Stoichiometric Homo-Aldol Coupling of Acetone, Cyclohexanone, and Acetophenone by the [(η^5-Cp^R)Co] (R = Me$_5$, 1,2,4-tri-*tert*-butyl) Moiety

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Keywords: Cobalt / Sandwich complexes / Aldol reactions / Ketones / C$_{sp3}$–H activation

Acetone, cyclohexanone, and acetophenone react with the toluene-bridged triple-decker complexes [{(η^5-Cp^R)Co}$_2$-μ-(η^4:η^4-toluene)] (R = Me$_5$ **3**; 1,2,4-tri-*tert*-butyl **4**) by toluene substitution and homo-aldol coupling of two ketone molecules to form the first oxadiene cobalt complexes. These reactions may involve a C$_{sp3}$–H activation step of the ketones by 14 e$^-$ [(η^5-Cp^R)Co] fragments generated from the triple-decker complexes **3** and **4**. If no acidic protons are present in the position α to the carbonyl carbon position in the ketone, no C$_{sp3}$–H activation occurs. In agreement with this, benzophenone does not react with complex **3**.

Introduction

During the last decade or so it has been well established, both spectroscopically and crystallographically, that carbonyl compounds are able to coordinate to transition metal fragments and, consequently, metal-mediated reactions, which are stoichiometric or even catalytic in nature, have been studied extensively.[1] The aldol reaction is generally regarded as one of the most powerful carbon–carbon bond forming reactions. The primary metal coordination site is at the C=O group, resulting in three different bonding situations A–C towards the transition metal center (Figure 1).[2] Recent results by Brookhart, who observed selective coordination of phthalaldehyde over acetone with the bis({trimethylsilyl}alkene)(η^5-Me$_5$C$_5$)Co complex **1** are striking.[3a] The bis-aldehyde complex **2**, which simultaneously displays coordination modes A and B is formed as the exclusive product from the activation of phthalaldehyde even though acetone was used as the reaction solvent (Scheme 1).[3a] Other examples of similar aldehyde over ketone reactivity are documented for the cobalt complex **1** by the same authors.[3b][3c]

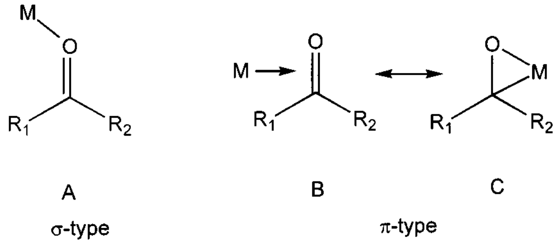
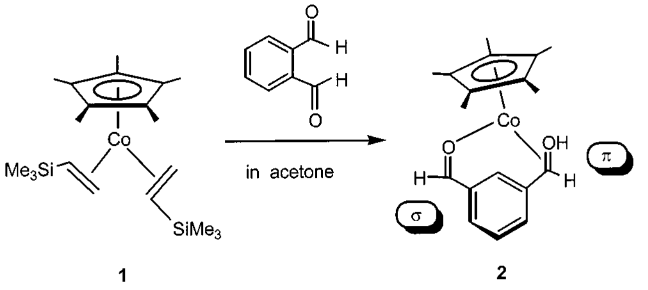


Figure 1. σ- and π-coordination modes of a transition metal fragment M to a ketone; R$_{1,2}$ = H or alkyl



Scheme 1

Herein we report on our studies on the synthesis and structure of cobalt-oxadiene complexes which are formed via a stoichiometric homo-aldol coupling reaction of acetone, cyclohexanone, and acetophenone mediated by 14-e [(η^5-Cp^R)Co] fragments.

Results and Discussion

Reaction of [{(η^5-Me$_5$C$_5$)Co}$_2$-μ-(η^4:η^4-toluene)] (3) and [{(η^5–1,2,4-tri-*tert*-butyl-C$_5$H$_2$)Co}$_2$-μ-(η^4:η^4-toluene)] (4) with Ketones

Reaction of the triple-decker compound [{(η^5-Me$_5$C$_5$)Co}$_2$-μ-(η^4:η^4-toluene)] (**3**) either in neat acetone as solvent or with a tenfold excess of acetone in ether results in the formation of the *s-cis*-oxadiene cobalt complex **5** (Scheme 2). No *s-trans* regioisomer was observed. The question of whether the product selectively adopts one of the regioisomers (Figure 2) is of interest since the two arrangements expose different faces of the α, β-unsaturated carbonyl moiety which may lead to different enantioselective additions to this complex.

The reaction of **3** with acetone proceeds stoichiometrically and no free 2-oxo-4-methylpent-3-ene was observed as the organic aldol coupling product resulting from a catalytic reaction sequence. The η^2-keto coordination is characterized by a significant ^{13}C high-field coordination shift of the carbonyl C-atom resonance of $\Delta\delta$ = –72 ppm relative to free acetone.

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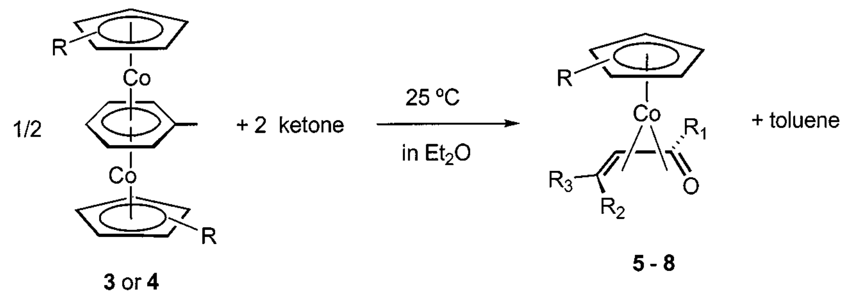


Scheme 2. General reaction scheme for the formation of Co-oxadiene complexes **5–8** via homo-aldol coupling of acetone, cyclohexanone and acetophenone. The characteristic η^4-oxadiene unit of **5–8** is depicted in bold.

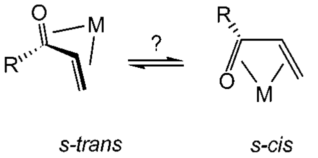
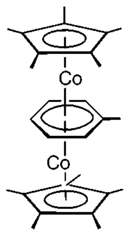


Figure 2. *s-cis* versus *s-trans* arrangement of a metal-oxadiene unit



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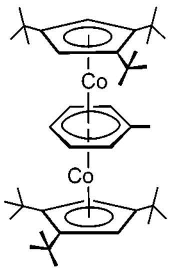

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A tenfold excess of acetophenone in diethyl ether reacts with **3** within 30 minutes to give the oxadiene cobalt complexes [{(η^5-Me$_5$C$_5$)Co(η^4-(*E*,*Z*)-3-methyl-1-oxo-1,3-diphenylbut-2-ene)} **(6)** as a mixture of *cis* and *trans* isomers (ratio 2:3) (Scheme 2). As in the case of **5**, a significant high-field coordination shift of $\Delta\delta = -49.2$ ppm for the resonance of C1 characterizes the η^2-keto coordination of the [(η^5-Me$_5$C$_5$)Co] fragment of **6**. The complete set of ^{13}C-NMR signals for both isomers is not observed probably just due to a low concentration of the sample studied.

When **3** is dissolved in neat cyclohexanone a reaction occurred within two days as judged from the color change from brown red to green black. The oxadiene cobalt complex [(η^5-Me$_5$C$_5$)Co(η^4-2-cyclohexylidenecyclohexane-1-one)] **7** is formed in moderate yields. (Scheme 2). ^{1}H- and ^{13}C-NMR spectroscopy shows the formation of only the *s-cis* isomer (assignment via 1D- and 2D-NMR techniques). In the ^{13}C-NMR spectrum the η^2-keto coordination is characterized by a coordination shift of $\Delta\delta = -75$ ppm for the resonance of C1 relative to free cyclohexanone.

To study the influence of the steric bulk of the [(Cp^R)Co] fragment on the homo-aldol coupling reaction we studied the reaction of acetone with the triple-decker complex **4**. The 1,2,4 tri-*tert*-butyl Cp ligand has already proven its versatility in kinetically stabilizing unusual metal coordination environments.[4,5] When **4** is dissolved together with a tenfold excess of acetone in diethyl ether the reaction proceeds within 12 hours to give the oxadiene complex [{(η^5-*t*Bu$_3$C$_5$H$_2$)Co(methyl-2-oxo-pent-3-ene)}] (**8**) whose structure is confirmed by its mass, IR and ^{1}H- and ^{13}C-NMR spectra (see Experimental Section) (Scheme 2). In **8**, as well as in the other oxadiene Co complexes **5–7**, the ν(C=O) stretching frequencies of the complexed η^2-carbonyl moieties are unfortunately obscured by the strong intensity of the stretching frequencies of the Me and 1,2,4-*tert*-butyl residues of the Cp ring ligands.

Molecular Structure of 5

An X-ray crystal structure determination[6] (Figure 3) of **5** reveals the *s-cis*-arrangement of the oxadiene moiety in agreement with the solution NMR results. The C1–O1 distance [1.310(5) Å] of the π-coordinated carbonyl group is in the same range as for the η^2-coordinated C=O group of the dialdehyde complex **1**[3a] as well as for other η^2 bound ketones.[1,7] This suggests a significant amount of π-backbonding from the Co^I d-orbitals into the π* orbitals of the carbonyl C atom. The Co–O [1.985(3) Å] and the Co1–C2 [1.994(4) Å] distances are in agreement with a symmetrical

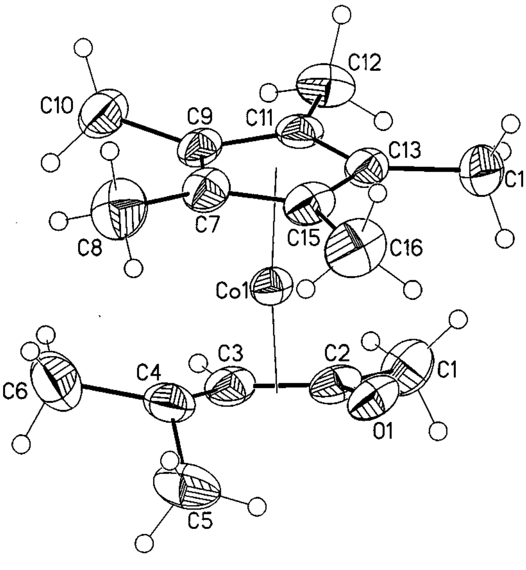


Figure 3. Molecular structure of **5** in the solid state; selected bond length [Å] and angles [°]: C(2)–O(1) 1.310(5),C(2)–C(3) 1.396(6), C(3)–C(4) 1.437(6),C(1)–C(2) 1.497(6), C(4)–C(5) 1.503(7), C(4)–C(6) 1529(6), Co(1)–C(2) 1.994(4), Co(1)–O(1) 1.985(3), Co(1)–C(3) 1.985(4), Co(1)–C(4) 2.041(5) O(1)–C(2)–C(3) 116.9(4), C(2)–C(3)–C(4) 119.0(4)

η^2-bonding of the $[Co(\eta^5\text{-}C_5Me_5)]$ fragment to the keto group. The atoms C2, C3, C4, and O1 define an almost ideal plane. The bond length deviation Co–C2 [1.994(4) Å], Co1–C3 [1.985(4) Å], Co1–C4 [2.041(5) Å], and Co1–O [1.985(3) Å] is within experimental error, thus the bonding can be regarded as symmetrical η^4. However, the distance C3–C4 [1.437(6) Å] within the planar oxadiene unit is significantly longer than C2–C3 [1.396(6) Å]. This indicates an intermediate bonding situation between a pure π-coordination mode **A** and a metallacyclic type coordination **B** for **5** in the solid state (Figure 4). **A** and **B** represent the two extremes of coordination for an $M(L)_x$ fragment to a oxadiene ligand system.

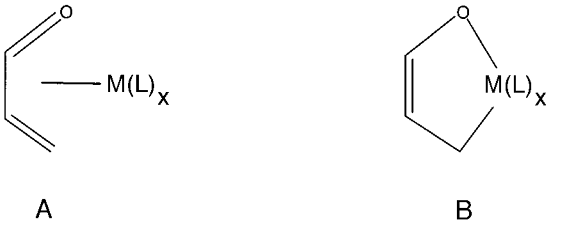
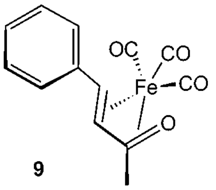


Figure 4. π-Metal coordination **A** versus σ-metallacycle formation **B** in an oxadiene complex

Discussion

Compounds **5–8** belong to a group of organometallic oxadiene complexes of which [(4-phenylbut-3-ene-2-one)-$Fe(CO)_3$] **(9)** represents the first example.[8] This and other enone complexes of a similar bonding type are accessible by standard complexation procedures.[9] In contrast, **5–8** are formed via a Co-mediated aldol-type coupling initiated by reactive 14 e $[(\eta^5\text{-}Cp^R)Co]$ (R = Me_5, 1,2,4-tri-*tert*-butyl) fragments. Their formation from the triple-decker complexes **3** and **4** was verified by detailed mechanistic studies.[5,10] Complexes **3** and **4** are valuable sources of either one or two $[(\eta^5\text{-}Cp^R)Co]$ fragments. The decay of **3** and **4** into $[(\eta^5\text{-}Cp^R)Co]$ (R = Me_5, 1,2,4-tri-*tert*-butyl) fragments (Scheme 3) proceeds in any common donor solvent and is especially fast in the presence of ketones (e.g. acetone).



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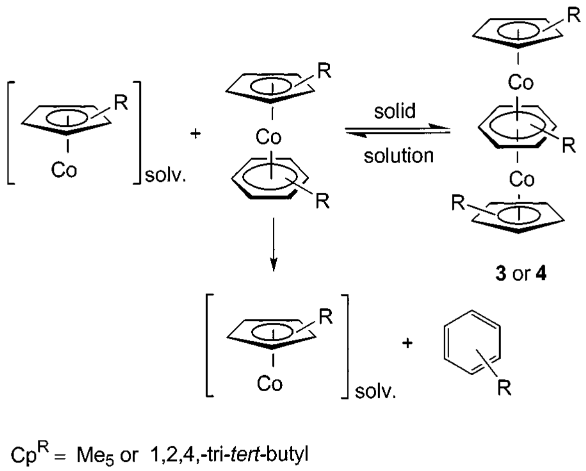
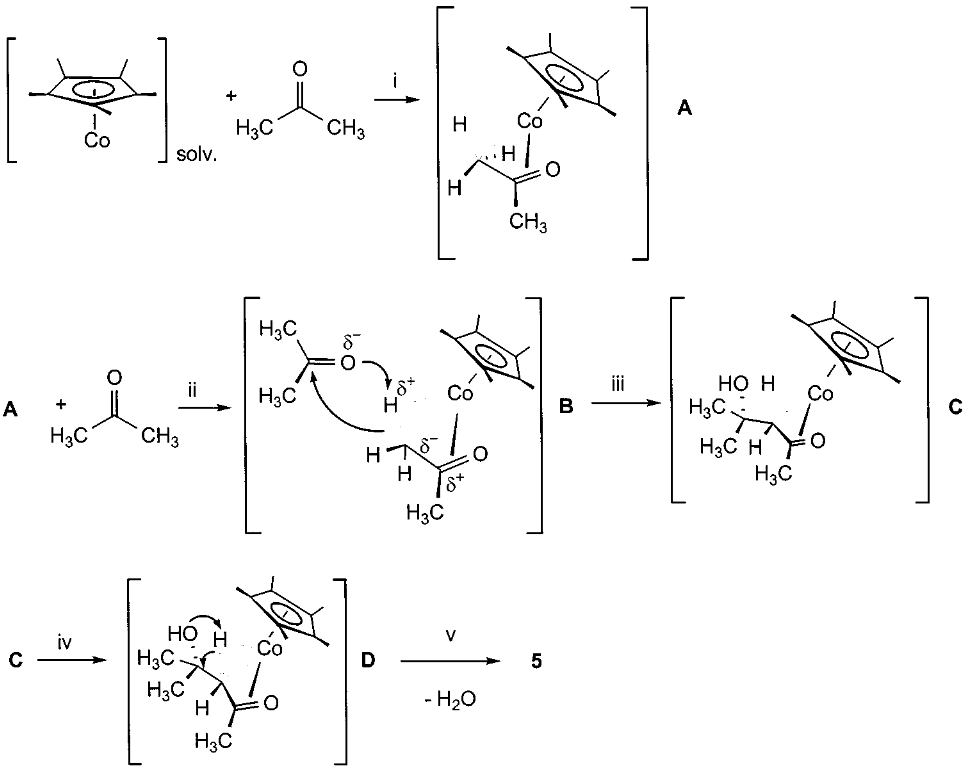
There has been quite intense research on the C–H bond activation by various transition metal complexes especially of the iron group triad which may be followed by functionalization of the activated substrate.[11] A process which combines C–H and C–C coupling reactions is the catalytic hydroacylation of olefins to form ketones at Rh^I centers studied by Bosnich.[12] However, such reactivity is usually not in the realm of first row transition metal chemistry and only a few cases are reported for organo cobalt complexes but to the best of our knowledge none so far for a C_{sp3}–H bond activation mediated by Co fragments. Extensive studies by Bergman[13], Jones,[14] and Graham[15] have established that 16 e species of the type $[(\eta^5\text{-}R_5C_5)ML]$ (M = Rh, Ir) generated in situ, undergo facile oxidative addition reactions with the C–H bonds of saturated hydrocarbons and arenes. For Co, Brookhart[3a,16] demonstrated facile oxidative addition of aldehydes via the 16 e $[(\eta^5\text{-}Me_5C_5)CoL]$ fragment. However, it is noteworthy with respect to our work that no activation of the less reactive acetone used as solvent is reported by these authors for the $[(\eta^5\text{-}Cp^R)CoL]$ fragment which is derived from **1**. Wadepohl[17] observed facile C_{sp2}–H activation processes of cycloalkenes in the course of the formation of polynuclear $[(\eta^5\text{-}Cp^R)Co]$-based clusters which are derived from the Jonas complex $[(\eta^5\text{-}Cp)Co(ethene)_2]$. Crucial for the ability of Co centers to participate in C–H-bond activation processes is the generation of reactive sites, especially the formation of either coordinatively unsaturated, electron deficient 16 e $[(\eta^5\text{-}Cp^R)Co(L_x)]$ or even 14 e $[(\eta^5\text{-}Cp^R)Co]$ fragments.[18] C–H activation is assumed to be a significant step in the homo-aldol coupling reaction of the ketones under study herein. This is based on results obtained from the reaction of benzophenone with **3**. Benzophenone contains no acidic protons at the α-carbon position, thus no homo-aldol coupling can be observed with benzophenone which is recovered unchanged from a reaction with **3**. A possible reaction pathway invoking C_{sp3}–H bond activation of acetone, cyclohexanone and acetophenone as crucial reaction step, leading to the oxadiene cobalt complex **5–8** is outlined in Scheme 4 exemplified for the reaction of **3** and acetone.



Scheme 3. Solid state versus solution equilibrium of the triple-decker complexes **3** and **4**[10]

Reactive 14 e $[(\eta^5\text{-}Me_5C_5)Co]_{solv}$ fragments are generated from **3**. These can first coordinate the keto group of acetone followed by an activation of the hydrogen atoms of the neighboring α-methyl group giving intermediate **A**. Reaction of intermediate **A** with the "acidic" carbonyl carbon

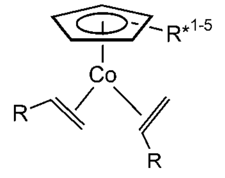


Scheme 4. Proposed reaction scheme for the Co-mediated homo-aldol coupling of acetone

atom of another acetone molecule forms (ii), **B** results in a C–C coupling, leading to intermediate **C** (iii). Finally **C** can eliminate water (v), **D** to yield complex **5**. This elimination of water parallels the classical base catalyzed aldol type coupling reaction.[19]

Conclusions

Our findings presented here indicate a pronounced reactivity enhancement of the arene triple-decker type complexes **3** and **4** over half sandwich complexes of type **10**, which in contrast to **3** and **4** do not show similar carbonyl coupling reactions and not even a reactivity towards acetone under similar conditions. This points to the fact that 14 e $[(\eta^5\text{-Cp}^R)\text{Co}]$ fragments derived from the triple-deckers **3** and **4** in contrast to 16 e $[(\eta^5\text{-Cp}^R)\text{CoL}]$ derived from **10** are able to activate ketones at their C_{sp3}-α-carbon atom under mild conditions. This is to the best of our knowledge the first C_{sp3}–H bond activation of ketones by an organocobalt compound leading to a C–C coupling under neutral and ambient conditions. It remains to be studied if this coupling proceeds regio- and/or stereospecifically with other ketones and if it can be tuned from stoichiometric to catalytic reactivity. Such investigations may open up new synthetic routes with respect to cobalt mediated cycloaddition reactions offering access to complex organic products as in the case of oxadiene complexes of Mo and W.[20]



$R^{*1\text{-}5}$ = H or alkyl

R = H, $SiMe_3$

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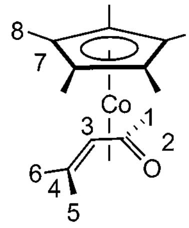
Experimental Section

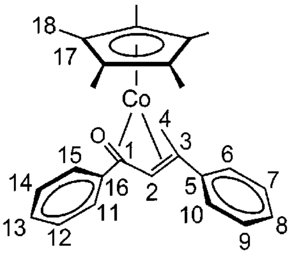
Compounds **3**[21] and **4**[5] were prepared according to published procedures. All ketones were commercial products (purity 99%), they were distilled prior to use and stored under nitrogen in the dark. – The NMR spectra were recorded on a Bruker AC 300 spectrometer (300 MHz for ^1H, 75 MHz for ^{13}C) and referenced against the residual protons of the deuterated solvent. – MS spectra were recorded on a MAT 8200 instrument under standard conditions (EI, 70 eV) and the fractional sublimation technique for compound inlet. – T_{vap} gives the individual vaporization temperature of the sublimation process during the MS experiment.

$[(\eta^5\text{-Me}_5\text{C}_5)\text{Co}(\eta^4\text{-4-methyl-2-oxopent-3-ene})]$ (5): Complex **3** (0.41 g, 0.85 mmol) was dissolved together with acetone (0.5 g, 8.6 mmol) in 30 mL of diethyl ether. Continued stirring for 24 hours resulted in a color change from red brown to greenish brown. Removal of all volatiles under vacuum gave a semi-solid residue which was dissolved in a minimum amount of pentane. Cooling to –78 °C afforded **5** (0.38 g, 1.31 mmol, 77%) as brown material. The same material resulted when the reaction was performed in acetone only. – MS (EI, 70 eV, T_{vap} 250 °C); *m/z* (%): 292 (100)

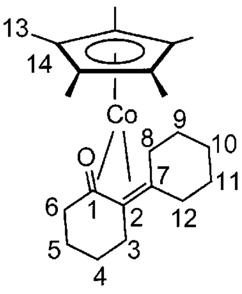
[M$^+$], 277 (3) [M$^+$ – CH$_3$], 249 (20) [M$^+$ – CH$_3$CO], 209 (13) [M$^+$ – (CH$_3$)$_2$C=CHCO], 192 (70) [(Me$_5$C$_5$)Co]. – ^{1}H NMR ([D$_6$]benzene, 300 MHz, 27 °C): δ = 0.95 (s, 3 H), 1.17 (s, 3 H), 1.50 (s, 15 H), 2.13 (s, 3 H), 4.03 (s, 1 H). – ^{13}C{^{1}H} NMR ([D$_6$]benzene, 75.1 MHz, 27 °C): δ = 9.4 (C7), 20.9 [C6(5)], 21.8 [C5(6)], 28.2 (C1), 77.9 (C3), 89.1 (C8), 127.2 (C4), 134.9 (C2). – IR (KBr): ṽ = 1473, 1448, 1431, 1385, 1351, 1364 (all vs, Me$_5$C$_5$), 1236, 1155, 1140, 1065, 1027, 911, 862, 602 (all vs) cm^{-1}. – $C_{16}H_{25}CoO$ (292.29): calcd. C 65.74, H 8.62, Co 20.16; found C 65.85, H 8.69, Co 20.22.



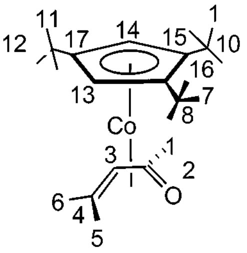
[{(η^5-Me$_5$C$_5$)Co(η^4-(*E*,*Z*)-3-methyl-1-oxo-1,3-diphenylbut-2-ene)}] (6): Synthetic procedure as described for **5**; crystallization from diethyl ether/pentane (2:1) gives **6** (0.28 g, 0.68 mmol, 63%) as a mixture of its (*E*)- (63%) and (*Z*)-isomers (37%). – MS (EI, 70 eV, T$_{vap}$: 100 °C); *m*/*z* (%): 416 (100) [M$^+$], 311 (3) [M$^+$ – C$_6$H$_5$CO], 281 (55) [M$^+$ – Me$_5$C$_5$], 192 10 [(Me$_5$C$_5$)Co]. – ^{1}H NMR ([D$_6$]benzene, 300 MHz, 27 °C): δ = 1.23 [s, 15 H, (*Z*)], 1.42 [s, 15 H, (*E*)], 1.54 [s, 3 H, (*E*)], 1.57 [s, 3 H, C4 (*Z*)], 4.99 [s, 1 H, (*E*)], 6.11 [s, 1 H, (*Z*)], 7.17 [m, arenes (*E* + *Z*)], 7.19 [m, arenes (*E* + *Z*)], 7.31 [m, arenes (*E* + *Z*)], 7.39 [m, 3 H, C12–C14 (*E*)], 7.41 [m, 3 H, C12–C14 (*Z*)], 8.16 [m, 2 H, C11, C15 (*E*)], 8.27 [m, 2 H, C11, C15 (*Z*)]. – ^{13}C{^{1}H} NMR ([D$_6$]benzene, 75.1 MHz, 27 °C): δ = 8.6 [C17 (*Z*)], 9.0 [C17 (*E*)], 17.1 [C4 (*Z*)], 27.40 [C4 (*E*)], 71.23 [C2 (*Z*)], 71.8 [C2 (*E*)], 89.6 [C18 (*E*)], 89.7 [C18 (*Z*)], 124.5, 124.5, 126.0, 126.7, 127.0, 127.3, 128.6, 129.2, 146.7 (C1). – IR (KBr): ṽ = 3055, 3034, 1540, 1488, 762, 695 (all strong, all phenyl), 1488, 1449, 1072, 1022 (all vs, all Me$_5$C$_5$) cm^{-1}. – $C_{26}H_{29}CoO$ (416.42): calcd. C 74.99, H 7.02; found C 74.36, H 7.02.



[{(η^5-Me$_5$C$_5$)Co(η^4-2-cyclohexylidenecyclohexan-1-one)}] (7): Synthetic procedure as described for **5**; crystallization from acetonitrile/ether mixture gives **7** (0.1 g, 0.27 mmol, 22%) as cube-shaped black crystals. – MS (EI, 70 eV, *T*$_{vap}$ 150 °C); *m*/*z* (%): 372 (100) [M$^+$], 354 (8) [M$^+$ – H$_2$O], 233 (17) [M$^+$ – C$_9$H$_{15}$], 194 (17) [Me$_5$Co]. – ^{1}H NMR ([D$_6$]benzene, 300 MHz, 27 °C): δ = 1.09 (m, 1 H), 1.52 (m, 2 H), 1.58 (m, 2 H), 1.61 [s, 15 H, C13], 1.77 (m, 2 H), 1.90 (m, 2 H), 1.94 (m, 2 H), 2.0 (m, 1 H), 2.14 (m, 1 H), 2.20 (m, 1 H), 2.32 [t (dd), 1 H], 2.45 (m, 1 H), 2.65 (ddd, 1 H). – ^{13}C{^{1}H} NMR ([D$_6$]benzene, 75.1 MHz, 27 °C): δ = 9.4 (C13), 24.2 (sec.), 24.4 (sec.), 26.3 (sec.), 28.1 (sec.), 28.4 (sec.), 28.6 (sec.), 31.0 (sec.), 31.6 (sec.), 32.1 (sec.), 35.7 (sec.), 63.0 (q, C7), 85.5 (q, C2), 88.7 (q, C14), 134.5 (q, C1). – $C_{22}H_{33}CoO$ (372.41): calcd. C 70.95, H 8.93, Co 20.16; found C 71.03, H 9.05.



[{(η^5-*t*Bu$_3$H$_2$C$_5$)Co(4-methyl-2-oxopent-3-ene)}] (8): Synthetic procedure fas described for **5**; crystallization from pentane at –78 °C affords **8** as a brown solid. – MS (EI, 70 eV, *T*$_{vap}$ = 120 °C); *m*/*z* (%): 390 (32) [M$^+$], 333 (100) [M$^+$ – *t*Bu], 57 (33) [*t*Bu]. – ^{1}H NMR ([D$_6$]benzene, 300 MHz, 27 °C): δ = 0.99 [s, 9 H, C11], 1.08 [s, 3 H, C5(6)], 1.18 [s, 3 H, C6(5)], 1.44 [s, 9 H, C7(9)], 1.77 [s, 9 H, C9(7)], 2.29 [s, 3 H, C1], 3.39 [s, 1 H, C13(14)], 4.14 [s, 1 H, C14(13)], 4.69 [s, 1 H, C3], in addition signals due to [{(η^5-*t*Bu$_3$H$_2$C$_5$)$_2$Co][22] were present in a 1:2 ratio. – ^{13}C{^{1}H} NMR ([D$_6$]benzene, 75.1 MHz, 27 °C): δ = 22.2 [C5(6)], 22.7 [C6(5)], 31.3 [C7(9,11)], 31.4 (C1), 32.7 [C9(7,11)], 33.2, 33.4, 35.1 [C11(7,9)], 76.3, 78.1, 79.21, 148.50 (CO). – IR (KBr): ṽ = 1486, 1458, 1391, 1242 (all vs, all *t*Bu), 1199, 1163, 1020, 990, 824, 668 (all m) cm^{-1}. – No satisfactory elemental analysis could be obtained due to trace amounts of [{(η^5-*t*Bu$_3$C$_5$)$_2$Co][22] already contained in the starting material **4**.



Reaction of 3 with Benzophenone: Complex **3** (0.31 g, 0.64 mmol) and benzophenone (0.46 g, 2.52 mmol) were dissolved in 30 mL of diethyl ether and stirred for 48 h. Although the color of the solution changed during this time from red-brown to orange-brown, removal of all volatiles gave mainly unchanged benzophenone. However, **3** was no longer present.

Acknowledgments

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[6] X-ray crystal structure investigation of **5**: A dark, thin plate-like crystal with the approximate dimensions 0.22 × 0.19 × 0.05 mm was investigated at room temperature with a Siemens-Smart System using Mo-K_α radiation. The orthorhombic crystal system has the cell dimensions a = 12.8021(5), b = 14.0394(6), c = 17.1475(6) Å, V = 3082.0(2) Å^3, Z = 8, ρ = 1.260 g cm^{-3}, μ = 1.101 mm^{-1}, space group *Pbca*. Full-sphere data collection of 21602 reflections (θ_{max} = 25.99°), data reduction (Siemens SAINT Vers. 4.05), empirical absorption correction (Siemens SADABS), max/min transmission 1.00/0.40, 2578 independent reflections [R_{merg} = 0.14 (F^2)], 1359 observed [$F_o > 4\sigma(F)$], structure solution with direct methods and refinement on F^2 of 163 parameters using Siemens SHELXTL Vers. 5.03 resulted in $R1$ = 0.0525 (obs. data) and $wR2$ = 0.1397 (all data), GoF = 0.887, maximum/minium residual electron densities 0.620/−0.286 eÅ^{-3}. Hydrogen atoms were treated as riding groups with the 1.2 fold (1.5 for methyl groups) isotropic U-values of the equivalent U-values that correspond to the attached C-atoms. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-130276 **(5)**. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44–1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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