Cofacial Dimer of a Diiminosuccinonitrile Complex Containing a $Co^{II}-Co^{II}$ Bond and its Reduction to the Monomeric Co^{I} Complex[**]

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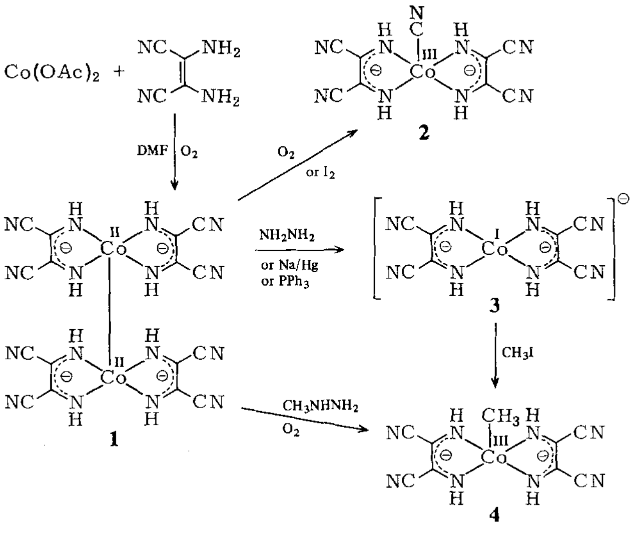
As a result of work on metal complexes with delocalized ground states, we report on two novel crystal structures of semidiiminosuccinonitrile (s-disn) complexes of cobalt (Scheme 1).



Scheme 1.

The blue binuclear complex $[Co^{II}(s\text{-}disn)_2]_2$ **1** was synthesized by the reaction of diaminomaleonitrile and $Co(OAc)_2$ in dimethylformamide (DMF), followed by oxidation. Suitable single crystals were grown by slow diffusion of air into the solution for one month. The structure of **1** consists of discrete DMF-solvated dimeric complexes, $\mathbf{1}\cdot(dmf)_3$ (Fig. 1). The complex **1** has a number of unusual features. First, it contains a short $Co^{II}-Co^{II}$ bond (2.633(3) Å), which is shorter than those in $[Co_2^{II}(CN)_{10}]^{6\ominus}$ (2.794 Å)[2] and $[Co_2^{II}(CNCH_3)_{10}]^{4\oplus}$ (2.734 Å)[3]. The Co atoms are displaced 0.19 Å from the plane formed by the four N atoms toward one another. Both findings indicate a reasonably strong Co–Co σ-bond. Secondly, the two diiminosuccinonitrile ligands are arranged in an eclipsed fashion and are separated by only 2.9 Å. Thirdly, the ligands have more localized double bond character than those in similar complexes, such as $[Ni^{II}(s\text{-}disn)_2]$[4], $[Co^{III}(CN)(s\text{-}disn)_2]$[1] **2**, and $[Co^{I}(s\text{-}disn)_2]^{\ominus}$ **3**. In order to account for all these structural features, it is proposed that, in addition to the $Co^{II}-Co^{II}$ σ-bond, a δ-type bond[5] exists between the two parallel s-disn ligands. These two types of bonds are synergic. The s-disn ligand in **1** has C_{2v} symmetry. Of the five π-electrons, four are in bonding orbitals (b_1, a_2) and one is in an antibonding orbital (b_1). The facial approach of two such monomeric units leads to a splitting of all the π-orbital pairs. Splitting of the antibonding states (b_1^*) and occupation of the lower set would lead to a net stabilization and the formation of one weak δ-type bond between the s-disn ligands. The proposed bonding scheme removes much of the antibonding character from the π* state and results in a more localized double bond arrangement of the s-disn ligands in this complex.

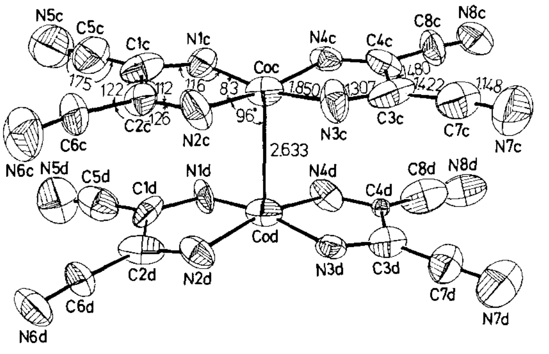


Fig. 1. ORTEP drawing of the crystal structure of **1**. $P\bar{1}$, $a=13.328(4)$, $b=27.999(26)$, $c=9.488(13)$ Å, $\alpha=85.91(10)$, $\beta=98.66(8)$, $\gamma=90.16(6)°$. $Z=4$. 3527 reflections with $F>3\sigma(F)$, 833 parameters, $R=0.082$, $R_w=0.077$. The crystals easily crack and have poor quality. The bond distances and angles are the average values of 16 chemically equivalent bond parameters. Estimated standard deviations; 0.02—0.04 Å and 1—2°, respectively [8].

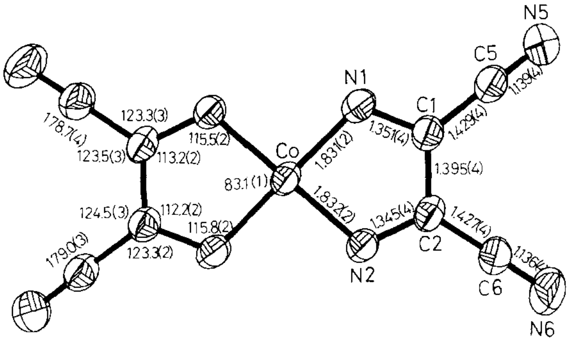


Fig. 2. ORTEP drawing of the anion **3** with 50 percent probability. $C2/c$, $a=22.731(4)$, $b=11.384(2)$, $c=11.549(3)$ Å, $\beta=93.23(2)°$. $Z=4$. 3188 reflections with $I>2\sigma(I)$, 193 parameters, $R=0.039$, $R_w=0.046$.

The reduction of **1** by hydrazine gives the monomeric complex anion $[Co^{I}(s\text{-}disn)_2]^{\ominus}$ **3**, which can be precipitated with the large cation $AsPh_4^{\oplus}$. Suitable single crystals can be grown from the salt $\mathbf{3}\cdot AsPh_4$. The structure of **3** is shown in Figure 2. The reduction of **1** results in a rupture of the Co–Co bond with formation of the square planar $[Co^{I}(s\text{-}disn)_2]^{\ominus}$ ion. The Co–N bond length, (1.831(2) Å) is short and comparable with that in $[Co^{I}(C_{10}H_{17}N_8)(CO)_6]$ (1.873 Å)[6] and with the M–N distances in complexes with delocalized ground states[1,4,7]. The C–C and C–N distances of the five-membered chelate rings in **3**, $[Co(CN)(s\text{-}disn)_2]$[1], $[Ni(s\text{-}disn)_2]$[4], and $[Pt(s\text{-}disn)_2]$[7] reveal the pronounced electron delocalization in the s-disn ligands of these complexes.

The anion **3** can be converted with CH_3I into the methylcobalt complex **4**, which can also be obtained directly from the dimer **1** by reaction with CH_3NHNH_2/O_2.

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[8] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD 51151, the authors names, and full citation of the journal.

E→*Z*-Photoisomerization of a Diphosphene on Carbonylmetal Complexes (M = Cr, Mo, W)**

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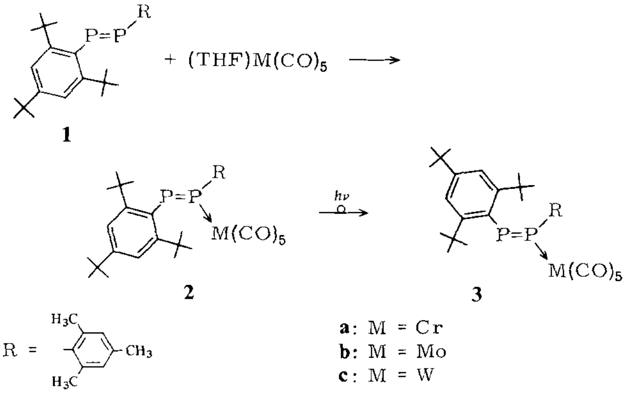
Recently, diphosphene-transition metal chemistry has developed very rapidly and extensively. We have been successful in the preparation and characterization of carbonylchromium(0), carbonylmolybdenum(0), and carbonyltungsten(0) complexes **2a**—**c** of *E*-mesityl-2,4,6-tri-*tert*-butylphenyldiphosphene **1** (THF = tetrahydrofuran). Transition-metal complexes involving formal P—P double bonds in the (*Z*)-configuration have been reported only very recently[1]. We now wish to report the first photoisomerization of (*E*)-diphosphenes on the pentacarbonylmetal complexes **2**.



a: M = Cr
b: M = Mo
c: M = W

In a typical experiment, **2a** (13.7 mg, 0.022 mmol) was dissolved in hexane (5.0 mL) and irradiated with a 100-W medium pressure Hg-lamp at 0°C for 15 min to give the (*Z*) isomer **3a** almost quantitatively. **3a** was purified by chromatography on silica gel at room temperature and recrystallization from pentane[2]. Similarly, upon irradiation, the molybdenum complex **2b** and the tungsten complex **2c** gave **3b** and **3c**, respectively. According to the ^{31}P-NMR spectra, the reaction rate decreases in the series Cr ≫ Mo > W. The FD-MS results were the same before and after irradiation[2].

Neither **2a** nor **1**, R = 2,4,6-tri-*tert*-butylphenyl[3] instead of mesityl, was isomerized on refluxing in CDCl$_3$ for several hours, whereas an *E/Z* equilibrium mixture has been formed upon laser irradiation of **1** at low temperature[4].

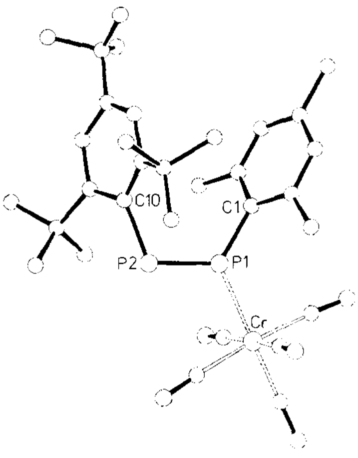


Fig. 1. Structure of **3a** in the crystal. $P2_1/c$, $a = 18.234(1)$, $b = 9.760(1)$, $c = 20.971(1)$ Å, $\beta = 114.72(1)°$, $Z = 4$. Mo$_{K\alpha}$-radiation, $\lambda = 0.7107$ Å, $R = 0.072$ for 2709 reflections with $I > 3\sigma(I)$. Important bond distances and bond angles, and the dihedral angle: P1—P2 2.039(3), P1—Cr 2.354(2) Å; Cr—P1—P2 116.3(1), Cr—P1—C1 124.9(3), P2—P1—C1 118.7(3), P1—P2—C10 109.6(3)°; *C1—P1—P2—C10 12.1(5)°. Further details of the crystal structure investigation can be obtained from the* Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2 (FRG), by quoting the depository number CSD 51177, the names of the authors, and the journal citation.

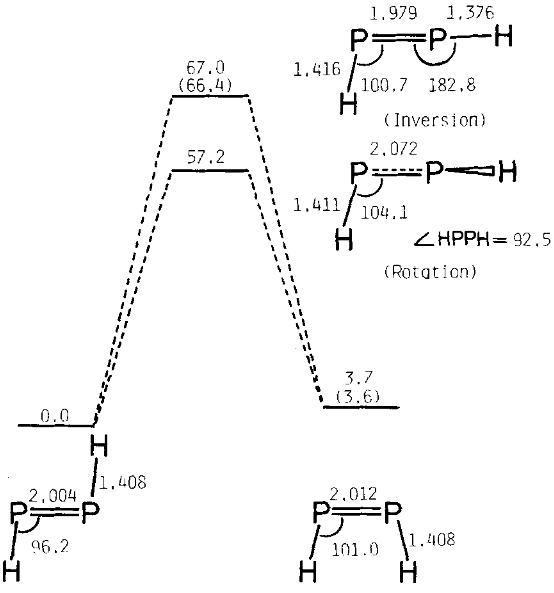


Fig. 2. Energies (kcal/mol) and geometries (Å, degrees) for the isomerization of HP=PH at the MP3/6-31G**//6-31G** level and the CI(S+D+Q)/6-31G**//6-31G** level (in parentheses). The rotational transition state is located by the use of complex molecular orbitals. See also the calculations of geometries optimized at the 3-21G level; T.-K. Ha, M. T. Nguyen, P. Ruelle, *Chem. Phys. 87* (1984) 23.

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