

Coordination Behavior of the S–C–S Monoanion and O–C–O and S–C–S Dianions toward Co^{II}

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Keywords: Cobalt / Anions / Pincer ligands / Density functional calculations

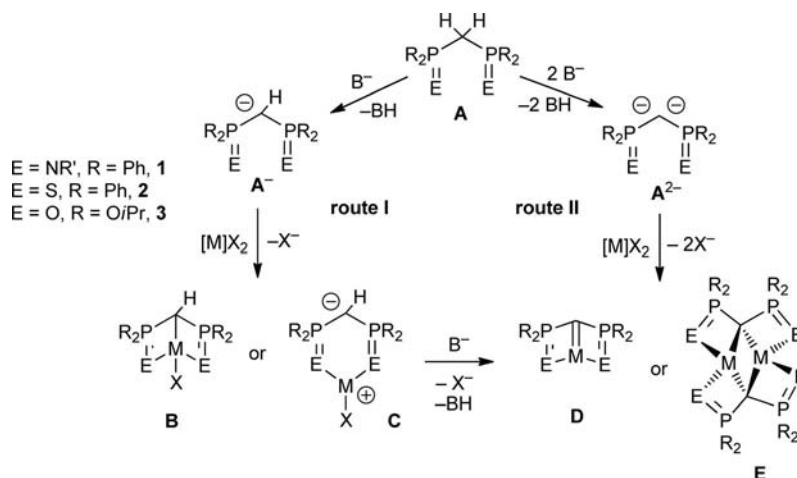
The reactivity of both the monoanionic and dianionic forms of bis(diphenylthiophosphinoyl)methane (**2**[−] and **2**^{2−}) as well as the dianion of tetrakisopropyl methylenediphosphonate (**3**^{2−}) was investigated towards the same Co^{II} precursor CoCl₂. Monoanion **2**[−] coordination yields a homoleptic zwitterionic Co^{II} complex. However, both dianions (**2**^{2−} and **3**^{2−})

give the same overall structure with a square Co₂C₂ core. Structures of all of the complexes have been confirmed by full NMR spectroscopic analysis and X-ray diffraction. Furthermore, DFT calculations have been carried out to rationalize the stability of such species.

Introduction

The coordination chemistry of the monoanions and dianions of bis(iminophosphorane), **1**^[1] and **1**^{2−},^[2] respectively, and of the dianion of bis(thiophosphinoyl)methane, **2**^{2−},^[3] has been studied in depth (Scheme 1), especially in the past decade.^[4] In particular, dianions **1**^{2−} and **2**^{2−} have

been shown to be excellent precursors to transition-metal carbenes^[5] as well as group 2,^[6] rare earth,^[7] and uranium^[8] carbene complexes. One of the strategies (“route I”, Scheme 1) toward the synthesis of such carbene complexes relies on a two-step sequence: coordination of monoanion **A**[−] followed by deprotonation of the ligand in the coordination sphere of the metal. In the very large majority of the



Scheme 1. Routes toward the synthesis of carbene complexes.

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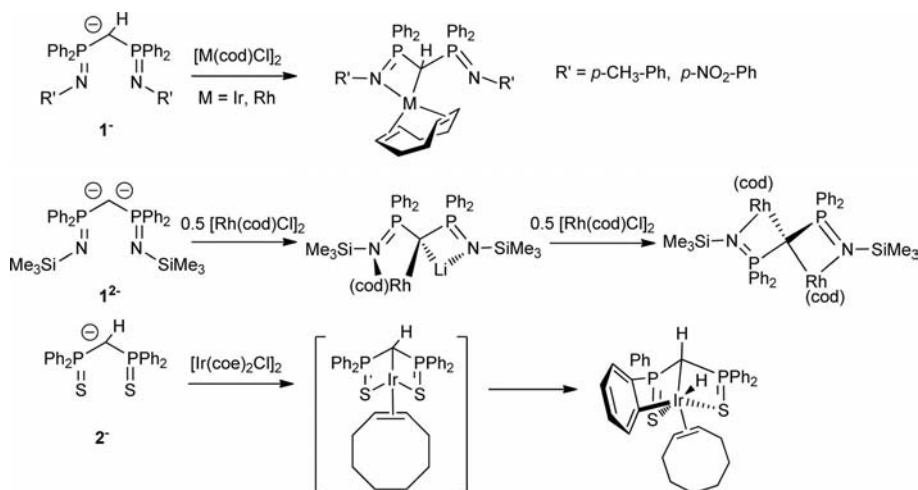
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cases, the intermediate structure **C** is obtained rather than structure **B** from the coordination of the monoanion to metal centers. This “route I” has been most extensively studied with the bis(iminophosphorane) ligands, **1**. On the other hand, the synthesis of transition-metal carbene complexes with ligand **2** almost only relied on the use of the geminal dianion, **2**^{2−}, as precursor (“route II”, Scheme 1). By choosing either “route I” or “route II”, the typical out-



Scheme 2. Examples of group 9 metal complexes synthesized using routes I and II (cod = cycloocta-1,5-diene; coe = cyclooctene).

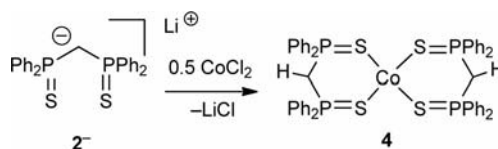
come of the reactions is the formation of the carbene complex (structure **D**) rather than dinuclear complex **E**. Notable examples of the “nontypical” cases are found mostly for group 9 complexes. Indeed, reactions of **1**[−] with either Rh^I or Ir^I precursors leads to a complex of type **B** (Scheme 2),^[9] and reaction of **1**^{2−} with one equivalent of Rh^I precursor resulted in the formation of a mixed Rh–Li complex. This complex could then be reacted with another equivalent of metal precursor to generate bimetallic complexes, in which the dianion acts as a bridging moiety, reminiscent of structure **E**.^[10] We have recently reported that the reaction of **2**[−] with one equivalent of Ir^I precursor led to the formation of an Ir^{III} complex resulting from the CH insertion in one phenyl substituent of the ligand.^[11] Finally, the reaction of two different ligands of type **1**[−] (R = C₆H₂Me₃ and C₆H₃iPr₂) with CoCl₂ is reported to form a complex of the type [(1)CoCl], yet their structures (**B** or **C**) are not known.^[12]

These peculiar results prompted us to study the coordination behavior of both the anions and dianions of **2** and **3** toward a Co^{II} precursor. We show here that coordination of **2**[−] leads to the formation of a complex that lacks Co–C bonding unlike the complexes of the heavier elements (Rh^I and Ir^I). The reactivity of dianions **2**^{2−} and **3**^{2−}, on the other hand, is shown to follow a path similar to the Rh analogue, leading to the dinuclear bridging species.

Results and Discussion

In the first stage, monoanion **2**[−] was synthesized by addition of methyllithium (1 equiv.) to 1,1-bis(diphenylthiophosphinoyl)methane (DPPMS₂) in toluene, diethyl ether, or THF.^[13] The 1:1 stoichiometric reaction between the ligand and CoCl₂, at room temperature in THF for 12 h, led to the formation of a green complex. This complex was characterized by a broad singlet in the ³¹P{¹H} spectrum at δ = +70 ppm, shifted downfield by approximately 33 ppm from the monoanion. The reaction performed with 2:1 stoichiometry resulted in the formation of the same spe-

cies, which was therefore postulated to be complex **4**. After evaporation of THF, dissolution of the complex in dichloromethane, and filtration to remove LiCl, complex **4** was obtained in good yield after evaporation of the solvent (80%; Scheme 3).



Scheme 3. Synthesis of complex **4**.

Surprisingly, the ³¹P NMR spectrum of **4** in dichloromethane showed a broad singlet at δ = +4 ppm, but when the complex was redissolved in THF after evaporation of dichloromethane, the ³¹P NMR spectrum showed the broad singlet at δ = +70 ppm. This points to a very large influence of the solvent on the chemical shift of **4**. Indeed, we found that this chemical shift depends on the ratio of the CH₂Cl₂/THF mixture, ranging from +4 ppm (100% dichloromethane) to +70 ppm (100% THF). Such solvent effects on Co^{II} complexes have already been reported in the literature.^[14] Complex **4** was further characterized by multinuclear NMR spectroscopy in CD₂Cl₂. The ¹H NMR spectrum exhibits only very broad signals for the various protons of the phenyl substituents, yet in the diamagnetic range (δ = 6.2 to 8.7 ppm), which suggests a moderate influence of the paramagnetic Co^{II} center on these chemical shifts. Neither the signal for the proton of the PC(H)P bridge (in the ¹H spectrum) nor the signal of the corresponding carbon (in the ¹³C spectrum) was observed. To gain more information on the bonding between the ligand and the metal center, a variable-temperature ³¹P NMR spectroscopic experiment was carried out. Lowering the temperature to −80 °C and warming back to 0 °C in CD₂Cl₂ did not show any change in the shape or intensity of the signal. However, the chemical shift was strongly affected, as chemical shifts were ob-

served between $\delta = -68$ and $+4$ ppm. Variations of the chemical shift of the phosphorus atoms relative to the temperature are shown in Table 1.

Table 1. Variation of the ^{31}P chemical shift of **4** with temperature (in CD_2Cl_2).

T [$^{\circ}\text{C}$]	-80	-70	-60	-50	-40
δ_{P} [ppm]	-68	-54	-43	-31	-22
T [$^{\circ}\text{C}$]	-30	-20	-10	0	20
δ_{P} [ppm]	-16	-11	-7	-3	+4

This phenomenon is indicative of ligand coordination to a paramagnetic center, and not of a dynamic process involving an equilibrium between a coordinated and uncoordinated C center to the Co atom.^[15] It is interesting to note that complex **4** does not react with dichloromethane, unlike ligand **2**⁻, which points to a strong C–Co interaction in the complex. At this point, no definitive answer regarding the presence or lack of Co–C could be drawn. Single crystals were grown from a concentrated solution of **4** in toluene at room temperature, and the solid-state structure of the complex was then obtained by X-ray diffraction analysis. A view of complex **4** is given in Figure 1, clearly showing that the two central carbon atoms of the monoanion are not coordinated to the cobalt center in the solid state. The Co–C distances [Co1–C1 3.230 Å, Co1–C2 3.824 Å] are far longer than the typical Co–C distances reported in the literature for pincer complexes.^[16] The geometry at the Co center is distorted tetrahedral, as shown by the very different angles of S–Co–S [between 93.21(4) and 123.46(4) $^{\circ}$]. Also, the P–C bond lengths within the ligand are similar to those found in monoanion **2**⁻^[13] [1.711 Å (av.) in **2**⁻ vs. 1.706 Å (av.) in **4** for P–C bonds], which shows that the stabilization of the charge at C is similar in both species. Thus, it appears that the stabilization of the lone pair at C by the two substituents PPh_2S is strong enough, and does not require further C–Co bonding interaction. Thus, complex **4** is a zwitter-

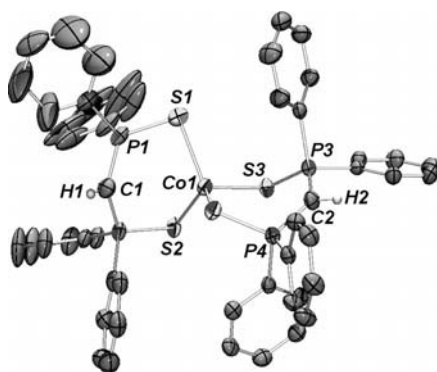
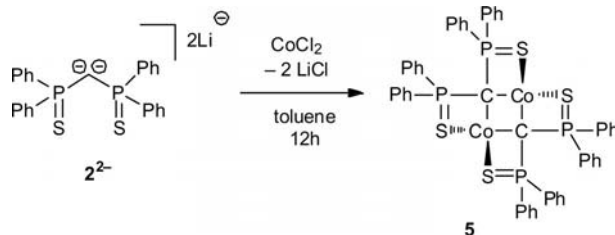


Figure 1. Molecular view of complex **4**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms on the phenyl rings and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [$^{\circ}$]: Co–S1 2.327(1), Co–S2 2.331(1), Co–S3 2.308(1), Co–S4 2.357(1), C1–P1 1.701(4), C1–P2 1.715(3), P1–S1 2.032(1), P2–S2 2.025(1), C2–P3 1.703(3), C2–P4 1.706(3), P3–S3 2.045(1), P4–S4 2.015(1); P1–C1–P2 125.3(2), P3–C2–P4 124.1(2), S3–Co–S1 105.08(4), S3–Co–S2 123.46(4), S3–Co–S4 110.29(3), S2–Co–S4 93.21(4).

ionic species consisting of a central Co^{2+} and two anionic ligands **2**⁻, which behave as bidentate ligands through the two S atoms and not as pincer anionic SCS ligands. This bonding of the monoanion with the d^7 Co^{II} center is therefore very different from that observed for analogous monoanionic ligands with d^8 Rh^{I} and Ir^{I} centers.

The absence of C bonding between the monoanionic ligand **2**⁻ and the metal prompted us to study the reactivity of dianion **2**²⁻ with the same cobalt precursor. Indeed, in all the cases studied so far, the dianion appeared as a very strong ligand, with the C atom always bound to either one or two metal centers (structures **D** or **E**, Scheme 1). Reaction of one equivalent of dianion **2**²⁻ with one equivalent of CoCl_2 was therefore carried out in toluene at room temperature, and followed by ^{31}P NMR spectroscopy (Scheme 4). After 12 h of stirring, the spectrum showed the complete formation of a new complex. After filtration and evaporation of the solvent, complex **5** was isolated as a brown solid in 75% yield. It was fully characterized by multinuclear NMR spectroscopy.



Scheme 4. Synthesis of complex **5**.

Complex **5** exhibits a low-field signal at $\delta = +187$ ppm in the ^{31}P NMR spectrum. This is a much higher chemical shift than what is usually observed for this ligand, which confirms the formation of a paramagnetic complex. The ^1H NMR spectrum presents signals ranging from $\delta = -9$ to $+13$ ppm for the phenyl hydrogen atoms, which are much more influenced by the paramagnetic Co^{II} center than those in complex **4**. In the ^{13}C NMR spectrum, no signal could be observed for the carbon of the PCP bridge nor for the ones associated with the protons at $\delta = -9$ ppm (in the *ortho* position on the phenyl rings) in the ^1H NMR spectra. The precise structure of complex **5** could not be deduced from the NMR spectroscopic data but was obtained by X-ray crystal structure analysis. Crystals were obtained by slow diffusion of hexanes into a concentrated solution of **5** in dichloromethane. A view of complex **5** is shown in Figure 2. Complex **5** features a planar Co–C–Co–C metallacycle (structure **E**, Scheme 1), with each ligand binding the two cobalt atoms. The Co–C distances [Co1–C1 2.044(3) Å, Co1–C1' 2.044(3) Å] are in the normal range of Co–C bonds observed in other complexes.^[16] The P–S bonds in **5** are only slightly shorter than in dianion **2**²⁻ (2.022 Å in average in **5** vs. 2.040 Å in **2**²⁻), whereas the P–C bonds are significantly longer than in **2**²⁻ (av. 1.735 Å vs. av. 1.676 Å).^[3] This latter point is directly correlated to the strength of the donation of the lone pairs at C to the metal

center(s) versus their stabilization by hyperconjugation into low-lying σ^* orbitals at the P substituent (P–Ph and P–S). These facts point to a relatively strong C–Co interaction. The Co–Co distance of 2.4710(7) Å suggests a bonding interaction between the two cobalt atoms (a search of the CCDC database for all complexes containing any type of Co–Co bond gave a distribution of the Co–Co distances centered on 2.5 Å). This Co–Co interaction has been studied by DFT calculations and the results are presented below. The evolution of the ^{31}P and ^1H NMR spectra was studied with respect to the temperature in CD_2Cl_2 . Note that here again, no reaction was observed between **5** and dichloromethane. The results are shown in Table 2.

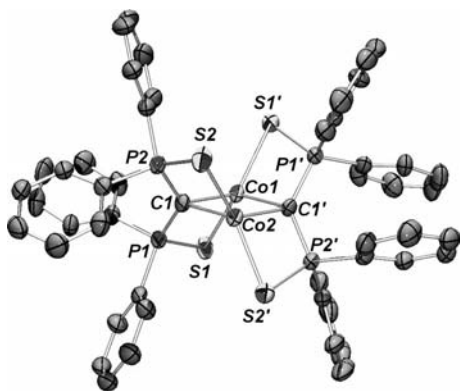


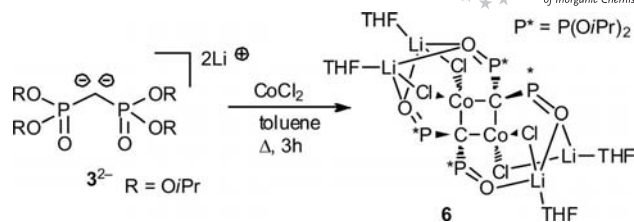
Figure 2. Molecular view of complex **5**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Co1–Co2 2.4710(7), Co1–C1 2.044(3), Co2–C1 2.044(3), Co1–S1 2.3408(8), Co2–S2 2.3627(8), C1–P1 1.728(3), C1–P2 1.742(3), P1–S1 2.024(1), P2–S2 2.021(1); P1–C1–P2 129.7(1), C1–Co2–C1' 105.6(2), C1–Co2–S2 84.20(8), Co1–C1–C1'–Co2 0.00.

Table 2. Evolution of the ^1H and ^{31}P chemical shifts of **5** with temperature in CD_2Cl_2 .

T [°C]	–80	–70	–60	–50	–40	25
δ_{P} [ppm]	147	150	154	158	161	187
$\delta_{\text{ortho-H}}$ [ppm]		–15			–13	–9

We had previously shown that dianions **2**^{2–} and **3**^{2–} reacted very differently towards Zr^{IV} . Indeed, when the bis-(thiophosphinoyl) ligand led to a monocarbene complex,^[17] the bis(phosphonate) led to a triscarbene complex.^[18] This prompted us to study the reactivity of **3**^{2–} with the same Co^{II} precursor. Ligand **3**^{2–} is insoluble in the solvents in which it does not react (toluene, Et_2O). In toluene, in which CoCl_2 is also insoluble, no reaction was seen even after three days. However, heating the suspension at 80 °C for 3 h allowed the formation of a novel species, as a purple precipitate, that was readily isolated by filtration (Scheme 5). Interestingly, no precipitation of the LiCl salt was observed during this reaction.

Once formed, the complex was soluble in THF, which allowed a full characterization. The ^{31}P NMR spectrum of this complex showed a singlet at $\delta = +63$ ppm, thus proving the conversion of the starting material into a single new species. Interestingly, this chemical shift is consistent with



Scheme 5. Synthesis of complex **6**.

either the complex being a diamagnetic species, or a paramagnetic complex with a weaker influence of the Co^{II} center on the ligand. A variable-temperature experiment was carried out, and the ^{31}P chemical shift did not evolve with temperature. The ^1H and ^{13}C NMR spectra were quite uninformative, except for the chemical shift of the proton of the *i*Pr substituent, which was observed at very low field ($\delta = 6.4$ ppm). The structure of the complex was elucidated by X-ray diffraction analysis. Single crystals of complex **6** were obtained by slow diffusion of hexanes into a concentrated solution of **6** in THF. A view of complex **6** is shown in Figure 3. The central core of the structure of complex **6** is similar to that of complex **5**. Both feature a C_2Co_2 square core. However, in **6** the oxygen atoms of the $\text{P}=\text{O}$ arms are not coordinated to the metal, which suggests that Cl^- is a better ligand than $\text{P}=\text{O}$. The stabilization of the complex is assisted by the presence of 4 lithium atoms. The $\text{P}=\text{O}$ bonds in **6** are longer than in the neutral ligand^[19] **3** [1.508(3) and 1.512(3) Å in **6** vs. 1.4840(12) and 1.4756(13) Å in **3**], whereas the two P–C bonds are significantly shorter [1.713(1) and 1.714(3) Å in **6** vs. 1.7924(17) and 1.7950(18) Å in **3**]. This indicates that the electron density initially on the C atom of the dianion is strongly stabilized by the substituents at P, rather than efficiently transferred to the metal centers. On the other hand, in complex **5** the P–C bonds are 1.728(3) and 1.742(3) Å, which clearly indicates a more efficient electron transfer from the carbon to the metals.

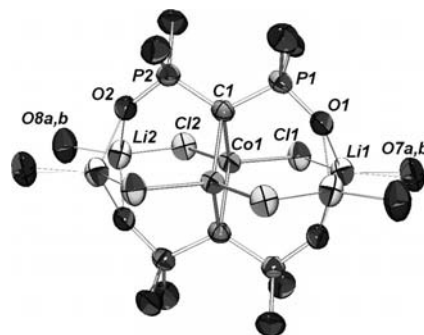
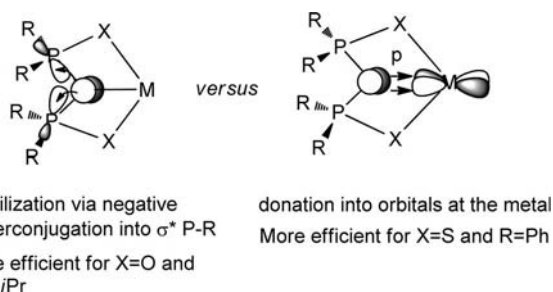


Figure 3. Molecular view of complex **6**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, isopropyl groups, and carbon atoms of the THF molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Co1–Co1' 2.724(1), Co1–C1 2.077(3), Co1'–C1 2.092(3), Co1–Cl1 2.353(1), Co1–Cl2 2.346(1), C1–P1 1.713(1), C1–P2 1.714(3), P1–O1 1.508(3), P2–O2 1.512(3); P1–C1–P2 123.4(2), C1–Co1'–C1' 98.4(1), Co1–C1–C1'–Co1' 0.0.

The Co–Co distance of 2.724(1) Å in **6** is longer than that in **5** [2.4710(7) Å] as are the Co–C distances [Co–C 2.077(3) and 2.092(3) Å in **6** vs. Co–C 2.044(3) and 2.044(3) Å in **5**], which also indicate a weaker interaction (Scheme 6). To obtain further insights in the bonding of the dinuclear complexes, DFT calculations were performed on complex **5** using the Gaussian03 set of programs.^[20] The PBEPBE^[21] functional was used in combination with the 6-31++G** for the core carbon atoms, 6-31+G* for the metal-bound atoms (P, S), 6-31G* for the *ipso*-carbon atoms, and 3-21G* for the remaining atoms (C, H of the phenyl groups). DZVP2^[22] was used for the cobalt (details on the optimized structures are given in the electronic Supporting Information). Two spin states have been considered for this species, a singlet and a triplet (5s, 5t). Both geometries have been optimized as minima on the potential-energy surface (PES) and the triplet turns out to be more stable by approximately 8 kcal mol^{−1} (G), in agreement with the experimental findings. A comparison of the structural parameters of the calculated structure and the experimental data is shown in Table 3. All calculated distances are in good agreement with the experimental data except for the Co–C distances that were found to be shorter, corroborated by the overestimation of the P–C bonds. Attempts to obtain more satisfying results were made by changing the basis sets (def2-qzvp, dzvp2) on C1 and C2 and the functional (b3lyp, opbe), but were not successful.



Scheme 6. Competition in the stabilization of the π lone pair at C: by the P substituent versus the metal.

Table 3. Comparison of bond lengths and angles in **5**.

Bond	RX	DFT	$ \Delta[RX - DFT] $
Co11–Co12	2.47	2.42	0.04
Co11–C1	2.05	1.93	0.12
C1–Co12	2.06	1.93	0.13
C1–P9	1.74	1.77	0.03
C1–P8	1.74	1.77	0.03
P9–S5	2.02	2.04	0.02
P8–S4	2.02	2.04	0.02
Co11–S5	2.35	2.33	0.02
Co11–S6	2.35	2.33	0.002

The relative stability of the triplet compared to the singlet can be explained when one looks at the frontier orbitals of **5** in both states. The SOMO–1 and the SOMO of complex **5** in the triplet state are shown in Figure 4. The SOMO–1 (Figure 4, left) shows an antibonding interaction of the two $d_{x^2-y^2}$ orbitals at the Co centers. This orbital

possesses a pure metal character as it does not have the right symmetry to overlap with orbitals at the ligands. On the other hand, the SOMO (Figure 4, right) is not a “pure d ” metal orbital, and presents an antibonding interaction of the Co centers with the ligands. This orbital therefore results from the overlap of the positive interaction of the two $d_{x^2-y^2}$ orbitals at the Co centers, in an antibonding fashion with two lone pairs at C (Scheme 7). This explains why these orbitals lie close in energy, thereby favoring the triplet state. In the optimized geometry of the singlet-state species, the Co–Co bond length is calculated at 2.54 Å, much longer than that in the triplet-state complex (2.42 Å). This is fully consistent with the transfer of an electron from the SOMO into the SOMO–1, increasing the antibonding interaction between the two Co centers.

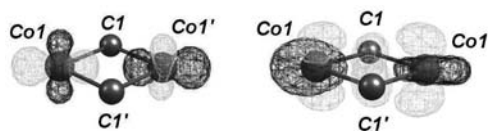
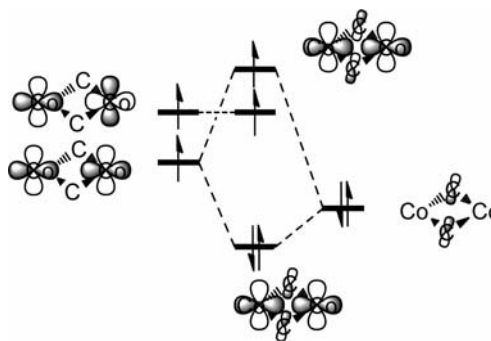


Figure 4. SOMO–1 (left) and SOMO (right) of complex **5**.



Scheme 7. Correlation diagram of orbitals in complex **5**.

Conclusion

We have presented here the first examples of the coordination of monoanion 2^- and dianions 2^{2-} and 3^{2-} toward Co^{II} . The reactivity of 2^- leads to the formation of a homoleptic complex, best seen as a paramagnetic zwitterionic species. The coordination of the two dianions results in the formation of related dinuclear species containing two bridging ligands. The metal–ligand interaction is much stronger in the case of ligand 2^{2-} , which transfers more efficiently its electronic density. On the other hand, the two lone pairs at C of the ligand 3^{2-} are more efficiently stabilized by the $\text{P}(\text{O})\text{OR}_2$ substituents. The formation of the paramagnetic complex **5** was rationalized by DFT calculations. The redox behavior of complexes **5** and **6** are currently being studied in our laboratory, as both oxidation and reduction should lead to profound modifications as illustrated by the shape of the SOMO orbitals of complex **5**.

Experimental Section

General: All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and glovebox techniques and dry deoxygenated solvents. Dry tetrahydrofuran and hexanes were distilled by using Na/benzophenone; dry dichloromethane was distilled by using P_2O_5 ; and dry toluene with Na. Nuclear magnetic resonance 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 . Solvent peaks were used as an internal reference relative to Me_4Si for 1H 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; br. s, broad singlet; t, triplet. Monoanion 2^- ,^[13] and dianions 2^{2-} and 3^{2-} were prepared according to literature procedures.^[3] $CoCl_2$ was bought as the hydrate and dried by heating under vacuum. All other reagents and chemicals were obtained commercially and used as received.

Synthesis of Complex 4: $CoCl_2$ (20.7 mg, 0.16 mmol) was added to a solution of monoanion 2^- (143.6 mg, 0.32 mmol) in toluene (4 mL) under an argon atmosphere at room temperature. The solution was left stirring for 15 h at room temperature, then filtered and dried. The solvent was evaporated under vacuum to give the title compound as a green solid (80%). Single crystals suitable for X-ray analysis were grown from a concentrated solution of **5** in toluene. 1H NMR (300 MHz, CD_2Cl_2): δ_H = 8.70 (br. s, *meta*-phenyl), 6.65 (br. s, *para*-phenyl), 6.32 (br. s, *ortho*-phenyl) ppm. ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ_C = 227.2 (br. s, C_{ipso}), 148.0 (s, CH *para*-phenyl), 146.4 (s, CH *meta*-phenyl), 129.2 (br. s, CH *ortho*-phenyl) ppm. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ_P = 4.1 (br. s) ppm. $C_{50}H_{42}CoP_4S_4 \cdot C_4H_8O$ (1026.1): calcd. C 63.21, H 4.92; found C 63.07, H 5.11.

Synthesis of Complex 5: $CoCl_2$ (41.4 mg, 0.32 mmol) was added to a solution of dianion 2^{2-} (143.6 mg, 0.32 mmol) in toluene (4 mL) under an argon atmosphere at room temperature. The solution was left stirring for 12 h at room temperature and was filtered. The title compound was obtained as a brown powder after evaporation of the solvent (75%). Single crystals suitable for X-ray analysis were obtained by a slow diffusion of hexanes into a concentrated solution of **5** in dichloromethane. 1H NMR (300 MHz, CD_2Cl_2): δ_H = 13.66 (s, 8 H, *ortho*-phenyl), 9.69 (s, 8 H, *meta*-phenyl), 9.05 (t, J = 7 Hz, 4 H, *para*-phenyl), 4.57 (t, J = 7 Hz, 4 H, *para*-phenyl), 2.79 (s, 8 H, *meta*-phenyl), –9.12 (s, 8 H, *ortho*-phenyl) ppm. ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ_C = 148.1 (s, *ortho*-phenyl), 136.2 (s, *para*-phenyl), 130.3 (s, *meta*-phenyl), 125.6 (s, *para*-phenyl), 121.4 (s, *meta*-phenyl) ppm. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ_P = 187 (s) ppm. $C_{50}H_{42}Co_2P_4S_4$ (1012.9): calcd. C 59.41, H 3.99; found C 59.69, H 3.88.

Synthesis of Complex 6: $CoCl_2$ (54.5 mg, 0.42 mmol) was added to a suspension of dianion **3** (150 mg, 0.42 mmol) in toluene (5 mL) under an argon atmosphere. The solution was heated at 80 °C for 3 h. The title compound was isolated as a purple-red solid after filtration and washing with toluene (3×2 mL; yield: 83%). Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexanes into a concentrated solution of **6** in THF. 1H NMR (300 MHz, $[D_8]THF$): δ_H = 6.4 [br. s, 4 H, $CH(CH_3)_2$], 1.23 [br. s, 12 H, $CH(CH_3)_2$], 1.06 [br. s, 12 H, $CH(CH_3)_2$] ppm. ^{13}C NMR (75.5 MHz, $[D_8]THF$): δ_C = 74.4 [br. s, $CH(CH_3)_2$], 25.9 [br. s, $CH(CH_3)_2$] ppm. ^{31}P NMR (121.5 MHz, $[D_8]THF$): δ_P = 63 (br. s) ppm. $C_{42}H_{88}Cl_4Co_2Li_4O_{16}P_4$ (1260.5): calcd. C 40.02, H 7.04; found C 39.86, H 6.87.

Supporting Information (see footnote on the first page of this article): Crystallographic details, computational details for calculations,

views of computed structures, cartesian coordinates, and the three lower frequencies for each optimized structure.

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