Pyridine as an *C*-Orthometalated and σ-*N*-Complexed Heteroarene Ligand on the Surface of a Co_3 Cluster

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Reaction of [(η^5-Cp*)(acac-*O,O'*)Co] (**1**) with potassium metal in pyridine results in reductive ligand transfer of the acac ligand to potassium and formation of a mixture of two organocobalt complexes which can be separated from each other by chromatography. Besides a mononuclear complex containing no pyridine unit the trinuclear cobalt cluster [{(η^5-Cp*)Co}$_3$-μ-pyridine] (**3**) is formed in a cyclometalation reaction in 57 % yield. The pyridine ligand in **3** is located on one edge of the Co_3 core according to the spectroscopic data and a preliminary X-ray crystal structure analysis.

Molecular metal cluster compounds containing μ-arene ligands in face-bridging modes are now well established in organometallic cluster chemistry since almost a decade or so[1].

These compounds may serve as unique model compounds to mimic the metal-surface/arene analogy established by the pioneering work of Muetterties[2], Rhodin[3], Somorjay[4] and co-workers.

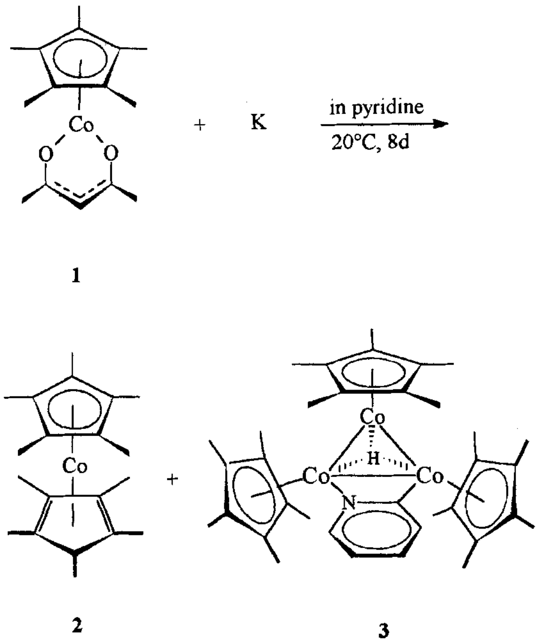
Concerning the synthesis of those compounds containing various arene ligands on the surface of a M_3 cluster unit, either the arene can be complexed on a preformed M_3L_3 cluster[5] or the M_3 cluster core can be build up stepwise on the surface of the arene[6]. Both ways work equally well and give rise to a variety of new and unusual M_3 systems with μ-(η:η:η-arene) ligands. In this communication is reported for the first time on the synthesis, spectroscopic, and in part structural characterization of a μ-pyridine ligand stabilized on a Co_3 cluster core.

Results and Discussion

Reductive ligand degradation of the mononuclear 17-VE cobalt complex [(η^5-Cp*)(acac-*O,O'*)Co] (**1**) with potassium metal in pyridine as solvent results in the formation of two organocobalt complexes (Scheme 1). They can be separated from the crude reaction mixture by chromatography. In 32% yield [(η^5-Cp*)(1,2,3,4,5-pentamethyl-η^4-cyclopentadiene)Co] (**2**)[7] was isolated as red crystals. In 30% yield brown crystals of [{(η^5-Cp*)Co}$_3$-μ-(C_5H_4N)] (**3**) were obtained as the second zone from the chromatography. Thermally, these crystals split off small amounts of [(η^5-Cp*)$_2$Co] by sublimation at about 150°C/10^{-3} Torr as identified by mass spectroscopy (*m/z*: 329 [M^+]). By raising the temperature of the sample probe to <160°C the [M^+] peak of **3** (*m/z*: 661) could be observed from the same sample.

Compound **3** exhibits ^{1}H-NMR resonances typical of an *o*-metalated pyridine ligand. The signal of the α proton of the pyridine ring in **3** is shifted downfield to $\delta = 8.30$ compared to free pyridine ($\Delta\delta = -0.20$). A hydridic resonance at $\delta = -24.3$ in the ^{1}H-NMR spectrum demonstrates that the second α proton of the pyridine ring is lost during this *o*-metalation reaction, but is still located on the metal core of the cluster. The IR spectrum of **3** with characteristic absorptions at $\tilde{\nu} = 730$ and 675 cm^{-1} gives additional evidence for an σ-*N* coordination of the pyridine ligand to an {(η^5-Cp*)Co} fragment. Examples of this bonding mode, although in mononuclear pyridine complexes, are found in [(η^5-Cp*)$_2$Lu(C_5H_4N)][8], [(η^5-Cp*)$_2$Y(C_5H_4N)][9], a couple of [(η^5-Cp)$_2$Ti−pyridine] complexes[10], and a number of [(*t*Bu$_3$SiO)$_3$Ta−(η^2-pyridine)] complexes[11]. However, attempts to detect 2-iodopyridine as a degradation product from the reaction of **3** with iodine[10] failed and resulted in complete degradation of the cluster and formation of [(η^5-Cp*)CoI$_2$][12]. The origin of the hydridic H in the ^{1}H-NMR

Scheme 1. Synthesis of **2** and **3** and possible coordination geometry of the pyridine ring ligand on the Co_3 cluster core of **3** as derived from the analytical data



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experiment from the pyridine ring and the pyridine σ-*N* coordination mode in **3** are furthermore independently confirmed by the synthesis of the perdeuterated derivative [D$_5$]-**3** (41% isolated yield) which can be prepared along with the monodeuterated [D$_1$]-**2** (30% isolated yield) in the same manner as described for **2** and **3** by the reaction of **1** with potassium metal in an excess of [D$_5$]pyridine. Absence of the resonance at $\delta = -24.3$ in the ^{1}H-NMR spectrum and a characteristic shift of the pyridine ring stretch to lower wave numbers in the IR spectrum of [D$_5$]-**3** as compared to **3** strongly supports the hypothesis of an *C-ortho*-metalated and σ-*N*-complexed pyridine ring.

Results of a preliminary X-ray crystal structure determination of **3**[13] reveal a trinuclear $\{(\eta^5\text{-Cp*})Co\}_3$ cluster core as shown in Scheme 1. The pyridine ring lies over one edge of the Co_3 triangle.

According to these and the spectroscopic results as well as the diamagnetism derived from the ^{1}H-NMR experiment the pyridine ligand in **3** acts as three-electron donor through a σ-N and σ-C bond of the ring to the Co_3 core resulting in an overall electron cluster count of 46 VE for **3**. The unusual coordination mode of the pyridine ligand in **3** might disrupt the aromaticity of the heteroarene and therefore distort its geometry to a significant extent which should be of further interest. However, from the experimental and spectroscopic data presently at hand it is obvious that in **3** pyridine is complexed in a hitherto new and unprecedented bonding mode on the surface of a Co_3 cluster. As it was pointed already out[11] for monometallic species with η-NC-bound pyridine ligands, clusters like **3** may also be relevant in C–H bond activation and related pyridine C-α functionalizations[14].

Experimental

All reactions were carried out under argon by using Schlenck-type glassware and techniques. Solvents were dried and distilled under argon prior to use. Al_2O_3 was activated by heating at 180°C/10^{-3} Torr for several days and stored under argon prior to use.

Synthesis of **2** *and* **3**: To a solution of 3.8 g (13 mmol) of **1** in 150 ml of pyridine 500 mg (13 mmol) of K was added in pieces. Treatment of this mixture for 10 min in an ultrasonic cleaning bath resulted in a fine suspension of the metal in the red pyridine solution of **1**. After stirring for 8 d all K had dissolved. All volatile compounds were removed in vacuo, and the oily residue was extracted with 150 ml of pentane and filtered to remove [K(acac)]. Removal of the pentane from the extract and dissolution of the residue in a minimum amount of THF was followed by adsorption of the obtained solution on Al_2O_3. Evaporization of the THF and chromatography of the Al_2O_3/crude reaction residue on Al_2O_3 (eluant: pentane) afforded two fractions; 460 mg (1.4 mmol, 32%) of **2** as red crystals (recrystallized from ether at −30°C); (eluant: pentane/ether, 1:1): **3**; brown crystals (1.6 g, 2.46 mmol, 57%). – **2**: identical spectroscopic data as reported[7]. – **3**: ^{1}H NMR (400 MHz, 27°C, [D$_6$]benzene) $\delta = -24.3$ (s, 1H), 1.95 (s, 45H, Cp*), 6.25 (td, 1H, *p*-H), 6.39 (dd, 1h, *m*-H), 7.82 (dt, 1H, *m*-H), 8.30 (dt, 1H, *o*-H). – IR (KBr): $\tilde{\nu}$ = 3075 cm^{-1} (w, py), 2850, 1370, 1020 (s, all Cp*), 730 (s, py), 675 (m, py). – MS (EI, 70 eV), *m/z* (%): 855 (>1) [M$^+$ + Cp*Co], 661 (31) [M$^+$], 578 (24), 442 (18), 329 (100), 315 (63), 79 (11). – $C_{35}H_{50}Co_3N$ (661.6): calcd. C 63.54, H 7.62, Co 26.72, N 2.12; found C 64.10, H 8.39, Co 24.71, N 1.39.

Synthesis of [D$_1$]-**2** *and* [D$_5$]-**3**: As described for **2** and **3** the deuterated compounds were prepared in an analogous manner from **1** and potassium metal in 30 and 41% yield, respectively, by using 30 ml of [D$_5$]pyridine (30-fold excess with respect to **1**) as solvent. Unreacted [D$_5$]pyridine was recovered by vacuum condensation. Further purification was as described for **2** and **3**. – Mixture of [D$_1$]-**2** (12%) and **2** (88%): MS (EI, 70 eV), *m/z* (%): 331 (3) [[D$_1$]-M$^+$], 330 (10), 329 (4), 317 (5), 316 (41) ([D$_1$]-M$^+$ − CH$_3$), 315 (100). – [D$_5$]-**3**: MS (EI, 70 eV), *m/z* (%): 860 (43) [M$^+$ + Cp*Co], 666 (6) [M$^+$], 634 (17), 329 (100), 84 (3). – ^{1}H NMR (400 MHz, 27°C, [D$_6$]benzene): δ = 2.01 (br. s, 45H, Cp*). – IR (KBr): $\tilde{\nu}$ = 2900 cm^{-1}, 2850 (s, all Cp*), 2265, 2280 (m, C–D, py), 1440, 1370, 1070, 1020 (s-m, all Cp*), 698 (s, py), 650 (s, py).

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