Available online at www.sciencedirect.com
ScienceDirect
Biochimica et Biophysica Acta 1767 (2007) 666 – 670
Biochimica et Biophysica Acta
BBA
www.elsevier.com/locate/bbabio

Synthesis and electrochemistry of Co(III) and Co(I) complexes having C_5Me_5 auxiliary

Takayuki Nagasawa *, Toshi Nagata

Research Center for Molecular-scale Nanoscience, Institute for Molecular Science, Myodaiji, Okazaki 444-8787, Japan

Received 23 October 2006; received in revised form 12 December 2006; accepted 13 December 2006
Available online 23 December 2006

Abstract

The synthesis and electrochemistry of half-sandwich type of Co(III) complexes $[(C_5Me_5)Co(bidentate)(CH_3CN)](BF_4)_2$ {bidentate = dppe (1, 2-bis(diphenylphosphino)ethane), dppp (1,3-bis(diphenylphosphino)propane), bpy (2,2′-bipyridine), en (ethylenediamine)) are reported. Cyclic voltammograms of $[(C_5Me_5)Co(bidentate)(CH_3CN)](BF_4)_2$ in CH_3CN s showed two redox couples assignable to Co(II)/Co(III) and Co(I)/Co(II). The Co(I) complex having C_5Me_5 and dppe was also prepared. Two redox couples of this Co(I) complex, $(C_5Me_5)Co(dppe)$, in CH_3CN coincided with those of $[(C_5Me_5)Co(dppe)(CH_3CN)](BF_4)_2$ in spite of the structural change around the metal center.

Keywords: Cobalt; Pentamethylcyclopentadienyl; Bidentate ligand; Cyclic voltammograms

1. Introduction

The use of fossil fuel as major energy source has risen up the amount of carbon dioxide in the atmosphere and brought several environmental problems like greenhouse effect or global warming. One possible solution is to use hydrogen as an energy source, which affords only water as its waste. Although hydrogen is at present mainly produced from hydrocarbons, it needs to be produced from water by use of natural energy for true environmental cleanness. In this context, photochemical splitting of water to hydrogen and oxygen has widely been studied [1]. On the other hand, natural photosynthesis produce oxygen and highly reducing NADPH by use of low-energy visible light with an elaborate set of molecular machinery. By mimicking photosynthesis at molecular level, we would get useful knowledge for artificial use of solar energy.

To achieve water splitting based on photosynthetic models, it is important to find suitable catalysts for reduction of H^+. There is a large amount of examples of Pt catalyst for the H_2 production [2] but Pt is a rare metal and resource is limited, so that it is desirable to find catalysts based on cheaper elements like first-row transition metals. One of the candidates is Co; the strong basicity of low-valent cobalt complexes [3–9] is beneficial for reduction of H^+, and indeed researches for the H_2 production utilizing Co complexes have been reported in the last two decades [10–12]. Spiro et al. examined hydrogen production from H_2O catalyzed by a Co porphyrin complex with a view toward an efficient electrocatalyst [10]. Koelle et al. described electrochemical reduction of H^+ by use of $(C_5H_5)Co(PR_3)_2$ and spectroscopic determinations of hydride complexes as intermediates in the reaction [11,12]. In the latter study, the electrochemistry of reduction of H^+ was examined, whereas no structural information of the metal core at different oxidation states was reported.

In this report, we describe synthesis of a series of Co(III) complexes $[(C_5Me_5)Co(bidentate)(CH_3CN)](BF_4)_2$ and demonstrate a reversible interconversion between Co(III) and Co(I) in CH_3CN solution by using cyclic voltammetry and X-ray crystallography. The structures of both oxidation states were elucidated and compared.

2. Materials and methods

2.1. General

All reactions and the manipulations of air-sensitive compounds were performed under an inert atmosphere using standard Schlenk and glovebox techniques. Solvents were dried, degassed, and distilled from sodium/

---

* Corresponding author. Tel.: +81 564 59 5534; fax: +81 564 59 5531.
E-mail address: tnaga@ims.ac.jp (T. Nagasawa).

0005-2728/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.bbabio.2006.12.005

Table 1
Summary of Crystallographic data for $[(C_5Me_5)Co(dppe)(CH_3CN)](BF_4)_2$ (**2**), $[(C_5Me_5)Co$ $(dppp)](BF_4)_2$ (**3**), $[(C_5Me_5)Co(bpy)(CH_3CN)](BF_4)_2$ (**4**), $[(C_5Me_5)Co$ $(en)(CH_3CN)](BF_4)_2$ (**5**), $[(C_5Me_5)Co(dppe)$ (**6**)

	(**2**)	(**3**)	(**4**)	(**5**)	(**6**)
Formula	$C_{38}H_{42}NCoP_2B_2F_8$	$C_{41}H_{47}N_2CoP_2B_2F_8$	$C_{24}H_{29}N_4Co\ B_2F_8$	$C_{14}H_{26}N_3\ CoB_2F_8$	$C_{36}H_{39}CoP_2$
Formula weight	807.24	862.32	606.06	468.92	592.58
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	Cc (No. 9)	$P2_1/n$ (No. 14)
a/Å	12.342 (7)	18.982 (6)	14.017 (5)	10.8800 (11)	8.349 (4)
b/Å	23.124 (12)	11.281 (3)	20.581 (6)	13.1745 (14)	18.687 (9)
c/Å	13.038 (8)	19.061 (5)	19.457 (6)	14.546 (2)	19.626 (10)
α/°					
β/°	92.953 (8)	92.999 (4)	90.846 (5)	95.450 (8)	90.488 (6)
γ/°					
V/Å^3	3716 (4)	4076 (2)	5612 (3)	2075.6 (4)	3062 (3)
Z	4	4	8	4	4
μ/cm^{-1}	6.18	5.688	6.855	9.005	6.884
No. reflections measured	29,289	31,397	43,970	7678	21,976
Unique reflections	8479	9299	12,767	4255	6625
GOF on F^2	1.000	1.002	1.134	0.843	1.000
$R1$ (I>2 (σ))[a]	0.072	0.067	0.078	0.041	0.059
w$R2$ (all data)[b]	0.212	0.234	0.187	0.111	0.219

$R\ 1=\Sigma\ ||Fo|-|Fc||/\Sigma\ |Fo|$, [b] $wR2=[\{\Sigma w\ (|Fo|-|Fc|)^2\}/\Sigma w(Fo^2)]^{1/2}$.

benzophenone ketyl (diethyl lether, THF) or from CaH_2 (CH_3CN) under argon. ^1H NMR spectra were recorded on a JEOL LAMBDA-500 (500 MHz) spectrometer, and chemical shifts were quoted in ppm relative to $SiMe_4$. All spectra were obtained at room temperature unless otherwise noted. Deuterated solvents were vacuum-transferred from CaH_2 (CD_3CN) or Na (benzene-d_6). Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer. The cyclic voltammograms were recorded on an ALS/CHI Model 660 voltammetric analyzer using glassy carbon electrode with Bu_4NClO_4 as the supporting electrolyte in CH_3CN. The potential was reported vs. $(C_5H_5)_2Fe$ (+0.55 V vs. NHE). The electrospray mass spectra were obtained on a Micromass LCT mass spectrometer. Elemental analyses were performed on a YANACO CHN CORDER MT-6. $[(C_5Me_5)Co(CO)_2]$ and $[CoCl(PPh_3)_3]$ were synthesized according to literature procedures [13–15]. The following reagents were used as received: SMe_2, C_5Me_5H, ethylenediamine (en) and 2,2′-bipyridine (bpy) (Tokyo-Kasei Co.); CH_3NO_2 (Sigma-Aldrich); 1,2-bis(diphenylphosphino) ethane (dppe) and 1,3-bis(diphenylphosphino)propane (dppp) (Kanto-Kagaku Co.).

2.2. Crystallography

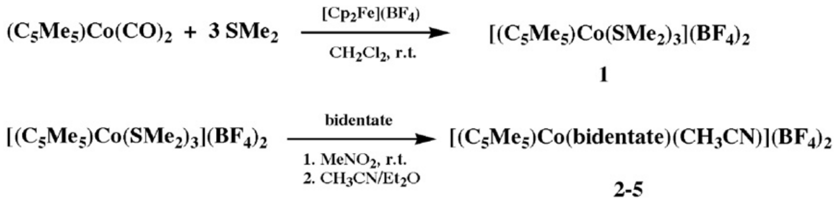
Crystal data, details of data collection, and refinement parameter for all structurally characterized complexes are summarized in Table 1. Single crystals of (**2**)–(**5**) were obtained by the slow diffusion of Et_2O to CH_3CN solutions and (**6**) was obtained from hexane. Crystals were immersed in Paraton-N oil on a nyron loop and transferred to a Mercury CCD diffractometer equipped with Rigaku GNNP low-temperature device. Diffraction data were collected −100 °C under a cold nitrogen stream using graphite monochromated MoKα radiation (λ=0.710690 Å). Equivalent reflections were merged, and the images were processed with the Crystal Clear (Rigaku) program. Corrections for Lorenz-polarization effects and absorption were performed. The structures were solved by direct method and refined on F^2 by the full-matrix least-square method using Crystal Structure (Rigaku) software package. The hydrogen atoms were put at calculated positions with C–H distances of 0.97 Å. The supplementary crystallographic data are available in CCDC-624423 (**2**), −624424 (**3**), −624425 (**4**), −624426 (**5**), −624427 (**6**).

3. Results and discussion

3.1. Synthesis of $[(C_5Me_5)Co(bidentate)(CH_3CN)](BF_4)_2$ (2)–(5)

The readily accessible pentamethylcyclopentadienyl complex $[(C_5Me_5)Co(SMe_2)_3](BF_4)_2$ (**1**) was utilized for the synthesis of a series of mononuclear Co(III) complexes. The strong coordination of a pentamethylcyclopentadienyl auxiliary ligand gives the complexes stability during redox changes and high solubility in organic solvents. It is also known that its steric bulkiness often avoids complexity arising from a cluster formation [16,17].

Synthesis of (**1**) was performed on the basis of the Kuhn's method which was described for $(C_5H_5)Co$ analogues [18]. The compound (**1**) was obtained as brown powder which could be stored in the glovebox for a prolonged period. Because of instability of (**1**) against moisture, it should be handled under anaerobic conditions for the following ligand substitution reactions.



$$(C_5Me_5)Co(CO)_2 + 3\ SMe_2 \xrightarrow[CH_2Cl_2,\ r.t.]{[Cp_2Fe](BF_4)} [(C_5Me_5)Co(SMe_2)_3](BF_4)_2$$

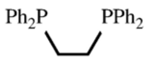
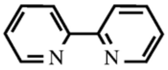
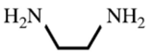
1

$$[(C_5Me_5)Co(SMe_2)_3](BF_4)_2 \xrightarrow[\substack{1.\ MeNO_2,\ r.t.\\ 2.\ CH_3CN/Et_2O}]{bidentate} [(C_5Me_5)Co(bidentate)(CH_3CN)](BF_4)_2$$

2-5

Scheme 1.

Table 2
Types of bidentates and yields of $[(C_5Me_5)Co(bidentate)(CH_3CN)](BF_4)_2$

Entry	Bidentate	Crystal color	Yield(%)
2		Orange	83
3		Orange	79
4		Red	83
5		Red	46

Addition of the bidentate ligands (dppe, dppp, bpy, en) to the CH_3NO_2 solution of (**1**) resulted in the introduction of the ligands to the $(C_5Me_5)Co(III)$ fragment. Removal of volatile SMe_2 under reduced pressure facilitated the reaction to complete. Recrystallization from CH_3CN/Et_2O gave to (**2**)–(**5**) in good yields. In analogy with Kuhn's results, we assume that two molecules of SMe_2 on (**1**) would be substituted by the bidentate ligand, and then the remaining SMe_2 was exchanged to CH_3CN during recrystallization from CH_3CN (Scheme 1 and Table 2).

3.2. Synthesis of $[(C_5Me_5)Co(dppe)]$ (6)

Kirchner reported the synthesis of (**6**) utilizing photoirradiation of $(C_5Me_5)Co(CO)_2$ in the presence of dppe [19]. However, we had difficulty in repeating this synthesis. Therefore, we decided to use $ClCo(PPh_3)_3$ as a starting material. Although Song et al. reported introduction of cyclopentadienyl derivatives (C_5H_4-R; R = CO_2Et, COMe) to obtain $(C_5H_4\text{-}R)Co(PPh_3)_2$ by reactions of $ClCo(PPh_3)_3$ and NaC_5H_4R in benzene/THF, synthesis of C_5Me_5 analogue in this method was not described [20]. Thus, at first, we tried to isolate $(C_5Me_5)Co(PPh_3)_2$ by the reaction of $ClCo(PPh_3)_3$ with $Li(C_5Me_5)$, but the obtained material from this reaction was a dimer compound and no $(C_5Me_5)Co(PPh_3)_2$ was isolated. The property and structure of this resulting dimer compound will be reported elsewhere. With this result, as the second trial, we chose to introduce dppe to the starting material. A reaction of PPh_3, dppe and $CoCl_2.6H_2O$ (1:1:1) followed by treatment with $NaBH_4$ gave a green powder, which is expected to contain $ClCo(PPh_3)$(dppe). The reaction of this green powder with $Li(C_5Me_5)$ resulted in a formation of red crystals of (**6**) in 21% yield (Scheme 2).

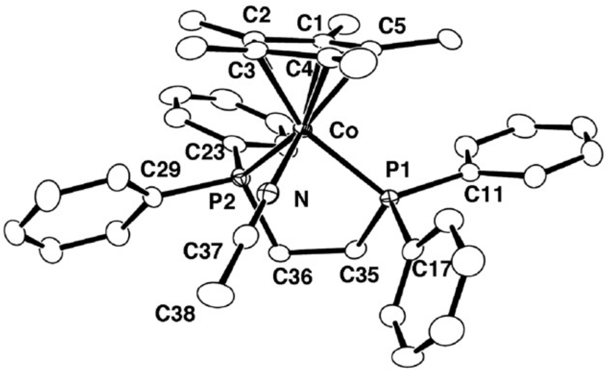


Fig. 1. Structure of the cationic part of (**2**).

3.3. Structures

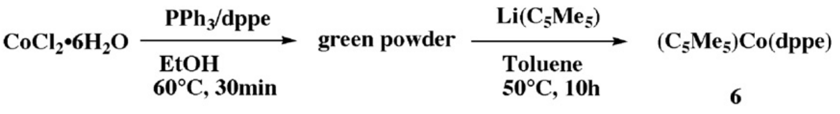
X-ray crystallographic analysis was performed for (2)–(5) and (6). The molecular structure of the cation part of (**2**) is shown in Fig. 1, and the structure of (**6**) is given in Fig. 2. Table 3 lists the selected bond distances and bond angles for (**2**) and (**6**). The divalent cationic part of (**2**) adopts a typical octahedral arrangement at Co with one C_5Me_5 ring, two phosphines and one CH_3CN. Compound (**6**) possesses a distorted trigonal bipyramidal coordination geometry, where C(2) and P(2) occupy the axial positions with C(2)–Co–P(2) angle 171.8° and P(1) and centers of C(3)–C(4) and C(1)–C(5) make up the triangle base. The P–Co–P angles in (**2**) and (**6**) do not differ much (87.67° for compound (**2**) and 87.30° for compound (**6**)), while the average length of Co–P bond is different. Despite the highly cationic property of (**2**), the average bond length of (**2**) (2.264 Å) is longer than that of (**6**) (2.109 Å) and it is suggested that a dπ–pπ interaction between electron-rich Co(I) center and aryl-phosphine ligand. Further, lower coordination numbers give shorter bond length in general.

The different coordination numbers of these complexes can be attributed to the 18 electron rule. The Co(III) complex (**2**) is 18-electron, whereas the Co(I) complex (**6**) has two more electrons but one less ligand (CH_3CN), resulting in the same 18-electron.

3.4. Voltammetry

Cyclic voltammograms were measured for compounds (**2**)–(**5**) and the half-wave potentials are listed in Table 4.

Each complex exhibits two one-electron reductions that are chemically reversible in CH_3CN solutions. The first reductions appearing from −0.56 to −0.98 V (vs. Cp_2Fe/Cp_2Fe^+) are assignable to Co(III)/Co(II) process and the second reductions, being over −1.13 V, are assignable to Co(II)/Co(I) process. No decrease of peak currents for each redox wave was observed



Scheme 2.

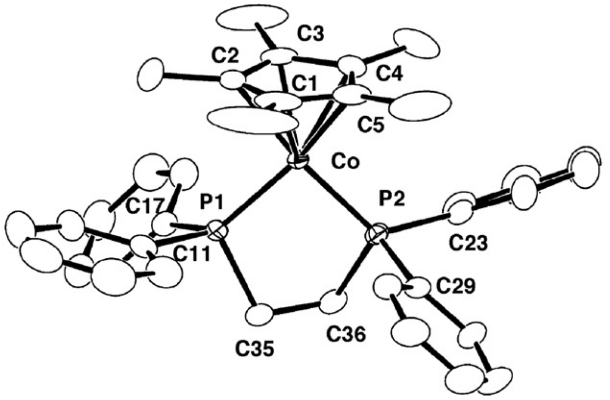
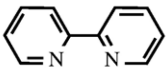
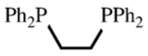


Fig. 2. Molecular structure of (**6**).

Table 3
Selected bond distances (Å) and angles (°) for [(C_5Me_5)Co(dppe)(CH_3CN)](BF_4)$_2$ (**2**) and (C_5Me_5)Co(dppe) (**6**)

[(C_5Me_5)Co(dppe)(CH_3CN))(BF_4)$_2$ (**2**)			
Bond length			
Co–P1	2.2733 (10)	P1–C11	1.824 (3)
Co–P2	2.2550 (10)	P1–C35	1.838 (3)
Co–N	1.913 (3)	P2–C23	1.828 (3)
Co–C1	2.071 (3)	P2–C36	1.835 (3)
Co–C2	2.120 (3)	C35–C36	1.526 (5)
Co–C3	2.127 (3)	C37–N	1.146 (4)
Co–C4	2.119 (3)	C37–C38	1.454 (5)
Co–C5	2.129 (3)		
Angles			
P1–Co–P2	87.69 (3)	C11–P1–C17	106.52 (16)
P1–Co–N	88.09 (9)	C23–P2–C29	103.33 (17)
P2–Co–N	88.34 (1)	P1–C35–C36	112.0 (2)
C1–Co–C5	39.88 (14)	P2–C36–C35	111.8 (2)
Co–N–C37	175.8 (3)	N–C37–C38	177.6 (4)
(C_5Me_5)Co(dppe) (**6**)			
Bond length			
Co–P1	2.1093 (7)	Co–C4	2.090 (3)
Co–P2	2.1077 (7)	Co–C5	2.072 (3)
Co–C1	2.094 (3)	P1–C35	1.858 (3)
Co–C2	2.072 (3)	C35–C36	1.530 (4)
Co–C3	2.112 (3)		
Angles			
P1–Co–P2	87.30 (3)	C11–P1–C17	102.2 (1)
C1–Co–C2	39.8 (2)	P1–C35–C36	105.3 (2)

Table 4
Cyclic voltammetric data of the compounds (**2**)–(**6**)

Entry	Bidentate	$E_{1/2}$(V vs. Cp_2Fe/Cp_2Fe^+)	
		Co(III)/Co(II)	Co(II)/Co(I)
2		−0.61	−1.13
3		−0.56	−1.26
4		−0.82	−1.15
5		−0.98	−2.25
6		−0.57	−1.12

Conditions:4.00 × 10^{-3} M in CH_3CN, 0.10 M $^nBU_4NClO_4$, highly polished glassy carbon working electrode (scan rate 0.100 Vs^{-1}).

during multiple sweeps. Interestingly, half-wave potentials for Co(II)/Co(I) process of (**5**) was much lower than those for (**2**)–(**4**). Such difference is reasonable, because dppe, dppp and bpy can relax the high electron density on the Co(I) center by accepting d electron to the π* orbitals in the process of Co(II)/Co(I) whereas ethylenediamine (en) cannot accept electron because it does not have π* orbitals. A cyclic voltammogram of the Co(I) complex (**6**) was also measured in CH_3CN solution and two chemically reversible one-electron oxidations were observed. The half-wave potentials were very close to those of (**2**) though the sweeping directions were opposite. These results suggest that, in these complexes, the two-electron redox process is accompanied by a reversible change between five-coordinated and six-coordinated structures, which comes from release and coordination of a CH_3CN molecule. During this process the structural motif "(C_5Me_5)Co(dppe)" is retained intact. Such durability against a variation of oxidation states will be essential to a catalytic activity involving electron donation to a substrate, such as reduction of H^+ to H_2.

As further investigation of this functionality, a cyclic voltammogram of (**2**) was measured in the presence of p-toluenesulfonic acid. Fig. 3 shows the cyclic voltammogram of (**2**) before (solid line) and after (dotted line) an addition of the acid. After the addition of acid, the oxidation wave from Co(I)

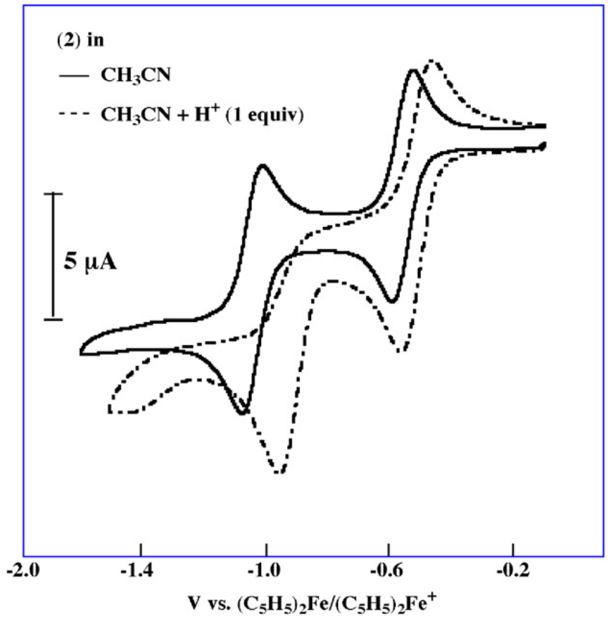


Fig. 3. Cyclic voltammograms of (**2**).

to Co(II) disappeared and while the oxidation wave from Co(II) to Co(III) remained unchanged. The reduction wave from Co(II) to Co(I) showed a positive shift, which suggests that the Co(I) species reacted with H^+ to give a Co–H complex [21]. This Co–H species was then converted to Co(II) with concurrent formation of H_2. There are two possible mechanisms for this step; one is that two molecules of the Co–H complex produce two Co(II) molecules and one molecule of H_2, and the other is that the Co–H species abstracts a hydrogen atom (H·) from the surrounding medium (the solvent or the supporting electrolyte). We prefer the former mechanism, because in the latter case, a 19-electron, seven-coordinated Co species "(C5Me5)CoH2 (dppe)" must be present as an intermediate, which is highly unlikely. We attempted the bulk electrolysis to detect H_2, but it was not successful because of the limited stability of the Co(I) species under these conditions. Trials to characterize the intermediates and to detect H_2 are currently under way.

4. Conclusion

An efficient synthesis of $[(C_5Me_5)Co(bidentate)(CH_3CN)](BF_4)_2$ is reported. By using SMe_2 ligand in the starting material, several bidentate ligands were cleanly introduced to the $(C_5Me_5)Co$ core to form a series of six-coordinated Co(III) complexes. The Co(I) five coordinated complex having similar components (C_5Me_5 and dppe) was synthesized. These Co complexes are electrochemically interconvertible between Co (III) and Co(I) in CH_3CN solutions with structural transformation. The durability of "$(C_5Me_5)Co(dppe)$" motif should be advantageous for catalytic reduction. Further investigation of the reduction of H^+ to H_2 by using these Co complexes is now in progress.

Acknowledgements

The authors thank Professor Hiroyuki Kawaguchi and Dr. Tsukasa Matsuo (Institute for molecular Science) for assistance in X-ray crystallography, Professor Koji Tanaka (Institute for molecular Science) permission to use the ESI-MS spectrometer and Seiji Makita (Institute for molecular Science) for elemental analysis.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.bbabio.2006.12.005.

References

[1] M. Yagi, M. Kaneko, Molecular catalysis for water oxidation, Chem. Rev. 101 (2001) 21–35.

[2] D. Wohrle, A.D. Pomogailo, Y. Amao, M. Kaneko, E.A. karakhanov, Y.S. Kang, A.L. Maximov, H. Nishide, T. Ohsaka, I. Okura, R.C. Raj, J. Won, Metal Complexes and Metal in Macromolecules, Wiley-VCH GmbH and Co. KGaA, Weinheim, Germany, 2003, pp. 573–600.

[3] M.C. Rakowski, E.L. Muetteries, Low valent cobalt triisopropyl phosphite complexes. Characterization of a catalyst for the hydrogenation of α, β-Unsaturated Ketones, J. Am. Chem. Soc. 99 (1977) 739–743.

[4] S.J. Carter, L.S. Stuhl, Low-valent cyanocobaltate chemistry. 3. Reactions of $[(\eta^5{-}C_5H_5)Co(CN)(CO)]^-$ with electrophiles, nucleophiles, and redox agents, Organometallics 7 (1988) 1909–1918.

[5] H.-L. Li, W.C. Anderson, J.Q. Chambers, D.T. Hobbs, Electrocatalytic reduction of nitrate in sodium hydroxide solution in the presence of low-valent cobalt-cyclam species, Inorg. Chem. 24 (1989) 863–868.

[6] M.G. Basallote, D.L. Hughes, M. Jimenez-Tenorio, Chemistry of cobalt complexes with 1,2-Bis(dimethylphosphino)ethane: hydrides, carbon disulfide complexes, and C–H cleavage in activated Alk-1-ynes. Crystal structure of $[CoH(C{\equiv}CCO_2Et)(Et_2PCH_2CH_2PEt_2)_2][BPh_4]$, J. Chem. Soc. Dalton Trans. (1993) 1841–1847.

[7] H.-F. Klein, M. Mager, A. Schmidt, Synthesis, structure, and magnetic properties of low-valent triangulo cobalt-hydride clusters $[XCO_3(\mu\text{-}CO)_3(PMe_3)_6]$, Inorg. Chem. 36 (1997) 4303–4306.

[8] H.K. Lee, C.H. Lam, S.-L. Li, Z.-Y. Zhang, T.C.W. Mak, Low-valent chemistry of cobalt amide. Synthesis and structural characterization of Cobalt(II) amido, aryloxide, and thiolate compounds, Inorg. Chem. 40 (2001) 4691–4695.

[9] X. Hu, I. Castro-Rodriguez, K. Meyer, Dioxygen activation by a low-valent cobalt complex employing a flexible tripodal N-heterocyclic carbene ligand, J. Am. Chem. Soc. 126 (2004) 13464–13473.

[10] T.G. Spiro, R.M. Kellet, Cobalt(I) porphyrin catalysis of hydrogen production from water, Inorg. Chem. 24 (1985) 2373–2377.

[11] T.G. Spiro, R.M. Kellet, Cobalt porphyrin electrode films as H_2 evolution catalysis, Inorg. Chem. 24 (1985) 2378–2382.

[12] U. Koelle, S. Ohst, Electrochemical reduction of protonated cyclopentadienylcobalt phosphine complexes, Inorg. Chem. 25 (1986) 2689–2694.

[13] S.A. Frith, J.L. Spencer, Synthesis of dicarbonyl (η^5-Pentamethyl cyclopentadienyl Cobalt(I) complex, Inorg. Synth. 23 (1985) 15–16.

[14] R.B. King, A. Efraty, Pentamethylcyclopentadienyl derivatives of trandition metals. II. Synthesis of pentamethylcyclopentadienyl metal carbonyls from 5-Acetyl-1,2,3,4,5-pentamethylcyclopentadiene, J. Am. Chem. Soc. 94 (1972) 3773–3779.

[15] Y. Wakatsuki, H. Yamazaki, Synthesis of Chloro(tris-triphenylphosphine) Cobalt(I) complex, Inorg. Synth. 26 (1989) 191–192.

[16] H. Kawaguchi, K. Yamada, J.-P. Lang, K. Tatsumi, A new entry into molybdenum sulfur chemistry: synthesis and reactions of mononuclear sulfido complexes of pentamethylcyclopentadienyl-Molybdenum(VI) and Tungsten(VI), J. Am. Chem. Soc. 119 (1997) 10346–10358.

[17] T. Nagasawa, H. Kawaguchi, K. Tatsumi, Isolation of pentamethylcyclopentadienyl tris(tert-buthylthiolato) complexes of tungsten(IV) and carbon-sulfur bond activation, J. Organomet. Chem. 592 (1999) 46–51.

[18] N. Kuhn, H. Bruggemann, M. Winter, Ein Einfacher Weg zur Synthese von Cyclopentadienylcobalt (III)-Dication, J. Organomet. Chem. 320 (1987) 391–400.

[19] N. Dudeney, J.C. Green, P. Grebenik, O.N. Kirchner, Synthesis and structural characterization of the electron rich complexes $Co(\eta\text{-}C_5Me_5)(R_2PCH_2CH_2PR_2)(R{=}Me, Ph)$; photoelectron spectroscopic studies of some pentamethylcyclopentadienyl phosphine cobalt complexes, J. Organomet. Chem. 252 (1983) 221–229.

[20] L.-C. Song, P.-C. Liu, Q.-M. Hu, G.-L. Lu, G.-F. Wang, Synthesis, characterization and properties of new organocobalt complexes containing η^5-functionally substituted cyclopentadienyl and [60]fullerene ligands, J. Organomet. Chem. 681 (2003) 264–268.

[21] A.J. Bard, L.R. Faulkner, Electrochemical Method; Fundamentals and Application Second Edition: Electrode Reactions with Coupled Homogeneous Chemical Reactions, John Wiley and Sons, Inc., New Jersey, USA, 2001, pp. 471–533.