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Reaction of the Acyl(hydrido)cobalt(III) Complex with 2-Propyn-1-ol

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Dedicated to Professor Dieter Fenske on the Occasion of his 65th Birthday

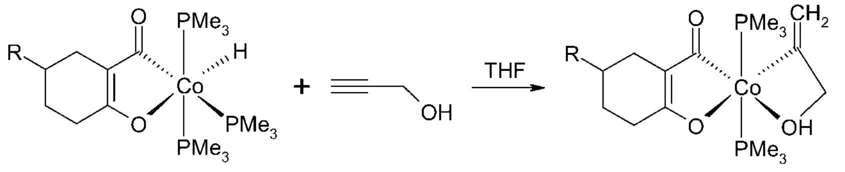
Abstract. Acyl(hydrido)cobalt(III) complexes *mer*-[$Co^{III}(O^\frown C{=}O)(H)(PMe_3)_3$] (**1** and **2**) stabilized by 2-acylphenolato-chelating ligands and with the support of trimethylphosphine react with 2-propyn-1-ol to generate inserting products of alkyne bond into Co-H bond bearing bis-chelating vinyl cobalt(III) complexes *cis*-[$Co^{III}(O^\frown C{=}O)(HO^\frown C{=}CH_2)(PMe_3)_2$] (**3** and **4**). In complexes **3** and **4** the vinyl chelating ligands form a novel four-membered chelate ring. Single crystal of complex **3** was analyzed by X-ray diffraction.

Keywords: Cobalt; Hydrido ligand; Trimethylphosphine; Alkyne

Introduction

The coordination chemistry of transition metal hydride complexes has always shown its attraction to both academe and industry. Transition metal hydrides are usually believed as actual active species in many catalytic processes rather than catalyst precursors in olefin oligomerization/polymerization and organic synthesis [1]. Therefore, the study on synthesis and properties of transition metal hydrides is one of the important research fields in organometallic chemistry [2]. During the last two decades, there have been considerable advances in this direction. Some metal hydrides were prepared through C-H activation method and most of the studies are focused on noble metals (Rh, Ru, Ir, etc) [3]. Practically, hydridocobalt complexes play a prominent role in some homogenous catalyses [4] owing to their low costs and relatively low environmental impacts, since 1998 *Klein* and co-workers have reported a series of acyl(hydrido)cobalt(III) complexes obtained via C-H activation of the aldehyde groups with chelate effect [5].

In this work, bis-chelate acyl enolato vinyl cobalt(III) complexes (**3** and **4**) with two chelating ligands are prepared by the reaction of acyl(hydrido)cobalt(III) complex (**1** and **2**) with 2-propyn-1-ol.



(1)

1, 2 **3, 4**

R = H C_6H_5

1, 3 **2, 4**

Results and Discussion

1. Reaction of acyl(hydrido)cobalt(III) complexes (1 and 2) with 2-propyn-1-ol

Addition of 2-propyn-1-ol to the solution of (2-acylphenolato)hydridocobalt(III) complexes **1** or **2** in THF afforded brown suspensions. The six-coordinate vinyl cobalt(III) complexes **3** or **4** could be isolated from the reaction solution (Eq. (1)). In the IR spectra the conspicuous ν(Co-H) absorption of the starting complex is absent. The ^{1}H NMR spectrum shows the vinyl signal of the CH_2 group at

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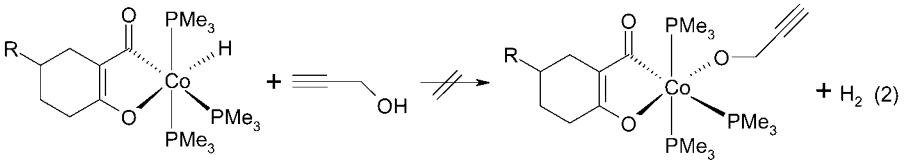

1, 2

(2)

4 ~ 5 ppm. ^{31}P NMR data present one signal for two *trans*-trimethylphosphine ligands. The molecular structure of **3** was confirmed by X-ray diffraction of single crystal.

Cobalt(III) complex **3** was isolated as orange red crystals, which are facile to be efflorescent. It was air-stable within several hours at ambient conditions and decomposes above 160 °C. The cobalt atom is in a distorted octahedral coordination (Fig. 1) bearing two chelate ligands: a five-membered acyl enolato chelate ligand ($O^\frown C=O$) and a four-membered vinyl hydroxy chelate ligand ($HO^\frown C=CH_2$) [6]. The addition of (Co-H) functionality to the ($C\equiv C$) bond is in line with the Markovnikov rule. Owing to the coordination of the O-donor atom of the hydroxyl group, the vinyl ligand turns to be a chelate ligand. The stability of complexes **3** and **4** is enhanced through the two chelating ligands. To the best of our knowledge, only a few examples of cobalt complexes with four-membered chelate ring had been published [7]. In addition, Co-O1 bond (1.9763 Å) was significantly shorter than Co-O3 bond (2.205 Å) showing the difference between a negatively charged enolato O-donor (O1) and a neutral hydroxyl O-donor atom (O3). The larger strain of the four-membered ring is another factor, which makes the (Co-O3) longer. The comparable Co-O(hydroxyl) distances (2.190 for Co^{III} and 2.109 Å for Co^{II}) were reported in the literature [8]. Because of the four-membered chelate ring the octahedral coordinarion configuration is extraordinarily distorted and the double bond C9-C10 (1.499 Å) is much longer than the normal C=C bond in olefins.

The hydrido ligand in acyl(hydrido)cobalt(III) complexes bears a partially negative charge [9]. Acyl(phenolato)hydridocobalt(III) complexes upon the reaction with acidic hydroxyl hydrogen of 2-nitrophenol or 2-nitronaphthol eliminate dihydrogen and afford bis-chelate 2-nitrophenolato or 2-nitronaphtholato cobalt(III) compounds [10]. Comparing with the pKa value of 2-nitrophenol (7.22) most of the aliphatic alcohols have the pKa values between 16 and 19. Therefore, it could be inferred that the neutralization of acyl(phenolato)hydridocobalt(III) complexes **1** and **2** with 2-proyn-1-ol did not occur and no substituted products were formed (Eq. (2)) because the acidity of the hydroxyl hydrogen of 2-proyn-1-ol is too weak.

2. *The Reaction of complex* 3 *with CO*

The reaction of complex **3** with carbon monoxide was carried out under 1 bar of carbon monoxide at room temperature for several days, complex **3** retained unchanged either in polar solvents or in non-polar solvents. Because of the low electronic density at the cobalt(III) atom it is difficult

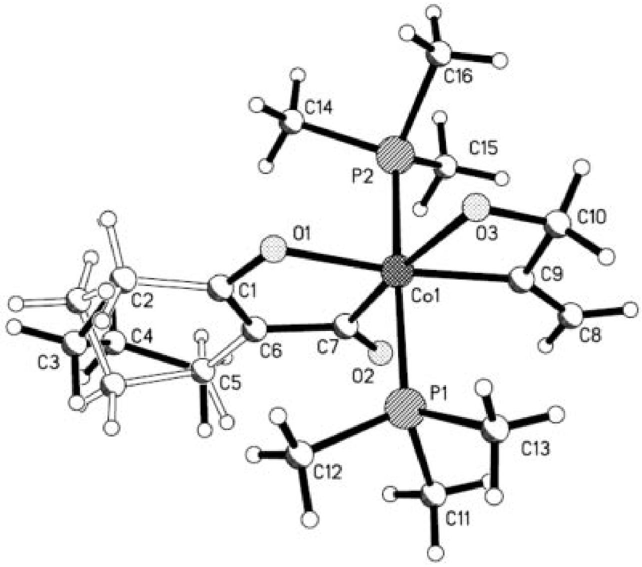

Fig. 1 Molecular structure of **3** with the representation of disorder of CH_2 groups C_2-C5. H atomic position on O3 could not be detected.

Selected distances /Å and angles /deg: Co1-C7 1.894(3), Co1-C9 1.914(3), Co1-O1 1.9763(19), Co1-O3 2.205(2), Co1-P2 2.2143(11), Co1-P1 2.2226(11), O3-C10 1.458(3), C9-C10 1.499(4), O1-C1 1.315(3), C1-C6 1.356(4), C6-C7 1.452(4), C7-Co1-C9 106.59(14), C7-Co1-O1 85.92(12), C9-Co1-O1 167.47(11), C7-Co1-O3 174.80(12), C9-Co1-O3 68.66(11), O1-Co1-O3 98.81(8), C7-Co1-P2 86.47(11), C9-Co1-P2 89.18(11), O1-Co1-P2 92.27(7), O3-Co1-P2 95.46(6), C7-Co1-P1 86.34(11), C9-Co1-P1 87.09(11), O1-Co1-P1 93.24(7), O3-Co1-P1 91.22(6), P2-Co1-P1 170.60(4).

for cobalt(III) complex to bear carbonyl ligand to form a p-back bonding. The examples of carbonyl cobalt(III) complexes were obtained as a result of an equilibrium between five-coordinated and six-coordinated species in solutions [11]. Under ambient condition, the unsaturated five-coordinated species with 16 valence electrons tends to combine a CO molecule to attain stable status with 18 valence electrons, whereas saturated six-coordinate complex **3** could not accept any CO ligand.

Conclusion

In conclusion, acyl(hydrido)cobalt(III) complexes **1** and **2** react with 2-propyn-1-ol forming bis-chelating vinylcobalt(III) complexes **3** and **4** via the addition of Co-H bond to C≡C bond. X-ray diffraction analysis of complex **3** indicates that the vinyl chelating ligand form a four-membered chelating ring. Under the experimental conditions no reaction of complexes **3** with carbon monoxide was observed.

Experimental Section

General Procedures and Materials

All air-sensitive and volatile materials were handled either in vacuo or under argon by using standard Schlenk techniques. Literature methods were applied in the preparation of (2-acylphenolatohydrido)cobalt(III) complexes **1** and **2** [9], 2-propyn-1-ol was used as purchased after distillation. All solvents were dehydrated and degassed by known procedures and used freshly distilled. Melting points/decomposition temperatures: Sealed capillaries, uncorrected values. IR: Nujol mulls between KBr disks, Bruker spectrophotometer type VECTOR 22. ^{1}H NMR, ^{31}P NMR and ^{13}C NMR spectra were recorded with Bruker AVANCE 400 and 300 spectrometers, respectively; ^{13}C and ^{31}P NMR resonances were obtained with broad-band proton decoupling.

Synthesis of (1-carbonyl-2-oxo-cyclohexenediyl)-(1-ethenyl-2-hydroxy-ethyl) -trans-bis(trimethylphosphan)cobalt(III) (3)

mer-Hydrido(1-carbonyl-2-oxo-cyclohexenediyl)tris(trimethylphosphine)cobalt(III) (**1**) (2.40 g, 5.81 mmol, dissolved in 50 mL THF) was added 1.07 g (19.1 mmol) of 2-propyn-1-ol in 20 mL of THF at −80 °C. The mixture was warmed to ambient temperature and turned brown-red rapidly. After stirring for 18 h the solvent was evaporated under vacuum, the residue was extracted with THF. Orange-red crystals were afforded at −27 °C in THF, which was found suitable for X-ray diffraction: yield 0.81 g of **3** (30 %), m.p.: 158 °C (dec.). $C_{16}H_{31}CoO_3P_2$ (392.3 g/mol): C 49.10 (calc. 48.99), H 7.84 (calc. 7.96) %.

IR (Nujol, cm^{-1}): ν(C=O) 1612 s; ν(C=C) 1569 s, 1538 m. **^{1}H NMR** (400 MHz, THF-d^8, 295 K, ppm): δ = 1.18 (d, 18H, $^2J_{P,H}$ = 3.2 Hz, PCH_3), 4.45 (s, 2H, C-CH_2-OH), 4.58 (t′, 1H, $|^4J_{P,H}+^2J_{H,H}|$ = 6.6 Hz, C=CH_2), 4.70 (s, 1H, C=CH_2), 1.45-1.92 (m, 8H, CH_2). **^{13}C NMR** (100 MHz, THF-d^8, 297 K): δ = 10.59 (t′, $|^1J_{P,C}+^3J_{P,C}|$ = 25.3 Hz, P*C*H$_3$), 67.1 (C-*C*H$_2$-OH), 114.4 (*C*-C=O), 119.0 (C=*C*H$_2$), 156.3 (*C*=CH$_2$), 181.4 (*C*-O), 198.1 (Co-*C*=O). **^{31}P NMR** (121 MHz, THF-d^8, 294 K) δ = 2.48 (s, *P*CH$_3$).

Synthesis of (1-carbonyl-2-oxo-5-phenyl-cyclohexendiyl)-(1-ethenyl-2-hydroxy-ethyl)-trans-bis(trimethylphosphan)cobalt(III) (4)

50 mL of THF solution of *mer*-hydrido(1-carbonyl-2-oxo-5-phenylcyclohexendiyl)tris(trimethylphosphine)cobalt(III) (**2**) (1.23 g, 2.50 mmol) and 1.76 g (31.4 mmol) of 2-propyn-1-ol in 20 mL of THF were combined at −80 °C. Upon warming to ambient temperature the mixture turned brown-red rapidly depositing some brown solid. After stirring for 18 h the solvent was removed under vacuum, the residue was extracted with ether and THF, respectively. Orange-red crystals were afforded at −27 °C in THF. Yield 0.33 g of **4** (28 %), m. p.: 130 °C (dec.). $C_{22}H_{35}CoO_3P_2$ (468.39 g/mol): C 56.29 (calc. 56.41), H 7.64 (calc. 7.53) %.

IR (Nujol, cm^{-1}): ν(C=O) 1613 s; ν(C=C) 1567 s. **^{1}H NMR** (300 MHz, THF-d^8, 294 K, ppm): δ = 1.40 (t′, 18H, $|^4J_{P,H}+^2J_{H,H}|$ = 9.3 Hz, PCH_3), 1.50-2.09 (m, 7H, CH_2), 4.66 (s, 2H, C-CH_2-OH), 4.77 (s, 1H, C=CH_2), 4.89 (s, 1H, C=CH_2), 6.98-7.37 (m, 5H, H_{arom}). **^{31}P NMR** (121 MHz, THF-d^8, 294 K) δ = 2.25 (s, *P*CH$_3$).

Crystallographic data for 3

$C_{16}H_{31}CoO_3P_2$, M_r = 392.3, crystal dimensions: 0.32 x 0.28 x 0.20 mm, monoclinic, space group $P2_1/n$, a = 9.8187 (18), b = 13.735 (2), c = 14.760 (3) Å, β = 95.058(3), V = 1982.9 (6) Å^3, T = 294(2) K, Z = 4, D_c = 1.311 g cm^{-3}, μ = 1.035 mm^{-1}. Bruker AXS SMART APEX. A total of 10937 reflections was collected, 4046 unique (Rint = 0.0391), θ_{max} = 26.42°, multi-scan absorption correction. R1 = 0.0404 (for 6678 reflections with $I > 2\sigma(I)$), wR2 = 0.1146 (all data). The structure was solved by direct methods and refined with full-matrix least-squares on all F^2(SHELXL-97) with non-hydrogen atoms anisotropic.

Crystallographic data have been deposited with the Cambridge Crystallgraphic Data Centre CCDC No 645481. These data can be obtained free of charge via www.code.cam.ac.uk/const/retrieving.html or from Cambridge Crystallographic Centre, 12, Union Road Cambridge CB2 1EZ, Uk; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk

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