Planar Discrimination in an SPS-Based Rhodium(I) Complex

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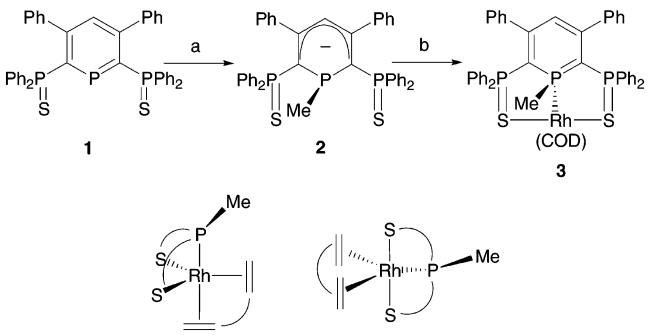
Received July 1, 2003

*Summary: This work describes the reactivity of the SPS-type pincer-based Rh^I complex **4** toward CO, O_2, CO_2, CS_2, and SO_2 to afford the corresponding Rh^I or Rh^{III} adducts. The SPS ligand is able to adopt a facial coordination mode in these trigonal-bipyramidal complexes. Differentiation of the two faces of the square-planar Rh^I complex **4** could be rationalized by a mechanical effect due to the rigidity of the central phosphinine backbone.*

Over the past few years, rigid pincer structures incorporating an aromatic ring as the central unit have emerged as a very important class of ligands, and their successful use in catalytic processes of importance has been emphasized by many reports.[1,2] It is now well established that the combination of three binding sites offers possibilities to subtly tune the electronic properties of the metal fragment. In this perspective, many efforts have been currently devoted to the design of new pincers featuring heteroatoms (N, O, S, P) as ancillary or central ligands.[1,3] So far, with sulfur, studies have mainly focused on the use of thiolate,[4] thioethers,[5] or sulfoxide[6] and only little attention has been paid to ligands bearing phosphine sulfides.[7]

Recently, we have developed a new class of SPS-based pincer system featuring a hypervalent phosphorus atom (λ^4-phosphinine) as the central unit and two phosphine sulfides as ancillary ligands.[8] Palladium(II) complexes of these new ligands proved to be particularly efficient in the catalyzed Miyaura cross-coupling process that allows the formation of C_{sp^2}−B bonds.[9] In pursuing our investigation, we recently found that rhodium(I) complexes are also particularly reactive. Herein we report on these preliminary results.

Scheme 1. Synthesis of 3[a]



[a] Legend: (a) MeLi (1 equiv), THF, −78 °C to room temperature; (b) $[RhCl(COD)]_2$ (1 equiv), THF, −78 °C to room temperature.

The rhodium(I) complex **3** is easily available from the reaction anion **2** with $^1/_2$ equiv of the $[RhCl(COD)]_2$ precursor (Scheme 1).[10] Complex **3**, which was isolated as a very stable orange solid, was fully characterized by NMR techniques and elemental analyses. Unfortunately, despite many attempts, **3** could not be crystallized and information about the spatial arrangement of the SPS ligand could not be obtained. Though ^{31}P NMR spectroscopy reveals that the PPh_2S groups are magnetically equivalent, two geometries can be proposed for **3**: one in which the ligand is located in the plane and a second in which it caps one face of the bipyramid (Scheme 1).

Therefore, experiments aimed at derivatizing complex **3** were undertaken. Displacement of the COD ligand by triphenylphosphine readily occurred in THF to yield the highly reactive complex **4**, which was structurally characterized. An ORTEP view of one molecule of **4** is presented in Figure 1. Only the ipso carbons of the phenyl groups of the SPS ligand have been kept for clarity. This structure is quite interesting and deserves several comments. The square-planar arrangement

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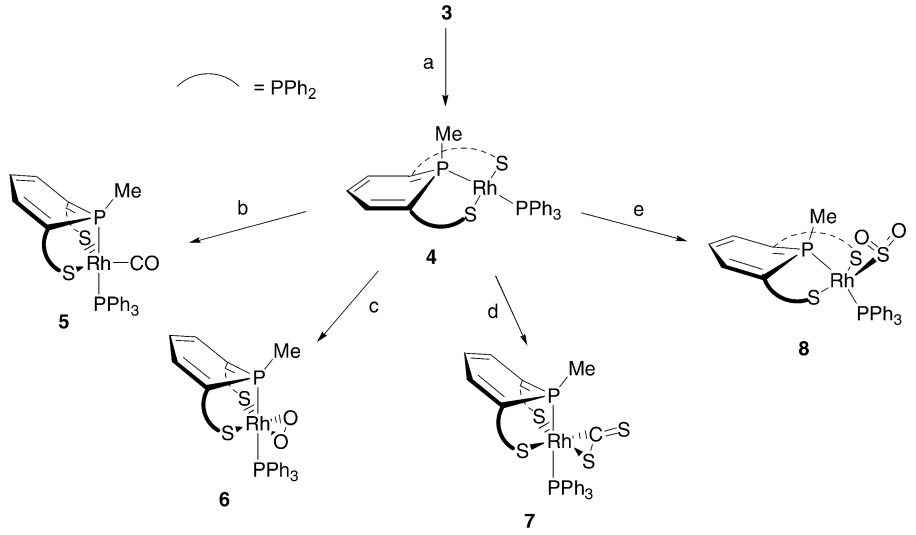
10.1021/om0305115 CCC: $25.00
Publication on Web 10/07/2003

Scheme 2. Synthesis and Reactions of 4[a]



[a] Legend: (a) PPh_3 (1 equiv), THF; (b) CO (1 atm), THF; (c) O_2 (1 atm), THF; (d) CS_2 (1 equiv), THF, −78 °C to room temperature; (e) SO_2 (1 atm), THF, −78 °C to room temperature

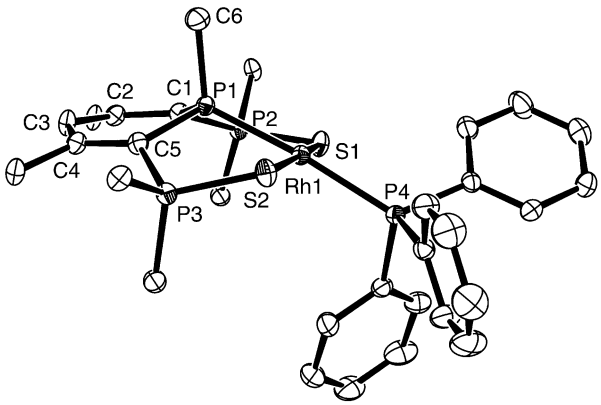


Figure 1. Molecular structure of **4** without hydrogen atoms. Phenyl groups of the phosphinine moiety have been omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−Rh1 = 2.2428(6), S1−Rh1 = 2.3197(6), S2−Rh1 = 2.3213(6), P4−Rh1 = 2.3034(6); S1−Rh−S2 = 172.51(2), P1−Rh−P4 = 174.65(2), P1−C1−P2 = 113.6(1), P1−C5−P3 = 111.1(1), (mean plane C1−C2−C4−C5)−P1 = 16.7, (mean plane C1−C2−C4−C5)−C3 = 7.1, S1−P2−C1−P1 = 4.3, S2−P3−C5−P1 = 13.0.

around the metal center is obvious, as expected for a ML_4 d^8 configuration. Although the SPS ligand occupies three coordination sites of the square-planar geometry, the ligand itself is not planar and the phosphorus atom is now located well above the plane defined by the ring carbon atoms (see Figure 1). The plane defined by C1−P−C5 deviates from the plane defined by C1−C2−C4 and C5 by 16.7°, and the phosphorus atom is highly pyramidal (∑(angles at P1) = 311.24°). The ORTEP plot clearly shows that the two faces of the rhodium center are differentiated and incoming reagents can approach either "syn" or "anti" to the methyl group. The very peculiar geometry for the ligand in complex **4** allows for the rationalization of the reactivity of this complex (vide supra). Apart from these features, the bond distances and angles are normal and deserve no further comments.

Several experiments were carried out to evaluate the reactivity of **4** toward small molecules. Some of these are summarized in Scheme 2. As can be seen, reaction with CO afforded the 18-VE Rh^I complex [Rh(**2**)(CO)(PPh_3)] (**5**), which was structurally characterized. Interestingly, its X-ray structure, which is not presented here, proves that the SPS pincer is sufficiently flexible to cap one face of a trigonal bipyramid.[11] This structural feature is important and markedly differs from what was observed with classical pincer ligands, which are structurally rigid and favor planar coordination. Complex **4** also reacted with molecular oxygen to yield the highly stable complex [Rh(**2**)(η^2-O_2)PPh_3] (**6**), which was also structurally characterized. Examination of the O−O distance (1.431(2) Å) reveals that **6** is a Rh^{III} peroxo complex.[12] Complex **6** appears to be the first example of a peroxo complex featuring sulfides as ligands.[11] As depicted in Scheme 2, it is important to note that attack of both CO (in **5**) and O_2 (in **6**) took place exclusively syn to P−Me. This attack results also in the displacement of the PPh_3 ligand away from the equatorial plane. It is now located on the main axis of the trigonal bypiramid, trans to the λ^4-phosphinine ligand.

Reaction of **4** with CO_2 was also attempted, but the corresponding complex proved to be too labile to be isolated and NMR data did not provide sufficiently clear information to propose a definitive formulation. A more gratifying result was obtained by reacting **4** with a

(11) Selected bond lengths (Å) and angles (deg) for complexes **5**, **6**, and **8** are as follows. **5**: P(phosphinine)−Rh = 2.2783(5), Ph_3P−Rh = 2.3248(5), S−Rh = 2.4846(5) and 2.5720(5), C−Rh = 1.820(2), C−O = 1.157(2); S−Rh−S = 87.49(2), P−Rh−P = 177.39(2), C−Rh−S = 143.52(7) and 128.97(7), Me−P−Rh−C = 5.0, S−P−C−P(phosphinine) = 33.8 and 36.9. **6**: P(phosphinine)−Rh = 2.2630(7), Ph_3P−Rh = 2.3655(7), S−Rh = 2.4057(8) and 2.3765(8), O−Rh = 2.050(2) and 2.004(2), O−O = 1.431(2); S−Rh−S = 98.68(3), P−Rh−P = 177.94(2), O−Rh−O = 41.32(6), Me−P−Rh−Centroid(O2) = 15.3, S−P−C−P(phosphinine) = 27.5 and 6.0. **8**: P(phosphinine)−Rh = 2.259(1), S−Rh = 2.3558(8) and 2.3756(8), S(sulfur dioxide)−Rh = 2.342(1), O1−S(sulfur dioxide) = 1.471(2), O2−S(sulfur dioxide) = 1.465(2); P−Rh−P = 172.86(3), S−Rh−S = 162.12(3), O−S−O = 112.0(1), S(sulfur dioxide)−Rh−S = 97.68(3) and 99.97(3), S−P−C−P(phosphinine) = 16.3 and 22.1.

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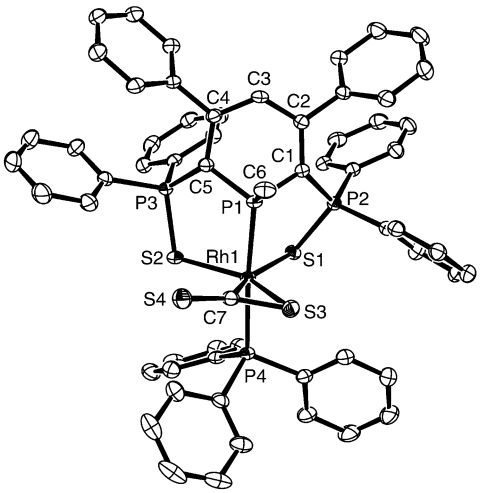
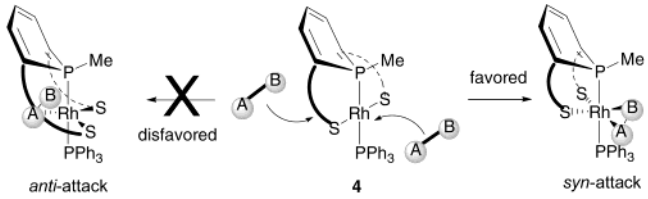


Figure 2. Molecular structure of **7** without hydrogen atoms. Selected bond lengths (Å) and angles (deg): P1−Rh1 = 2.2771(8), S1−Rh1 = 2.5040(8), S2−Rh1 = 2.4193-(7), P4−Rh1 = 2.379(1), C7−Rh1 = 2.003(3), S3−Rh1 = 2.3866(7), C7−S3 = 1.670(3), C7−S4 = 1.631(3); P1−Rh1−P4 = 174.81(2), S1−Rh1−S2 = 92.26(3), S3−C7−S4 = 140.2(2), P1−C1−P2 = 115.2(1), P1−C5−P3 = 116.7(1), (mean plane C1−C2−C4−C5)−P1 = 26.3, (mean plane C1−C2−C4−C5)−C3 = 8.6, S1−P2−C1−P1 = 26.6, S2−P3−C5−P1 = 13.3.

stoichiometric amount of CS_2. Coordination readily took place in THF at room temperature to yield the [Rh(**2**)-(η^2-SC═S)PPh_3] complex **7**, which was fully characterized. An ORTEP view of one molecule of **7** is presented in Figure 2. Crystal data and structural refinement details are presented in Table 1. As can be seen, the complex adopts a trigonal-bipyramidal geometry like that of **6** and coordination of CS_2 occurs through one of the C═S bonds. So far, only two (η^2-CS_2)Rh complexes have been structurally characterized, neither featuring a phosphine sulfide as ligand.[13] In contrast to its CO_2 analogue, complex **7** is not labile and its structure is preserved in solution, as attested by the ^{31}P NMR spectrum, which exhibits two different signals for the ancillary phosphorus atoms. As can be seen in Figure 2, the attack of CS_2 also occurred syn to the P−Me group.

Finally, reaction with SO_2 was attempted. Coordination readily occurred in THF by bubbling SO_2 into a solution of **4** at −78 °C. The geometry of complex **8** could not be unambiguously established on the sole basis of NMR data. Indeed, though the spectra revealed that the complex is symmetrical, discrimination between three possible modes of coordination (pyramidal or η^1-S planar, η^1-O or η^2-O,S bonded) of SO_2 is not possible. However, the presence of two characteristic stretching frequencies of the SO bond at 1028 and 1148 cm^{-1} in the IR spectrum strongly suggested a pyramidal geometry, which was definitively proved by X-ray crystallography.[11] Here again, the incoming ligand reacted syn to the P−Me group. The IR and X-ray data of this complex are very similar to those of [RhCl(tpp)(SO_2)] (tpp = bis(3-diphenylphosphino)propyl)phenylphosphine).[14]

Scheme 3. Planar Discrimination of 4



How can the regiospecificity of the various reactions presented here, in favor of the attack of the incoming reactant syn to the P−Me group, be rationalized? Two main factors that may operate to different extents can be put forward: steric requirements and SPS ligand mechanical effects. Let us consider the variation in geometries of the different complexes during the considered reaction. In the synthesis of **8**, which adopts a square-pyramidal geometry, the initial arrangement found in **4** is not perturbed to a great extent and the SPS ligand keeps the same geometry: i.e., the steric requirements likely predominate. Thus, the attack from the anti face, where two axial phenyl rings are found, is disfavored versus the syn attack. In the three other cases, leading to **5**−**7**, the final geometry is trigonal bipyramidal. There, no matter how much the sterics are involved (likely favoring the syn attack also), the rigidity of the phosphinine ring results in a mechanical effect that does not allow the two PPh_2S moieties to bend toward the syn face (Scheme 3). Moreover, the two phenyl groups would collide with the interacting molecule. The anti attack is thus forbidden, and the sole product results from the attack on the syn face.

In conclusion, a highly reactive rhodium(I) complex featuring an SPS-based pincer ligand has been synthesized. Preliminary experiments have shown that this complex **4** reacts with small molecules such as CO, O_2, CO_2, CS_2, and SO_2. Interestingly, a mechanical effect resulting from the rigidity of the central phosphinine ring allows the differentiation of the two faces of the square-planar complex **4**. A new interesting challenge will now consist in introducing chirality at the phosphorus atom. Indeed, one may expect that the presence of a chiral substituent at P would help to differentiate the two diastereotopic sides of the SPS-based pincer complex. This would provide a unique way for controlling enantioselectivity in derived catalysts. Experiments aimed at validating this hypothesis are currently underway in our laboratories.

Acknowledgment. We thank the CNRS, the Ecole Polytechnique, and the DGA for supporting this work.

Supporting Information Available: Text detailing the preparation of compounds **2**−**8** and giving a description of the X-ray procedures and tables of X-ray data, positional and thermal parameters, and bond lengths and angles and ORTEP diagrams for complexes **4** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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