4838 *Organometallics* **2005,** *24,* 4838−4841

Notes

A Bis(thiophosphinoyl)methylene Ruthenium Carbene Complex: Synthesis, X-ray Crystal Structure, and DFT Calculations of Its Thermally Promoted Reverse α-Hydride Migration Process

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Received May 26, 2005

*Summary: The synthesis and X-ray crystal structure of a new (S,C,S)-based carbene ruthenium complex (**2**) are presented. The thermally promoted rearrangement of this new complex to complex **3** involves a reverse α-hydride migration, which has been investigated by DFT calculations.*

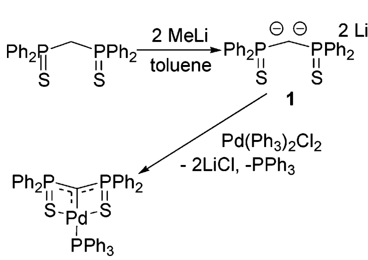
Introduction

The chemistry of metallocarbenes has undergone an impressive revival over the past few years due to the discovery of stable and isolable carbene ligands.[1] Although different methods for generating free carbenes are now available, the development of new synthetic approaches leading to new and inexpensive precursors for the synthesis of carbene complexes having well-tailored and adjustable electronic properties is still desirable. We recently reported on the quantitative synthesis of dianion **1**, which was obtained by double deprotonation of bis(diphenylthiophosphinoyl)methane. During this study, we also showed that this dianion could serve as an efficient source of a nucleophilic Pd(II) carbene complex (Scheme 1) which involves a new bonding mode of the carbene ligand (coordination through the $2p_z$ orbital at carbon).[2] This new type of complex can be regarded as the sulfur analogue of Cavell's complexes.[3] In this article we report on the synthesis and reactivity of a Ru(II) complex of this dianion.

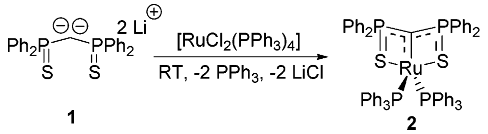
Results and Discussion

Reaction of **1** with 1 equiv of $[RuCl_2(PPh_3)_4]$ at room temperature immediately yielded a dark brown solution and a dark brown precipitate (Scheme 2). The ^{31}P NMR spectrum recorded from the crude mixture showed the presence of free triphenylphosphine and the formation of a single symmetrical complex featuring four phosphorus atoms as assessed by a new A_2X_2 spin system ($\delta(A) = 48.8$ ppm, $\delta(X) = 57.6$ ppm, $^3J(P,P) = 11.8$ Hz, CD_2Cl_2, 298 K).

Scheme 1



Scheme 2



After usual workup aimed at eliminating LiCl and free PPh_3, complex **2**, which proved to be stable toward air and water, was fully characterized by NMR spectroscopy (^1H, ^{13}C) and elemental analyses. ^1H and ^{13}C spectra both confirm the absence of a methylenic proton and, as expected, the carbenic carbon is characterized by a triplet of triplets at 130.8 ppm ($^1J(C,P) = 33.2$ Hz, $^2J(C,P) = 1.9$ Hz, CD_2Cl_2, 298 K). This chemical shift is

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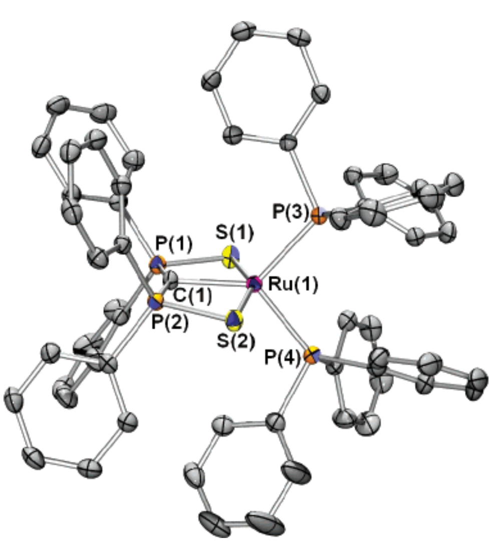

Figure 1. View of one molecule of **2** (thermal ellipsoids set at 50% probability). The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ru(1)−C(1) 2.053(2), C(1)−P(1) 1.675(2), C(1)−P(2) 1.676(2), Ru(1)−S(1) 2.4739(5), Ru(1)−S(2) 2.4843(5), Ru(1)−P(3) 2.2656(5), Ru(1)−P(4) 2.2641(5), P(1)−S(1) 2.0269(7), P(2)−S(2) 2.0206(6), P(1)−C(1)−P(2) 156.5(1), P(1)−C(1)−Ru(1) 100.7(1), P(2)−C(1)−Ru(1) 102.26(8), S(1)−Ru(1)−S(2) 155.18(2), P(3)−Ru(1)−P(4) 95.75(2).

considerably upfield relative to other ruthenium carbene complexes (220−320 ppm),[4] suggesting that a significant negative charge remains on the carbon atom.

X-ray quality crystals of **2** were obtained by diffusing diethyl ether in a solution of the complex in methylene chloride (Figure 1).[5]

The observed structure is consistent with the spectroscopic data and validates the presence of a central carbenic carbon. The ruthenium center lies in a distorted trigonal bipyramid (as expected for ML_5-d^8 center). Interestingly, the overall geometry around the carbene moiety is planar (sum of angles: 359.5°). The situation is completely different from the one observed in the previously reported palladium complex in which the metal is located in a plane quasi-perpendicular to the carbene fragment. Although the geometry in **2** seems, at a first glance, quite common for a carbene complex, the ruthenium−carbon bond is relatively long (2.053(2) Å) compared to other Ru−C double bonds (1.92 Å).[6] In fact, it is only marginally shorter than Ru−C(sp^3) single bonds (2.11 Å) or in N-heterocyclic carbene ruthenium complexes (2.08 Å)[6] and falls in the range of Ru−C(sp^2) single bonds (2.06 Å).[7] This bond length suggests a weak π-bonding between the carbon and the metal center in **2**. A striking feature is the very short P−C(1) bonds of 1.675(2) and 1.676(2) Å, which are similar to bond lengths found in carbodiphosphoranes and their complexes.[8] These short bonds very likely result from negative hyperconjugation from carbon to phosphorus σ* orbitals.

The electronic structure of complex **2** was investigated by DFT calculations using a model complex (**2-[H]**, B3LYP/[6-31+G*(H,C,P,S),LANL2DZ+f(Ru)] level of theory).[9] The optimized structure is in very good agreement with the experimental structure, and a long Ru−C bond was obtained (2.034 Å). In line with both structural and spectroscopic data, the Wiberg index calculated for the ruthenium carbon bond (equal to 0.67) reveals a very weak double-bond character in **2-[H]**. The frontier orbitals (HOMO and LUMO) for complex **2-[H]** are shown in Figure 2.

The HOMO is an antibonding π* orbital between the ruthenium center and the sulfur lone pairs. Interestingly, the LUMO (Figure 2) corresponds to an antibonding π* interaction between the carbene's n_p orbital and the metal centered d_{xy} orbital, as opposed to the situation in the palladium complex, in which this π* orbital is doubly occupied and constitutes its HOMO.[2] Complex **2** then formally results from the double oxidation of its palladium analogue (see d^8 vs d^{10}) and presents a planar geometry commonly observed for carbene complexes.

As far as reactivity is concerned, complex **2** was found to be very resistant and can be stored for days in the air at room temperature without any degradation. This complex does not react with methanol or with water. The two triphenylphosphine ligands were not displaced by chelating diphosphines, such as bis(diphenylphosphino)ethane (dppe), or by bulky phosphines, such as PCy_3. The reactivity of **2** was further assessed by reactions with various electrophiles and nucleophiles. In particular, complex **2** did not react with methyllithium or methyliodide and so exhibits no pronounced electrophilic or nucleophilic character. Without addition of any substrate, heating a solution of complex **2** (toluene, 120 °C, 15 h) affords a single complex, **3**, which results from metalation of one phenyl group and formal protonation at the carbene center (Scheme 3). Complex **3** was fully characterized by NMR spectroscopy (^1H, ^{13}C, and ^{31}P) and elemental analyses. Crystals suitable for X-ray diffraction analysis were grown by diffusing

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[5] Crystal data for **2**: $C_{61}H_{50}P_4RuS_2$; M_r = 1072.08; monoclinic; a = 18.4040(10) Å, b = 16.1150(10) Å, c = 17.3300(10) Å; β = 104.5900(10)°; V = 4974.0(5) Å^3; T = 150.0(1) K; space group $P2_1/c$; Z = 4; μ = 0.569 cm^{-1}; 23 879 reflections measured, 14 470 unique, 10 950 used reflections, criterion $I > 2\sigma(I)$; R_{int} = 0.0250; wR2 = 0.0902. Crystal data for **3**: see Supporting Information. CCDC-268363 (**2**) and CCDC-268364 (**3**) 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 CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[6] Average values obtained using the CSD program VISTA (*Vista−a program for the analysis and display of data retrieved from the CSD*, CCDC, Cambridge, UK, 1996) on a search of the Cambridge Structural Database (Allen, F. H. *Acta Crystallogr. Sect. B* **2002**, *58*, 380−388) using the program Conquest (Bruno, I. J.; Cole, J. C.; Eddington, P. R.; Kessler, M.; Mcrae, C. F.; McGabe, P.; Pearson, J.; Taylor, R. *Acta Crystallogr. Sect. B* **2002**, *58*, 389−397).

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[8] See for example: Vincent, A. T.; Wheatley, P. J. *J. Chem. Soc., Dalton Trans.* **1972**, 617−622. Hardy, G. E.; Zink, J. I.; Kaska, W. C.; Baldwin, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 8001−8002. Petz, W.; Weller, F.; Uddin, J.; Frenking, G. *Organometallics* **1999**, *18*, 619−626.

[9] B3LYP[8a] is a hybrid functional consisting of Becke's exchange,[8b] Slater's exchange,[8c] exact Hartree−Fock exchange, VWN correlation,[8d] and the nonlocal (gradient) part of the LYP correlation[8e] functionnals. The basis set LANL2DZ[8f] plus an f-type polarization function with an exponent of 1.235 was used for Ru. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Becke, A. D. *Phys. Rev. A* **1998**, *38*, 3098. (c) Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864. Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133. Slater, J. C. In *Quantum Theory of Molecular and Solids Vol. 4: The Self-Consistent Field for Molecular and Solids*; McGraw-Hill: New York, 1974. (d) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200. (e) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200. (f) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

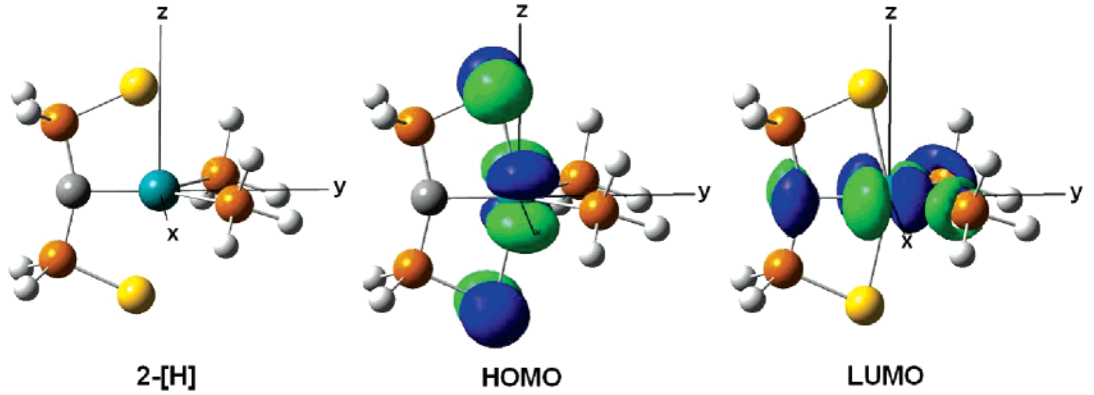
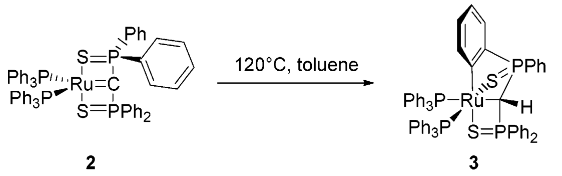
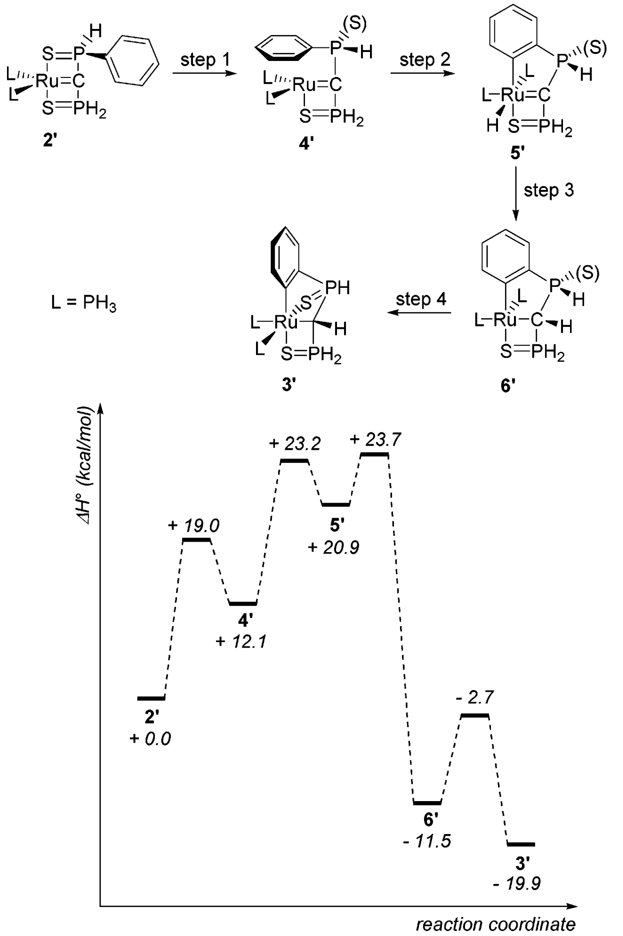


Figure 2. View of the optimized structure of complex **2-[H]** and its frontier orbitals, obtained by DFT calculations.

Scheme 3



Scheme 4



2-propanol in a solution of **3** in dichloroethane.[5] Its molecular structure reveals the reaction to be diastereoselective (the *RR*/*SS* racemic mixture was obtained (see ESI))[10] and shows a significant lengthening of the ruthenium carbon bond (2.053(2) Å in **2** vs 2.262(4) Å in **3**).

This unusual transformation of complex **2** into **3** was investigated by DFT calculations. A model complex (**2′**), in which the innocent phenyl rings were replaced by H, was used, and calculations were carried out at the B3LYP/[6-31+G*(H,C,P,S),LANL2DZ+f(Ru)] level of theory.[9] The calculated mechanism is presented in Scheme 4.

As can be seen, the rate-limiting step turns out to be the first one. It consists in the decoordination of one thiophosphinoyl ligand and results in the formation of the unsaturated d^8-ruthenium(0) complex **4′**. A significant shortening of the Ru–C bond is observed (from 2.03 Å in **2′** to 1.97 Å in **4′**), which indicates a more pronounced multiple-bond character in **4′** and therefore a greater electronic donation from the carbon atom to the metal. Complex **4′** is thus better described as a d^8-ruthenium(0) carbene complex. This step is a prerequisite for the following oxidative addition of a C–H bond to yield **5′** (note that in this case no additional reduction is required to form the ruthenium(0) intermediate).[11] Then the hydride complex **5′** rearranges through a reverse α-hydride migration (to **6′**) to finally afford the saturated d^6-ruthenium(II) complex **3′** upon recoordination of the sulfur ligand. This pathway is consistent not only with the required temperature (about 100 °C) but also with the observed complete diastereoselectivity which stems from the *cis* 1,2-H shift (**5′** to **6′**).

The 1,2[H] migration process is commonly employed in the syntheses of carbene complexes from alkyl complexes. If reverse hydrogen shift (migration from the metal to the carbon, step 3) is less common in carbene complexes, it has been often observed in the case of hydrido-carbyne complexes.[12] Both experimental and theoretical investigations on α-H migrations (from a transition metal center to a carbene ligand) have been recently carried out.[13,14] These studies have pointed out that hydrido-carbene complexes and alkyl complexes could be engaged in an equilibrium.[14] Stabilization of the carbene center by either the metal center or the carbenic substituents was shown to be the key factor to the shift of this equilibrium toward the hydrido-carbene complex.[14] On the other hand, in our case, the thermo-

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[10] This selectivity was also observed by Cavell and co-workers whose platinum carbene complex [(η^4-cod)Pt{=C(Ph$_2$P=NSiMe$_3$)$_2$-$\kappa C,\kappa N$}] undergoes a similar orthometalation and carbene protonation (see ref 3h).

[11] Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403–424.

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dynamic balance definitely validates the completeness of the reaction ($\Delta H°(\mathbf{2'}\rightarrow\mathbf{3'}) = -19.9$ kcal/mol). The overall transformation involves the cleavage of one σ C−H and the formal Ru═C π bond and the formation of one σ C−H and one σ Ru−C. Thus, the very large exothermicity of the reaction clearly indicates that a weak Ru═C π bond at best is involved in **2**. Consequently, the stabilization of the carbene center in complex **2** is provided by the two P═S arms. Upon decoordination of one thiophosphinoyl unit, stabilization by the ruthenium center is not sufficient to ensure the carbene stability, and the thermal isomerization proceeds toward its alkyl form (**3**).

Conclusion

In conclusion, the (S,C,S) scaffold has been shown to stabilize a new type of ruthenium carbene complexes. Structural and spectroscopic studies have shown that a weak Ru═C π bond was involved in carbene complex **2**. In terms of reactivity, its thermal conversion to the orthometalated complex **3** has been studied. A mechanism of this transformation has been proposed and validated by DFT calculations. It nicely accounts for the experimental observations (in terms of diastereoselectivity, temperature, and thermodynamic balance) and confirms the almost negligible π Ru═C character in **2**. Further studies are now focusing on the full understanding of the electronic structure of this complex as well as on the reactivity of dianion **1** toward other transition metal centers.

Experimental Section

General Procedures. All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and glovebox techniques and dry deoxygenated solvents. Dry THF, ether, and hexanes were obtained by distillation from Na/benzophenone. Dry dichloromethane was distilled on P_2O_5 and dry toluene on Na. Nuclear magnetic resonance spectra were recorded on a Bruker AC-300 SY spectrometer operating at 300.0 MHz for ^{1}H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P. Solvent peaks are used as internal reference relative to Me_4Si for ^{1}H and ^{13}C chemical shifts (ppm); ^{31}P chemical shifts are relative to a 85% H_3PO_4 external reference. Coupling constants are given in hertz. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; v, virtual. Elemental analyses were performed by the “Service d'analyse du CNRS”, at Gif sur Yvette, France. $[RuCl_2(PPh_3)_4]$ and bis(diphenylthiophosphinoyl)methane were prepared according to literature procedures. All other reagents and chemicals were obtained commercially and used as received.

Synthesis of Carbene Complex 2. One equivalent of $[RuCl_2(PPh_3)_4]$ (490 mg, 0.40 mmol) was added to a solution of dianion **1** in toluene (3 mL, 0.13 mol/L, 0.40 mmol) at room temperature. The resulting mixture immediately turned dark brown, and ^{31}P NMR spectroscopy showed the reaction to be complete. LiCl salt was eliminated via centrifugation after addition of 10 mL of methylene chloride. Evaporation of the solvent afforded a dark brown solid, which was washed three times with hexanes (5 mL). Pure complex **2** was finally isolated in 91% yield (390 mg, 0.36 mmol). Selected data: ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 6.87−7.42 ppm (m, 50H; H of phenyl). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 25 °C, 85% H_3PO_4 as external standard): δ 48.8 (t, $^3J_{PP} = 11.8$ Hz), 57.6 ppm (t, $^3J_{PP} = 11.8$ Hz). $^{13}C\{^1H\}$ NMR (75.465 MHz, CD_2Cl_2, 25 °C, CD_2Cl_2: δ 53.73 ppm as internal reference): δ 127.3−139.6 (m; C of phenyl), 138.0 ppm (tt, $^1J_{CP} = 33.2$ Hz, $^2J_{CP} = 1.9$ Hz; carbenic carbon). Anal. Calcd for $C_{61}H_{50}P_4RuS_2$: C, 68.34; H, 4.70. Found: C, 68.39; H, 4.71.

Synthesis of Complex 3. A solution of complex **2** (250 mg, 0.23 mmol) in toluene (20 mL) was heated in a sealed tube at 120 °C for 15 h. Evaporation of the solvent afforded a yellow solid, which was washed with methanol (10 mL). Complex **3** was thus obtained in a pure form in 95% yield (237 mg, 0.22 mmol). Selected data: ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 1.42 (dt, $^2J_{HP} = 5.7$ Hz, $^3J_{HP} = 4.3$ Hz, 1H; PCHP), 5.26 (dd, $^3J_{HH}$=7.6 Hz, $^4J_{HP} = 2.5$ Hz, 1H; H of ortho-phenyl), 5.88 (vtt, $^3J_{HH} = 7.5$ Hz, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.3$ Hz, $^5J_{HP} = 1.3$ Hz, 1H; H of ortho-phenyl), 6.51 (vq, $^3J_{HH} = 7.3$ Hz, $^3J_{HH} = 7.5$ Hz, $^4J_{HP} = 7.3$ Hz, 1H; H of ortho-phenyl), 6.71 (ddd, $^4J_{HH} = 1.3$ Hz, $^3J_{HH} = 7.3$ Hz, $^3J_{HP} = 11.6$ Hz, 1H; H of ortho-phenyl), 6.83−7.60 ppm (m, 45H; H of phenyl). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 25 °C, 85% H_3PO_4 as external standard): δ −9.0 (t, $^3J_{PP} = 7.3$ Hz; ortho-Ph-PhP(S)), 48.9 (m, $\sum J_{PP} = 45.3$ Hz; PPh_3), 50.8 (dd, $^2J_{PP} = 23.8$ Hz, $^3J_{PP} = 7.3$ Hz; PPh_3), 62.5 ppm (d, $^3J_{PP} = 12.1$ Hz; PPh_2(S)). $^{13}C\{^1H\}$ NMR (75.465 MHz, CD_2Cl_2, 25 °C, CD_2Cl_2 δ 53.73 ppm as internal reference): δ 1.0 (s; PC(H)P), 118.8 (d, $^3J_{CP} = 15.2$ Hz; C of ortho-phenyl), 123.4 (d, $^4J_{CP} = 3.5$ Hz; C of ortho-phenyl), 126.6 (d, $^3J_{CP}$=18.7 Hz; C of ortho-phenyl), 126.9−138.5 (m; C of phenyl), 145.0 (m, $\sum J_{CP} = 19.5$ Hz; C of ortho-phenyl), 149.8 (dt, $^1J_{CP} = 107.6$ Hz, $^3J_{CP} = 2.4$ Hz; CP of ortho-phenyl), 183.2 ppm (m, $\sum J_{CP} = 41.3$ Hz; CRu of ortho-phenyl). Anal. Calcd for $C_{61}H_{50}P_4RuS_2$: C, 68.34; H, 4.70. Found: C, 68.14; H, 4.75.

Acknowledgment. The authors thank the CNRS (Centre National de la Recherche Scientifique) and the Ecole Polytechnique for the financial support of this work and IDRIS (Orsay, Paris XI) for the allowance of computer time.

Supporting Information Available: CIF files and tables giving crystallographic data for **2** and **3** (including atomic coordinates, bond lengths and angles, and anisotropic displacement parameters) and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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