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Diamagnetic versus Paramagnetic Structure of SPS-Type Pincer-Based Co^{I}, Rh^{I}, and Ir^{I} Complexes

Marjolaine Doux,[a] Pascal Le Floch,[a] and Yves Jean*[a]

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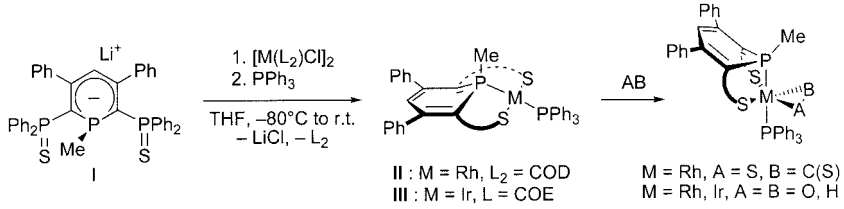
The lowest singlet and triplet states of SPS-type pincer-based [M(SPS)(PPh_3)] complexes (M = Co, Rh, and Ir) were studied by means of DFT/B3PW91 calculations on the model complexes in which the nine phenyl substituents were replaced by H atoms. Although the Rh and Ir compounds were found to be diamagnetic with a square-planar geometry, the yet unknown Co complex was predicted to be paramagnetic ($\Delta E_{S/T}$ = –22.4 kcal·mol^{-1}) with two unpaired electrons localized on the metal center. Three minima were actually located on the triplet potential energy surface that differ by the arrangement of the ligands (nearly tetrahedral or butterfly geometries), two of them being close in energy (ΔE = 2.5 kcal·mol^{-1}). Finally, the paramagnetism of the Co complex was confirmed by calculations on the real complex at the B3PW91//ONIOM(B3PW91:UFF) level of theory ($\Delta E_{S/T}$ = –29.6 kcal·mol^{-1}).

Introduction

Since the pioneering work of Shaw in 1976,[1] the development of pincer-based ligands has been flourishing and many of these polydentate systems have found numerous applications in coordination chemistry, homogeneous and heterogeneous catalysis.[2–4] Whereas the first studies focussed on PCP-based systems, it rapidly appeared that the introduction of heteroatoms (N, O, P, S) either as central or ancillary ligands could be used to finely tune the electronic properties of the corresponding complexes.[5–7] However, the use of oxygen and sulfur as ancillary ligands remains limited compared to their nitrogen (amine, amide, imine), phosphorus (phosphane, phosphite, phosphaalkene), or carbon (NHC) counterparts. Sulfur-based systems are of great interest as they can be used to modelize enzyme active sites.[8] Sulfur ligands can be found either as thioethers,[9–12] thiolates,[13,14] sulfoxides,[15] or phosphanyl sulfides.[16–19]

Recently, we described the synthesis and the coordination chemistry of the anionic SPS-based pincer ligand **I**, which features two ancillary P=S ligands and a phosphorus atom as the central binding site (Scheme 1).[20] In a series of papers we showed that these ligands can accommodate various metal fragments in different oxidation states (Re^{I}, Mn^{I}, Rh^{I}, Rh^{II}, Rh^{III}, Ir^{I}, Ir^{III}, Ni^{II}, Pd^{II}, Pt^{II}, Au^{I}, Cu^{I}).[21–24] Some of these complexes have found applications in catalysis,[25] photochemistry[21] and activation of small molecules.[26–28] Among these complexes, the 16 VE square-planar Rh^{I} complex [Rh(SPS)(PPh_3)] (**II**) proved to be particularly reactive towards small molecules such as CO, SO_2, O_2, CS_2, and H_2 and the corresponding Rh^{III} complexes, [Rh(η^2-O_2)(SPS)(PPh_3)], [Rh(η^2-CS_2)(SPS)(PPh_3)], and [Rh$(H)_2$(SPS)(PPh_3)], or Rh^{I} complexes, [Rh(η^1-CO)(SPS)(PPh_3)] and [Rh(η^1-SO_2)(SPS)(PPh_3)], were isolated and structurally characterized in most cases



Scheme 1.

(Scheme 1).[23,28] Later it was found that the iridium counterpart of **II**, the [Ir(SPS)(PPh_3)] complex **III**, could also activate O_2 and H_2.[27,28] Moreover, the attack of the small molecule proved to be stereospecific and only led to a single isomer (the attack occurring *syn* to the P–Me moiety). This

[a] Laboratoire "Hétéroéléments et Coordination", UMR CNRS 7653 (DCPH), Ecole Polytechnique,
91128 Palaiseau Cédex, France
Fax: +33-1-69-33-39-90
E-mail: yves.jean@polytechnique.fr
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planar discrimination has been studied in the case of O_2,[27] CO,[26] and H_2.[28]

We now wish to report on a theoretical study of the cobalt complex [Co(SPS)(PPh_3)], analog of **II** and **III**. In order to shed some light on the electronic structure of these SPS-based complexes, examination of the singlet and triplet states of this yet unknown cobalt complex is presented herein and a comparison is drawn with its Rh and Ir analogs.

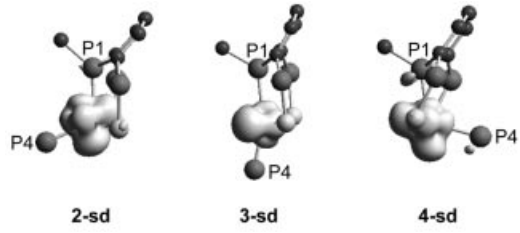

Figure 2. Total spin density (**sd**) surfaces computed for the triplet state of the cobalt complexes **2**, **3**, and **4**. Hydrogen atoms are omitted for clarity.

Results and Discussion

The geometry of the [Co(SPS)(PH_3)] model complex was first optimized in the singlet state without any symmetry constraint. The optimized structure (**1**, Figure 1) came out to be nearly of C_s symmetry with an almost perfect square-planar (SP) arrangement around the metal center (S1–Co–S2 = 178.4° and P1–Co–P4 = 177.8°), a geometry usual for a diamagnetic complex of the d^8-[ML_4] type.

The optimization of the triplet state led to three minima of C_s symmetry (**2**, **3**, and **4**, Figure 1), which differ by the arrangement of the ligands around the metal center. A pseudotetrahedral (*Td*) geometry was found for **2** ($^3A'$) with S1–Co–S2 and P1–Co–P4 angles of 128.3 and 113.1°, respectively. The two other minima can be described as butterfly structures: in **3** ($^3A''$) there is a large P1–Co–P4 angle (164.2°) and a smaller S1–Co–S2 angle (124.2°), while the reverse is true for **4** ($^3A'$) (111.5 and 169.3°, respectively). Such a change in the geometry in going from the singlet to the triplet state is consistent with qualitative molecular orbital arguments: moving away from the square-planar geometry towards tetrahedral or butterfly structures reduces the energy gap between the frontier MOs of d^8-[ML_4] complexes,[29] a trend which is favorable for the triplet state. The total spin density (**sd**) surface is pictured in Figure 2 and, for each complex, it was found to be mainly developed on the metal center with a Mulliken spin density of 1.970, 1.993, and 1.857 for **2**, **3**, and **4**, respectively.

From an energetic point of view, complex **2** was found to be more stable than **3** and **4** by 2.5 and 12.9 kcal·mol^{-1}, respectively. Interestingly, all these triplet-state structures are lower in energy than the singlet-state **1**, as $\Delta E_{S/T}$ = –22.4 kcal·mol^{-1} between **1** (singlet state) and **2** (lowest triplet state) (Figure 1). Note that **2** and **3**, which differ by their symmetry ($^3A'$ and $^3A''$) and their geometry [nearly tetrahedral (**2**) and butterfly-type with a wide P1–Co–P4 angle (**3**)], are predicted to be competitive in energy (ΔE = 2.5 kcal·mol^{-1}). It is remarkable that large changes in the metal–ligand bond angles induce rather small energy changes on the triplet potential energy surface. Note, however, that relative energies and even orderings can depend critically on the amount of HF exchange included in the functional. The energy separation of the four structures was therefore tested by single-point ab initio calculations at the MP2 level. The same energy ordering is found: **2** (0.0) < **3** (+4.1) < **4** (+14.1) < **1** (+34.5) (in kcal·mol^{-1}), the main change being an increase of the singlet–triplet energy separation (34.5 instead of 22.4 kcal·mol^{-1} at the B3PW91 level). These values are large enough to conclude unambiguously that the model complex [Co(SPS)(PH_3)] is paramagnetic. The energy ordering of the three triplet-state structures can be qualitatively traced to two factors: (i) the energy required to distort the complex in its singlet state from the equilibrium square-planar geometry to the actual geometry in the triplet-state structure. This distortion energy (in kcal·mol^{-1}) increases in the order **3** (14.0) < **2** (19.8) < **4** (23.7) (restricted B3PW91 calculations); (ii) the energy gap

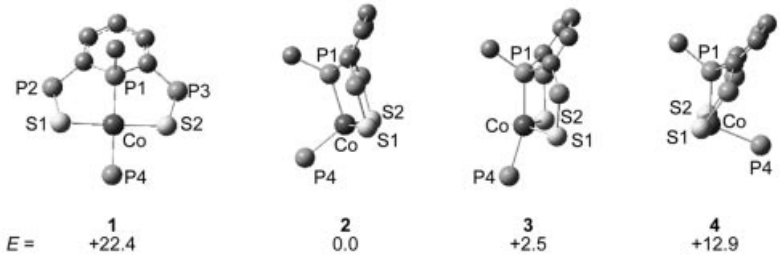

Figure 1. Optimized geometries for the [Co(SPS)(PH_3)] complex in its singlet (**1**) and triplet (**2**, **3**, and **4**) states. Hydrogen atoms are omitted for clarity. *E*: relative energies (at the B3PW91 level) are given in kcal·mol^{-1}. Selected geometrical parameters (bond lengths in Å and bond angles in °): **1**: Co–S 2.292, Co–P1 2.175, Co–P4 2.203; S1–Co–S2 178.4, P1–Co–P4 177.8. **2**: Co–S 2.455, Co–P1 2.324, Co–P4 2.288; S1–Co–S2 128.3, P1–Co–P4 113.1. **3**: Co–S 2.513, Co–P1 2.317, Co–P4 2.308; S1–Co–S2 124.2, P1–Co–P4 164.2. **4**: Co–S 2.568, Co–P1 2.286, Co–P4 2.340; S1–Co–S2 169.3, P1–Co–P4 111.5.

between the two singly occupied MOs in the triplet state (a small value favoring a low-lying triplet state), which increases in the order **2** (10.7) < **3** (23.8) < **4** (29.5). Therefore structure **4** appears to be the least favorable, while the two factors work in opposite direction for structures **2** and **3**, which were actually found to be close in energy.

For the sake of comparison, similar calculations were performed on the rhodium and iridium analogs, the energetic results and the main geometrical parameters being reported in Table 1. A nearly square-planar geometry was found for the singlet state[26,27] and three minima were located for the triplet state. Their geometries are close to that pictured in Figure 1 for the cobalt complex and two of them (**2** and **3**) are still found to be close in energy. However, the singlet state is now located well below the lowest triplet state, by 19.0 and 26.2 kcal·mol^{-1} for M = Rh and Ir, respectively (Table 1). The electronic ground state of the Rh and Ir complexes is thus found to be diamagnetic, in agreement with NMR spectroscopic data.[23,27] Therefore, the trend for the first-row transition metals to form high-spin complexes is large enough to induce a change of the magnetic properties in this family of SPS-based complexes.

Table 1. Relative energies (given in kcal·mol^{-1}) at the B3PW91 level of the lowest square-planar (SP) singlet state (**1**) and triplet states [**2** (pseudo-*Td*), **3** (butterfly-1), and **4** (butterfly-2)] of the [M(SPS)(PH$_3$)] model complexes (M = Co, Rh, and Ir).[a]

	1 (SP) ^{1}A′	**2** (pseudo-*Td*) ^{3}A′	**3** (butterfly-1) ^{3}A′′	**4** (butterfly-2) ^{3}A′
Co	+22.4	0.0	+2.5	+12.9
Rh	0.0	+19.0	+19.9	+27.8
Ir	0.0	+26.7	+26.2	+39.7

[a] Selected geometrical parameters (bond lengths in Å and bond angles in °) for Rh and Ir complexes: **Rh(1)**: Rh–S 2.401, Rh–P1 2.259, Rh–P4 2.303; S1–Rh–S2 173.9, P1–Rh–P4 174.3. **Rh(2)**: Rh–S 2.551 (av.), Rh–P1 2.335, Rh–P4 2.304; S1–Rh–S2 138.1, P1–Rh–P4 106.6. **Rh(3)**: Rh–S 2.568, Rh–P1 2.358, Rh–P4 2.369; S1–Rh–S2 111.3, P1–Rh–P4 170.4. **Rh(4)**: Rh–S 2.642, Rh–P1 2.309, Rh–P4 2.332; S1–Rh–S2 168.3, P1–Rh–P4 103.2. **Ir(1)**: Ir–S 2.380, Ir–P1 2.274, Ir–P4 2.272; S1–Ir–S2 172.7, P1–Ir–P4 171.4. **Ir(2)**: Ir–S 2.461, Ir–P1 2.275, Ir–P4 2.240; S1–Ir–S2 128.6, P1–Ir–P4 106.5. **Ir(3)**: Ir–S 2.509, Ir–P1 2.304, Ir–P4 2.300; S1–Ir–S2 106.0, P1–Ir–P4 166.5. **Ir(4)**: Ir–S 2.453, Ir–P1 2.266, Ir–P4 2.284; S1–Ir–S2 163.1, P1–Ir–P4 107.6.

Finally, optimizations of both the singlet and triplet states were performed at the ONIOM(B3PW91:UFF) level of calculation on the real complex (**rc**) [Co(SPS)(PPh$_3$)] bearing nine phenyl substituents. The square-planar singlet state (**1-rc**) and the two lowest structures optimized for the triplet state (**2-rc** and **3-rc**) are pictured in Figure 3.[30] Complex **2-rc** is a slightly distorted tetrahedral complex with S1–Co–S2 and P1–Co–P4 angles of 119.8 and 112.2°, respectively, and **3-rc** adopts a butterfly-type structure with S1–Co–S2 and P1–Co–P4 angles of 103.2 and 150.9°, respectively. From an energetic point of view, complex **2-rc** was found to be more stable than **3-rc** by 6.2 kcal·mol^{-1}, the two triplet-state structures being lower in energy than the singlet-state **1-rc** ($\Delta E_{S/T}$ = –20.3 kcal·mol^{-1} between **2-rc** and **1-rc**). Finally, the influence of a QM treatment of the phenyl ligands was tested by single-point calculations at the B3PW91//ONIOM(B3PW91:UFF) level (Figure 3). A triplet ground state was still found, with **2-rc** and **3-rc** very close in energy (only 0.4 kcal·mol^{-1} in favor of **3-rc**) and significantly more stable than the square-planar singlet-state **1-rc** ($\Delta E_{S/T}$ = –29.6 kcal·mol^{-1} between **3-rc** and **1-rc**). Both from the geometrical and energetic points of view, the results of these calculations on the real complex are similar to those from the study of the model complex (Figure 1).

Conclusion

According to DFT calculations, there is a change in the nature of the electronic ground state when Rh or Ir is replaced by Co in the family of SPS-based pincer-based [M(SPS)(PH$_3$)] model complexes. While Rh and Ir compounds are found to be diamagnetic, a triplet ground state is predicted for the yet unknown cobalt complex, a conclusion confirmed by calculations on the real complex [Co(SPS)(PPh$_3$)] with nine phenyl substituents. This change in the electronic ground state in going from (Rh, Ir) to Co is likely to result in a different chemical behavior of the Co complex compared to its rhodium or iridium analogs. This

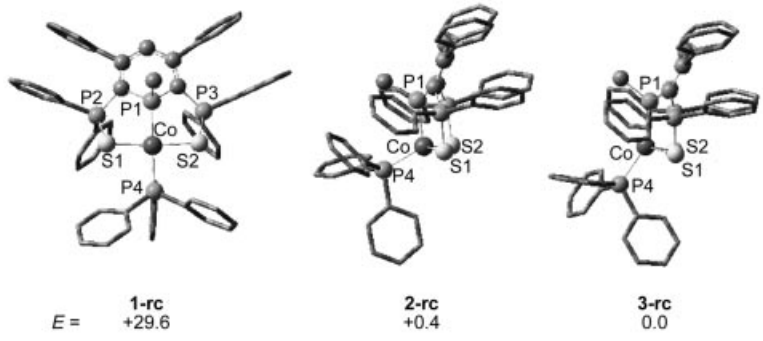

Figure 3. Optimized geometries for the real complex [Co(SPS)(PPh$_3$)] in its singlet (**1-rc**) and triplet (**2-rc** and **3-rc**) states. Hydrogen atoms are omitted for clarity. *E*: relative energies [at the B3PW91//ONIOM(B3PW91:UFF) level] are given in kcal·mol^{-1}. Selected geometrical parameters (bond lengths in Å and bond angles in °): **1-rc**: Co–S1 2.290, Co–S2 2.283, Co–P1 2.176, Co–P4 2.244; S1–Co–S2 172.5, P1–Co–P4 173.2. **2-rc**: Co–S1 2.405, Co–S2 2.367, Co–P1 2.285, Co–P4 2.278; S1–Co–S2 119.8, P1–Co–P4 112.2. **3-rc**: Co–S1 2.428, Co–S2 2.420, Co–P1 2.277, Co–P4 2.299; S1–Co–S2 103.2, P1–Co–P4 150.9.

result has prompted us to synthesize this interesting Co derivative and to study its reactivity towards small molecules.

Computational Details

Calculations on the model complexes (quoted as [M(SPS)(PH_3)] with M = Co, Rh, and Ir), in which the phenyl groups were replaced by H atoms, were performed with the GAUSSIAN 03 series of programs.[31] Density functional theory (DFT)[32,33] was applied with the B3PW91 functional.[34] A quasirelativistic effective core potential operator was used to represent the 10 innermost electrons of the cobalt atom, the 28 innermost electrons of the rhodium atom, and the 60 innermost electrons of the iridium atom.[35] The basis set for the metal atom was that associated with the pseudopotential, with a standard double-ζ LANL2DZ contraction[35] completed by a set of polarization *f* functions.[36] Geometry optimizations were performed with the 6-31+G* basis for phosphorus and sulfur atoms, 6-31G* for the carbon atoms, and 6-31G for hydrogen atoms[37–40] (basis set A) and the minimum energy structures were characterized by vibration frequency calculations. Finally, the energies were recomputed by single-point calculations on the optimized structures using the same basis set for the metal center and the 6-31+G* basis set for all the other atoms (basis set B). Note that the changes in relative energies were found to be lower than 0.7 kcal·mol^{-1} in going from basis set A to basis set B. The restricted singlet-state wave function was reoptimized in the Co complex **1**, as an RHF → UHF instability was detected (single-point calculation on the geometry optimized at the restricted level). The geometry of the real complex (**rc**) [Co(SPS)(PPh_3)] with nine phenyl substituents was optimized and characterized by vibration frequency calculations by means of QM/MM calculations at the ONIOM(B3PW91:UFF) level with the phenyl substituents in the MM part.[41] The QM part was treated at the DFT/B3PW91 level with the basis set A (see above) and the UFF force field was used for the MM part.[42] Finally, DFT-B3PW91 single-point calculations were performed on the optimized structures [B3PW91//ONIOM(B3PW91:UFF) calculations] using the 6-31G basis set for the phenyl substituents and the basis set A for the other atoms.

Supporting Information (see footnote on the first page of this article): Optimized geometry and frequencies of **1**–**4**, **1-rc**, **2-rc**, **3-rc**, **Rh(1)**, **Rh(2)**, **Rh(3)**, **Rh(4)**, **Ir(1)**, **Ir(2)**, **Ir(3)**, and **Ir(4)**.

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