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Mixed (P=S/P=O)-Stabilized Geminal Dianion: Facile Diastereoselective Intramolecular C–H Activations by a Related Ruthenium–Carbene Complex

Hadrien Heuclin,[a] Xavier F. Le Goff,[a] and Nicolas Mézailles*[a, b]

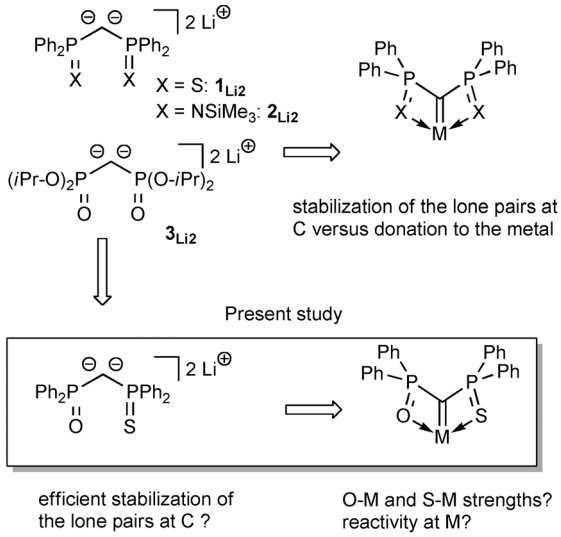
In memory of Pascal Le Floch

Abstract: A new unsymmetrical geminal dianion that contained both a phosphine oxide moiety and a phosphine sulfide moiety has been synthesized. Its reactivity towards Ru^{II} was explored, which led to the formation of a highly reactive carbene complex that evolved at room temperature to yield a kinetic orthometalated Ru^{II} complex through C–H activation of the phenyl group of the phosphine oxide moiety. This insertion was found to be thermally reversible and a second C–H insertion occurred at a phenyl group of the phosphine sulfide moiety to form the thermodynamic orthometalated Ru^{II} complex in a diastereospecific manner. DFT calculations fully rationalized the experimental findings in terms of the relative energies of the kinetic and thermodynamic products and allowed the mechanism of this process to be fully understood.

Keywords: carbenes · coordination modes · density functional calculations · dianions · ruthenium

Introduction

The use of phosphorus-stabilized geminal dianions[1] as precursors of carbene complexes has emerged as a powerful synthetic tool over the past decade. Part of the interest in using such species lays in their potential donation of the four electrons in the metal–carbon interactions. As a consequence, carbene complexes of not only transition metals[2] and main-group elements,[3] but also of rare-earth metals[4,5] and actinides,[6] have been synthesized with ligands $\mathbf{1}_{Li2}$–$\mathbf{3}_{Li2}$.[7] These latter cases have been studied in great details because the understanding of the electronic nature of the M=C bond, as well as its reactivity, is of fundamental interest. An alternative approach to these complexes relies on the double deprotonation of the coordinated neutral ligand, although it requires the synthesis of a precursor complex that features two strongly basic ligands. Theoretical calculations on two dianionic species, $\mathbf{1}_{Li2}$ and $\mathbf{3}_{Li2}$ (Scheme 1), have shown that the stabilization of the two lone pairs on the same carbon atom depends, to the greatest extent, on the different substituents on the phosphorus atom, through the accepting antibonding P–X orbitals.[1f] Not surprisingly then, the stabilization by the PPh_2=S moiety appeared to be weaker than that by the $P(OR)_2$=O moiety. In turn, the overall donation toward the metal center will be in competition with the stabilization by the substituent at the carbon center; that is, the stronger the stabilization is, the weaker the donation will be. Thus, it is of interest to have access to a wide range of dianions to be able to finely tune these parameters. These dianions possess the important additional feature of being tridentate ligands. Thus, we envisaged that the chemistry at the metal could also be tuned by the strength of the X–M bond. This new property relies on



Scheme 1. Coordination patterns of the geminal dianions to metal centers.

[a] H. Heuclin, Dr. X. F. Le Goff, Dr. N. Mézailles
Laboratoire Hétéroéléments et Coordination
Ecole Polytechnique, CNRS
Route de Saclay, 91120 Palaiseau (France)

[b] Dr. N. Mézailles
Current address: Laboratoire Hétérochimie Fondamentale et Appliquée, Université Paul Sabatier, CNRS
118 Route de Narbonne, 31062 Toulouse cedex 9 (France)
Fax: (+33) 561558204
E-mail: mezailles@chimie.ups-tlse.fr

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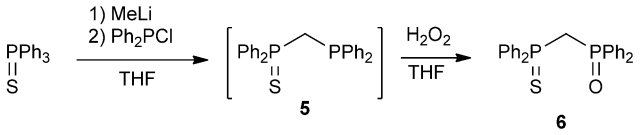
access to a geminal dianion of mixed P=S/Y ligands, for which only two examples have been reported so far ($\mathbf{4a_{Li2}}$: Y = PPh_2NSiMe_3,[1j] $\mathbf{4b_{Li2}}$: Y = SO_2Ph).[1k]

Herein, in the first part, we report the synthesis of the monoanion and geminal dianion of a mixed P=S/P=O ligand. The coordination behavior of the dianion with a Ru^{II} precursor is then reported. An unprecedented room-temperature C–H activation on a phenyl ring of the PPh_2=O moiety, in a diastereospecific fashion, was observed. This C–H activation was thermally reversible and a second C–H activation occurred on a phenyl ring of the PPh_2=S moiety, also in diastereospecific manner. A comprehensive DFT study was performed to rationalize these experimental findings and the results are also presented herein.

Results and Discussion

As mentioned above, the dianions of compounds **1** and **3** have already been reported. No information is yet available for a dianion that is derived from the bis(oxide) of dppm (1,1-bis(diphenylphosphino)methane), but the monoanion has been synthesized. Therefore, we reasoned that the double deprotonation of compound **6** should be possible. The synthesis of the neutral ligand was achieved in two steps: Diphenylphosphino(methyl)diphenylphosphinesulfide **5** was synthesized according to a literature procedure[8] and was further oxidized in situ to yield compound **6** in an overall yield of 70% (Scheme 2). In the ^{31}P NMR spectrum,

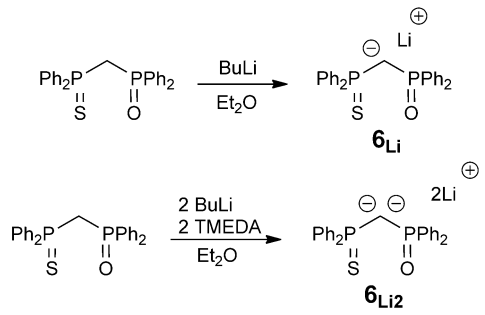


Scheme 2. Synthesis of compound **6**.

compound **6** exhibits an AB system at $\delta = 33.6$ and 21.0 ppm ($^2J(P,P) = 15$ Hz). The central protons are found as a doublet of doublet ($^2J(P,H) = 12$ Hz, $^2J(P,C) = 15$ Hz) at $\delta = 3.75$ ppm in the ^1H NMR spectrum and at $\delta = 37.1$ ppm (dd, $^1J(P,C) = 45$ Hz, $^1J(P,C) = 60$ Hz) in the corresponding ^{13}C NMR spectrum. To investigate the structural parameters of compound **6**, single crystals were grown by the slow evaporation of a concentrated solution of compound **6** in CH_2Cl_2 (for details of the structure of compound **6**, see the Supporting Information).[9] The bond lengths and angles in compound **6** are all standard.

Next, the single deprotonation of compound **6** was attempted (Scheme 3). The reaction of compound **6** with one equivalent of an alkyl lithium reagent (MeLi, BuLi, *t*BuLi) in toluene, THF, or Et_2O led to a color change from colorless to yellow, concomitant with an evolution of gas.

After 15 min (1 h in toluene), a pale-yellow solid precipitated from the crude mixture. This new compound was isolated and showed poor solubility in common solvents. However, it was highly soluble in pyridine, which allowed its characterization by multinuclear NMR spectroscopy. In its ^{31}P NMR spectrum, an AB system at $\delta = 35.3$ and 33.8 ppm ($^2J(P,P) = 24$ Hz) was observed. Furthermore, in the ^1H NMR spectrum, a broad doublet ($^2J(P,H) = 4$ Hz, 1H) at $\delta = 2.33$ ppm, which corresponded to a signal at $\delta = 22.3$ ppm (dd, $^1J(P,C) = 105$ Hz, $^1J(P,C) = 135$ Hz) in the ^{13}C NMR spectrum, was identified as the central proton. Confirmation of the successful monodeprotonation of compound **6** was provided by X-ray diffraction analysis. Single crystals of compound $\mathbf{6_{Li}}$ were grown by the diffusion of pentane into a concentrated solution of $\mathbf{6_{Li}}$ in pyridine (Figure 1). Compound $\mathbf{6_{Li}}$ crystallized as a dimer in the solid state with two pyridine molecules acting as solvent for the Li^+ cations.



Scheme 3. Synthesis of compounds $\mathbf{6_{Li}}$ and $\mathbf{6_{Li2}}$.

Compared to neutral derivative **6**, compound $\mathbf{6_{Li}}$ features elongated PO and PS bond lengths (1.524(2) Å and

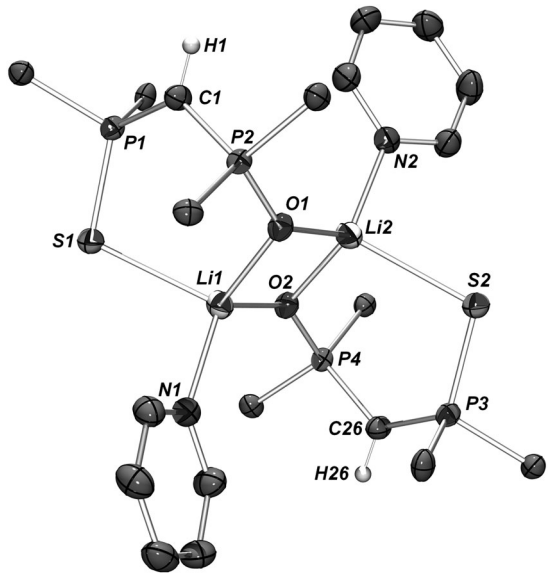


Figure 1. ORTEP plot of compound $\mathbf{6_{Li}}$; ellipsoids are set at 50% probability. Hydrogen atoms (except for H1 and H26) and the phenyl rings (except for the *ipso* carbon atoms) on the P atoms have been omitted for clarity. Selected bond lengths [Å]: C1–P1 1.721(3), C1–P2 1.703(3), P1–S1 1.994(1), P2–O1 1.524(2), O1–Li1 1.951(5), O1–Li2 1.922(5), C26–P3 1.721(3), C26–P4 1.702(3), P3–S2 1.992(1), P4–O2 1.523(2), O2–Li1 1.910(5), O2–Li2 1.922(5).

1.994(1) Å in compound $\mathbf{6_{Li}}$ versus 1.495(1) Å and 1.949(1) Å in compound **6** for the PO and PS bonds, respectively). On the contrary, the two PC bond lengths are significantly shorter (1.721(3) Å and 1.703(3) Å in compound $\mathbf{6_{Li}}$ versus 1.819(2) Å and 1.818(2) Å in compound **6**). Following this result, we tried to synthesize dianion $\mathbf{6_{Li2}}$ (Scheme 3) but the synthesis was not successful when following literature procedures.[1] After optimization of the reaction conditions, two equivalents of *n*-butyllithium, together with two equivalents of TMEDA (tetramethylethylenediamine), were used in Et_2O.[10] Compound $\mathbf{6_{Li2}}$ precipitated from the reaction mixture and was easily isolated in a very good 75% yield. Compound $\mathbf{6_{Li2}}$ showed very poor solubility in toluene, 1,2-dimethoxyethane (DME), and Et_2O and decomposed in THF and pyridine, thus rendering its NMR characterization difficult. Interestingly, despite its very low solubility, compound $\mathbf{6_{Li2}}$ could be recrystallized from a saturated solution in benzene and was characterized by X-ray diffraction (Figure 2).

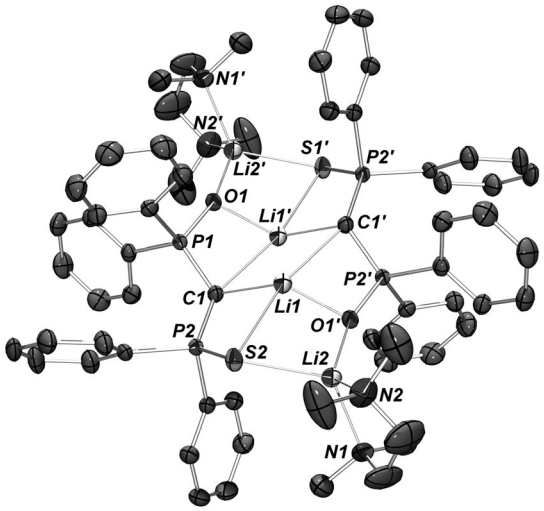
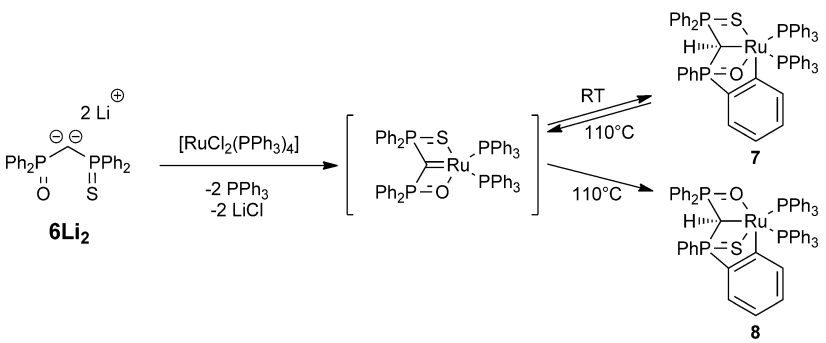


Figure 2. ORTEP plot of compound $\mathbf{6_{Li2}}$; ellipsoids are set at 50% probability. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å]: C1–P1 1.671(2), C1–P2 1.681(2), P1–O1 1.535(1), P2–S1 2.0418(6), C1–Li1 2.189(3), C1–Li1′ 2.425(3), O1–Li1′ 1.928(3), S2–Li1 2.599(3).

In the solid state, compound $\mathbf{6_{Li2}}$ crystallizes as a dimer; two molecules of TMEDA complete the coordination sphere of the external lithium atoms and three benzene molecules (not shown). The geometrical changes that were observed in compound $\mathbf{6_{Li}}$ are more pronounced in compound $\mathbf{6_{Li2}}$. The PC bonds are even shorter (1.671(2) Å and 1.681(2) Å) and the PS and PO bonds are longer (2.0418(6) Å and 1.535(1) Å, respectively). This result is in line with previous findings and has been rationalized by DFT calculations.[1i] A trapping experiment with D_2O was carried out to confirm the double deprotonation. The reaction of compound $\mathbf{6_{Li2}}$ with an excess of D_2O in Et_2O yielded the doubly deuterated compound $\mathbf{2_{D2}}$ after work up and purification. The ^1H NMR spectrum of compound $\mathbf{2_{D2}}$ showed the absence of any signals at $\delta = 3.75$ ppm in CH_2Cl_2, which was indicative of quantitative deuteration. The difference in bond length (0.5 Å) between the PS and the PO bonds is particularly interesting. Indeed, in carbene complexes of transition metals that incorporate geminal dianions as ligands, the M–C distance is, on average, 2.393 Å (CCDC search on 57 structures). Therefore, 4-membered metallacycles that contain the PO moiety should be much more strained than their PS counterparts and, hence, confer specific reactivity on their corresponding complexes. To verify our hypothesis, we studied the coordination of compound $\mathbf{6_{Li2}}$ with a Ru^{II} center. The reaction of compound $\mathbf{6_{Li2}}$ with $[RuCl_2(PPh_3)_4]$ in toluene was carried out and followed by ^{31}P NMR spectroscopy (Scheme 4). After 15 min, the spectrum showed the presence of free triphenylphosphine, as well as numerous unresolved peaks. After several hours, four well-defined peaks were observed, each of which integrated to one phosphorus atom ($\delta = 73.7$, 64.1, 46.7, and 14.0 ppm) and the signal for free triphenylphosphine integrated to two phosphorus atoms. After purification, a new complex (**7**) was isolated and characterized by multinuclear NMR spectroscopy. Unlike what was observed with the symmetrical $[(PPh_2S)_2CLi_2]$ dianion, complex **7** was not the expected ruthenium carbene.[11] Indeed, its ^1H NMR spectrum showed a multiplet at $\delta = 1.41$ ppm, which corresponded to a proton on the P–C–P bridge.

Moreover, four separate signals at $\delta = 6.92$, 6.65, 6.28, and 6.06 ppm were observed for the four aromatic protons that were located on the same phenyl ring (determined by COSY) at high field for aromatic protons. These patterns are reminiscent of a Ru^{II} complex that was synthesized in our group that resulted from the C–H activation of a phenyl ring on the ligand.[2d] X-ray diffraction analysis confirmed this hypothesis. Single crystals of compound **7** were grown by the slow diffusion of pentane into a concentrated solution in CH_2Cl_2 (Figure 3).



Scheme 4. Synthesis of complexes **7** and **8**.

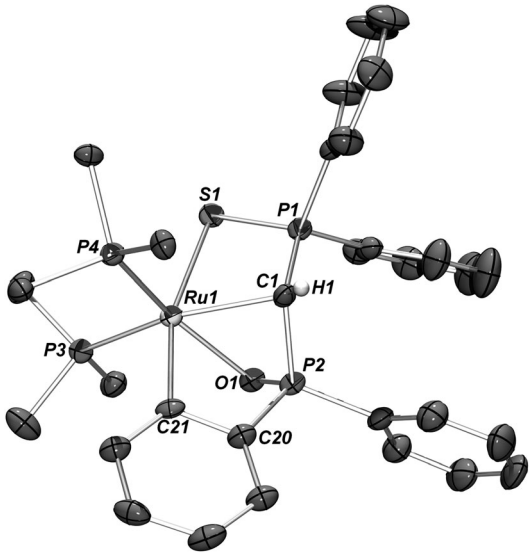


Figure 3. ORTEP plot of complex **7**; ellipsoids are set at 50% probability. Hydrogen atoms (except for H1) and the phenyl rings of the PPh_3 substituents (except for the *ipso* carbon atoms) have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–P1 1.762(5), C1–P2 1.816(5), P1–S1 2.000(2), P2–O1 1.526(4), Ru1–C1 2.267(5), Ru1–S1 2.580(1), Ru1–O1 2.319(3), Ru1–C21 2.067(5), P2–C20 1.769(5), C20–C21 1.407(7), Ru1–P3 2.330(1), Ru1–P4 2.271(1); P1–C1–P2 116.6(3), C1–Ru1–P4 160.5(1), S1–Ru1–C21 162.8(1), P4–Ru1–O1 162.5(1).

Indeed, complex **7** resulted from a C–H activation of the ligand, which constitutes a formal C–H addition to the Ru=C bond. Such behavior has already been reported with similar ligands by the group of Cavell and by ourselves.[2c,d,12] The Ru1–C21 distance (2.067(5) Å) is much shorter than the Ru1–C1 distance (2.267(5) Å) and falls within the range of other reported orthometalated ruthenium(II) complexes.[13] The C20–C21 distance (1.407(7) Å) is longer than the other C–C bonds in the orthometalated phenyl ring. The ruthenium atom adopts a distorted octahedral geometry. One phenyl ring on the PPh_2O moiety is now orthometalated and the aromatic proton is now located on the central carbon atom. Two triphenylphosphine ligands remain on the metal center. Interestingly, only one pair of diastereoisomers is observed by ^{31}P NMR spectroscopy (*SR*/*RS* couple). In an attempt to explore the reactivity of complex **7**, a solution of compound **7** was heated at 110°C in toluene. The reaction mixture turned progressively from dark green to orange. After heating for 12 h, the ^{31}P NMR spectrum showed the complete conversion of compound **3** into a new complex that was characterized by an NMR pattern that was very similar to that of complex **7** (note that no free triphenylphosphine was observed during the process). Indeed, four distinct signals, each of which integrated to one phosphorus atom, were observed at $\delta = 53.4$, 47.0, 45.4, and -12.8 ppm, respectively. After evaporation of the solvent, complex **8** was isolated. Its ^1H NMR spectrum also showed the presence of a central proton on the P–C–P bridge ($\delta =$ 1.51 ppm), as well as four high-field signals that were attributed to an orthometalated phenyl ring. The exact structure of complex **8** was ascertained by X-ray diffraction analysis (Figure 4).[14] Its structure resembles that of complex **7**, except that the C–H activation took place on a phenyl ring of the PPh_2S moiety. All of the bond lengths and angles in complex **8** are comparable to those in compound **7**. Compound **8** features disordered phenyl rings on the triphenylphosphine substituents. Here, again, one pair of diastereoisomers is observed (*RR*/*SS*). Interestingly, the diastereoselectivity is opposite to that observed for complex **7**.

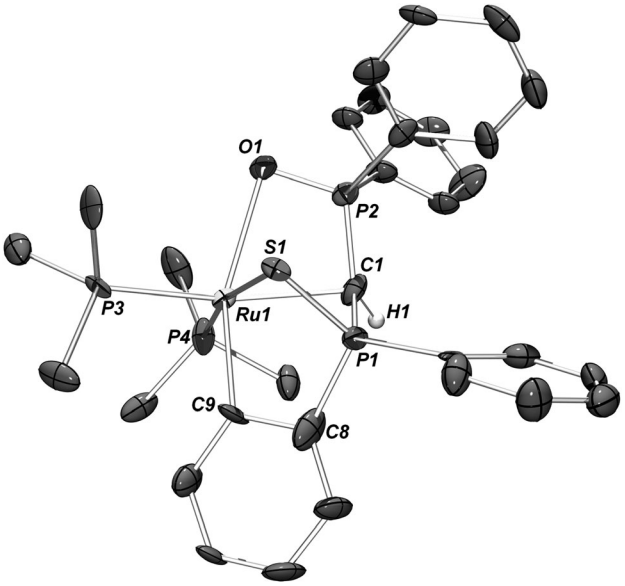


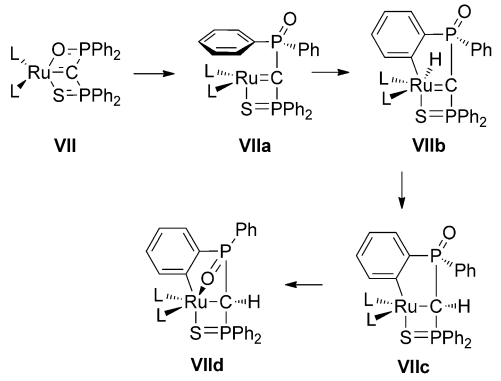
Figure 4. ORTEP plot of complex **8**; ellipsoids are set at 50% probability. Hydrogen atoms (except for H1) and the phenyl rings of the PPh_3 substituents (except for the *ipso* carbon atoms) have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–P1 1.80(1), C1–P2 1.80(2), P1–S1 2.002(4), P2–O1 1.513(7), Ru1–C1 2.28(1), Ru1–S1 2.499(2), Ru1–O1 2.428(7), Ru1–C9 2.04(1), P1–C8 1.75(2), C8–C9 1.43(1); P1–C1–P2 122.0(6), P3–Ru1–C1 160.5(3), C9–Ru1–O1 158.8(3), P4–Ru1–S1 168.4(1).

DFT calculations were carried out to rationalize the diastereoselectivity and reversibility of this process. For this purpose, we used the full model of compounds **7** and **8** (named **VII** and **VIII**, respectively). The calculations were performed by using the Gaussian 03 set of programs[15] with the b3pw91 functional[16] in combination with the 6-31G* basis set for the metal-bound atoms (P, S, C, O), 6-31G for the other atoms (C, H) in the orthometalated phenyl ring, 6-311++G** for the migrating H atom, and STO-3G for all other atoms (C, H).[17] The LANL2DZ basis set was used for the Ru atoms, with an additional f-polarization function (for full details on the theoretical calculations, see the Supporting Information).[18,19] Because of our experimental observations, four C–H activation pathways were computed. Thus, our proposed mechanism for the transformation is: 1) Decoordination of the X atom (X = O, S) by rotation of the P=X arm; 2) insertion of ruthenium into the aromatic C–H bond; 3) hydrogen transfer from the ruthenium center to the central carbon atom; 4) recoordination of the X atom

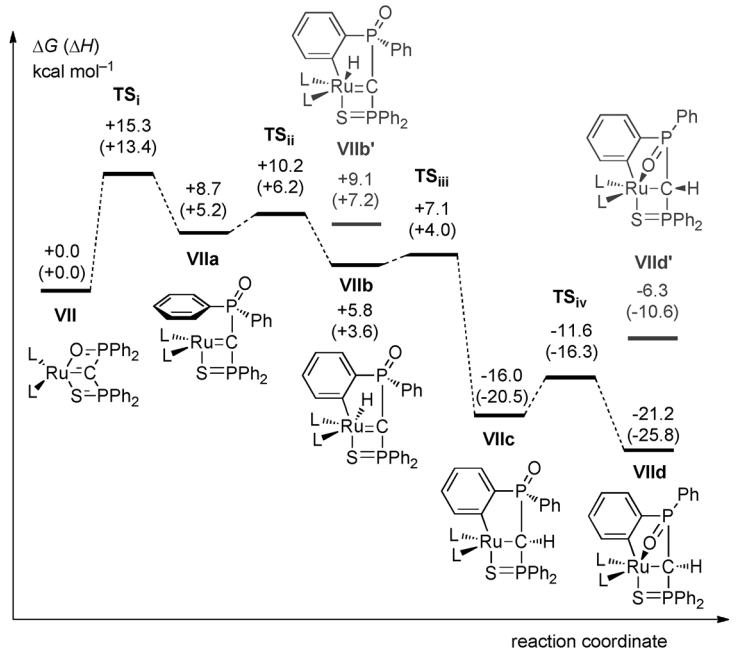
to the ruthenium center. The key step in determining the selectivity of the process is the formation of the ruthenium–hydride intermediate. Indeed, insertion of the ruthenium atom into the C–H bond can occur in two ways: In the first case, both the heteroatom (O, S) and the hydride are in the same plane (defined by the Ru–C–P–Y atoms), whereas, in the second case, they are in opposite planes.

Formation of complex 7: The calculated mechanism and the energy diagram for the formation of compound **7** are presented in Scheme 5 and Scheme 6, respectively.

The overall transformation is exergonic with a total $\Delta G = -21.2$ kcal mol^{-1}. The first step (decoordination of the phosphine oxide moiety) is the rate-determining step, with a calculated barrier of 15.3 kcal mol^{-1}. This barrier, which is much smaller than the related decoordination of PS (see above), as expected from the ring strain, is consistent with a transformation that occurs at room temperature. From the unsaturated complex (**VIIa**), the C–H insertion is very facile, with a TS that is a mere 1.5 kcal mol^{-1} higher in energy, thus leading to Ru–carbene–hydride complex **VIIb**, in which the H and O atoms are in opposite planes. The formation of the ruthenium–alkyl species (**VIIc**) is then the most favorable step ($\Delta G = -23.1$ kcal mol^{-1}), again with a very low activation energy ($\Delta G^{\neq} = 1.3$ kcal mol^{-1}). It has been shown that hydride–carbene complexes and alkyl complexes could be found in equilibrium through an α-H-transfer reaction.[20] Here, the formation of alkyl complex **VIIc** is highly favorable, thereby resulting in the sole formation of the alkyl complex. Finally, recoordination of the O atom takes place to yield the final ruthenium(II) product. The alternative C–H insertion was also calculated; the corresponding intermediate, complex **VIIb′**, in which the hydrogen atom is located in the same plane as the oxygen atom, is 3.3 kcal mol^{-1} higher in energy than complex **VIIb**. Moreover, the final product (**VIId′**), which results from complex **VIIb′**, was calculated to be about 15 kcal mol^{-1} higher in energy than complex **VIId**. Because those two complexes are higher in energy than complexes **VIIb** and **VIId**, even if the path were energetically accessible, only the formation of the most stable complex (**VIIb**) would be possible. These first calculations clearly explain why the starting carbene complex is not observed in solution at room temperature, because it rapidly evolves into complex **7**. Moreover, the calculations show that the energy that is required for this process to be reversible is 36.5 kcal mol^{-1}. Thus, they corroborate the observation that transformation of complex **7** only proceeds upon prolonged heating at reflux in toluene.



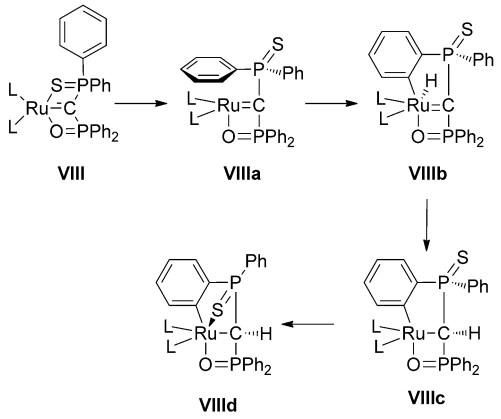
Scheme 5. Proposed mechanism for the formation of complex **7**.



Scheme 6. Computed energies of the intermediates in the formation of complex **7**.

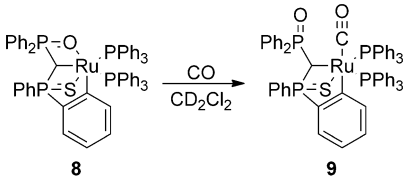
Formation of complex 8: The same method was applied to model compound **VIII**. The calculated mechanism is given in Scheme 7 and the corresponding energies are given in Scheme 8. Here, also, the rate-determining step in the mechanism for the formation of complex **8** is the decoordination of the thiophosphinoyl ligand ($\Delta G = 29.4$ kcal mol^{-1}). This decoordination cannot be achieved at room temperature, but is compatible with a reaction temperature of 110 °C. As mentioned above, this barrier is much higher than the one for the decoordination of the PO moiety. The rest of the mechanism is very much like the previous one for complex **VII**.

The overall process is exothermic ($\Delta G = -25.8$ kcal mol^{-1}). In this case, the rever-



Scheme 7. Proposed mechanism for the formation of complex **8**.

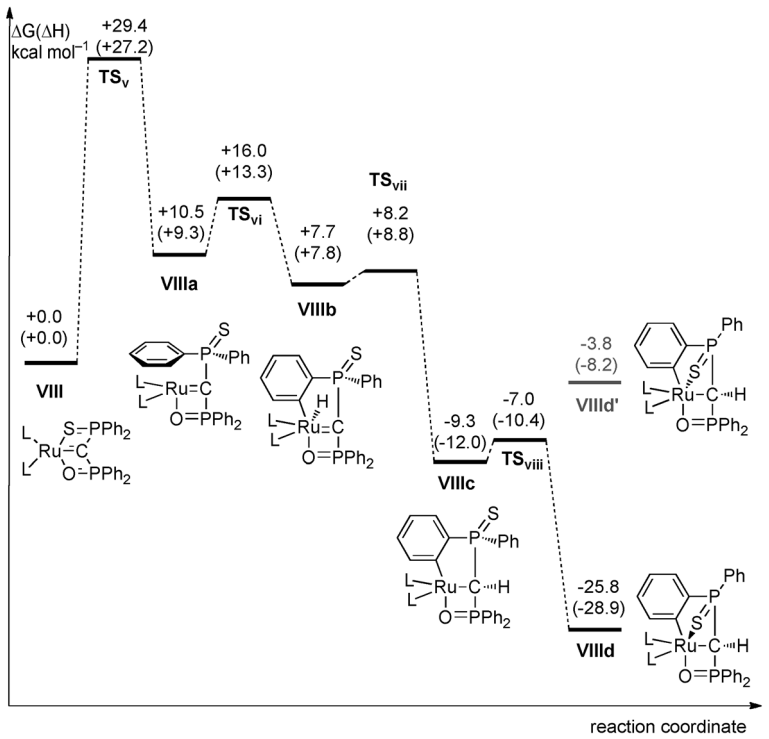
sibility is unachievable because the reverse process would require an activation energy of 55.2 kcal mol^{-1}. Complex **VIIId** is about 4 kcal mol^{-1} lower in energy than complex **VIId**, which rationalizes the fact that only one product is obtained in each case (at low or high temperature). These calculations confirm our initial hypothesis of the higher reactivity of the phosphine oxide moiety compared to the thiophosphinoyl moiety (decoordination energy of 15.3 kcal mol^{-1} for PO versus 29.4 kcal mol^{-1} for PS). This higher reactivity was further confirmed by reacting compounds **7** and **8** with carbon monoxide. The reactions were performed in an NMR tube that was plugged with a CO balloon. The reaction of compound **7** with CO was not clean and the ^{31}P NMR spectrum showed the formation of several unidentified products, as well as some unreacted starting material. The reaction with complex **8** was much more clear cut and complete conversion of the starting complex into a single new product (complex **9**, Scheme 9), as characterized by



Scheme 9. Synthesis of complex **9**.

four signals in the ^{31}P NMR spectrum ($\delta = 52.2$, 47.5, 30.5, 7.3 ppm), was observed within 30 min. ^{13}C NMR analysis confirmed the coordination of CO to the metal center: a highly coupled signal was observed at $\delta = 206.8$ ppm (which was seen as a singlet in the $^{13}C\{^{31}P\}$ NMR spectrum). The exact structure of compound **9** was determined by X-ray diffraction analysis. Single crystals of compound **9** were grown by the slow diffusion of pentane into a concentrated solution in CH_2Cl_2 (Figure 5).

As expected, the phosphine oxide moiety has been replaced by one molecule of CO in the coordination sphere of the metal, *trans* to the orthometalated carbon atom. The metal center still adopts a distorted octahedral geometry. The Ru1–C1 distance is shortened by the coordination of the CO molecule (2.260(2) Å in compound **9** versus 2.28(1) Å in compound **8**).



Scheme 8. Computed energies of the intermediates in the formation of complex **8**.

Conclusion

In conclusion, we have developed an easy and efficient synthesis of a new type of unsymmetrical geminal dianion that contains both a phosphine oxide moiety and a thiophosphinoyl moiety. Coordination to a Ru^{II} center showed that the expected carbene complex was not formed. Rather, the weaker coordination of the P=O arm, because of ring strain, resulted in a hemilabile behavior at room temperature. Following the decoordination of the P=O arm, a facile C–H activation on a phenyl ring of the ligand occurred in a diastereospecific fashion. The reversibility of this process could

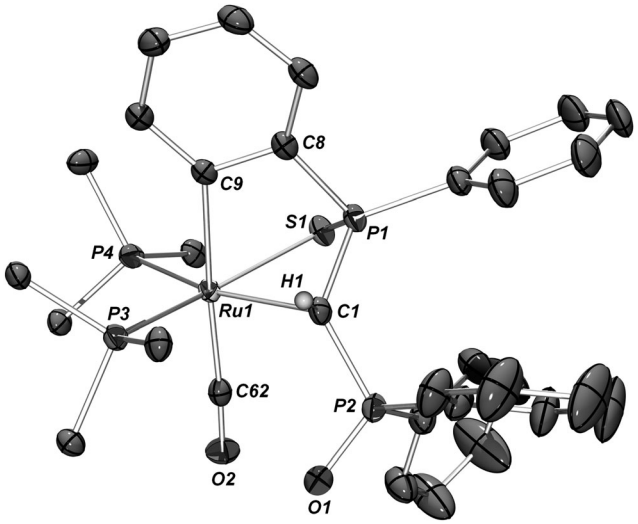


Figure 5. ORTEP plot of complex **9**; ellipsoids are set at 50% probability. Hydrogen atoms (except for H1) have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–P1 1.766(2), C1–P2 1.789(2), P1–S1 2.0063(7), P2–O1 1.487(1), Ru1–C1 2.260(2), Ru1–C9 2.172(2), Ru1–C62 1.900(2), Ru1–S1 2.5149(5), Ru1–P3 2.3524(5), Ru1–P4 2.3842(5), P1–C8 1.784(2), C62–O2 1.149(2), C8–C9 1.412(2); P1–C1–P2 125.9(1), C1–Ru1–P4 162.38(5), C9–Ru1–C62 175.85(7), Ru1–C62–O2 176.6(2), S1–Ru1–P3 164.88(2).

be thermally promoted with this kinetic complex. A second diastereospecific C–H activation was then observed, thereby leading to the thermodynamic complex. These experimental findings were fully rationalized by DFT calculations. An investigation of the reactivities of both the kinetic and the thermodynamic complexes is currently underway in our laboratory.

Experimental Section

All reactions were performed under an inert atmosphere of argon or nitrogen by using Schlenk and glovebox techniques and dry deoxygenated solvents. Dry Et_2O, CH_2Cl_2, toluene, petroleum ether, and THF were obtained by using a MBRAUN SPS-800 purifying system. NMR spectra were recorded on a Bruker AC-300 SY spectrometer operating at 300.0 MHz for ^1H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P nuclei. Solvent peaks were used as an internal reference relative to $SiMe_4$ for ^1H and ^{13}C chemical shifts; ^{31}P chemical shifts are reported relative to an external reference (85% H_3PO_4). Coupling constants are given in Hz. The following abbreviations are used: s: singlet, d: doublet, dd: doublet of doublet, br d: broad doublet, t: triplet, dt: doublet of triplets, m: multiplet, br: broad signal. $[RuCl_2(PPh_3)_4]$ was prepared according to a literature procedure.[21] TMEDA was heated at reflux for 2 h over KOH and distilled. Triphenylphosphine sulfide was obtained by the sulfuration of triphenyl phosphine with elemental sulfur in THF. All other reagents and chemicals were obtained commercially and used as received.

CCDC-893613 (**6**), CCDC-893614 (**6_{Li}**), CCDC-893615 (**6_{Li2}**), CCDC-893616 (**7**), CCDC-893617 (**8**), and CCDC-893618 (**9**) 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.

Synthesis of compound 6: To a solution of triphenylphosphinesulfide (4.23 g, 14.4 mmol) in THF (20 mL) was added methyllithium (1.6 M, 9 mL, 14.4 mmol) at −78 °C. The reaction mixture was left to warm to RT and stirred overnight. The resulting dark-red solution was transferred with a cannular into a solution of Ph_2PCl (2.65 mL, 14.4 mmol) in THF (10 mL) at 0 °C. The reaction was left to stir for 4 h and H_2O_2 (35 wt.% in H_2O, 1.4 mL, 14.4 mmol) was added at 0 °C. Stirring for 3 h prompted the precipitation of compound **6** as a white solid that was extracted by filtration, washed with THF (2×10 mL) and Et_2O (3×15 mL), and dried under vacuum (4 g, 9.25 mmol, 64%). ^1H NMR (300.0 MHz, CD_2Cl_2): $\delta = 7.96$–7.88 (m, 4H; H_{ortho} Ph_2PS), 7.77–7.63 (m, 4H; H_{ortho} Ph_2PO), 7.54–7.37 (m, 12H; H_{arom}), 3.75 ppm (dd, $^2J(P,H) = 12.4$ Hz, $^2J(P,H) = 14.5$ Hz, 2H; PCH_2P); ^{13}C NMR (75.5 MHz, CD_2Cl_2): $\delta = 133.7$ (dd, $J(P,C) = 2.6$ Hz, $J(P,C) = 104$ Hz; C_{ipso}), 133.1 (dd, $J(P,C) = 1.5$ Hz, $J(P,C) = 84$ Hz; C_{ispo}), 132.0 (m, 8C; CH_{arom}), 131.1 (m, 4C; CH_{arom}), 128.7 (m, 8C; CH_{arom}), 37.1 ppm (dd, $^1J(P,C) = 45$ Hz, $^1J(P,C) = 59$ Hz; PCH_2P); ^{31}P NMR (121.5 MHz, CD_2Cl_2): $\delta = 33.6$ (d, $^2J(P,P) = 14.5$ Hz; PS), 21.0 ppm (d, $^2J(P,P) = 14.5$ Hz; PO).

Synthesis of compound 6_{Li}: To a suspension of compound **6** (139.3 mg, 0.32 mmol) in Et_2O (5 mL) was added *n*-butyllithium (1.6 M, 0.2 mL, 0.32 mmol) at −78 °C. The solution turned yellow and was left to warm to RT and stirred for 1 h. A yellow solid precipitated that was extracted, washed with Et_2O (2×3 mL), and dried (120 mg, 85%). ^1H NMR (300.0 MHz, C_6D_5N): $\delta = 8.24$–8.17 (m, 10H; H_{arom}), 8.13–8.07 (m, 5H; H_{arom}), 8.03–7.96 (m, 5H; H_{arom}), 2.33 ppm (br d, $J(P,H) = 4$ Hz, 1H; PC(H)P); ^{13}C NMR (75.5 MHz, C_6D_5N): $\delta = 144.0$ (dd, $^3J(P,C) = 4$ Hz, $^1J(P,C) = 80$ Hz; C_{ipso}), 142.8 (dd, $^3J(P,C) = 6$ Hz, $^1J(P,C) = 100$ Hz; C_{ipso}), 132.5 (d, $J(P,C) = 10$ Hz; CH_{arom}), 131.8 (d, $J(P,C) = 10$ Hz; CH_{arom}), 130.0 (d, $J(P,C) = 3$ Hz; CH_{para}), 129.7 (d, $J(P,C) = 3$ Hz; CH_{para}), 128.3 (d, $J(P,C) = 10$ Hz; CH_{arom}), 128.2 (d, $J(P,C) = 10$ Hz; CH_{arom}), 23.5 ppm (dd, $^1J(P,C) = 105$ Hz, $^1J(P,C) = 135$ Hz; PCHP); ^{31}P NMR (121.5 MHz, C_6D_5N): $\delta = 35.3$ (d, $^2J(P,P) = 24$ Hz; PS), 33.8 ppm (d, $^2J(P,P) = 24$ Hz; PO); elemental analysis calcd (%) for $C_{30}H_{26}LiNOP_2S\cdot(C_5H_5N)_2$: C 71.09, H 5.37, N 6.22; found: C 69.80, H 5.23, N 6.45.

Synthesis of compound 6_{Li2}: To a suspension of compound **6** (1.0 g, 2.32 mmol) in Et_2O (10 mL) was added TMEDA (0.4 mL, 2.66 mmol). At −78 °C, *n*-butyllithium (1.6 M, 3 mL, 4.8 mmol) was added and the solution turned dark orange. After 1 h, compound **6_{Li2}** precipitated as a bright-yellow solid and the reaction was stirred for a further 2 h. Compound **6_{Li2}** was isolated by centrifugation, washed with Et_2O (2×5 mL) and pentane (2×8 mL), and dried (960 mg, 1.74 mmol, 75%). Elemental analysis calcd (%) for $C_{62}H_{72}Li_4N_4O_2P_4S_2$: C 66.43, H 6.47, N 5.00; found: C 66.31, H 6.51, N 4.87.

Synthesis of compound 6_{D2}: To a suspension of compound **6_{Li2}** (100 mg, 0.18 mmol) in Et_2O (4 mL) was added D_2O (40 μL, 2 mmol). An instant color change from yellow to white was observed and the reaction was left to stir for 2 h. The addition of CH_2Cl_2, filtration, drying over $MgSO_4$, and evaporation of the solvents afforded compound **6_{D2}** as a white solid (77 mg, 98%). ^1H NMR (300.0 MHz, [D_8]THF): $\delta = 7.93$–7.85 (m, 4H; H_{arom}), 7.68–7.61 (m, 4H; H_{arom}), 7.48–7.35 ppm (m, 12H; H_{arom}); ^{13}C NMR (75.5 MHz, [D_8]THF): $\delta = 133.6$ (dd, $^3J(P,C) = 2.7$ Hz, $^1J(P,C) = 104$ Hz; C_{ipso}), 133.1 (dd, $^3J(P,C) = 1.5$ Hz, $^1J(P,C) = 84$ Hz; C_{ipso}), 132.1 (d, $J(P,C) = 3$ Hz; CH_{para}), 131.9 (d, $J(P,C) = 11$ Hz; CH_{arom}), 131.8 (d, $J(P,C) = 3$ Hz; CH_{para}), 131.1 (d, $J(P,C) = 11$ Hz; CH_{arom}), 128.7 (pseudo-t, $\Sigma J(P,C) = 24$ Hz; $2\times CH_{arom}$), 36.6 ppm (m; PCD_2P); ^{31}P NMR (121.5 MHz, [D_8]THF): $\delta = 33.6$ (d, $^2J(P,P) = 14.5$ Hz; PS), 21.0 ppm (d, $^2J(P,P) = 14.5$ Hz; PO).

Synthesis of complex 7: To a suspension of compound **6_{Li2}** (100 mg, 0.18 mmol) in toluene (6 mL) was added $[RuCl_2(PPh_3)_4]$ (220 mg, 0.18 mmol). The solution was left to stir at RT for 3 h and turned dark green. Centrifugation allowed the elimination of LiCl and the remaining supernatant was dried under vacuum. Washing with petroleum ether (3×5 mL) and drying under vacuum allowed the isolation of complex **7** as a green powder (160 mg, 84%). ^1H NMR (300.0 MHz, CD_2Cl_2): $\delta = 7.57$–7.50 (m, 6H; H of phenyl), 7.42–7.11 (m, 28H; H of phenyl), 7.06–8.97 (m, 7H; H of phenyl), 6.92 (1H; H_a), 6.83–6.77 (m, 5H; H of phenyl), 6.65 (m, 1H; H_b), 6.28 (m, 1H; H_c), 6.06 (m, 1H; H_d), 1.41 ppm (m, 1H; PC(H)P); ^{13}C NMR (75.5 MHz, CD_2Cl_2): $\delta = 145.0$ (dd, $J(P,C) = 2$ Hz, $J(P,C) = 15$ Hz; C_d), 137.6 (d, $J(P,C) = 43$ Hz; C of phenyl), 136.9 (d, $J(P,C) = 34$ Hz; C of phenyl), 135.7 (d, $J(P,C) = 10$ Hz; CH of phenyl),

134.8 (m, CH of phenyl), 134.5 (br d, J(P,C) = 15 Hz; C_a), 134.0 (br s; CH of phenyl), 132.2 (br s; CH of phenyl), 131.5 (d, J(P,C) = 2 Hz; CH of phenyl), 130.8 (d, J(P,C) = 10 Hz; CH of phenyl), 130.7 (d, J(P,C) = 10 Hz; CH of phenyl), 130.5 (d, J(P,C) = 10 Hz; CH of phenyl), 130.4 (d, J(P,C) = 11 Hz; CH of phenyl), 128.9 (br s; CH of phenyl), 128.8 (br s; CH of phenyl), 128.6 (br s; CH of phenyl), 128.0 (br s; CH of phenyl), 127.9 (d, J(P,C) = 11 Hz; CH of phenyl), 127.7 (d, J(P,C) = 3 Hz; CH of phenyl), 127.7 (d, J(P,C) = 11 Hz; CH of phenyl), 127.5 (d, J(P,C) = 11 Hz; CH of phenyl), 125.2 (d, J(P,C) = 3 Hz; C_c), 119.5 (d, J(P,C) = 15 Hz; C_b), 7.7 ppm (m; PC(H)P); ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ = 73.7 (d, J(P,P) = 27 Hz; 1P), 64.1 (d, J(P,P) = 6 Hz; 1P), 46.7 ppm (m; 1P), 14 (m; 1P); elemental analysis calcd (%) for $C_{61}H_{50}OP_4RuS$: C 69.36, H 4.77; found: C 69.42, H 5.01.

Synthesis of complex 8: To a suspension of compound $\mathbf{6_{Li2}}$ (100 mg, 0.18 mmol) in toluene was added $[RuCl_2(PPh_3)_4]$ (220 mg, 0.18 mmol). The solution was left to stir at 110 °C overnight, during which time it turned orange. Centrifugation allowed the elimination of LiCl and the remaining supernatant was dried under vacuum. Washing with petroleum ether (3 × 5 mL) and further drying under vacuum allowed the isolation of complex **8** as a yellow powder (170 mg, 89 %). ^{1}H NMR (300.0 MHz, CD_2Cl_2): δ = 7.73 (m, 5H; H of phenyl), 7.43–6.78 (m, 41H; H of phenyl), 6.37 (ddd, J(H,H) = 1.5 Hz, J(H,H) = 7.3 Hz, J(P,H) = 12.5 Hz; H_a), 6.25 (m; H_b), 5.63 (m; H_c), 4.81 (m; H_d), 1.51 ppm (m; PC(H)P); ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ = 175.9 (m; RuC), 153.0 (br d, J(P,C) = 108 Hz; Ph2P(S)C), 144.6 (dd, J(P,C) = 2.4 Hz, J(P,C) = 15 Hz; C_d), 139.7 (d, J(P,C) = 35 Hz; C of phenyl), 139.2 (br s; C of phenyl), 139.1 (br s; C of phenyl), 136.9 (dd, J(P,C) = 10 Hz, J(P,C) = 95 Hz; C of phenyl), 136.9 (dd, J(P,C) = 4 Hz, J(P,C) = 40 Hz; C of phenyl), 134.8 (d, J(P,C) = 5 Hz; CH of phenyl), 134.4 (d, J(P,C) = 10 Hz; CH of phenyl), 131.3 (d, J-(P,C) = 3 Hz; CH of phenyl), 131.1 (d, J(P,C) = 3 Hz; CH of phenyl), 130.9 (d, J(P,C) = 11 Hz; CH of phenyl), 130.6 (d, J(P,C) = 11 Hz; CH of phenyl), 129.9 (d, J(P,C) = 3 Hz; CH of phenyl), 129.3 (d, J(P,C) = 11 Hz; CH of phenyl), 128.7–128.2 (m; CH of phenyl), 127.7 (d, J(P,C) = 10 Hz; CH of phenyl), 127.4 (d, J(P,C) = 10 Hz; CH of phenyl), 127.3 (d, J-(P,C) = 11 Hz; CH of phenyl), 126.0 (d, J(P,C) = 16 Hz; C_a), 123.9 (d, J-(P,C) = 4 Hz; C_c), 118.1 (d, J(P,C) = 15 Hz; C_b), 15.0 ppm (m; PC(H)P); ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ = 53.4 (dd, J(P,P) = 6.6 Hz, J(P,P) = 24 Hz; PPh_3), 47.0 (dt, J(P,P) = 10 Hz, J(P,P) = 24 Hz; $PPPh_3$), 45.4 (m; P(O)), −12.8 ppm (m; P(S)).

Synthesis of complex 9: To a solution of complex **8** (50 mg) in CD_2Cl_2 (0.6 mL) was added CO (balloon). The solution turned from orange to yellow. Complete conversion was determined by ^{31}P NMR spectroscopy and the mixture was evaporated to dryness (50 mg, 98 %). ^{1}H NMR (300.0 MHz, CD_2Cl_2): δ = 7.78–6.95 (m, H; H of phenyl+H_a), 6.64 (m, 1H; H_b), 5.96 (m, 1H; H_c), 5.8 (m, 1H; H_d), 2.05 ppm (m, 1H; PC(H)P); ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ = 206.8 (m; CO), 183.5 (m; RuC), 148.0 (m; C of phenyl), 144.0 (m; CH_d), {138.4, 137.8, 136.4} (C of phenyl), 132.5 (d, J(P,C) = 10 Hz; CH of phenyl), 131.9 (d, J(P,C) = 10 Hz; CH of phenyl), 131.8 (d, J(P,C) = 3 Hz; CH of phenyl), 131.2 (d, J(P,C) = 3 Hz; CH of phenyl), 130.6 (br s; CH of phenyl), 129.9 (br s; CH of phenyl), 129.8 (br s; CH of phenyl), 128.8 (d, J(P,C) = 10 Hz; CH of phenyl), 128.7 (d, J(P,C) = 10 Hz; CH of phenyl), 128.1 (br s; CH of phenyl), 128.0 (d, J-(P,C) = 2 Hz; CH of phenyl), 127.8 (d, J(P,C) = 2 Hz; CH of phenyl), 127.4 (br d, J(P,P) = 8 Hz; CH of phenyl), 127.2 (d, J(P,C) = 11 Hz; CH of phenyl), 126.4 (d, J(P,C) = 20 Hz; CH_a), 125.0 (d, J(P,C) = 3 Hz; CH_c), 121.4 (d, J(P,C) = 13 Hz; CH_b), 24.6 ppm (m; PC(H)P); ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ = 52.2 (dd, J(P,P) = 8 Hz, J(P,P) = 21 Hz; PPh_3), 47.5 (dt, J(P,P) = 6 Hz, J(P,P) = 21 Hz; PPh_3), 30.5 (d, J(P,P) = 6 Hz; PO), 7.6 ppm (t, J(P,P) = 8 Hz; PS); elemental analysis calcd (%) for $C_{62}H_{50}O_2P_4RuS$: C 68.68, H 4.65; found: C 68.40, H 4.61.

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[9] Data collection for compound **6**: $C_{25}H_{22}OP_2S$; $M_w = 432.43$; crystal dimensions 0.24 mm × 0.20 mm × 0.10 mm; orthorhombic; space group $P2_12_12_1$; $a = 8.661(1)$, $b = 11.153(1)$, $c = 22.508(1)$ Å; $\alpha = 90.00$, $\beta = 90.00$, $\gamma = 90.00°$; $V = 2174.2(4)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.257$ g cm^{-3}; $\mu = 0.361$ cm^{-1}; $F(000) = 904$; $T = 150.0(1)$ K; $\theta_{max} = 25.02°$; *hkl* ranges: −9 to 10, −12 to 10, −26 to 15; 6071 reflections collected; 3430 unique reflections ($R_{int} = 0.0234$); 3323 reflections with $I > 2\sigma(I)$; 263 parameters refined; GOF = 1.056; $R1 = 0.0310$ and $wR2 = 0.0694$; difference peak/hole (e Å^{-3}) 0.264(0.040)/−0.221(0.040).
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[14] In the X-ray crystal structure of complex **8**, a disorder on one phenyl substituent of the $Ph_3P(4)$ ligand is present, but has been omitted in Figure 4 for reasons of clarity. See the Supporting Information for details.
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