  $\mbox{m}$  in Et<sub>2</sub>O, 0.2 mL, 0.32 mmol) at -78 °C. The solution was warmed to room temperature and stirred for 1.5 h. The solution changed from colorless to yellow. [Rh(COD)Cl]<sub>2</sub> (78.9 mg, 0.16 mmol) was added at room temperature. The solution was left to stir for 1 h. The solution was concentrated to ca. 0.5 mL and petroleum ether (5 mL) was added to allow the precipitation of LiCl and a yellow solid. The solid mixture was collected by filtration, washed twice with petroleum

ether (3 mL), and dried. Yellow complex **6** was extracted with toluene after the removal of LiCl (198 mg, 94%). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 36.1 (d,  $J_{RhP}$  = 5 Hz) ppm. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.92–7.83 (m, 8 H, H<sub>arom</sub>), 6.85–6.78 (m, 12 H, H<sub>arom</sub>), 4.14 (br. s, 4 H, CH of COD), 1.84–1.72 (m, 4 H, CH<sub>2</sub> of COD), 1.79 (bt,  $J_{PH}$  = 2 Hz, 1 H, PC*H*P), 1.35–1.27 (m, 4 H, CH<sub>2</sub> of COD) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 137.7 (d,  $J_{PC}$  = 90 Hz, C<sub>quat</sub>), 131.0 (pseudo-t, CH<sub>arom</sub>), 129.5 (s, CH<sub>arom</sub>), 127.2 (pseudo-t, CH<sub>arom</sub>), 80.3 ( $J_{RhC}$  = 12 Hz, CH of COD), 30 (s, CH<sub>2</sub> of COD), 12.3 (td,  $J_{PC}$  = 93,  $J_{RhC}$  = 4 Hz, PCHP) ppm.

Synthesis of 7: To a solution of 6 (100 mg, 0.15 mmol) in THF was added 2,6-dimethylphenyl isocyanide (39.8 mg, 0.30 mmol). The solution immediately went from orange to red. It was left to stir for 15 min at room temperature and concentrated to ca. 0.5 mL. Petroleum ether (5 mL) was added, which allowed the precipitation of a yellow solid that was extracted by centrifugation and washed twice with petroleum ether (117 mg, 96%).  ${}^{31}P{}^{1}H$  NMR ([D<sub>8</sub>]toluene):  $\delta = 54$  (br. s) ppm. <sup>1</sup>H NMR ([D<sub>8</sub>]toluene):  $\delta = 7.83$  (br. s, 8 H, H<sub>arom</sub>), 7.12 (br. s, 12 H, H<sub>arom</sub>), 7.02–6.90 (singlets, H<sub>arom</sub> isocyanides), 2.58 (td,  $J_{RhH}$  = 1.5,  $J_{PH}$  = 8 Hz, PCHP), 2.14 (s, 12 H, CH<sub>3</sub> isocyanides) ppm. <sup>13</sup>C NMR ([D<sub>8</sub>]toluene):  $\delta = 160$  (d,  $J_{\rm RhC}$  = 69 Hz, CN), 137.1 (dd,  $J_{\rm PC}$  = 4,  $J_{\rm PC}$  = 75 Hz,  $C_{ipso}$ ), 134.8 [s,  $C(CH_3)$  isocyanide], 132.9 (d,  $J_{PC}$  = 11 Hz,  $C_{ortho}$ ), 130.8 (d,  $J_{PC}$ = 4 Hz,  $C_{para}$ ), 128.4 (s,  $C_{meta}$  isocyanide), 128.0 (d,  $J_{PC}$  = 12 Hz, C<sub>meta</sub>), 127.5 (s, C<sub>para</sub> isocyanide), 19.5 (s, CH<sub>3</sub> isocyanide), 6.2 (m, PCHP) ppm. C<sub>43</sub>H<sub>39</sub>N<sub>2</sub>P<sub>2</sub>RhS<sub>2</sub> (812.77): calcd. C 63.54, H 4.84; found C 63.25, H 4.92.

**Synthesis of 8:** To a solution of **6** (100 mg, 0.15 mmol) in THF was added CO with a balloon for 5 min. The solution immediately went from orange to brown. It was left to stir for 15 min at room temperature and dried under vacuum to isolate a brown solid (77 mg, 85%). <sup>31</sup>P{<sup>1</sup>H} NMR ([D<sub>8</sub>]toluene):  $\delta = 62$  (d,  $J_{RhP} = 10$  Hz) ppm. <sup>1</sup>H NMR ([D<sub>8</sub>]toluene):  $\delta = 7.74-7.62$  (m, 8 H, H<sub>arom</sub>), 7.18–6.87 (m, 12 H, H<sub>arom</sub>), 2.68 (td,  $J_{RhH} = 1.8$ ,  $J_{PH} = 8$  Hz, PCHP) ppm. <sup>13</sup>C NMR ([D<sub>8</sub>]toluene):  $\delta = 185.6$  (d,  $J_{RhC} = 70$  Hz, CO), 135.2 (dd,  $J_{PC} = 4$ ,  $J_{PC} = 76$  Hz,  $C_{ipso}$ ), 132.2 (d,  $J_{PC} = 11$  Hz,  $C_{meta}$ ), 131.8 (d,  $J_{PC} = 3$  Hz,  $C_{para}$ ), 128.5 (d,  $J_{PC} = 13$  Hz,  $C_{ortho}$ ), 0.0 (m, PCHP) ppm. C<sub>27</sub>H<sub>21</sub>O<sub>2</sub>P<sub>2</sub>RhS<sub>2</sub> (606.43): calcd. C 53.47, H 3.49; found C 53.40, H 3.67.

CCDC-847285 (for 1), -847286 (for  $1-Li^+$ ), -847287 (for 3), -847288 (for 4), -847289 (for 5), -847290 (for 6), and -847291 (for 7) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

**Supporting Information** (see footnote on the first page of this article): Crystallographic details, computational details for calculations, view of computed structures, Cartesian coordinates and the three lowest frequencies for each optimized structure.

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