ChemPubSoc Europe

DOI: 10.1002/chem.201605222

CHEMISTRY A European Journal Full Paper

Reaction Mechanisms

Alkene Metalates as Hydrogenation Catalysts

Philipp Büschelberger,[a] Dominik Gärtner,[b] Efrain Reyes-Rodriguez,[b] Friedrich Kreyenschmidt,[c] Konrad Koszinowski,[c] Axel Jacobi von Wangelin,*[b] and Robert Wolf*[a]

Abstract: First-row transition-metal complexes hold great potential as catalysts for hydrogenations and related reductive reactions. Homo- and heteroleptic arene/alkene metalates(1−) (M = Co, Fe) are a structurally distinct catalyst class with good activities in hydrogenations of alkenes and alkynes. The first syntheses of the heteroleptic cobaltates [K([18]crown-6)][Co(η^4-cod)(η^2-styrene)$_2$] (**5**) and [K([18]crown-6)][Co(η^4-dct)(η^4-cod)] (**6**), and the homoleptic complex [K(thf)$_2$][Co(η^4-dct)$_2$] (**7**; dct = dibenzo[*a*,*e*]cyclooctatetraene, cod = 1,5-cyclooctadiene), are reported. For comparison, two cyclopentadienylferrates(1−) were synthesized according to literature procedures. The isolated and fully characterized monoanionic complexes were competent precatalysts in alkene hydrogenations under mild conditions (2 bar H_2, r.t., THF). Mechanistic studies by NMR spectroscopy, ESI mass spectrometry, and poisoning experiments documented the operation of a homogeneous mechanism, which was initiated by facile redox-neutral π-ligand exchange with the substrates followed by H_2 activation. The substrate scope of the investigated precatalysts was also extended to polar substrates (ketones and imines).

Introduction

Metal-catalyzed hydrogenations are among the largest technical processes and constitute key operations in numerous chemical syntheses.[1] In recent decades, the use of highly active platinum-group metal catalysts has grown to maturity and enabled efficient hydrogenations of unsaturated C=C and C=X bonds.[2] Apart from nickel,[3] 3 d transition-metal catalysts have received much less attention, despite their higher abundance and often lower toxicity.[4] The emphasis on stringent economic and environmental criteria has placed the development of sustainable hydrogenation methods with base-metal catalysts into the limelight of current research activities.[5]

Great progress was only recently made with the development of low-valent iron-group metal catalysts (Fe, Co, Ni) for olefin hydrogenations under very mild reaction conditions. Special ligand architectures allowed the stabilization of catalytically active species in low oxidation states. Budzelaar and co-workers reported the first application of (pyridyldiimine)cobalt catalysts to hydrogenations of mono- and disubstituted olefins (Figure 1, top left).[6] Significantly, Chirik and co-workers introduced new catalyst derivatives and expanded the scope to include bulky alkenes; they were also able to hydrogenate geminal-disubstituted olefins enantioselectively (Figure 1, top left).[7] Hanson and co-workers reported PNP pincer cobalt complexes to be active in the hydrogenation of alkenes, aldehydes, ketones, and imines and to undergo transfer hydrogenations (Figure 1, top center).[8] Iron and cobalt complexes with

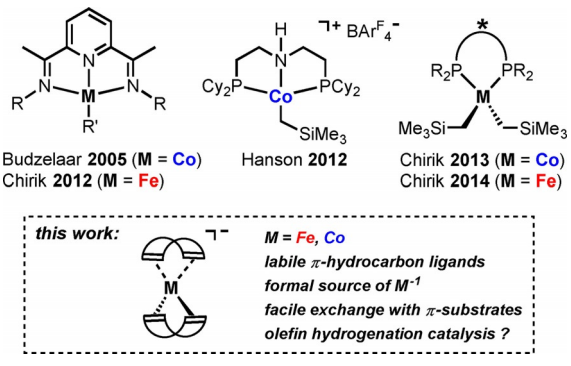


Figure 1. Cobalt- and iron-based hydrogenation catalysts (top) and the design concept of alkene metalate catalysts (bottom). $BAr^F{}_4^-$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

[a] *P. Büschelberger, Prof. R. Wolf*
Institute of Inorganic Chemistry, University of Regensburg
Universitätsstr. 31, 93040 Regensburg (Germany)
E-mail: robert.wolf@ur.de

[b] *Dr. D. Gärtner, E. Reyes-Rodriguez, Prof. A. Jacobi von Wangelin*
Institute of Organic Chemistry, University of Regensburg
93040 Regensburg (Germany)
E-mail: axel.jacobi@ur.de

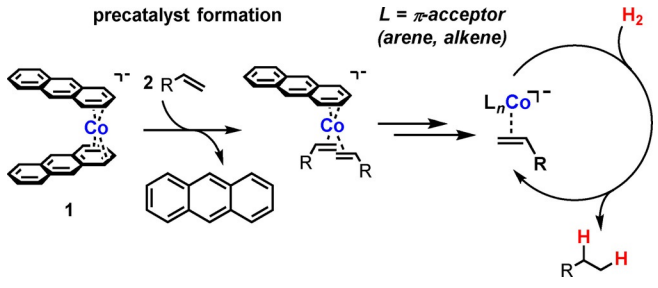
[c] *F. Kreyenschmidt, Prof. K. Koszinowski*
Institut für Organische und Biomolekulare Chemie
Georg-August-Universität Göttingen, Tammannstr. 2
37077 Göttingen (Germany)

Supporting information and ORCID identification number from the author of this article are available on the WWW under http://dx.doi.org/10.1002/chem.201605222.

bis(phosphine) ligands were also used for (asymmetric) alkene hydrogenation (Figure 1, top right), whereas a catalyst with a tridentate tris(phosphane) (=triphos) ligand was shown to reduce esters and carboxylic acids.[9,10] To date, there have been many more examples, especially for PNP pincer complexes, that show impressive catalytic activities.[11] Recently, the groups of Kempe and Kirchner used PNP pincer cobalt and iron complexes for selective hydrogenations of polar bonds with high tolerance of other unsaturated bonds.[12] Moreover, effective cobalt catalysts based on NNP, PBP, and CCC pincers have been reported.[13–15]

Arenes are one of the most abundant and versatile classes of unsaturated organic compounds and also entertain a rich coordination chemistry with low-valent transition metals.[16,17] Our groups recently initiated a research program with the aim of developing metalate catalysts with simple and cheap arenes as stabilizing ligand motifs (Figure 1, bottom).[18] Initial experiments focused on homoleptic bis(η^4-anthracene) metalates **1** (M=Co) and **2** (M=Fe) originally reported by Ellis and co-workers.[19,20] The closed-shell 18-electron complex **1** and the open-shell 17-electron complex **2** constitute two isolable representatives of homogeneous Fe^- and Co^- sources.[17]

The bis(η^4-anthracene)metalates **1** and **2** exhibited good activity in hydrogenations of various alkenes under mild conditions; cobaltate **1** was also active in catalytic hydrogenations of alkynes, ketones, and imines.[18] Based on our preliminary mechanistic investigations with the precatalysts **1** and **2**, we postulated a new catalytic approach to hydrogenation reactions that involved 1) facile synthetic access to a variety of modular catalyst compositions from simple starting materials (alkene/arene, metal salt, reductant); 2) the presence of highly reduced, anionic iron or cobalt species, providing sufficient reducing power for the key H_2 activation; and 3) the presence of a cheap hydrocarbon ligand that could be easily replaced with structurally very similar substrates of olefin hydrogenations. The exchange of labile π ligands with the substrates is redox-neutral; requires only little structural reorganization; and can, in principle, be traceless, if the ligands undergo complete hydrogenation themselves under the reaction conditions (Scheme 1). In an effort to explore the scope of this new mechanistic paradigm further, we prepared a series of monoanionic alkene/arene metalates (M=Co, Fe) and studied their catalytic activity in alkene hydrogenations. Herein, we give a full account of these catalytic studies and describe the results of reaction monitoring and poisoning experiments designed to reveal the catalyst activation step and the homo- or heterogeneous nature of the catalytically active species.

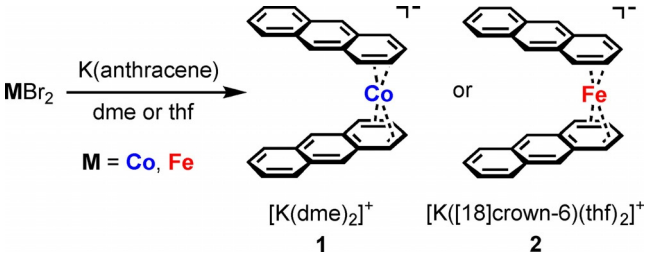


Scheme 1. Catalytic concept: activation of arene metalate precatalysts for hydrogenation reactions by π-ligand exchange with olefinic substrates.

Results and Discussion

Precatalyst syntheses

The potassium bis(η^4-anthracene)metalates **1** (M=Co) and **2** (M=Fe) were prepared in good yields, according to the method by Ellis and co-workers, through the reduction of metal dibromides with potassium in the presence of anthracene (Scheme 2).[19–21] In a similar manner, treatment of the in

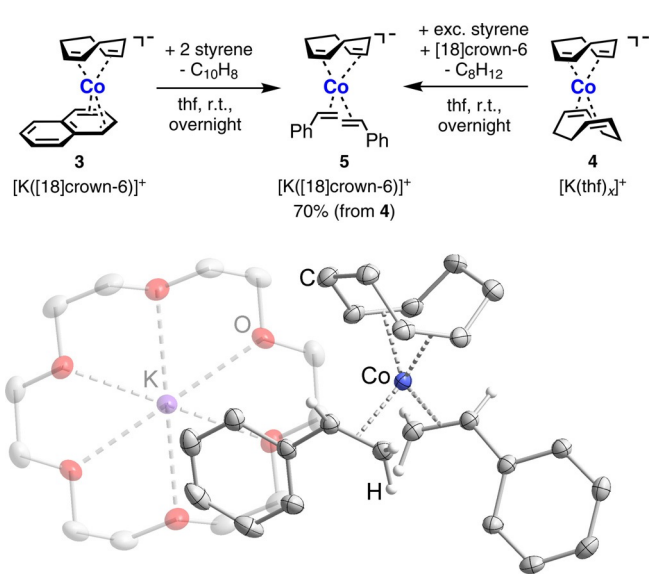


Scheme 2. Synthesis of bis(anthracene) metalates **1** and **2**;[19–21] dme=dimethoxyethane.

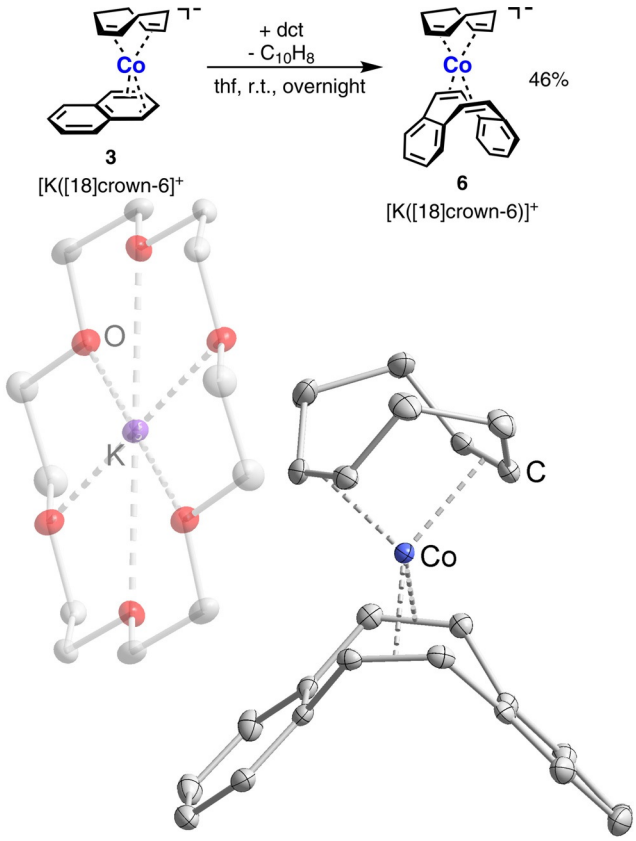
situ prepared [Co(η^4-naphthalene)$_2$]$^-$ with one equivalent of 1,5-cyclooctadiene (cod) gave the heteroleptic complex [K([18]crown-6)][Co(η^4-naphthalene)(η^4-cod)] (**3**).[22] Following a protocol of Jonas and co-workers, we synthesized homoleptic [K(thf)$_x$][Co(η^4-cod)$_2$] (**4**) by the reduction of cobaltocene with a slight excess of potassium in the presence of cod (3 equiv) in THF.[23] Upon ligand exchange of **3** and **4** with styrene, we succeeded in the first preparation of the heteroleptic complex [K([18]crown-6)][Co(η^4-cod)(η^2-styrene)$_2$] (**5**), which constituted a potential intermediate of styrene hydrogenations with cobaltate precatalysts (see below).

Reaction of **3** with 2.2 equivalents of styrene in THF at room temperature gave the bis(η^2-styrene) complex **5** in 61% yield (Scheme 3, top). The analogous reaction of **4** with styrene in THF at room temperature required a large excess of styrene (30 equiv) and addition of [18]crown-6 to allow the isolation of bis(η^2-styrene) complex **5** in 70% yield. Isolation of a solid product was not possible in the absence of the crown ether. The formation of a putative homoleptic complex [Co(η^2-styrene)$_4$]$^-$ was not observed. Complex **5** crystallized as bright orange blocks from a solution in THF layered with *n*-hexane and was characterized by single-crystal XRD (Scheme 3, bottom), NMR spectroscopy, and elemental analysis. The compound is very air sensitive. Exposure of solid **5** to air is followed by immediate decomposition to a dark brown solid. A dark precipitate is formed in solution upon contact with air or moisture.

In the molecular structure of **5**, the coordination environment of the cobalt atom is distorted tetrahedral with a twist angle of 56.3°, which is somewhat smaller than that for



Scheme 3. Synthesis and molecular structure of **5**. Ellipsoids are at the 50% probability level; H atoms are omitted for clarity.



Scheme 4. Synthesis and molecular structure of **6**. Ellipsoids are at the 50% probability level; H atoms are omitted for clarity.

[K([2,2,2]cryptand)][Co(η^4-cod)$_2$] (67.3°) reported by Ellis et al.[19b] The bite angle of the cod ligand is 90.0(3)°, and the angle between the two styrene ligands and Co is 104.3(3)°. The average C=C bond length of the styrene ligands is 1.423(1) Å, which is 0.08 Å longer than that of free styrene.[24]

The ^{1}H NMR spectrum of **5** ([D$_8$]THF) shows two sets of signals with different intensities, which indicates the presence of a major and a minor isomer in solution (Figure S1 in the Supporting Information). These isomers are likely to arise from species with differing relative orientations of the phenyl rings, but the same overall composition.[25] According to ^{1}H NMR integration, the ratio between the major and minor isomers is 4:1.

Similar to the preparation of **5**, [K([18]crown-6)][Co-(η^4-cod)(η^4-dct)] (**6**; dct = dibenzo[*a*,*e*]cyclooctatetraene), containing the rigid, nonplanar, tub-like diene ligand dct,[26,27] was synthesized by adding one equivalent of dct to **3** in THF at room temperature (Scheme 4, top). Ligand exchange is incomplete; thus, complex **6** could not be obtained as a pure compound. Various samples were contaminated with a minimum of 18% [K([18]crown-6)][Co(η^4-dct)$_2$], even after several recrystallizations.

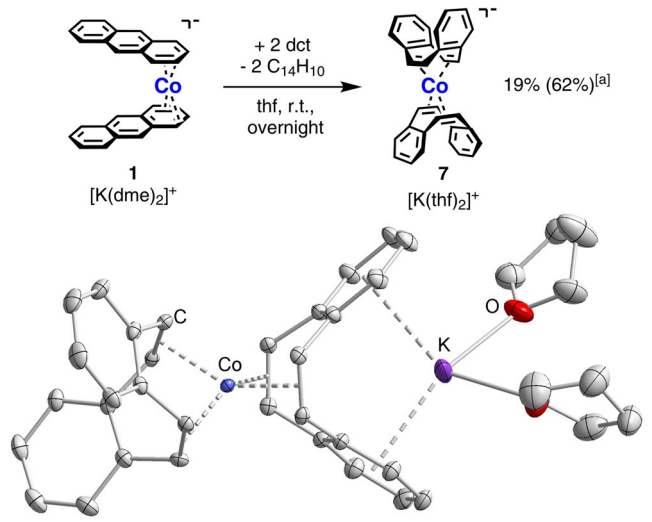
X-ray-quality crystals of yellow–orange **6** were obtained from a solution in THF layered with diethyl ether. The crystallographically determined molecular structure (Scheme 4, bottom) is similar to those of **5** and [K([2,2,2]cryptand)][Co(η^4-cod)$_2$].[19b] Cobalt has a distorted tetrahedral coordination environment with a twist angle of 59.0°. The average C=C bond length (1.419 Å) of the coordinated dct molecules is very similar to the value found for cod in [K([2,2,2]cryptand)][Co(η^4-cod)$_2$].[19b]

The ^{1}H NMR spectrum of the isolated product mixture recorded in [D$_8$]THF corroborates the composition of **6**. The spectrum clearly shows one set of signals assigned to **6** with the expected broad multiplets for dct and cod ligands in a 1:1 ratio, including the typical AA′BB′ spin system arising from the arene protons of dct (multiplets at δ = 6.45 and 6.32 ppm). In addition, a second set of minor signals can be assigned to [K([18]crown-6)][Co(η^4-dct)$_2$].

Treatment of **4** with dct (1.2 equiv) resulted in a mixture of unreacted **4**, the mono-substitution product [K(solv)][Co(η^4-cod)(η^4-dct)], and homoleptic [K(thf)$_2$][Co(η^4-dct)$_2$] (**7**). The formation of such a mixture is probably due to ligand-exchange equilibria, which need to be considered when using dct as a catalyst poison (see below).[27]

The desired homoleptic complex **7** was cleanly produced by reacting **1** with two equivalents of dct in THF at room temperature (Scheme 5, top) and was isolated in 19% yield by recrystallization from THF/*n*-hexane. The relatively low yield is explained by the need for several recrystallizations to remove free anthracene and dct. It seems noteworthy that the yield of **7** considerably increased when styrene (2 equiv) was added to the reaction mixture. In this case, pure **7** was isolated in 62% yield after only one crystallization step from the clear orange reaction solution. The higher yield in this case might be due to the formation of an intermediary styrene complex, such as **5**, which is subsequently converted into **7** by reaction with dct.

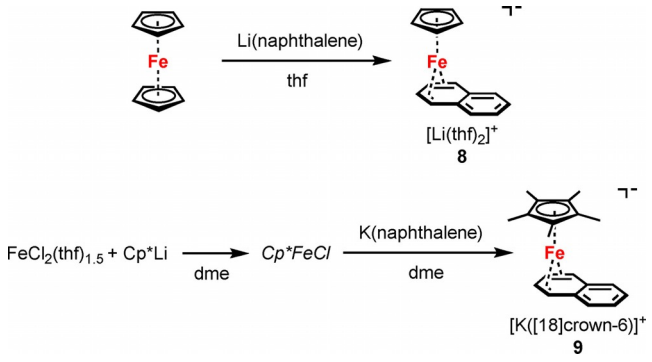
Orange blocks of **7** suitable for X-ray crystallography were obtained from THF/Et$_2$O. Single-crystal X-ray analysis revealed an ion-contact structure (Scheme 5, bottom) in which the coordination environment of cobalt is overall similar to that in



Scheme 5. Synthesis and molecular structure of **7**. Ellipsoids are at the 50% probability level; H atoms are omitted for clarity. [a] Yield of isolated compound obtained in the presence of styrene (2 equiv).

[K([2,2,2]cryptand)][Co(η^4-cod)$_2$].[19b] The twist angle of 55.0(1)° is significantly smaller than that of the former compound (67.3°). One set of dct signals is observed in the ^{1}H NMR spectrum of **7** in [D$_8$]THF, which is consistent with the homoleptic structure of the complex.

The aforementioned series of arene and alkene metalates was complemented with two cyclopentadienyl iron complexes (Scheme 6). [Li(thf)$_2$][CpFe(η^4-naphthalene)] (**8**; Cp = C$_5$H$_5$) was



Scheme 6. Synthesis of cyclopentadienylferrates **8** and **9**.

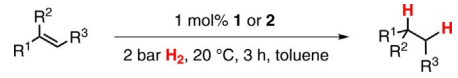
prepared according to a method reported by Jonas from ferrocene by reduction with Li in the presence of naphthalene.[28b] The compound was isolated in 60% yield. Its purity was confirmed by ^{1}H NMR spectroscopy and elemental analysis. The synthesis of the related complex [K([18]crown-6)][Cp*Fe(η^4-naphthalene)] (**9**; Cp* = C$_5$Me$_5$) was reported previously by our group.[29] The reduction of Cp*FeCl, in situ prepared from FeCl$_2$(thf)$_{1.5}$ and Cp*Li in DME, with potassium naphthalenide (2 equiv) in the presence of [18]crown-6 at −60 °C in DME gave **9** in 40% yield.

Catalytic hydrogenations

Our preliminary study of catalytic hydrogenations with 1 mol% of the potassium bis(η^4-anthracene) metalates(1−) **1** and **2** revealed superior activity of cobaltate **1** (Table 1).[18] Various α-, β-, and ring-substituted styrenes were hydrogenated in excellent yields in toluene at 2 bar H$_2$ and room temperature. The conversion of terminal, internal, and di- and trisubstituted aliphatic alkenes and alkynes required a higher catalyst loading, as well as elevated pressure and temperature (5 mol%, 10 bar H$_2$, 60 °C). The 17 valence electron precatalyst **2** exhibited good activity only with unbiased styrenes and 1-alkenes, but fared much poorer with deactivated olefins (electron-donating group (EDG)-substituted styrenes, internal alkenes). Rapid deactivation and unwanted side reactions were observed when the substrate contained ester and free amino groups. No significant effect of the crown ether coordinated to the potassium counterion on the catalytic activity was observed.

We then set out to evaluate the series of monoanionic alkene and arene metalates **1**–**9** as precatalysts in parallelized olefin hydrogenations under identical conditions. Styrene and 1-dodecene (dod) were chosen as model substrates (Table 2).

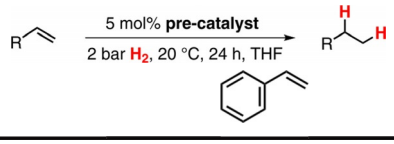
Table 1. Hydrogenation of alkenes with bis(anthracene) complexes **1** and **2**.[a]

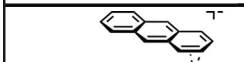
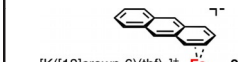
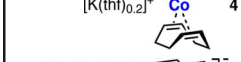
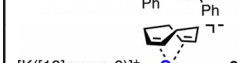
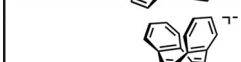
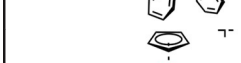
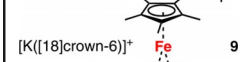
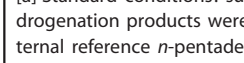


Entry	Alkene	R	Yield [%] 1	2
1		H	95	89
2		4-F	100	100
3		4-CO$_2$Me	89	2
4		2-OMe	95	50
5		3-Me	96	27
6		4-NH$_2$	27	0
7		OMe	97[b]	58
8		OAc	69	–
9		Me	100[c]	–
10		Ph	100[d]	–
11		Me	100[c]	–
12		Ph	100[c]	–
13		CO_2Et	76[d]	–
14		$n=8$	88[d,e]	73[d,e]
15		$n=12$	92[d,e]	72[d,e]
16			92[d]	–
17			100[c]	–
18			63[d,f]	–
19			79[d]	<5[d]
20	Ph—≡—Ph		99[d,g]	<5[d,h]

[a] Standard conditions: substrate (0.5 mmol) in toluene (2 mL); yields of hydrogenation products were determined by quantitative GC versus the internal reference *n*-pentadecane. [b] 2 bar. [c] 60 °C, 2 bar, 24 h. [d] 5 mol% cat., 60 °C, 10 bar, 24 h. [e] <8% 2-alkene. [f] 1-Menthene. [g] Bibenzyl. [h] (*E*)-Stilbene.

Table 2. Hydrogenation of alkenes with precatalysts **1**–**9**.[a]



Precatalyst			
	**1**	94	58 (27)
	**2**	72	15 (7)
	**3**	99	93 (0)
	**4**	93	62 (29)
	**5**	72	85 (8)
	**6**	36	71 (24)
	**7**	0	0 (0)
	**8**	90	84 (15)
	**9**	6	72 (24)

[a] Standard conditions: substrate (0.5 mmol) in THF (2 mL); yields of hydrogenation products were determined by quantitative GC versus the internal reference *n*-pentadecane. In parentheses: yields of alkene isomerization products.

The standard conditions involved reaction with 5 mol% precatalyst under an atmosphere of 2 bar H_2 in THF (due to the better solubility of the complexes compared with that in toluene) at room temperature for 24 h in a stainless-steel Parr™ reactor (Figure 2). In general, styrene was converted in excellent yields with most precatalysts, except **6** and **7**, containing dct as a ligand. This observation is in accordance with the postulate that dct is a competent catalyst poison for homogeneous low-valent monometal species (see above).[27] The strong coordination of dct, and to a lesser extent of cod, to the formal Co^- catalytic center slows down ligand exchange with the substrate styrene. At the same time, dct is not hydrogenated and

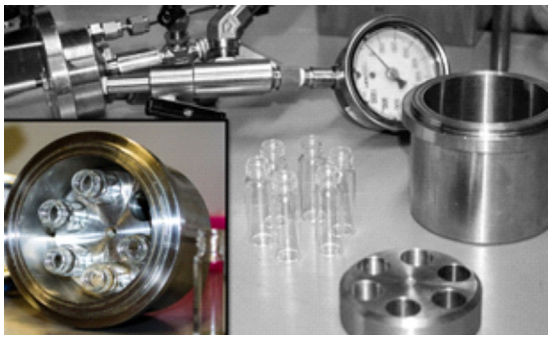


Figure 2. Parallelized hydrogenation setup in Parr™ pressure reactors.

the hydrogenation of cod is slow. The iron complexes **2**, **8**, and **9** showed slightly lower activity.

With dod, similarly good catalytic hydrogenation activities were observed for the precatalysts **1**, **3**, **4**, **5**, and **8** with up to 93% alkene hydrogenation and $<29\%$ alkene isomerization. The best activity and selectivity was determined in the reaction with **3**, which resulted in no observable isomerization to internal alkenes. Again, bis(η^4-dct)cobaltate **7** was catalytically inactive due to strong dct coordination to the Co center, which rendered this complex inert with respect to ligand substitution and ligand hydrogenation.[27] From both model reaction series, it became clear that, despite only small stereoelectronic differences between precatalysts **1**–**9**, the nature of the π-hydrocarbon ligands and the central metal ion had a strong influence on the overall catalytic activity. Precatalysts containing naphthalene or anthracene exhibited generally higher activity, presumably due to the reestablishment of aromaticity upon exchange of the polyarene ligand with the better π^*-accepting alkenes.[16d,30] Cobaltate complexes were more active and selective than their iron counterparts.

Mechanistic studies

The investigated precatalysts **1** and **2** did not react with dihydrogen at ambient temperature (J. Young NMR tube experiment, up to 4 bar H_2, [D_8]THF). We therefore believe that the proposed mechanism of alkene hydrogenation is initiated by the substitution of the labile arene ligand by the π-substrate followed by reaction of the resulting metal catalyst with dihydrogen (Scheme 1). In preliminary studies with bis(η^4-anthracene)cobaltate **1**, we monitored this catalyst activation step by redox-neutral π-ligand exchange in homogeneous phase through NMR spectroscopy experiments. Figure 3 shows the ^{1}H NMR spectra of precatalyst **1** in [D_8]THF after the addition of styrene (20 equiv) to the solution of complex at room temperature and the reaction mixture after 3 h under 4 bar H_2 pressure. The observation of resonances of noncoordinated anthracene in spectra a and b in Figure 3 clearly supports the notion of ligand exchange prior to styrene hydrogenation. The signals of ethylbenzene are apparent in spectrum b in Figure 3. There were no further resonances observed in the high-field section that would indicate the formation of hydride complexes under a dihydrogen atmosphere. The observed line broadening is

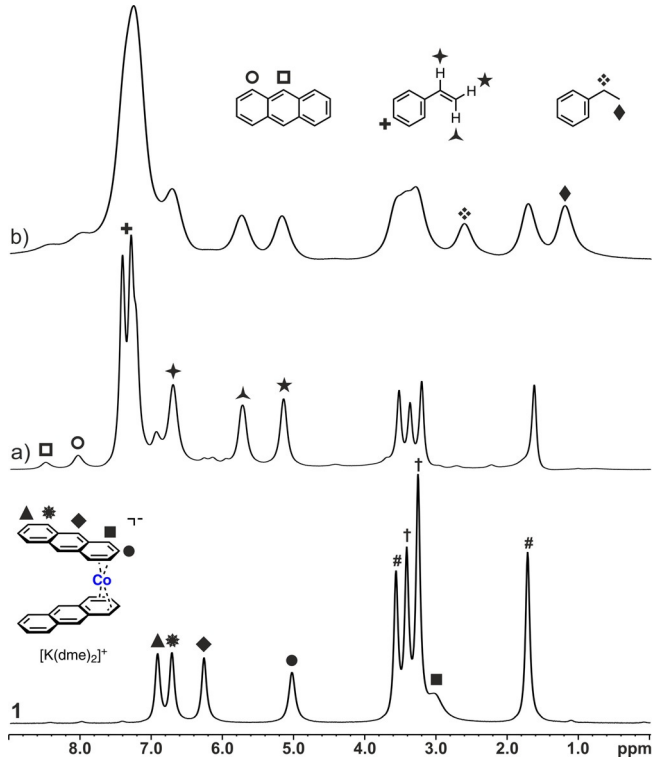


Figure 3. ^{1}H NMR spectroscopy monitoring ([D$_8$]THF: #) of styrene hydrogenation with precatalyst **1** (dme: †): a) 3 h after the addition of styrene (20 equiv); and b) 3 h after the addition of hydrogen.

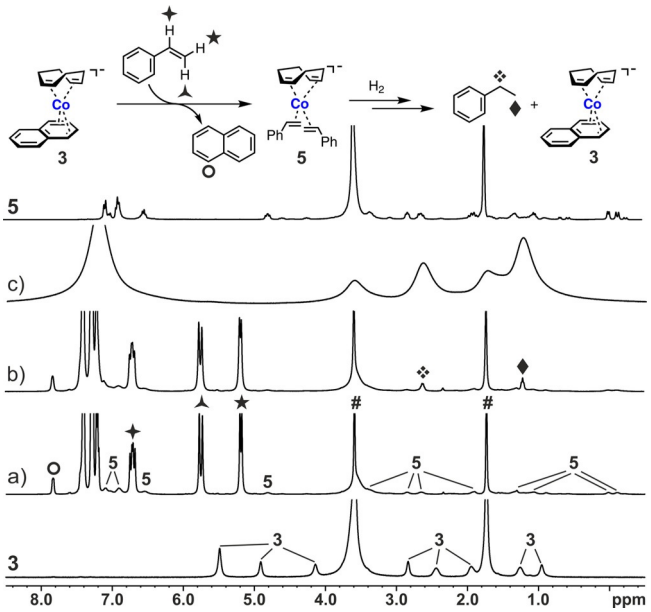


Figure 4. ^{1}H NMR spectroscopy monitoring ([D$_8$]THF: #) of styrene hydrogenation with precatalyst **3**: a) 1.5 h after the addition of styrene (20 equiv), and b) 1.5 and c) 24 h after the addition of hydrogen; the spectrum of a clean sample of **5** is shown on top.

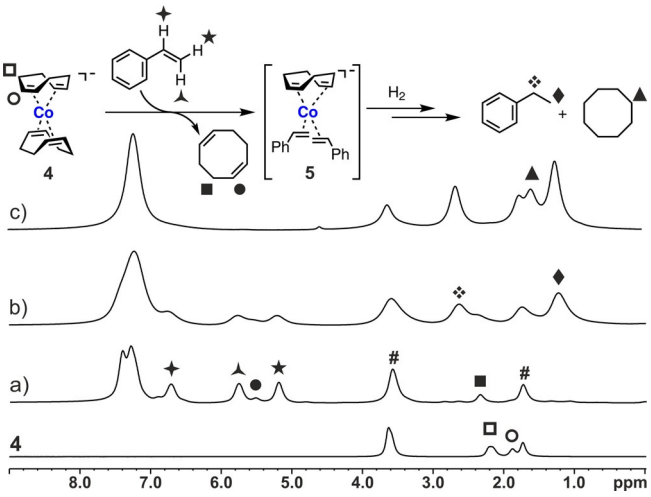


Figure 5. ^{1}H NMR spectroscopy monitoring ([D$_8$]THF: #) of styrene hydrogenation with precatalyst **4**: a) 1.5 h after the addition of styrene (20 equiv), and b) 1.5 and c) 96 h after the addition of hydrogen.

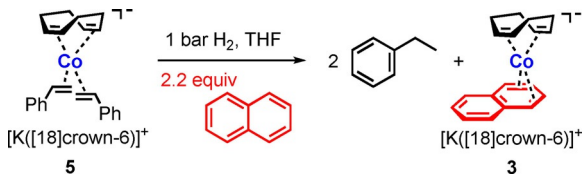
tentatively attributed to the slow formation of cobalt nanoparticles.

We extended the ^{1}H NMR spectroscopy monitoring studies to complexes **3** and **4**. When assuming precatalyst activation by π-ligand exchange of the weakest ligand with the substrate, both **3** and **4** should funnel through the same catalytic intermediate. We tested this mechanistic hypothesis by adding 20 equivalents of styrene to solutions of **3** and **4** in [D$_8$]THF (Figures 4 and 5, respectively). Indeed, the recorded ^{1}H NMR spectra showed the clean formation of the anticipated bis(η^2-styrene)cobaltate **5** in both cases, alongside resonances of free naphthalene (from **3**) and cod (from **4**). This observation strongly supports our mechanistic proposal. Upon application of an atmosphere of H_2 to the NMR-scale reactions, clean conversion of the substrate styrene was observed (Figures 4 and 5). Furthermore, the rate of substrate conversion can be qualitatively assessed from these experiments.

The loss of the styrene π-ligand upon complete hydrogenation with precatalyst **3** after 24 h at 2 bar H_2 and a significantly slower conversion of cod (and naphthalene) resulted in the reconstitution of the original precatalyst **3** by naphthalene coordination, as indicated by the red color of the complex. This complex is difficult to detect in the reaction mixture by ^{1}H NMR spectroscopy, but its formation was clearly proven by a separate experiment (Scheme 7, see below). NMR spectroscopy monitoring of the related **4**-catalyzed hydrogenation of styrene showed full conversion of the substrate and the ligand cod after 96 h (Figure 5). Likewise, as in the case of **1**, NMR spectroscopy monitoring of complexes **3** and **4** did not show any high-field signals of hydride species.

We prepared and fully characterized the catalytically active bis(η^4-styrene) complex **5** (Scheme 3, see above), the role of which as a key intermediate in styrene hydrogenations with alkene cobaltate precatalysts was clear from the NMR spectroscopy experiments discussed above (Figures 4 and 5). Application of an H_2 atmosphere (1 bar) to a bright orange solution of **5** in [D$_8$]THF effected an immediate color change to black due to the hydrogenative consumption of the π-ligands that stabilize this cobaltate species (Figure S4 in the Supporting Information). ^{1}H NMR spectra of the crude mixture and GC analyses

confirmed the instantaneous formation of major amounts of ethylbenzene and cyclooctane and only minor amounts of cyclooctene. With precatalyst **3**, with a much less reactive naphthalene ligand, sufficiently differing rates of hydrogenation, styrene > cod ≫ naphthalene, allowed the reconstitution of the original precatalyst by a release–catch mechanism after the complete hydrogenation of the reactive alkenes (Figure 4, top). A similar outcome was observed in reactions of bis(η^2-styrene) complex **5** with excess naphthalene under 1 bar H_2 pressure (Scheme 7). The chemoselective conversion of styrene and inertness of naphthalene under the mild hydrogenation conditions also led to the formation of **3**, which was isolated as a dark red solid by evaporation of the volatile compounds (Figure S5 in the Supporting Information).



Scheme 7. Demonstration of the ligand release–catch concept by the conversion of **5** into **3** upon chemoselective hydrogenation of styrene.

Because the abovementioned results do not rule out the operation of a heterogeneous catalytic pathway as a background reaction,[27] we turned to reaction progress analyses by quantitative GC analysis of all reaction components (Figure 6). The early reaction phase of the **1**-catalyzed hydrogenation of styrene (< 20 min) showed no induction period and no sigmoidal curvature, which would indicate a nucleation step en route to nanoclusters and nanoparticles. Identical behavior was observed from the hydrogenation of styrene with 5 mol% of precatalyst **3**. Without any detectable induction period, styrene was completely hydrogenated within 45 min at 2 bar H_2. The conversion of the ligands cod and naphthalene largely commenced after the substrate styrene had been entirely converted into ethylbenzene (Figure 7).

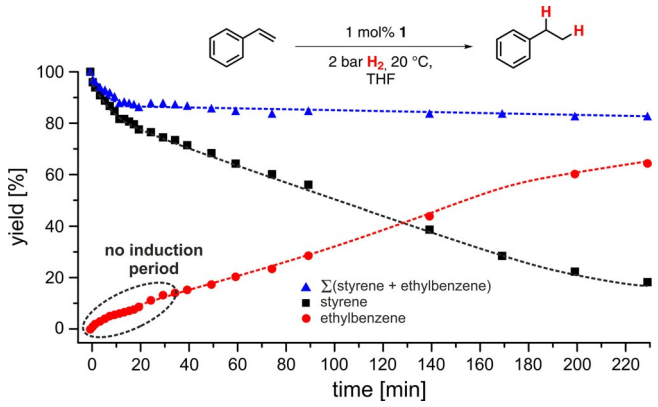


Figure 6. Reaction progress analysis: **1**-catalyzed hydrogenation of styrene under standard conditions without any detectable induction period. Dashed lines are only visual guides.

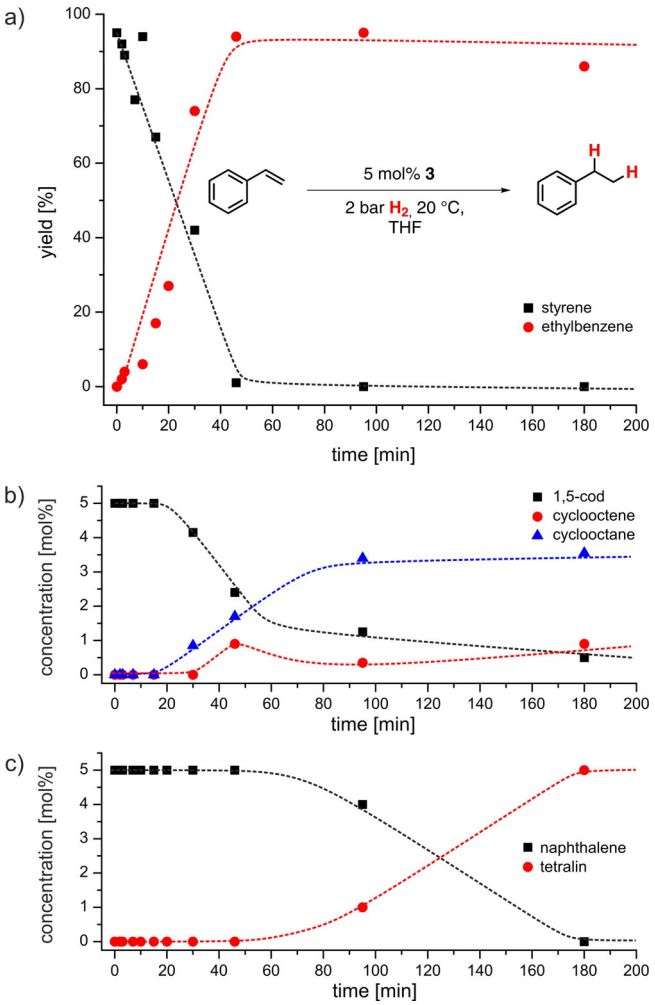


Figure 7. Reaction progress analysis: **3**-catalyzed hydrogenation. Conversions of styrene (a), cod (b), and naphthalene (c). Dashed lines are only visual guides.

To gain further information with respect to the homo- versus heterogeneous nature of the operating catalyst, we performed kinetic poisoning studies with a scavenger reagent selective for mononuclear late-transition-metal species in low oxidation states: dct.[26,27] Upon addition of only 2 mol% dct to a catalytic hydrogenation of styrene with 1 mol% **1** after 35 min (≈17% conversion), complete inhibition of catalyst turnover was observed; this is indicative of a homogeneous mechanism (Figure 8). Inhibition of a potential heterogeneous pathway by amalgamation was not observed.[27]

In an extended study, we performed the two model reactions (styrene, dod) with the two most active precatalysts, **1** and **3**, in the presence of scavengers (Hg, PMe_3, and dct; Table 3). Filtration of the freshly prepared precatalyst solution through a polytetrafluoroethylene (PTFE) syringe filter (pore size < 0.1 μm) prior to the addition of the substrate gave unaltered hydrogenation activity of precatalyst **1**. The addition of 300 mol% mercury only slightly affected the catalyst activity. However, the formation of amalgams between mercury and 3d transition metals is very slow.[31] A pronounced reaction in-

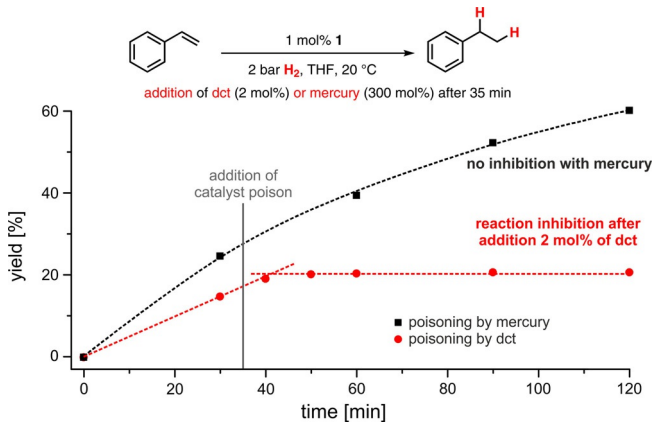
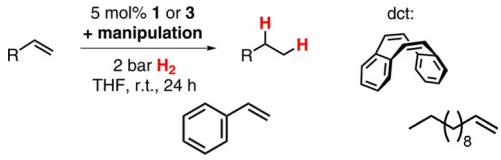


Figure 8. Poisoning studies with precatalyst **1** by the addition of 300 mol% Hg and 2 mol% dct, respectively. Dashed lines are only visual guides.

Table 3. Poisoning experiments of hydrogenations with arene cobaltate precatalysts **1** and **3**.[a]



Catalyst				
manipulation	**1**	**3**	**1**	**3**
none	94	99	58[b]	93
<0.1 µm filter	91	–	46[c]	–
300 mol% Hg	81	75	29[d]	40
1.25 mol% PMe_3	69	91	47[e]	94
11 mol% dct	**14**	81	**3**[f]	66

[a] Standard conditions: substrate (0.5 mmol) in THF (2 mL). [b] 27% isomerization. [c] 34% isomerization. [d] 34% isomerization. [e] 6% isomerization. [f] 31% isomerization.

hibition was only observed by the addition of dct to the catalytic hydrogenation with precatalyst **1**. This suggests the formation of a catalytically inactive homoleptic cobaltate containing dct ligands, which is in perfect agreement with the observation of 0% conversion in alkene hydrogenations with precatalyst **7** (see Table 2). The rapid formation of **7** from **1** and dct was already demonstrated (Scheme 6). Further support comes from ^{1}H NMR spectroscopy experiments of a solution of **7** in THF with 20 equivalents of styrene, which showed no substitution of the dct ligands over the course of 1.5 h (Figure 9).

The observation of good catalytic activity of a mixture of precatalyst **3** and dct in Table 3 is a direct consequence of the presence of the strongly coordinating ligand cod in **3**, which undergoes little or no substitution with equimolar dct. This results in the exclusive substitution of the naphthalene ligand of **3** by dct and formation of the heteroleptic cobaltate **6** as the dominant catalyst species. Our catalytic experiments showed that **6** had good activity in hydrogenations of styrene and dod (Table 2, see above).

Given the anionic nature of the putative catalyst species, we also used negative-ion mode ESI-MS for their selective detection and analysis. Under carefully optimized conditions, this method is capable of detecting even highly reactive organometallics in intact form,[32] including low-valent transition-metal complexes.[33] Indeed, negative-ion mode ESI of a solution of **1** in THF afforded the free $[Co(anthracene)_2]^-$ anion with high signal intensity (Figure S6 in the Supporting Information). In addition, the potassium-bound dimer $[K\{Co(anthracene)_2\}_2]^-$ was also observed. Presumably, this species was not present in the diluted sample solution, but formed due to the concentration increase during the ESI process; similar behavior has been found in other cases as well.[32e,34] ESI of a solution of heteroleptic complex **3** produced not only $[Co(\eta^4\text{-cod})(\eta^4\text{-naphthalene})]^-$, as well as small quantities of $[K\{Co(\eta^4\text{-cod})(\eta^4\text{-naphthalene})\}_2]^-$, but also its homoleptic counterpart $[Co(\eta^4\text{-cod})_2]^-$ (Figure S7 in the Supporting Information). This observation clearly demonstrates the operation of an intermolecular exchange process in solution. ESI-MS analysis of solutions of **4** and **5** also resulted in the detection of the expected anionic complexes as the main signals (Figures S8 and S9, respectively, in the Supporting Information).

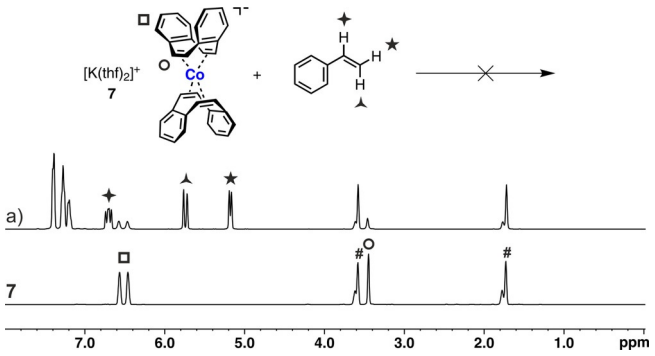


Figure 9. ^{1}H NMR spectrum ([D_8]THF: #) of complex **7**, and a) 1.5 h after the addition of styrene (20 equiv).

After treating solutions of **1** and **3** with an excess of styrene, we observed the formation of cobaltates **10** and **5**, respectively (Figure 10a and b). In both complexes, two styrene molecules replaced one of the originally bound ligands (also compare Figure 4). For the heteroleptic complex **3**, only naphthalene, but not the cod ligand, was released. This behavior is fully in line with the higher binding energy of the latter, which we had already derived from NMR spectroscopic experiments. The reaction of **1** with styrene also gave the homoleptic complex $[Co(styrene)_3]^-$ in very small abundance. The lack of any detectable $[Co(styrene)_4]^-$ suggested that this species did not form in solution or that its stability was too low to survive the ESI process. When **1** was treated with an excess of dod, the replacement of naphthalene by dod proceeded only to a small extent (Figure 10c). This finding is consistent with the lower reactivity of dod observed in the synthetic studies (see above).

Interestingly, the cobaltate complexes incorporating two molecules of styrene were accompanied by ions, the *m/z* ratios of which were shifted by two units to lower values, which clearly resulted from dehydrogenation reactions. According to the principle of microscopic reversibility, the catalytic activity of the cobaltate complexes with respect to hydrogenation re-

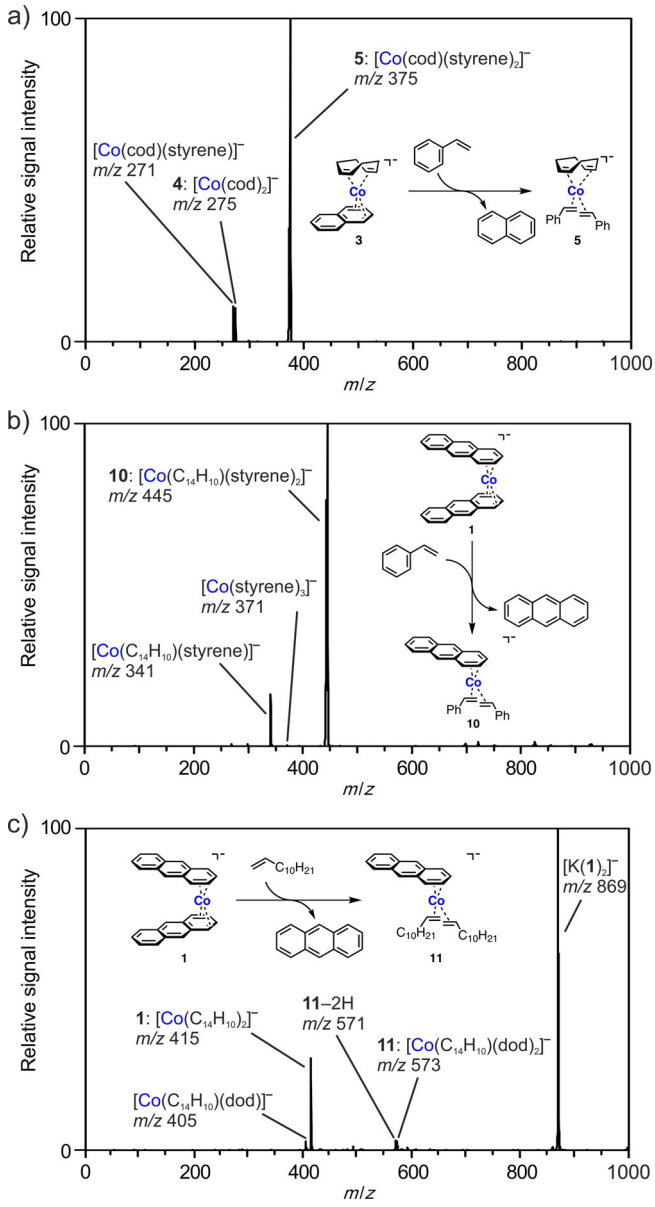


Figure 10. Negative-ion mode ESI mass spectra of the products formed upon reaction of a) **3** (7.5 mM) with 10 equivalents of styrene; b) **1** (7.5 mM) with 20 equivalents of styrene; c) **1** (7.5 mM) with 20 equivalents of 1-dodecene (dod) in THF.

actions implies that they can also catalyze dehydrogenations.[35] The absence of any ions with *m/z* ratios shifted by four units moreover indicates that the dehydrogenation reactions involve a coupling of two styryl units, which most likely result in 1,4-diphenylbuta-1,3-diene. Possibly, this diene originated from the dehydrogenation of one cobalt-bound styrene molecule and the addition of a second cobalt-bound styrene to the resulting C≡C triple bond. Low-valent cobalt complexes are known to catalyze related C–H activation reactions.[36]

Finally, we probed the unimolecular gas-phase reactivity of the mass-selected cobaltate complexes. These experiments have the advantage of excluding any interference from dynamic equilibria, counterion, or solvent effects, which may operate in solution. Gas-phase fragmentation of **3** led to the loss of cod and naphthalene, whereas **5** and **10** only released styrene (Figures S10–S13 in the Supporting Information).

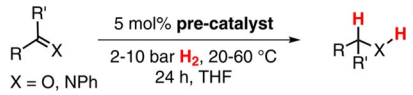
In conclusion, our investigations on catalytic alkene hydrogenations documented the formation of 18 valence electron (18e) bis(alkene) complexes in the reaction mixtures. These species are presumably resting states, which serve as the reservoir for the catalytically active cobalt species. One may speculate that H_2 activation is initiated by loss of an alkene ligand, forming an unsaturated and reactive 16e monoalkene complex.

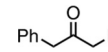
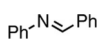
Methodology extensions

We also applied precatalysts **1**–**9** to hydrogenations of ketones and imines. Generally, hydrogenations of such polar unsaturated compounds are accelerated by the presence of a Lewis acidic catalyst in higher oxidation states. However, the precatalyst complexes contain a weakly Lewis acidic K^+ counterion. We observed very poor catalytic activities under standard conditions at 2 bar H_2 and room temperature. Elevated pressure and temperature (10 bar H_2, 60 °C, see Table 4) led to good activity of potassium bis(anthracene)cobaltate **1** in the hydrogenation of dibenzylketone and *N*-benzylideneaniline (>91% yield). The cod-containing complexes **3** and **4** exhibited moderate activity in the ketone hydrogenation (60–65%). Surprisingly, both complexes were rather inactive in the hydrogenation of the imine.

The most active ketone hydrogenation catalyst **1** was subjected to a series of other carbonyl compounds (Table 5).[18] Good catalytic activity was only observed at elevated temperature and pressure. Importantly, the employment of carbonyl compounds as hydrogenation substrates could, in principle, trigger three unwanted side reactions: deprotonation at the α-carbonyl position, direct reduction of the carbonyl moiety by metalate addition or single-electron transfer (SET), and deprotonation of any formed alcohol. Indeed, we have observed the operation of the last two pathways under the present reaction

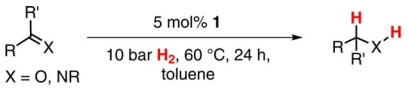
Table 4. Hydrogenation of ketone and imine with precatalysts **1**–**9**.[a]

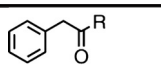
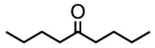
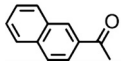
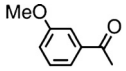
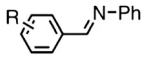
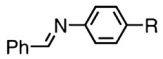


Precatalyst		
1	11 (**91**)	0 (**99**)
2	14 (14)	0 (2)
3	4 (**65**)	0 (15)
4	5 (**60**)	0 (3)
5	5	3 (3)
7	0 (17)	0 (26)
8	6 (4)	0 (15)
9	2 (4)	4 (6)

[a] Standard conditions: substrate (0.5 mmol) in THF (2 mL); yields of hydrogenation products determined by quantitative GC versus the internal reference *n*-pentadecane. Yields from reactions at 10 bar H_2, 60 °C, in parentheses.

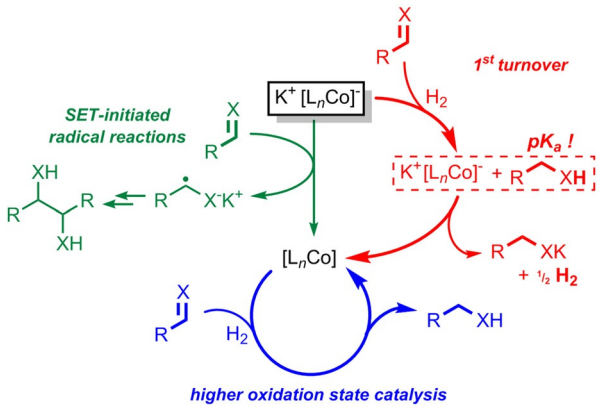
Table 5. Hydrogenation of ketones and imines with cobaltate precatalyst **1**.



Entry	Substrate	R	Yield [%]
1		Me	99, 91[b]
2		Bn[c]	96
3			100
4			88
5			71
6		H	96, 99[b]
7		2-Me	98
8		3-Me	100
9		4-OMe	100
10		CO_2Et	79[d]
11		Br	0

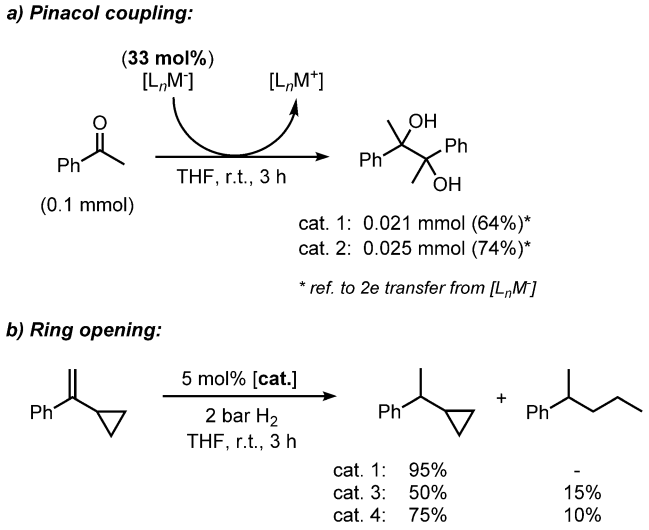
[a] Standard conditions: substrate (0.5 mmol) in toluene (2 mL); yields of hydrogenation products determined by quantitative GC versus the internal reference *n*-pentadecane. [b] Solvent: THF. [c] Bn = benzyl. [d] 7.5 mol% **1**, 70 °C, 10 bar H_2.

conditions. The catalytic hydrogenation reaction generates an acidic proton in the resulting alcohol and amine products, both with pK_a values of about 29 (in DMSO).[37] After the first turnover, this is very likely to alter the catalytic mechanism by catalyst oxidation and H_2 evolution (Scheme 8).[38] Considering catalyst oxidation after direct electron transfer to the ketone or after the first hydrogenation catalysis turnover, we postulate the formation of a cobalt(+I) catalyst that displays lower catalytic activity, and therefore, requires harsher conditions. The formation of dihydrogen was observed by ^{1}H NMR spectroscopy in an equimolar reaction between **1** and 1,3-diphenyl-2-propanol. Furthermore, a transfer hydrogenation experiment between 4-methylstyrene and 4 equivalents of 1,3-diphenyl-2-propanol afforded 18% yield of ethylbenzene in the presence of 5 mol% **1**.[18]



Scheme 8. Change of mechanism, H_2 evolution, and catalyst oxidation in the hydrogenation of polar substrates.

Direct SET reduction of acetophenone was observed in the presence of **1** and **2**, respectively, to give the pinacol product in good yields (Scheme 9a).[39] With an olefinic radical probe, such behavior was much less pronounced under standard reaction conditions (Scheme 9b). Catalyst **1** showed no ring opening of α-cyclopropylstyrene, but clean hydrogenation of the double bond. Significant radical character was observed in reactions with the cod-bearing catalysts **3** and **4**.



Scheme 9. Observation of radical side reactions.

Conclusions

We showed that bis(η^4-anthracene)metalates **1** and **2** exhibited good activity in catalytic hydrogenation reactions. The bis(η^4-anthracene)cobaltate **1** was a highly active precatalyst for the hydrogenation of a variety of alkenes, ketones and, imines at ambient H_2 pressure and temperatures. The iron analogue, **2**, showed significantly lower catalytic activity.[18]

In a greatly extended study, we have now compared the catalytic activity of **1** and **2** with that of structurally related alkene and arene metalates **3**–**9**. Complexes **5**–**7** were synthesized for the first time. Complexes **1**–**6**, as well as **8** and **9**, were competent precatalysts for the hydrogenation of alkenes under mild conditions. Unlike **1** and **2**, bis(η^4-styrene) complex **5** rapidly reacts with H_2 (1 bar) with release of ethylbenzene. Kinetic studies and ^{1}H NMR spectroscopy monitoring experiments presented herein now lead to the conclusion that the olefin hydrogenation reaction is initiated by the substitution of one labile arene ligand by a π-acceptor substrate. Furthermore, we proved the concept of the release–catch mechanism of catalyst activation by ^{1}H NMR spectroscopy monitoring of π-ligand exchange reactions and by negative-ion mode ESI-MS investigations. The selective formation of a bis(η^2-monoalkene)cobaltate is believed to be key to rapid dihydrogen activation because, unlike coordinated cod and naphthalene or anthracene, the monoalkene ligands of such a species are readily hydrogenated.

Poisoning experiments with dct and mercury supported the hypothesis that the active species had a homogeneous nature. The validity of the Crabtree dct test for cobaltate complexes was confirmed by the formation of **7** and **6**. Bis(η^4-dct) complex **7** was not a competent precatalyst, presumably because the dct ligands were not substituted or hydrogenated under the reaction conditions. By contrast, complex **6** still showed some catalytic activity because of its more labile cod ligand.

Extensions to polar substrates (ketones and imines) were also investigated, but these reactions most likely proceeded through a different mechanism than that of alkene hydrogenations because of the operation of unwanted radical and acid–base reactions. Both pathways most likely involve oxidation of the metalate complexes to a higher oxidation manifold, which ultimately exhibits lower catalytic activity. However, the rapid onset of SET reactions with polar substrates appears to be a promising entry to future studies of radical reactions catalyzed by such alkene metalates. The general concept of redox-neutral alkene ligand substitution with metalate complexes has only recently been tapped for catalytic reaction developments. Further variations of this motif in the context of small-molecule hydrogenation and hydrofunctionalization will be reported in due course.

Experimental Section

General procedures

All experiments were performed under an atmosphere of dry argon by using standard Schlenk and glove box techniques. Solvents were purified, dried, and degassed by standard techniques. NMR spectra were recorded (300 K) with Bruker Avance 300 and Avance 400 spectrometers internally referenced to residual solvent resonances. NMR spectroscopy assignments were based on COSY, HSQC, and NOESY 2D NMR spectroscopy experiments. Melting points were measured on samples in sealed capillaries and are uncorrected. Elemental analyses were determined by the Analytical Department of the University of Regensburg.

Precatalysts **1**,[19,21] **2**,[20] **3**,[22] **4**,[23] **8**,[28b] and **9**[29] were prepared according to procedures reported in the literature. The THF content of **4** varied, according to ^{1}H NMR spectroscopy and elemental analysis ($x = 0.15$–0.3).

[K([18]crown-6)][Co(η^4-cod)(η^2-styrene)$_2$] (5)

Method 1 (from 3): A solution of styrene (57.4 mg, 0.551 mmol, 2.20 equiv) in THF (2 mL) was added dropwise to a solution of **3** (150 mg, 0.251 mmol, 1.00 equiv) in THF (5 mL) at room temperature. The resulting clear, orange solution was stirred overnight. Afterwards, the solvent was removed in vacuo. The solid, orange residue was washed several times with diethyl ether (10 mL overall). The crude product was dissolved in THF (5 mL); the resulting solution was filtered and concentrated. Orange, X-ray-quality crystals of **5** (105 mg, 62%) formed after layering of the solution in THF with *n*-hexane (1:2). M.p. 125 °C (decomp); ^{1}H NMR (300.13 MHz, [D$_8$]THF): major isomer: $\delta = -0.15$ (d, $J = 11.1$ Hz, 2H; styrene CH$_2$), -0.02 (d, $J = 7.3$ Hz, 2H; styrene CH$_2$), 0.92–1.16 (m, 2H; cod CH), 1.22–1.44 (m, 2H; cod CH$_2$), 1.78–2.04 (m, 2H; cod CH$_2$), 2.62 (dd, $J = 13.4$, 7.9 Hz, 2H; cod CH$_2$), 2.27–2.93 (m, 2H; cod CH), 3.27–3.39 (m, 2H; cod CH$_2$), 4.77 (dd, $J = 11.1$, 7,3 Hz, 2H; styrene CH), 6.38–6.64 (m, 2H; styrene *p*-Ar-H), 6.89 (t, $J = 7.4$ Hz, 4H; styrene *m*-Ar-H), 7.15–6.97 ppm (m, 4H; styrene *o*-Ar-H); minor isomer: -0.63 (d, $J = 6.8$ Hz), -0.26 (d, $J = 11.2$ Hz), 0.55 (d, $J = 11.2$ Hz), 0.65 (d, $J = 6.8$ Hz), 0.87–0.89 (m), 2.29–2.39 (m), 3.02–3.10 (m), 4.17–4.27 (m), 4.50–4.62 ppm (m); ^{13}C{^{1}H} NMR (100.61 MHz, 300 K, [D$_8$]THF): $\delta =$ 29.4 (cod CH$_2$), 37.8 (cod CH$_2$), 47.0 (styrene CH$_2$), 60.4 (styrene CH), 71.0 ([18]crown-6 CH$_2$), 81.6 (cod CH), 89.5 (cod CH), 117.7 (styrene *p*-Ar-CH), 124.2 (styrene *m*-Ar-CH), 127.0 (styrene *o*-Ar-CH), 154.6 ppm (styrene C$_{quart.}$-Ar); minor isomer: $\delta = 29.0$, 29.4, 38.5, 117.6, 118.0, 124.4, 126.9, 127.5 ppm; elemental analysis calcd (%) for $C_{36}H_{52}O_6CoK$ (678.84): C 63.70, H 7.72; found: C 63.04, H 7.47.

Method 2 (from 4): Styrene (2.09 mL, 18.2 mmol, 30.0 equiv) was added to a solution of **4** (200 mg, 0.608 mmol, 1.00 equiv) and [18]crown-6 (162.5 mg, 0.608 mmol, 1.00 equiv) in THF (5 mL) at room temperature. The resulting clear, orange solution was stirred for 5 h. All volatile components were removed in vacuo afterwards. The resulting orange solid was washed with diethyl ether (5 mL), taken up in THF, and layered with *n*-hexane. Compound **5** was obtained as orange blocks by storage at room temperature (290 mg, 70%). The ^{1}H NMR spectrum of the sample prepared by method 2 was identical to that prepared by method 1.

[K([18]crown-6)][Co(η^4-cod)(η^4-dct)] (6)

A solution of dct (73.6 mg, 0.360 mmol, 1.50 equiv) in THF (7 mL) was added dropwise to **3** (143.7 mg, 0.240 mmol, 1.00 equiv) in THF (10 mL) at room temperature. The resulting clear, yellow solution was stirred overnight. Afterwards, the solvent was removed in vacuo. The yellow–orange solid residue was washed three times with diethyl ether (15 + 10 + 5 mL). The crude product was dissolved in THF (7 mL) and filtered. Yellow–orange, X-ray-quality crystals of **6** formed after layering the filtrate with diethyl ether (1:1). Compound **6** was contaminated with varying amounts of **7** that could not be removed by recrystallization. A minimum of 18% impurity was observed. Yield: 76.3 mg (46%), referring to a mixture of **6** (82%) and **7** (18%); ^{1}H NMR (400.13 MHz, [D$_8$]THF): $\delta = 1.98$–2.06 (m, 4H; CH$_2$ of cod or dct), 2.24–2.34 (m, 4H; CH$_2$ of cod or dct), 2.71 (br s, 4H; alkene-CH of cod or dct), 2.93 (s, 4H; alkene-CH of cod or dct), 6.27–6.36 (m, 4H; Ar-H), 6.42–6.49 ppm (m, 4H; dct Ar-H); in addition, one set of signals assigned to the [Co(dct)$_2$]$^-$ anion of [K([18]crown-6)][Co(η^4-dct)$_2$] was observed.

[K(thf)$_2$][Co(η^4-dct)$_2$] (7)

Method 1 (from 1): A solution of dct (733 mg, 3.59 mmol, 2.00 equiv) in THF (60 mL) was added to a solution of **1** (1.14 g, 1.79 mmol, 1.00 equiv) in THF (100 mL) at -80 °C, and the mixture was slowly warmed to room temperature. The resulting black suspension was concentrated, filtered, and layered with *n*-hexane. A dark precipitate was isolated after 3 days. Repeated recrystallization (3× from THF/*n*-hexane 1:3) was necessary to remove remaining dct and anthracene. Compound **7** was obtained as bright orange crystals (220 mg, 19%). M.p. 112 °C (decomp); ^{1}H NMR (400.13 MHz, [D$_8$]THF): $\delta = 1.77$ (m, THF), 3.45 (s, 8H; dct CH), 3.61 (m, THF), 6.45–6.48 (m, 8H; dct Ar-H), 6.56–6.58 ppm (m, 8H; dct Ar-H); ^{13}C{^{1}H} NMR (100.61 MHz, 300 K, [D$_8$]THF): $\delta = 26.3$ (THF), 68.1 (THF), 87.6 (CH), 122.8 (C-Ar), 124.9 (C-Ar), 152.9 ppm (C$_{quart}$-Ar); elemental analysis calcd (%) for $C_{40}H_{40}O_2CoK$ (650.79): C 73.82, H 6.20; found: C 73.45, H 6.04.

Method 2 (from 1): A solution of dct (600 mg, 2.94 mmol, 2.00 equiv) and styrene (612 mg, 5.88 mmol, 4.00 equiv) in THF (50 mL) was added to a solution of **1** (932 mg, 1.47 mmol,

1.00 equiv) in THF (120 mL) at room temperature. The mixture was stirred overnight and filtered. Concentration of the clear orange solution to 60 mL and layering with diethyl ether (1:1) gave **7** as orange crystals. The isolated compound had the composition $[K(thf)_{0.75}][Co(\eta^4\text{-dct})_2]$ after drying in vacuo for 1 h, according to ^{1}H NMR spectroscopy and elemental analysis. Yield: 512 mg (62%). The ^{1}H NMR spectrum of samples prepared by this method was identical to that of samples prepared by method 1.

General procedure for hydrogenation reactions

A dry 5 mL vial with a screw cap and PTFE septum was charged with a magnetic stirrer bar and a solution of the precatalyst (0.025 mmol) in THF (1 mL). After adding a solution of the substrate (0.5 mmol) in THF (1 mL) with a pipette, the vial was closed and the septum was punctured with a short needle (Braun). The vial was placed into a high-pressure reactor (Parr Instr.), which was sealed, removed from the glove box, placed on a magnetic stirrer plate, and purged with hydrogen. After 24 h at room temperature under an atmosphere of hydrogen (2 bar), the pressure was released, the vial was removed, and the reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (1 mL). For quantitative GC-FID analysis, *n*-pentadecane was added as an internal standard. The mixture was extracted with diethyl ether and the combined organic layers were dried over Na_2SO_4.

General procedure for poisoning and filtration experiments

The poisoning experiments were carried out according to the general procedure for hydrogenation reactions. In the case of poisoning with PMe_3, the precatalyst was dissolved in THF (0.5 mL) before a stock solution of the phosphane (0.5 mL; $c = 1.25 \times 10^{-2}$ mol L^{-1}) in THF was added. For experiments with dct, the catalyst poison was added to the solid precatalyst before dissolving both together in THF. When using elementary mercury as the catalyst poison, the liquid metal was added directly to the dissolved precatalyst with a syringe before the addition of the substrate solution. For the filtration experiments, the precatalyst solution was filtered through a PTFE syringe filter (Puradisc 13, Whatman, pore size < 0.1 μm) before the substrate solution was added.

General procedure for ^{1}H NMR spectroscopy monitoring

Reaction monitoring by ^{1}H NMR spectroscopy was carried out in a sealed J. Young NMR tube. A solution of the precatalyst (5×10^{-3} mmol, 5 mol%) in [D_8]THF (0.5 mL) was transferred to a NMR tube, and the first ^{1}H NMR spectrum was measured. In the glove box, styrene (10 mg, 0.1 mmol, 1.0 equiv) was added to the solution of precatalyst. After storing the sample for 90 min, the second ^{1}H NMR spectrum was recorded. Subsequently, the atmosphere was exchanged with dihydrogen by the freeze–pump–thaw technique. Subsequent spectra were recorded after further 90 min and then at irregular intervals until the substrate was fully consumed or until no further consumption was detected.

General procedure for reaction progress analysis

Reaction progress was monitored in a 50 mL Schlenk flask. A solution of styrene (260 mg, 2.50 mmol, 1.00 equiv) in THF (5 mL) was added to a solution of the precatalyst (0.125 mmol, 5 mol%) in THF (5 mL). For quantitative GC-FID analysis, *n*-pentadecane was added as an internal standard. The reaction was started by replacing the atmosphere in the Schlenk flask by dihydrogen (2 bar). Samples of 0.1 mL were taken at regular intervals through a septum. Each sample was worked up according to the general procedure for hydrogenation reactions. Quantification of starting material and hydrogenation products was performed by GC-FID analysis.

ESI-MS

Sample solutions were transferred into a gas-tight syringe and infused into the ESI source of a HCT quadrupole ion trap mass spectrometer (Bruker Daltonik) at a flow rate of 8 μL min^{-1}. For the ESI process and the transfer of ions into the helium-filled quadrupole ion trap, mild conditions similar to those reported previously were applied.[32] Mass spectra were recorded over a typical range of *m*/*z* 50–1000. Gas-phase fragmentation was accomplished by subjecting the mass-selected ions to excitation voltages of amplitudes, V_{exc}, and allowing them to collide with the helium gas.

X-ray crystallography

The single-crystal XRD data were recorded on an Agilent Technologies SuperNova diffractometer in case of compound **5** and on an Agilent Technologies Gemini Ultra diffractometer in case of **6** and **7**, by using $Cu_{K\alpha}$ radiation for **5** and **6** and $Mo_{K\alpha}$ radiation for **7**. Empirical multiscan and analytical absorption corrections were applied to the data.[40,41] By using Olex2,[42] the structures were solved with SHELXS or SHELXT.[43,44] Least-squares refinements were carried out with SHELXL.[43]

CCDC 1513657, 1513658, and 1513659 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Acknowledgements

This work was generously supported by the Deutsche Forschungsgemeinschaft (DFG: WO 1496/6-1, JA 1107/6-1, KO 2875/8-1) and the European Research Council (ERC: 683150). E.R.R. is a doctoral fellow of the Deutsche Bundesstiftung Umwelt (DBU). We thank Christoph Ziegler and Julia Märsch for the preparation and activity studies of complexes **5** and **6** as a part of their B.Sc. projects, Matteo Villa for the preparation of α-cyclopropylstyrene, and Stefan Pelties for crystallographic support.

Keywords: cobalt · hydrogenation · iron · reaction mechanisms · transition metals

[1] a) *Catalytic Hydrogenation* (Ed.: L. Cerveny), Elsevier, Amsterdam, **1986**; b) *The Handbook of Homogeneous Hydrogenation* (Eds.: J. G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim, **2007**.

[2] a) J. A. Osborn, F. H. Jardine, J. F. Young, G. Wilkinson, *J. Chem. Soc.* **1966**, 1711–1732; b) W. S. Knowles, M. J. Sabacky, B. D. Vineyard, D. J. Weinkauff, *J. Am. Chem. Soc.* **1975**, *97*, 2567–2568; c) H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, A. F. England, T. Ikariya, R. Noyori, *Angew. Chem. Int. Ed.* **1998**, *37*, 1703–1707; *Angew. Chem.* **1998**, *110*, 1792–1796; d) Á. Molnár, A. Sárkány, M. Varga, *J. Mol. Catal. A* **2001**, *173*, 185–221.

[3] a) M. Raney, US patent 1628190, **1927**; b) I. M. Angulo, A. M. Kluwer, E. Bouwman, *Chem. Commun.* **1998**, 2689–2690; c) S. Kuhl, R. Schneider, Y. Fort, *Organometallics* **2003**, *22*, 4184–4186; d) T. Hibino, K. Makino, T. Sugiyama, Y. Hamada, *ChemCatChem* **2009**, *1*, 237–240.

[4] a) W. Hess, J. Treutwein, G. Hilt, *Synthesis* **2008**, *40*, 3537–3562; b) M. S. Holzwarth, B. Plietker, *ChemCatChem* **2013**, *5*, 1650–1679; c) I. Bauer,

H. J. Knölker, *Chem. Rev.* **2015**, *115*, 3170 – 3387; d) P. Röse, G. Hilt, *Synthesis* **2016**, *48*, 463 – 492.
[5] S. Enthaler, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2008**, *47*, 3317 – 3321; *Angew. Chem.* **2008**, *120*, 3363 – 3367.
[6] Q. Knijnenburg, A. D. Horton, H. van der Heijden, T. M. Kooistra, D. G. H. Hetterscheid, J. M. M. Smits, B. de Bruin, P. H. M. Budzelaar, A. W. Gal, *J. Mol. Catal. A* **2005**, *232*, 151 – 159.
[7] a) S. Monfette, Z. R. Turner, S. P. Semproni, P. J. Chirik, *J. Am. Chem. Soc.* **2012**, *134*, 4561 – 4564; b) R. P. Yu, J. M. Darmon, J. M. Hoyt, G. W. Margulieux, Z. R. Turner, P. J. Chirik, *ACS Catal.* **2012**, *2*, 1760 – 1764.
[8] a) G. Zhang, B. L. Scott, S. K. Hanson, *Angew. Chem. Int. Ed.* **2012**, *51*, 12102 – 12106; *Angew. Chem.* **2012**, *124*, 12268 – 12272; b) G. Zhang, K. V. Vasudevan, B. L. Scott, S. K. Hanson, *J. Am. Chem. Soc.* **2013**, *135*, 8668 – 8681; c) G. Zhang, S. K. Hanson, *Chem. Commun.* **2013**, *49*, 10151 – 10153.
[9] a) M. R. Friedfeld, M. Shevlin, J. M. Hoyt, S. W. Krska, M. T. Tudge, P. J. Chirik, *Science* **2013**, *342*, 1076 – 1080; b) M. R. Friedfeld, G. W. Margulieux, B. A. Schaefer, P. J. Chirik, *J. Am. Chem. Soc.* **2014**, *136*, 13178 – 13181; c) J. M. Hoyt, M. Shevlin, G. W. Margulieux, S. W. Krska, M. T. Tudge, P. J. Chirik, *Organometallics* **2014**, *33*, 5781 – 5790.
[10] T. J. Korstanje, J. I. van der Vlugt, C. J. Elsevier, B. de Bruin, *Science* **2015**, *350*, 298 – 302.
[11] For selected examples, see: a) X. Yang, *ACS Catal.* **2011**, *1*, 849 – 854; b) G. Bauer, K. A. Kirchner, *Angew. Chem. Int. Ed.* **2011**, *50*, 5798 – 5800; *Angew. Chem.* **2011**, *123*, 5918 – 5920; c) R. Langer, G. Leitus, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* **2011**, *50*, 2120 – 2124; *Angew. Chem.* **2011**, *123*, 2168 – 2172; d) R. Xu, S. Chakraborty, H. Yuan, W. D. Jones, *ACS Catal.* **2015**, *5*, 6350 – 6354; e) A. Z. Spentzos, C. L. Barnes, W. H. Bernskoetter, *Inorg. Chem.* **2016**, *55*, 8225 – 8233.
[12] a) S. Rösler, J. Obenauf, R. Kempe, *J. Am. Chem. Soc.* **2015**, *137*, 7998 – 8001; b) N. Gorgas, B. Stöger, L. F. Veiros, K. Kirchner, *ACS Catal.* **2016**, *6*, 2664 – 2672.
[13] a) D. Srimani, A. Mukherjee, A. F. G. Goldberg, G. Leitus, Y. Diskin-Posner, L. J. W. Shimon, Y. Ben David, D. Milstein, *Angew. Chem. Int. Ed.* **2015**, *54*, 12357 – 12360; *Angew. Chem.* **2015**, *127*, 12534 – 12537; b) Z. Shao, S. Fu, M. Wei, S. Zhou, Q. Liu, *Angew. Chem. Int. Ed.* **2016**, *55*, 14653 – 14657; *Angew. Chem.* **2016**, *128*, 14873 – 14877; c) S. Fu, N.-Y. Chen, X. Liu, Z. Shao, S.-P. Luo, Q. Liu, *J. Am. Chem. Soc.* **2016**, *138*, 8588 – 8594.
[14] a) T.-P. Lin, J. C. Peters, *J. Am. Chem. Soc.* **2013**, *135*, 15310 – 15313; b) T.-P. Lin, J. C. Peters, *J. Am. Chem. Soc.* **2014**, *136*, 13672 – 13683.
[15] K. Tokmic, C. R. Markus, L. Zhu, A. R. Fout, *J. Am. Chem. Soc.* **2016**, *138*, 11907 – 11913.
[16] a) S.-B. Choe, K. J. Klabunde, *J. Organomet. Chem.* **1989**, *359*, 409 – 418; b) S. Sun, C. A. Dullaghan, G. B. Carpenter, A. L. Rieger, P. H. Rieger, D. A. Sweigart, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2540 – 2542; *Angew. Chem.* **1995**, *107*, 2734 – 2737; c) S. Sun, L. K. Yeung, D. A. Sweigart, T.-Y. Lee, S. S. Lee, Y. K. Chung, S. R. Switzer, R. D. Pike, *Organometallics* **1995**, *14*, 2613 – 2615; d) J. K. Seaburg, P. J. Fischer, V. G. Young, Jr., J. E. Ellis, *Angew. Chem. Int. Ed.* **1998**, *37*, 155 – 158; *Angew. Chem.* **1998**, *110*, 163 – 167.
[17] For a review, see: J. E. Ellis, *Inorg. Chem.* **2006**, *45*, 3167 – 3186.
[18] D. Gärtner, A. Welther, B. R. Rad, R. Wolf, A. Jacobi von Wangelin, *Angew. Chem. Int. Ed.* **2014**, *53*, 3722 – 3726; *Angew. Chem.* **2014**, *126*, 3796 – 3800.
[19] For the preparation of [K(L)][Co(anthracene)$_2$] and related compounds, see: a) W. W. Brennessel, V. G. Young, Jr., J. E. Ellis, *Angew. Chem. Int. Ed.* **2002**, *41*, 1211 – 1215; *Angew. Chem.* **2002**, *114*, 1259 – 1263; b) W. W. Brennessel, J. E. Ellis, *Inorg. Chem.* **2012**, *51*, 9076 – 9094.
[20] For [K([18]crown-6)(thf)$_2$)][Fe(anthracene)$_2$], see: W. W. Brennessel, R. E. Jilek, J. E. Ellis, *Angew. Chem. Int. Ed.* **2007**, *46*, 6132 – 6136; *Angew. Chem.* **2007**, *119*, 6244 – 6248.
[21] Compound **1** was prepared according to a slightly modified procedure detailed in ref. [18].
[22] W. W. Brennessel, V. G. Young, J. E. Ellis, *Angew. Chem. Int. Ed.* **2006**, *45*, 7268 – 7271; *Angew. Chem.* **2006**, *118*, 7426 – 7429.
[23] a) K. Jonas, R. Mynott, C. Krüger, J. C. Sekutowski, Y.-H. Tsay, *Angew. Chem.* **1976**, *88*, 808 – 809; b) K. Jonas, US patent 4169845, **1979**.
[24] W. Caminati, B. Vogelsanger, A. Bauder, *J. Mol. Spectrosc.* **1988**, *128*, 384 – 398.
[25] In total, four isomers with differing relative orientations of the phenyl groups are conceivable for **5**, two of which have C_2 symmetry and two have C_s symmetry.
[26] a) S. Chaffins, M. Brettreich, F. Wudl, *Synthesis* **2002**, *9*, 1191 – 1194; b) G. Franck, M. Brill, G. Helmchen, *Org. Synth.* **2012**, *89*, 55 – 65.
[27] a) D. R. Anton, R. H. Crabtree, *Organometallics* **1983**, *2*, 855 – 859; b) J. A. Widegren, R. G. Finke, *J. Mol. Catal. A* **2003**, *198*, 317 – 341; c) R. H. Crabtree, *Chem. Rev.* **2011**, *111*, 1536 – 1554.
[28] a) A. J. Frings, Ph.D. dissertation, University of Bochum, Germany, **1988**; b) K. Jonas, *Pure Appl. Chem.* **1990**, *62*, 1169 – 1174.
[29] E.-M. Schnöckelborg, M. M. Khusniyarov, B. de Bruin, F. Hartl, T. Langer, M. Eul, S. Schulz, R. Pöttgen, R. Wolf, *Inorg. Chem.* **2012**, *51*, 6719 – 6730.
[30] a) S. Zhang, J. K. Shen, F. Basolo, T. D. Ju, R. F. Lang, G. Kiss, C. D. Hoff, *Organometallics* **1994**, *13*, 3692 – 3702; b) G. Zhu, K. E. Janak, J. S. Figueroa, G. Parkin, *J. Am. Chem. Soc.* **2006**, *128*, 5452 – 5461.
[31] P. Paklepa, J. Woroniecki, P. K. Wrona, *J. Electroanal. Chem.* **2001**, *498*, 181 – 191.
[32] a) B. H. Lipshutz, J. Keith, D. Buzard, *J. Organomet. Chem.* **1999**, *18*, 1571 – 1157; b) K. Koszinowski, P. Böhrer, *Organometallics* **2009**, *28*, 100 – 110; c) A. Putau, K. Koszinowski, *Organometallics* **2011**, *30*, 4771 – 4778; d) T. K. Trefz, M. A. Henderson, M. Linnolahti, S. Collins, J. S. McIndoe, *Chem. Eur. J.* **2015**, *21*, 2980 – 2991; e) C. Schnegelsberg, S. Bachmann, M. Kolter, T. Auth, M. John, D. Stalke, K. Koszinowski, *Chem. Eur. J.* **2016**, *22*, 7752 – 7762.
[33] T. Parchomyk, K. Koszinowski, *Chem. Eur. J.* **2016**, *22*, 15609 – 15613.
[34] a) N. G. Tserkezos, J. Roithová, D. Schröder, M. Ončák, P. Slavíček, *Inorg. Chem.* **2009**, *48*, 6827 – 6896; b) A. Putau, H. Brand, K. Koszinowski, *J. Am. Chem. Soc.* **2012**, *134*, 613 – 622.
[35] We also analyzed sample solutions prepared under a hydrogen atmosphere (1 bar), which should disfavor dehydrogenation reactions. However, we still observed signals of the dehydrogenated complexes. Possibly, these species formed in the ESI source, where no hydrogen atmosphere could be maintained.
[36] B. J. Fallon, E. Derat, M. Amatore, C. Aubert, F. Chemla, F. Ferreira, A. Perez-Luna, M. Petit, *J. Am. Chem. Soc.* **2015**, *137*, 2448 – 2451.
[37] a) http://www.chem.wisc.edu/areas/reich/pkatable/ (October 15th, 2016); b) W. N. Olmstead, Z. Margolin, F. G. Bordwell, *J. Org. Chem.* **1980**, *45*, 3295 – 3299; c) F. G. Bordwell, D. J. Algrim, *J. Am. Chem. Soc.* **1988**, *110*, 2964 – 2968.
[38] a) G. E. Dobereiner, R. H. Crabtree, *Chem. Rev.* **2010**, *110*, 681 – 703; b) G. Zhang, S. K. Hanson, *Org. Lett.* **2013**, *15*, 650 – 653.
[39] a) B. S. Terra, F. Macedo, Jr., *ARKIVOC* **2012**, 134 – 151; b) B. E. Kahn, R. D. Rieke, *Chem. Rev.* **1988**, *88*, 733 – 745.
[40] a) SCALE3ABS, CrysAlisPro, Aglient Technologies Inc., Oxford, UK, **2015**; b) G. M. Sheldrick, SADABS, Bruker AXS, Madison, USA, **2007**.
[41] a) R. C. Clark, J. S. Reid, *Acta Crystallogr. Sect. A* **1995**, *51*, 887; b) CrysAlisPro, version 171.37.35, Agilent Technologies Inc., Oxford, UK, **2015**.
[42] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339 – 341.
[43] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112 – 122.
[44] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3 – 8.

Manuscript received: November 9, 2016
Accepted Article published: December 27, 2016
Final Article published: February 6, 2017

