DOI: 10.1002/anie.201105055

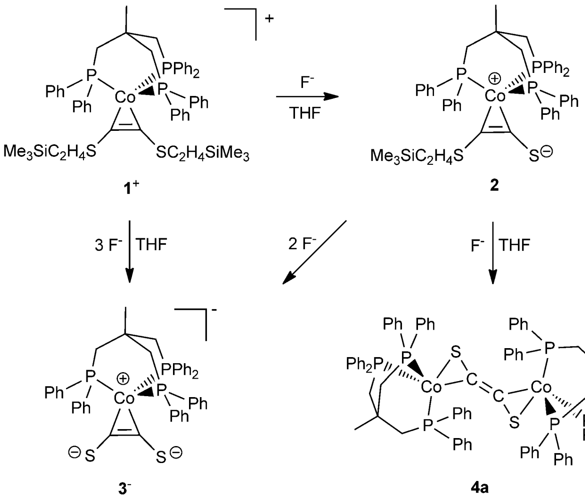
Ethenedithione (S=C=C=S): Trapping and Isomerization in a Cobalt Complex[**]

Wolfram W. Seidel, Matthias J. Meel, Stephen R. Hughes, Florian Hupka, and Alexander Villinger*

Dedicated to Professor Gerhard Erker on the occasion of his 65th birthday

Heterocumulenes composed of carbon and terminal chalcogen atoms are moderately stable if the number of carbon atoms is uneven. C_3O_2 ($K_\mathrm{p} = 7\,^\circ\mathrm{C}$, accessible by dehydration of malonic acid[1]) and C_3S_2 ($F_\mathrm{p} = -0.5\,^\circ\mathrm{C}$, obtained by discharge in the presence of CS_2[2]) can be isolated and handled at low temperature. In contrast, C_2O_2 and C_2S_2 are very elusive, which can be simply attributed to the triplet ground state of this species and the corresponding high reactivity.[3] Generally, carbon suboxides are a prominent research topic owing to the relationship with graphene oxide and CO_2-free combustion of hydrocarbons.[4] The sulfur congeners are intriguing because of the relation to the CS polymer.[5] Presumable structural patterns in $(CS)_n$ have been disclosed by the investigation of molecular compounds with slightly differing composition, such as C_6S_8 and C_8S_9.[6] Furthermore, ethenedithione (C_2S_2), has attracted much interest regarding its electronic ground state and the respective singlet–triplet gap.[3,7] Until now, C_2S_2, generated by flash vacuum pyrolysis, has been either detected by neutralization reionization mass spectrometry[8] or isolated in an argon matrix and characterized by combination of IR and UV spectroscopy and ab initio calculations.[7,9] While small elusive sulfur species, such as SO,[10] NS,[10d,11] PS,[12] or S_2^-,[13] could be stabilized by coordination, and CS complexes are well-established,[5,14] C_2S_2 complexes are unknown to date. In the course of our work on acetylenedithiolate (acdt^{2-}) complexes,[15] we were now able to generate ethenedithione in a dinuclear cobalt complex that is stable at ambient temperature. Interestingly, even coordinated ethenedithione reveals an inclination to isomerization.

The generation of C_2S_2 building blocks in complexes can be favorably achieved by use of appropriate alkyne complexes of acetylenedisulfides and subsequent removal of the respective S-protecting groups.[15] Accordingly, the cobalt(I) alkyne complex $[(\text{triphos})\text{Co}\{\eta^2\text{-}C_2(SC_2H_4SiMe_3)_2\}](PF_6)$ (**1**, triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane; Scheme 1) reacts quickly with an equimolar amount of $[Bu_4N]F$ in THF even at −40 °C to yield the neutral complex $[(\text{triphos})\text{Co}\{\eta^2\text{-}C_2(S)(SC_2H_4SiMe_3)\}]$ (**2**) that bears one terminal sulfur atom. In contrast, the removal of the second trimethylsilylethyl group turned out to be much slower and it was sensitive to the quantity of fluoride salt applied. Reaction of complex **2** with two equivalents of $[Bu_4N]F$ in THF led to the acetylenedithiolate complex $(Bu_4N)[(\text{triphos})\text{Co}(\eta^2\text{-}C_2S_2)]$ (Bu_4N-**3**).[15d] Surprisingly, by using only one equivalent instead, a dinuclear complex of the composition $[Co_2(\text{triphos})_2C_2S_2]$ (**4a**) is formed according to mass spectrometry. The compound crystallized from the reaction mixture in yields of up to 43%. A single-crystal X-ray study on **4a** revealed an unprecedented coordination mode of the C_2S_2 bridging moiety (Figure 1). The C_2S_2 ligand adopts a transoid constitution and coordinates in a η^2-*C,S* fashion to both cobalt centers. The bond lengths of the central C1−C2 bonds for the two independent molecules in the crystal amount to 1.318(5) and 1.316(5) Å, in close agreement with a classical double bond. Accordingly, the stretching frequency of the central C−C bond is detected at 1571 cm^{-1} in the Raman spectrum. Furthermore, the cobalt carbon and cobalt sulfur distances



Scheme 1. Formation of **4a** in line with acdt complex generation.

---

[*] W. W. Seidel, A. Villinger
Universität Rostock, Institut für Chemie
Albert-Einstein-Strasse 3a, 18059 Rostock (Germany)
E-mail: wolfram.seidel@uni-rostock.de
W. W. Seidel, M. J. Meel, S. R. Hughes, F. Hupka
Westfälische Wilhelms-Universität Münster
Institut für Anorganische und Analytische Chemie
Corrensstrasse 30, 48149 Münster (Germany)

[**] We are grateful to the Deutsche Forschungsgemeinschaft for generous financial support and to the Fonds of Chemical Industry (VCI) for an award (M.J.M). We thank Dr. E. Bill (MPI Mülheim) for the SQUID and EPR measurements.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201105055.

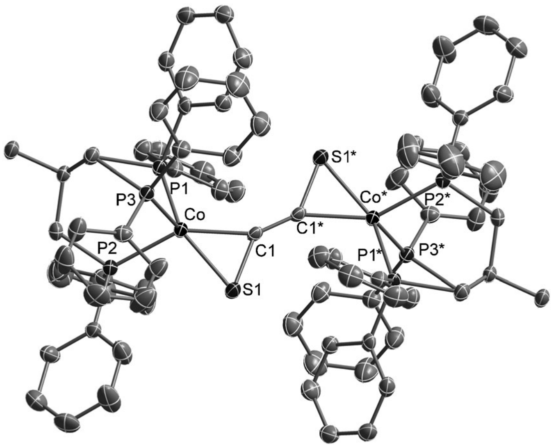


Figure 1. Molecular structure of one individual molecule of complex **4a** in crystals of **4a**·3.5 THF with thermal ellipsoids set at 40% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–C1* 1.318(5), C1–S1 1.719(2), Co1–C1 1.992(2), Co1–S1 2.185(1), Co1–P1 2.177(1), Co1–P2 2.194(1), Co1–P3 2.240(1), Co–Co* 5.172(1); C1*-C1-S1 137.4(3), C1*-C1-Co1 150.5(3).

(mean values 1.981(2) Å and 2.188(1) Å) resemble those determined for side-on CS_2 and related complexes of cobalt.[16] However, the significantly shorter Co–C(CS_2) bonds in [(triphos)Co(η^2-CS_2)] (1.88(1) Å) and in [(η^5-C_5H_5)(PMe_3)Co(η^2-CS_2)] (1.89(1) Å) reveal an even weaker cobalt carbon interaction in **4a**. Consequently, complex **4a** is best rationalized as an ethenedithione complex in which C_2S_2 is stabilized by double side-on coordination of cobalt triphos moieties. Accordingly, the oxidation state of 0 with d^9 configuration is assigned to cobalt, implying two 17-valence-electron centers in the complex. This perception is corroborated by the magnetic moment μ_{eff} of 2.29 μ_B measured at room temperature in the solid state. This value is close to the expected value of 2.45 μ_B for two coupled $S = 1/2$ centers ($g = 2$) in the complex according to $\mu_{\mathrm{eff}}/\mu_B = g\{S_1(S_1+1) + S_2(S_2+1)\}^{1/2}$.

Evidence for the generation of dinuclear species **4a** from **2** by reaction with fluoride ions was sought from ^{31}P NMR investigations. The reaction mixture contains, apart from the starting material **2** (32 ppm) and the acdt complex **3**$^-$ (−25 ppm), a third species (25 ppm) that could be assigned to H-**3** with protons coming from the water content of [Bu_4N]F. According to this premise, the formation of **4a** might be rationalized by a concerted step with elimination of HS–C≡C–$SC_2H_4SiMe_3$ from one of the [(triphos)Co] moieties. This pathway is repressed with an excess of fluoride ions either by the strong basicity of fluoride or because of the accelerated removal of the trimethylsilylethyl group at complex **2**.

Under anaerobic conditions and in the solid state, complex **4a** is stable for weeks. However, solutions of **4a** in polar solvents such as CH_2Cl_2 show a distinct color change from brown to deep red in the course of hours. Monitoring this process by UV/Vis spectroscopy reveals a kinetically well-defined conversion by the observation of an increasing maximum at 525 nm and an isosbestic point at 485 nm (Figure 2). However, MALDI mass spectrometry of the final product demonstrated an unaltered composition of [Co_2(triphos)$_2C_2S_2$]. The retention of the molecular mass of 1455 pointed to the identity of the new complex **4b** as an isomer of **4a**. Similar to **4a**, the effective magnetic moment of **4b** determined in CH_2Cl_2 solution by the Evans method amounts to 2.59 μ_B.

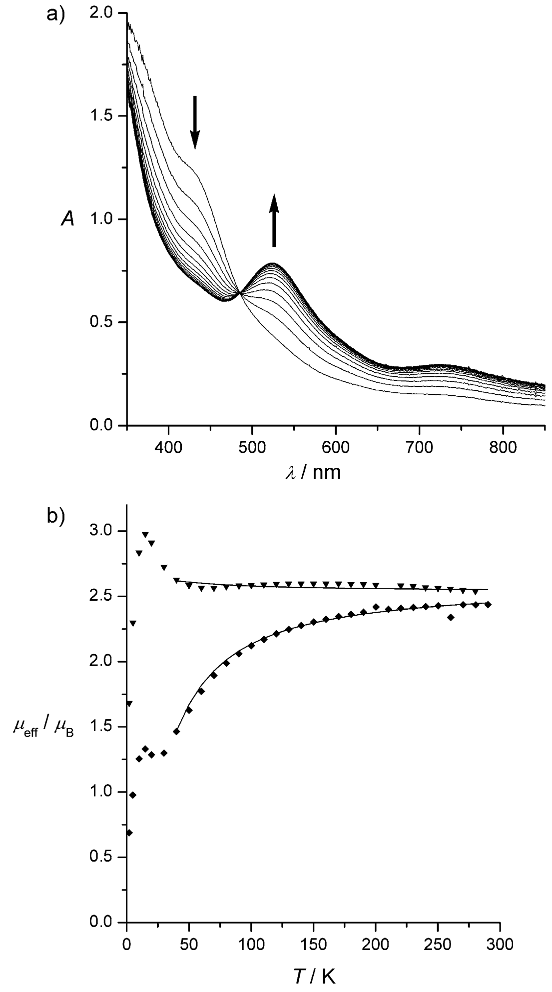


Figure 2. a) Electronic spectra monitoring the conversion of **4a** into **4b** in CH_2Cl_2. b) Temperature dependence of magnetic moments: **4a** (◆), **4b** (▼), lines: simulation using $H = -2J\mathbf{S}_1\mathbf{S}_2 + \Sigma\mu_B g_i \mathbf{S}_i \mathbf{B}_i$ with $J = -38\ \mathrm{cm}^{-1}$ and $g = 2.05$ for **4a** and $J = +10\ \mathrm{cm}^{-1}$ and $g = 2.00/2.05$ for **4b** (the behavior below 40 K has not been accounted for).

Temperature-dependent magnetic measurements using a SQUID magnetometer uncovered however an opposing behavior of **4a** and **4b** (Figure 2). The dinuclear complex **4a** shows a moderate antiferromagnetic coupling of the two spins with $J = -38\ \mathrm{cm}^{-1}$, according to expectations. In contrast and rather surprisingly, the spins are slightly ferromagnetically coupled in complex **4b** ($J = +10\ \mathrm{cm}^{-1}$), indicating again a distinct change in the bonding motive of the bridging moiety by the isomerization observed in the electronic spectra. Formation of crystals of this isomeric complex **4b** that were suitable for crystal structure analysis turned out to be cumbersome. However, the general connectivity could be unequivocally derived from the best result out of a number of X-ray diffraction studies, which is depicted in Figure 3. The C_2S_2 moiety now adopts a η^2-C,C'-κ^2-S,S'-bridging mode with a cis configuration of the sulfur donors, which has already been observed in polynuclear complexes with acdt^{2-}.[15] The five-membered dithiolene-like chelate ring is largely planar and coplanar with the CoC_2 ring (deviation 1.1°). The Co–C and the C1–C2 bond lengths within the alkyne complex unit (Co–C1 1.781(6), Co–C2 1.773(6), C1–C2 1.353(8) Å) are similar with those in related acdt complexes within the margin of error. However, the Co–S1 and Co–S2 distances (2.328(2), 2.315(2) Å) are markedly longer than those of related cobalt dithiolene complexes, such as $[(\text{triphos})\text{Co}(S_2C_6H_4)]^{n+}$ (2.216, 2.225 Å for $n = 0$ and 2.164, 2.174 Å for $n = 1$).[17]

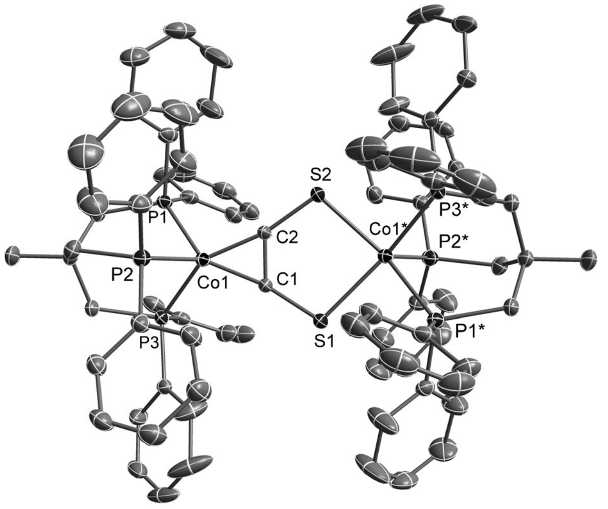


Figure 3. Molecular structure of complex **4b** in crystals of **4b**·2 CH_2Cl_2 with thermal ellipsoids set at 40% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–C2 1.353(8), Co1–C1 1.781(6), Co1–C2 1.773(6), C1–S1 1.687(6), C2–S2 1.683(6), Co1*–S1 2.328(2), Co1*–S2 2.315(2), Co–P1 2.181(1), Co–P2 2.196(1), Co–P3 2.187(1), Co–Co* 4.729(1); C1-C2-S2 123.8(5), C2-C1-S1 122.9(5), S1-Co1*-S2 87.3(1).

The formation of dipolar **4b** from centrosymmetric **4a** is apparently solvent-dependent and probably driven by the higher stability of a five-membered chelate ring in **4b**, compared with the exclusive η^2 side-on bonding in **4a**. The conversion must include some kind of flipping over of one carbon and one sulfur atom within the pocket formed by the two {Co(triphos)} units. Curiously, complex **4b** does not form by a rational synthesis of K-**3** with [Co(triphos)Br] in THF, which was shown by UV/Vis spectroscopic monitoring. Furthermore, the reverse reaction of **4b** to **4a** cannot be observed owing to the low solubility of both **4a** and **4b** in THF.

The inclination of CS building blocks to redox-dependent coordination isomerism has recently been demonstrated for the system tetrathiooxalate/ethylentetrathiolate.[18] The different magnetic behavior of both isomers raises the question of whether the constitutional isomerism is involved together with valence isomerism. With respect to the magnetic behavior, two alternative formulations for **4b** are conceivable. First, both cobalt centers can be considered to have an oxidation state of zero, with the presence of a neutral C_2S_2 as in **4a**. In contrast, if the bridging moiety is regarded as dianionic (acdt^{2-}), a sulfur-coordinated low-spin Co^{II} center ($S = \frac{1}{2}$)[17] is coupled with a carbon-bound Co^0 center ($S = \frac{1}{2}$).

Unfortunately, EPR measurements revealed both **4a** and **4b** to be virtually EPR silent down to a temperature of 30 K. This observation can be rationalized by an effectual zero-field splitting of an $S = 1$ state by dipolar interaction of the spins. Furthermore, anisotropic exchange coupling might contribute to the zero-field splitting. DFT calculations at the UB3LYP/6-311G(d) level of theory support a comparable charge distribution in **4a** and **4b**. A natural population analysis with **4b** disclosed a rather balanced population of the 3d 4s 4p valence orbitals at both cobalt atoms (10.15 for Co–S and 10.02 for Co–C). The NPA analysis of **4a** also showed an even smaller population value for the corresponding orbitals in isomer **4a** (9.91). The calculated spin density of the triplet species is predominantly localized at both cobalt centers, both in **4a** and in **4b**. A (4,4)-CAS calculation using the reduced model complex $[\{Co[CH(CH_2PH_2)_3]\}_2(\mu\text{-}C_2S_2)]$ confirmed this result (see the Supporting Information for details). Interestingly, the residual spin density in the bridging ligand is localized in **4a** in the σ framework with respect to the C_2S_2 plane, whereas in **4b** it is in the π system. This result could be related to the opposite magnetic coupling of both isomers. Accordingly, the singlet-state broken-symmetry solution[19] of **4a** is more stable than the triplet state, whereas the opposite holds true for **4b**.

In conclusion, we have shown for the first time that ethenedithione can be stabilized at ambient temperature by coordination. In complex **4a**, the C_2S_2 ligand has a μ-η^2-C,S-η^2-C',S' binding mode linking two cobalt centers. Furthermore, the high reactivity of ethenedithione even in the complex is evident, as **4a** converts in polar solvents into complex **4b** by an unusual isomerization. In complex **4b**, the C_2S_2 ligand adopts a cis configuration, leading to a μ-η^2-C,C'-κ^2-S,S' bridging mode. Further investigations are directed to the generation of bis(thiocarbonyl) complexes starting from related ethenedithione complex species.

Received: July 19, 2011
Published online: November 30, 2011

Keywords: bridging ligands · cobalt · coordination modes · s ligands · through-bond interactions

---

[1] a) O. Diels, G. Meyerheim, *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 355–363; b) H. Staudinger, S. Bereza, *Ber. Dtsch. Chem. Ges.* **1908**, *41*, 4461–4465; c) E. Ott, K. Schmidt, *Ber. Dtsch. Chem. Ges. B* **1922**, *55*, 2126–2130; d) H. Hopff, G. Hegar, *Helv. Chim. Acta* **1961**, *44*, 2016–2021.

[2] a) B. von Lengyel, *Ber. Dtsch. Chem. Ges.* **1893**, *26*, 2960–2968.

[3] a) N. L. Ma, M. W. Wong, *Angew. Chem.* **1998**, *110*, 3587–3589; *Angew. Chem. Int. Ed.* **1998**, *37*, 3402–3404; b) D. Talbi, G. S. Chandler, *J. Phys. Chem. A* **2000**, *104*, 5872–5881; c) C. Trindle, *Int. J. Quantum Chem.* **2003**, *93*, 286–293.

[4] a) A. Fridman, A. Gutsol, A. Dolgopolsky, E. Shtessel, *Energy Fuels* **2006**, *20*, 1242 – 1249; b) D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff, *Chem. Soc. Rev.* **2010**, *39*, 228 – 240.

[5] E. K. Moltzen, K. J. Klabunde, A. Senning, *Chem. Rev.* **1988**, *88*, 391 – 406.

[6] a) D. D. Doxsee, C. P. Galloway, T. B. Rauchfuss, S. R. Wilson, X. Yang, *Inorg. Chem.* **1993**, *32*, 5467 – 5471; b) J. Beck, J. Weber, A. B. Mukhopadhyay, M. Dolg, *New J. Chem.* **2005**, *29*, 465 – 473; c) J. Beck, J. Daniels, A. Roloff, N. Wagner, *Dalton Trans.* **2006**, 1174 – 1180.

[7] G. Maier, H. P. Reisenauer, J. Schrot, R. Janoschek, *Angew. Chem.* **1990**, *102*, 1475 – 1477; *Angew. Chem. Int. Ed.* **1990**, *29*, 1464 – 1466.

[8] a) D. Sülzle, H. Schwarz, *Angew. Chem.* **1988**, *100*, 1384 – 1386; *Angew. Chem. Int. Ed.* **1988**, *27*, 1337 – 1339; b) M. W. Wong, C. Wentrup, R. Flammang, *J. Phys. Chem.* **1995**, *99*, 16849 – 16856.

[9] a) C. Wentrup, P. Kambouris, R. A. Evans, D. Owen, G. Macfarlane, J. Chuche, J. C. Pommelet, A. B. Cheikh, M. Plisnier, R. Flammang, *J. Am. Chem. Soc.* **1991**, *113*, 3130 – 3135; b) R. B. Bohn, Y. Hannachi, L. Andrews, *J. Am. Chem. Soc.* **1992**, *114*, 6452 – 6459.

[10] early examples: a) L. Markó, B. Markó-Monostory, T. Madach, H. Vahrenkamp, *Angew. Chem.* **1980**, *92*, 225 – 226; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 226 – 227; b) W. A. Schenk, J. Leißner, C. Burschka, *Angew. Chem.* **1984**, *96*, 787 – 788; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 806 – 807; c) I.-P. Lorenz, J. Messelhäuser, W. Hiller, K. Haug, *Angew. Chem.* **1985**, *97*, 234 – 235; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 228 – 229; d) K. K. Pandey, *Prog. Inorg. Chem.* **1992**, *40*, 445 – 502.

[11] a) T. Chivers, F. Edelmann, *Polyhedron* **1986**, *5*, 1661 – 1699; b) M. Herberhold, *Comments Inorg. Chem.* **1988**, *7*, 53 – 72; c) K. Dehnicke, *Z. Anorg. Allg. Chem.* **2003**, *629*, 729 – 743.

[12] C. E. Laplaza, W. M. Davis, C. C. Cummins, *Angew. Chem.* **1995**, *107*, 2181 – 2183; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2042 – 2044.

[13] J. T. York, E. C. Brown, W. B. Tolman, *Angew. Chem.* **2005**, *117*, 7923 – 7926; *Angew. Chem. Int. Ed.* **2005**, *44*, 7745 – 7748.

[14] a) P. V. Broadhurst, *Polyhedron* **1985**, *4*, 1801 – 1846; b) W. Petz, *Coord. Chem. Rev.* **2008**, *252*, 1689 – 1733; for poly(thiocarbonyl)complexes, see: c) L. W. Yarbrough, G. V. Calder, J. G. Verkade, *J. Chem. Soc. Chem. Commun.* **1972**, 705 – 706; d) A. E. Fenster, I. S. Butler, *Inorg. Chem.* **1974**, *13*, 915 – 920; e) A. F. Hill, J. D. E. T. Wilton-Ely, *Organometallics* **1996**, *15*, 3791 – 3797.

[15] a) W. W. Seidel, M. Schaffrath, T. Pape, *Angew. Chem.* **2005**, *117*, 7976 – 7979; *Angew. Chem. Int. Ed.* **2005**, *44*, 7798 – 7800; b) W. W. Seidel, M. Schaffrath, T. Pape, *Chem. Commun.* **2006**, 3999 – 4000; c) W. W. Seidel, M. J. Meel, U. Radius, M. Schaffrath, T. Pape, *Inorg. Chem.* **2007**, *46*, 9616 – 9629; d) W. W. Seidel, M. J. Meel, F. Hupka, J. J. Weigand, *Dalton Trans.* **2010**, *39*, 624 – 631.

[16] a) H. Werner, K. Leonhard, C. Burschka, *J. Organomet. Chem.* **1978**, *160*, 291 – 298; b) C. Bianchini, C. Mealli, A. Meli, A. Orlandini, L. Sacconi, *Angew. Chem.* **1979**, *91*, 739 – 740; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 673 – 674; c) C. Bianchini, C. Mealli, A. Meli, A. Orlandini, L. Sacconi, *Inorg. Chem.* **1980**, *19*, 2968 – 2975; d) H. Werner, O. Kolb, U. Schubert, K. Ackermann, *Chem. Ber.* **1985**, *118*, 873 – 879; e) R. Drews, F. Edelmann, U. Behrens, *J. Organomet. Chem.* **1986**, *315*, 369 – 382.

[17] a) S. Vogel, G. Huttner, L. Zsolnai, *Z. Naturforsch. B* **1993**, *48*, 641 – 652; b) V. Körner, A. Assam, G. Huttner, L. Zsolnai, M. Büchner, *Z. Naturforsch. B* **1994**, *49*, 1183 – 1192; c) C. A. Ghilardi, F. Laschi, S. Midollini, A. Orlandini, G. Scapacci, P. Zanello, *J. Chem. Soc. Dalton Trans.* **1995**, 531 – 540.

[18] O. P. Lam, F. W. Heinemann, K. Meyer, *Angew. Chem.* **2011**, *123*, 6088 – 6091; *Angew. Chem. Int. Ed.* **2011**, *50*, 5965 – 5968.

[19] An explicit determination of the exchange coupling would require a more rigorous treatment according to F. Neese, *J. Phys. Chem. Solids* **2004**, *65*, 781 – 785.