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FULL PAPER

Alkene Metalates as Hydrogenation Catalysts

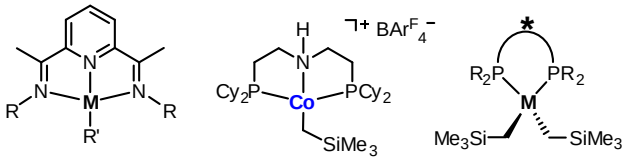
Philipp Büschelberger,[a] Dominik Gärtner,[b] Efrain Reyes-Rodriguez,[b] Friedrich Kreyenschmidt,[c] Konrad Koszinowski,[c] Axel Jacobi von Wangelin,*[b] and Robert Wolf*[a]

Abstract: First-row transition metal complexes hold great potential as catalysts for hydrogenations and related reductive reactions. Homoleptic 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**), [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 found to be competent pre-catalysts in alkene hydrogenations under mild conditions (2 bar H_2, r.t., THF). Mechanistic studies by NMR, electrospray-ionization (ESI) mass spectrometry, and poisoning experiments documented the operation of a homogeneous mechanism, which is initiated by facile redox-neutral π-ligand exchange with the substrates followed by H_2 activation. The substrate scope of the investigated pre-catalysts 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] Over the past decades, the use of highly active platinum group metal catalysts has grown to maturity which enabled efficient hydrogenations of unsaturated C=C and C=X bonds.[2] Apart from nickel,[3] 3d 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 the catalytically active species in low oxidation states. Budzelaar and coworkers reported the first application of (pyridyldiimine)cobalt catalysts to hydrogenations of mono- and disubstituted olefins (Figure 1, top left).[6] Significantly, Chirik and coworkers 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 coworkers 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 bearing bis(phosphine) ligands were also used for (asymmetric) alkene hydrogenation (Figure 1, top right), while a catalyst with a tridentate tris(phosphane) (= triphos) ligand was shown to reduce esters and carboxylic acids.[9],[10] To date there are many more examples especially for PNP-pincer complexes which 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],[14],[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 aiming at the development of metalate catalysts that bear simple and cheap arenes as stabilizing ligand motifs (Figure 1, bottom).[18] Initial experiments focused on the homoleptic bis(η^4-anthracene) metalates **1** (M = Co) and **2** (M = Fe) originally reported by Ellis and coworkers.[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]



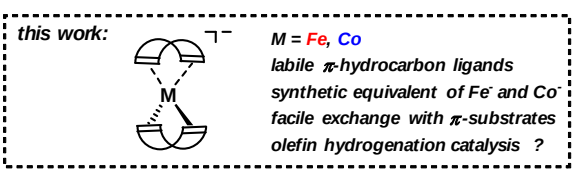


Figure 1. Cobalt- and iron-based hydrogenation catalysts (top) and design concept of alkene metalate catalysts (bottom).

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

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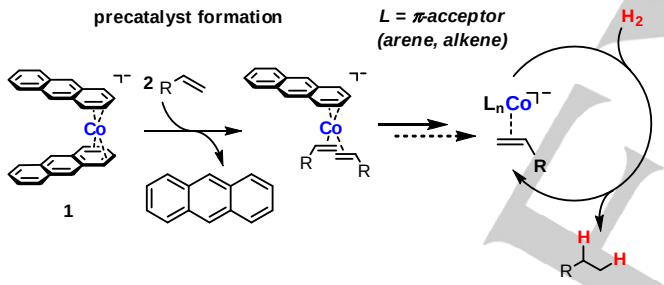
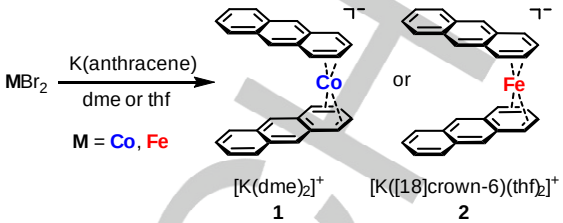
The bis(η^4-anthracene)metalates **1** and **2** exhibited good activity in hydrogenations of various alkenes under mild conditions; cobaltate **1** was also active in catalytic hydrogenations of alkynes, ketones, and imines.[18] Based on our preliminary mechanistic investigations with the pre-catalysts **1** and **2**, we postulated a new catalytic approach to hydrogenation reactions which involves *(i)* the facile synthetic access to a variety of modular catalyst compositions from simple starting materials (alkene/arene, metal salt, reductant), *(ii)* the presence of highly reduced, anionic iron or cobalt species, providing sufficient reducing power for the key H_2 activation, *(iii)* the presence of a cheap hydrocarbon ligand that can be easily replaced with the structurally very similar substrates of olefin hydrogenations. The exchange of the 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 mono-anionic alkene/arene metalates (M = Co, Fe) and studied their catalytic activity in alkene hydrogenations. Here, 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 homogeneous or heterogeneous nature of the catalytically active species.



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

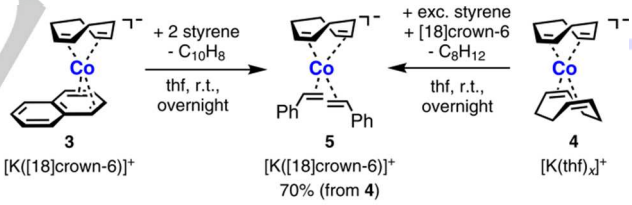
Results and Discussion

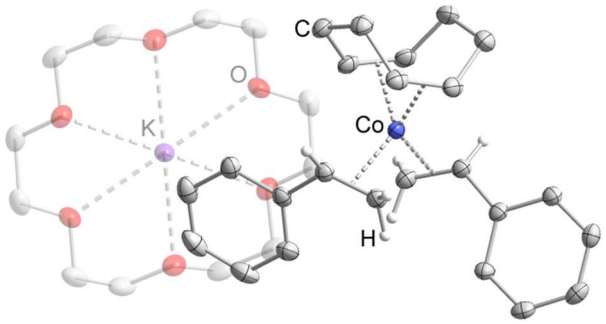
Pre-catalyst syntheses. The potassium bis(η^4-anthracene)-metalates **1** (M = Co) and **2** (M = Fe) were prepared in good yields according to the method by Ellis and coworkers by reduction of the metal dibromides with potassium in the presence of anthracene (Scheme 2).[19],[20],[21] In a similar manner, treatment of the *in situ* prepared [Co(η^4-naphthalene)$_2$]$^-$ with one equivalent of cod (1,5-cyclooctadiene) gave the heteroleptic complex [K([18]crown-6)][Co(η^4-naphthalene)-(η^4-cod)] (**3**).[22] Following a protocol of Jonas and coworkers, we synthesized the homoleptic [K(thf)$_x$][Co(η^4-cod)$_2$] (**4**) by reduction of cobaltocene with a slight excess of potassium in the presence of 3 equiv. of cod 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 constitutes a potential intermediate of styrene hydrogenations with cobaltate pre-catalysts (*vide infra*).



Scheme 2. Synthesis of bis(anthracene) metalates **1** and **2**.[19],[20],[21]

Reaction of [K([18]crown-6)][Co(η^4-naphthalene)(η^4-cod)] (**3**) with 2.2 equiv. 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 [K(thf)$_x$][Co(η^4-cod)$_2$] (**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 the 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 THF solution layered with *n*-hexane and was characterized by single crystal X-ray diffraction (Scheme 3, bottom), NMR spectroscopy, and elemental analysis. The compound is very air-sensitive. Exposure of solid **5** to the air is followed by immediate decomposition to a dark brown solid. A dark precipitate is formed in solution upon contact with air or moisture.





Scheme 3. Synthesis and molecular structure of [K([18]crown-6)][Co(η^4-cod)(η^2-styrene)$_2$] (**5**). Ellipsoids are at the 50% probability level; H atoms are omitted for clarity.

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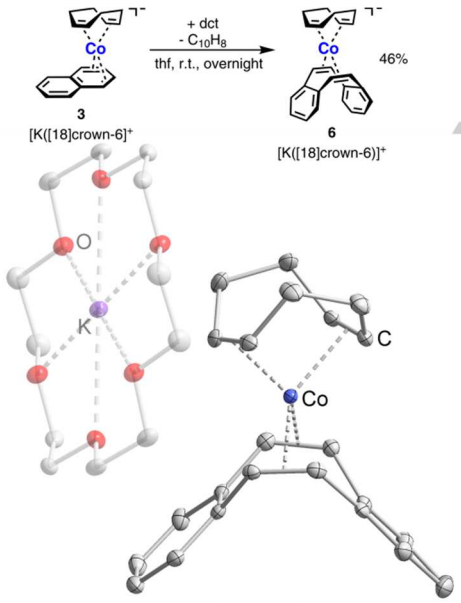
In the molecular structure of **5**, the coordination environment of the cobalt atom is distorted tetrahedral with a twist angle of 56.3°, which is somewhat smaller than the one for [K([2,2,2]cryptand)][Co(η^4-cod)$_2$] (67.3°) reported by Ellis.[19] The bite angle of the cod ligand is 90.0(3)°, and the angle between the two styrene ligands and Co is 104.3(3)°. The average C=C bonds length of the styrene ligands is 1.423(1) Å, which is 0.08 Å longer than the value of free styrene.[24]

The ^{1}H NMR spectrum of **5** (THF-d_8) shows two sets of signals with different intensities, which indicates the presence of a major and a minor isomer in solution (SI, Figure S1). These isomers likely 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 main and the minor isomer is 4:1.

Similar to the preparation of **5**, [K([18]crown-6)][Co(η^4-cod)(η^4-dct)] (**6**), containing the rigid, non-planar, tub-like diene ligand dct (dibenzo[*a,e*]cyclooctatetraene),[26],[27] was synthesized by adding 1 equiv. of dct to **3** in THF at room temperature (Scheme 4, top). Ligand exchange is incomplete, thus, **6** could not be obtained as a pure compound. Various samples were contaminated with a minimum of 18% of [K([18]crown-6)][Co(η^4-dct)$_2$], even after several recrystallizations.



Scheme 4. Synthesis and molecular structure of [K([18]crown-6)][Co(η^4-cod)(η^4-dct)] (**6**). Ellipsoids are at the 50% probability level; H atoms are omitted for clarity.

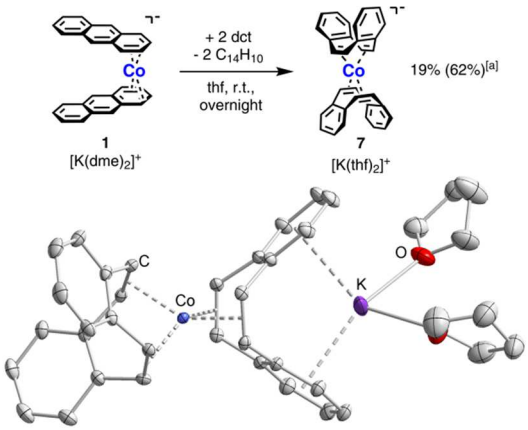
X-ray quality crystals of yellow-orange **6** were obtained from a THF solution layered with diethyl ether. The crystallographically determined molecular structure (Scheme 4, bottom) is similar to that of **5** and of [K([2,2,2]cryptand)][Co(η^4-cod)$_2$].[19] Cobalt has a distorted tetrahedral coordination 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)$_2$].[19]

The ^{1}H NMR spectrum of the isolated product mixture recorded in THF-d_8 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 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 [K(thf)$_x$][Co(η^4-cod)$_2$] (**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 (*vide infra*).[27]

The desired homoleptic complex **7** was cleanly produced by reacting [K(dme)$_2$][Co(η^4-anthracene)$_2$] (**1**) with two equivalents of dct in THF solution 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 in order 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 to **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) where the coordination environment of cobalt is overall similar to that in [K([2,2,2]cryptand)][Co(η^4-cod)$_2$].[19] The twist angle of 55.0(1)° is significantly smaller than for the former compound (67.3°). One set of dct signals is observed in the ^{1}H NMR spectrum of **7** in THF-d_8 , consistent with the homoleptic structure of the complex.



Scheme 5. Synthesis and molecular structure of [K(thf)$_2$][Co(η^4-dct)$_2$] (**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.).

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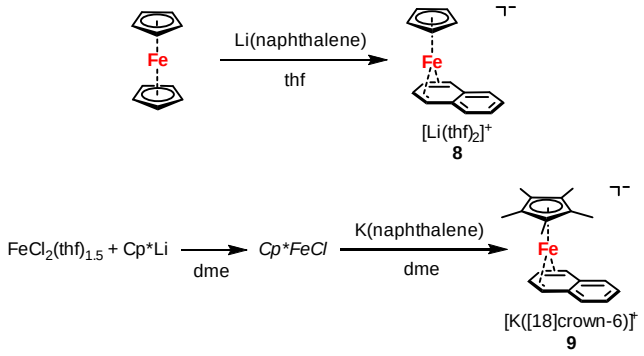
The aforementioned series of arene and alkene metalates was complemented with two cyclopentadienyl iron complexes (Scheme 6). [Li(thf)$_2$][CpFe(η^4-naphthalene)] (**8**, Cp = C_5H_5) was prepared according to Jonas and coworkers from ferrocene by reduction with Li in the presence of naphthalene.[28] The compound was isolated in 60% yield. Its purity was confirmed by ^{1}H NMR and elemental analysis. The synthesis of the related complex [K([18]crown-6)][Cp*Fe(η^4-naphthalene)] (**9**, Cp* = C_5Me_5) was reported earlier by our group.[29] The reduction of Cp*FeCl, *in situ* prepared from $FeCl_2(thf)_{1.5}$ and Cp*Li in DME, with 2 equiv. of potassium naphthalenide in the presence of [18]crown-6 at –60 °C in DME gave **9** in 40% yield.

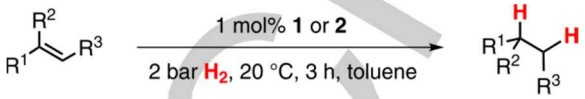


Scheme 6. Synthesis of cyclopentadienylferrates **8** and **9**.

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 the cobaltate **1** (Table 1).[18] Various α-, β-, and ring-substituted styrenes were hydrogenated in excellent yields in toluene solution at 2 bar H_2 and room temperature. The conversion of terminal, internal, di- and tri-substituted 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 pre-catalyst **2** exhibited good activity only with unbiased styrenes and 1-alkenes, but fared much poorer with deactivated olefins (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 pre-catalysts in parallelized olefin hydrogenations under identical conditions. Styrene and 1-dodecene were chosen as model substrates (Table 2). The standard conditions involved reaction with 5 mol% pre-catalyst under an atmosphere of 2 bar H_2 in THF (due to the better solubiltity of the complexes compared to 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 pre-catalysts except **6** and **7** containing dct as ligand. This observation is in accord with the postulate that dct is a competent catalyst poison for homogeneous low-valent monometal species (*vide supra*).[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 the hydrogenation of cod is slow. The iron complexes **2**, **8**, and **9** showed slightly lower activity.

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



Entry	Alkene	R	1 yield [%]	2 yield [%]
1		H	95	89
2		4-F	100	100
3		4-CO_2Me	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	2
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
15		n = 12	92[d, e]	72
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: 0.5 mmol substrate in 2 mL toluene; yields of hydrogenation products determined by quantitative GC vs. 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] 80 °C. [g] bibenzyl. [h] (*E*)-stilbene.

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

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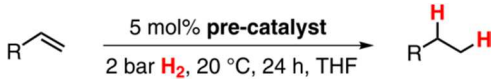
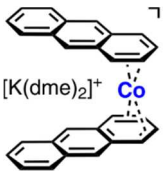
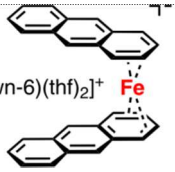
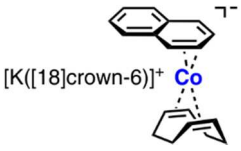
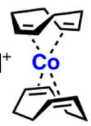
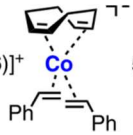
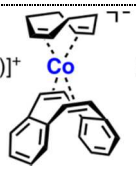
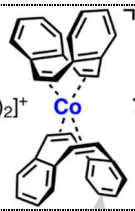
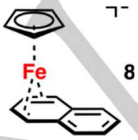
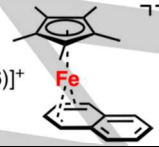
Table 2. Hydrogenation of alkenes with pre-catalysts **1**–**9**.[a]



Pre-catalyst			
	**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: 0.5 mmol substrate in 2 mL THF; yields of hydrogenation products determined by quantitative GC vs. internal reference *n*-pentadecane. In parentheses: yield of alkene isomerization products.

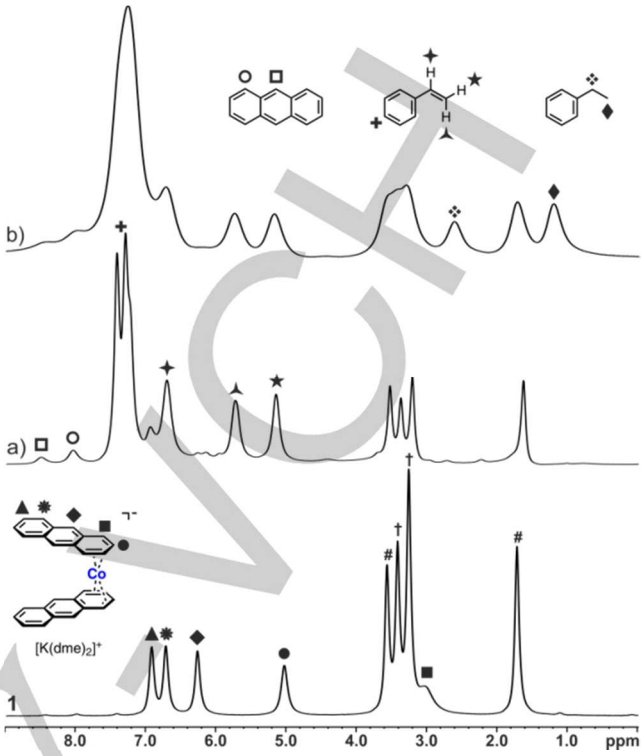


Figure 3. ^{1}H NMR monitoring (THF-d_8: #) of styrene hydrogenation with pre-catalyst **1** (dme: †); a) 3 h after the addition of 20 equiv. of styrene; b) 3 h after addition of hydrogen.

With 1-dodecene, similarly good catalytic hydrogenation activities were observed for the pre-catalysts **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, the bis(η^4-dct)cobaltate **7** was catalytically inactive due to the strong dct-coordination to the Co center, which renders this complex inert with respect to ligand substitution and ligand hydrogenation.[27] From both model reaction series, it became obvious that, despite only small stereoelectronic differences between the pre-catalysts **1** – **9**, the nature of the π-hydrocarbon ligands and the central metal ion has a strong influence on the overall catalytic activity. Pre-catalysts containing naphthalene or anthracene exhibited generally higher activity, presumably due to the re-establishment of aromaticity upon exchange of the polyarene ligand with the better π*-accepting alkenes.[30] Cobaltate complexes were more active and selective than their Fe counterparts.

Mechanistic studies. The investigated pre-catalysts **1** and **2** did not react with dihydrogen at ambient temperature (J. Young NMR tube experiment, up to 4 bar H_2, THF-d_8). 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

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activation step by redox-neutral π-ligand exchange in homogeneous phase through NMR experiments. Figure 3 shows the ^{1}H NMR spectra of pre-catalyst **1** in THF-d_8, the reaction mixture after 3 h resulting from the addition of 20 equiv. styrene to the complex solution at room temperature (spectrum a), and the reaction mixture after 3 h under 4 bar H_2 pressure (spectrum b). The observation of resonances of non-coordinated anthracene in the spectra a) and b) clearly supports the notion of ligand exchange prior to styrene hydrogenation. The signals of ethylbenzene are apparent in spectrum b). There were no further resonances observed in the high-field section which would indicate the formation of hydride complexes under dihydrogen atmosphere. The observed line broadening is tentatively attributed to the slow formation of cobalt nanoparticles.

We extended the ^{1}H NMR monitoring studies to the [Co(η^4-cod)(η^4-L)]$^-$ complexes **3** (L = naphthalene) and **4** (L = cod). When assuming a pre-catalyst 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 equiv. of styrene to THF-d_8 solutions of **3** and **4**, respectively (Figures 4 and 5). 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.

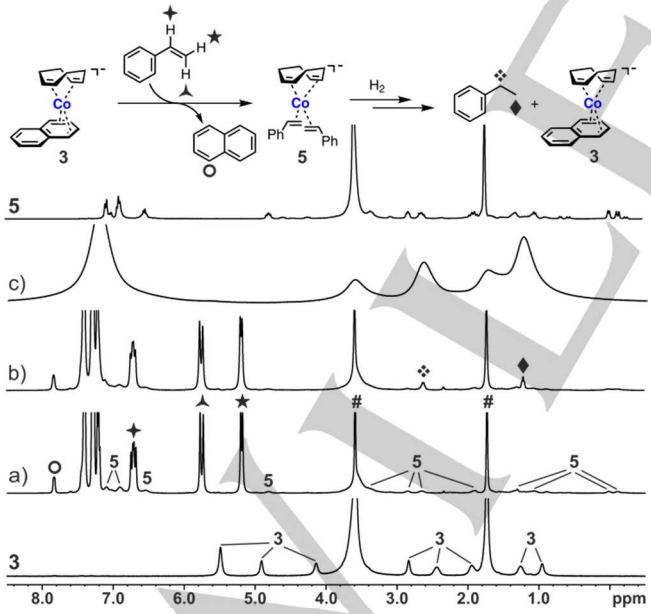

Figure 4. ^{1}H NMR monitoring (THF-d_8: #) of styrene hydrogenation with pre-catalyst **3**; a) 1.5 h after the addition of 20 equiv. of styrene; b) 1.5 h, and c) 24 h after addition of hydrogen; the spectrum of a clean sample of **5** is shown on top.

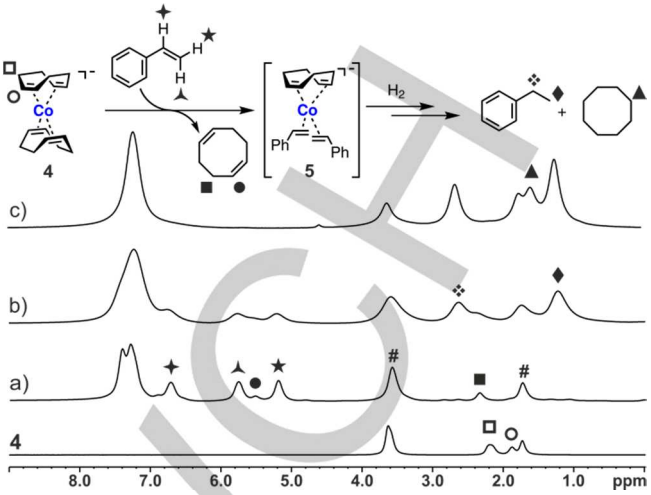

Figure 5. ^{1}H NMR monitoring (THF-d_8: #) of styrene hydrogenation with pre-catalyst **4**; a) 1.5 h after the addition of 20 equiv. of styrene; b) 1.5 h, and c) 96 h after addition of hydrogen.

The loss of the π-ligand styrene upon complete hydrogenation with pre-catalyst **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 pre-catalyst **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, but its formation was clearly proven by a separate experiment (Scheme 7, *vide infra*). The NMR 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**, the NMR 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, *vide supra*), whose role as a key intermediate in styrene hydrogenations with alkene cobaltate pre-catalysts was obvious from the NMR-spectroscopic experiments discussed above (Figures 4 and 5). Application of an H_2 atmosphere (1 bar) to a bright orange THF-d_8 solution of **5** effected an immediate color change to black due to the hydrogenative consumption of the π-ligands which stabilize this cobaltate species (SI, Figure S4). ^{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 pre-catalyst **3**, bearing a much less reactive naphthalene ligand, the sufficiently differing rates of hydrogenation, styrene > cod >> naphthalene allowed the reconstitution of the original pre-catalyst 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 the (η^4-cod)(η^4-naphthalene)cobaltate **3**, which was isolated as a dark red solid by evaporation of the volatiles (SI, Figure S5).

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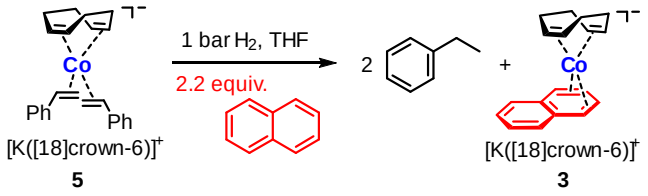

Scheme 7. Demonstration of the ligand release-catch concept by conversion of **5** to **3** upon chemoselective hydrogenation of styrene.

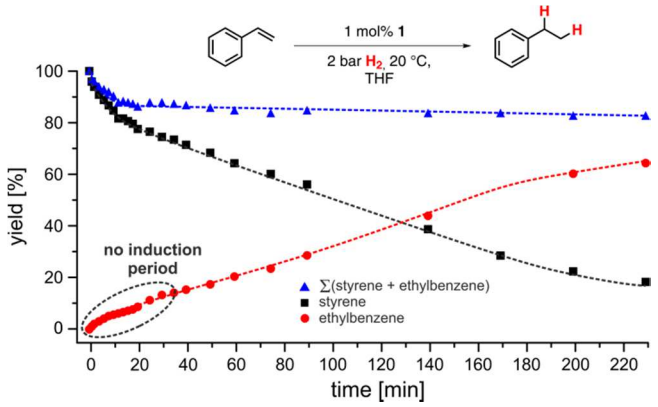

Figure 6. Reaction progress analysis: **1**-catalyzed hydrogenation of styrene under standard conditions without any detectable induction period. Dashed lines are only visual guides.

As 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. An identical behavior was observed from the hydrogenation of styrene with 5 mol% of pre-catalyst **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 to ethylbenzene (Figure 7).

To gain further information with respect to the homogeneous vs. heterogeneous nature of the operating catalyst, we performed kinetic poisoning studies with a scavenger reagent that is selective for mononuclear late transition metal species in low oxidation states: dibenzo[*a*,*e*]cyclooctatetraene (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), a complete inhibition of catalyst turnover was observed, which is indicative of a homogeneous mechanism (Figure 8, *vide supra*). Inhibition of a potential heterogeneous pathway by amalgamation was not observed.[27]

In an extended study, we performed the two model reactions (styrene, 1-dodecene) with the two most active pre-catalysts **1** and **3** in the presence of scavengers (Hg, PMe_3 and dct; Table 3).

Filtration of the freshly prepared pre-catalyst solution through a PTFE syringe filter (pore size <0.1 µm) prior to the addition of the substrate gave unaltered hydrogenation activity of pre-catalyst **1**. The addition of 300 mol% mercury did only slightly affect the catalyst activity. However, the formation of amalgams between mercury and 3d transition metals is very slow.[31] A pronounced reaction inhibition was only observed by addition of dct to the catalytic hydrogenation with the bis(η^4-anthracene)cobaltate pre-catalyst **1**. This suggests the formation of a catalytically inactive homoleptic cobaltate bearing dct ligands, which is in perfect agreement with the observation of 0% conversion in alkene hydrogenations with the pre-catalyst $[K(thf)_2][Co(\eta^4\text{-dct})_2]$ (**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 experiments of a THF solution of **7** and 20 equiv. of styrene, which showed no substitution of the dct ligands over a course of 1.5 h (Figure 9).

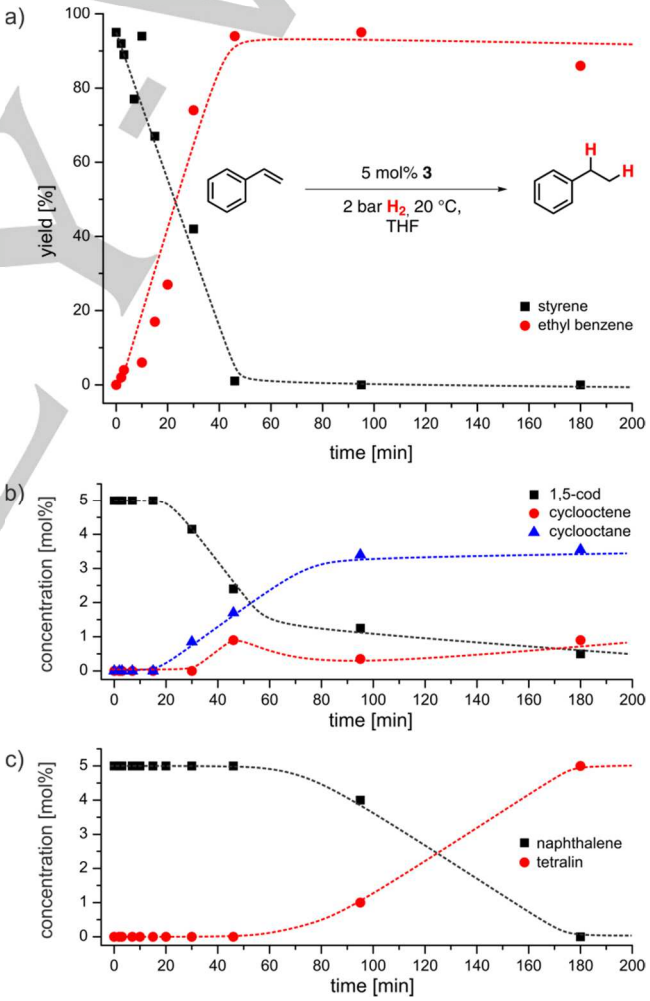

Figure 7. Reaction progress analysis: **3**-catalyzed hydrogenation. Conversions of styrene (a), cod (b), and naphthalene (c). Dashed lines are only visual guides.

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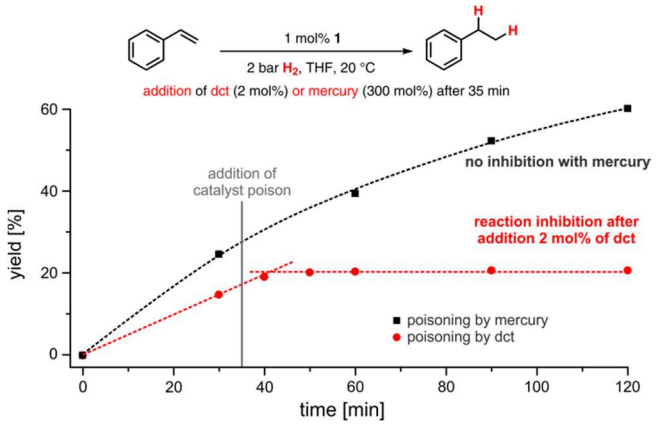
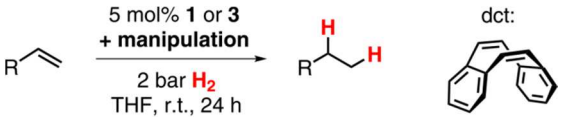


Figure 8. Poisoning studies with pre-catalyst **1** by addition of 300 mol% Hg and 2 mol% dct, respectively. Dashed lines are only visual guides.

Table 3. Poisoning experiments of hydrogenations with arene cobaltate pre-catalysts **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: 0.5 mmol substrate in 2 mL THF. Isomerization: [b] 27%, [c] 34%, [d] 34%, [e] 6%, [f] 31%.

The observation of good catalytic activity of a mixture of pre-catalyst **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 [K([18]crown-6)][Co(η^4-cod)(η^4-dct)] (**6**) has a good activity in hydrogenations of styrene and 1-dodecene (Table 2, *vide supra*).

Given the anionic nature of the putative catalyst species, we also used negative-ion mode ESI mass spectrometry for their selective detection and analysis. Under carefully optimized conditions, this method is well 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 in high signal intensity (SI, Figure S6). 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.[32],[34] ESI of a solution of the heteroleptic complex **3** produced not only [Co(η^4-cod)(η^4-naphthalene)]$^-$ as well as small quantities of [K{Co(η^4-cod)(η^4-naphthalene)}$_2$]$^-$, but also its homoleptic counterpart [Co(η^4-cod)$_2$]$^-$ (SI, Figure S7). This observation clearly demonstrates the operation of intermolecular exchange process in solution. ESI-mass spectrometric analysis of solutions of **4** and **5**, respectively, also resulted in the detection of the expected anionic complexes as main peaks (SI, Figures S8 and S9).

After treating solutions of **1** and **3** with an excess of styrene, we observed the formation of the cobaltates **10** and **5**, respectively (Figure 10a and 10b). In both complexes, two styrene molecules had 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 the NMR spectroscopic experiments. The reaction of **1** with styrene also furnished the homoleptic complex [Co(styrene)$_3$]$^-$ in very small abundance. The lack of any detectable [Co(styrene)$_4$]$^-$ suggests 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 1-dodecene, the replacement of naphthalene by 1-dodecene proceeded only to a small extent (Figure 10c). This finding is consistent with the lower reactivity of 1-dodecene observed in the synthetic studies (*vide supra*).

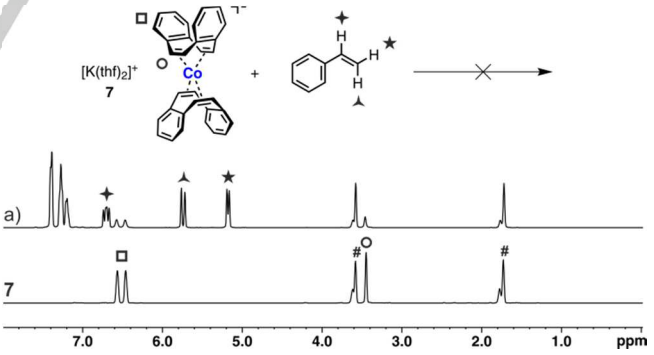


Figure 9. ^{1}H NMR spectrum (THF-d_8: #) of complex **7**, and a) 1.5 h after the addition of 20 equiv. of styrene.

Interestingly, the cobaltate complexes incorporating two molecules of styrene were accompanied by ions whose *m*/*z* ratios were shifted by 2 u to lower values, which obviously resulted from dehydrogenation reactions. According to the principle of microscopic reversibility, the catalytic activity of the cobaltate complexes with respect to hydrogenation reactions implies that they can also catalyze dehydrogenations.[35] The absence of any

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ions with *m*/*z* ratios shifted by 4 u moreover indicates that the dehydrogenation reactions involved a coupling of two styryl units, which most likely gave 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]

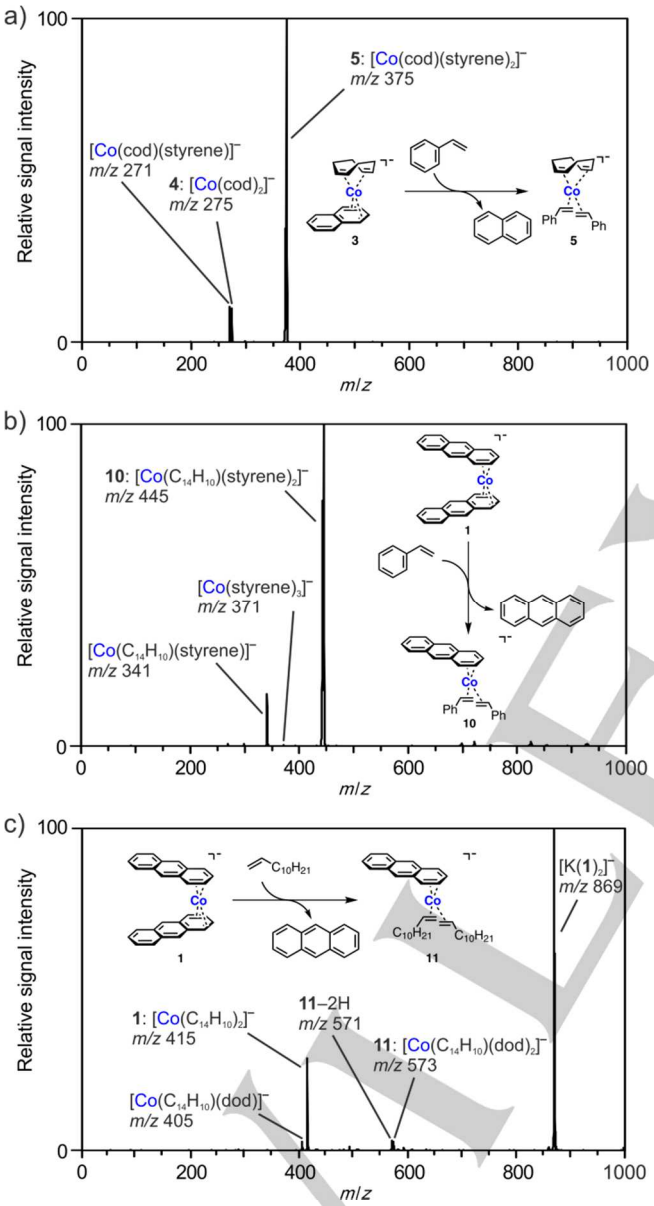
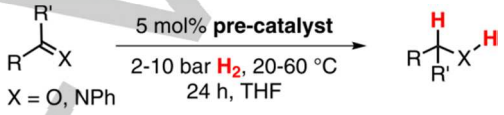


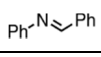
Figure 10. Negative-ion mode ESI mass spectra of the products formed upon reaction of: a) **3** (7.5 mM) with 10 equiv. of styrene; b) **1** (7.5 mM) with 20 equiv. of styrene; c) **1** (7.5 mM) with 20 equiv. of 1-dodecene (dod) in THF.

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, counter-ion or solvent effects, which may operate in solution. Gas-phase fragmentation of the complex **3** led to the loss of cod and naphthalene, whereas **5** and **10** only released styrene (SI, Figures S10−S13).

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 presumably are 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.

Table 4. Hydrogenation of ketone and imine with pre-catalysts **1**−**9**.[a]



Pre-catalyst		
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: 0.5 mmol substrate in 2 mL THF; yields of hydrogenation products determined by quantitative GC vs. internal reference *n*-pentadecane. Yields from reactions at 10 bar H_2, 60 °C in parentheses.

Methodology extensions. We also applied the pre-catalysts **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 pre-catalyst complexes contain a weakly Lewis acidic K^+ counterion. We observed very poor catalytic activities under the 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.

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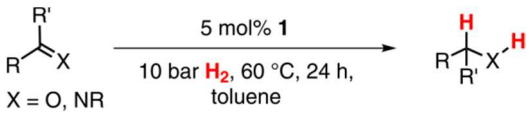
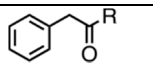
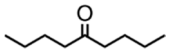
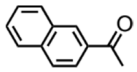
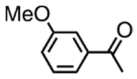
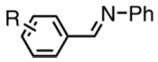
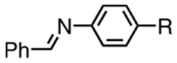
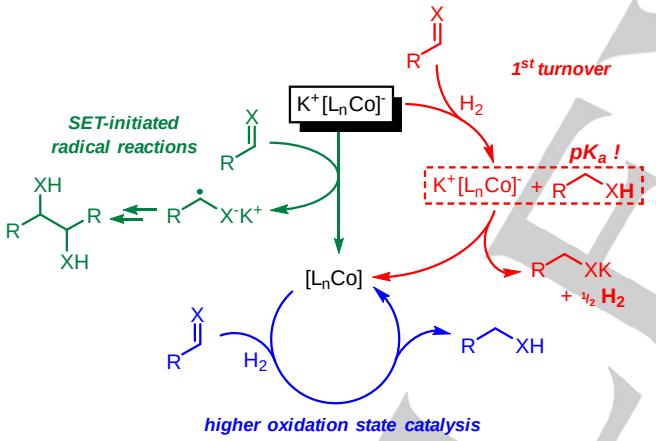
Table 5. Hydrogenation of ketones and imines with cobaltate pre-catalyst **1**.



Entry	Substrate	R	yield [%]
1		Me	99, 90[b]
2		Bn	96
3			100
4			88
5			71
6		H	96,100[b]
7		2-Me	98
8		3-Me	100
9		4-OMe	100
10		CO_2Et	79[c]
11		Br	0

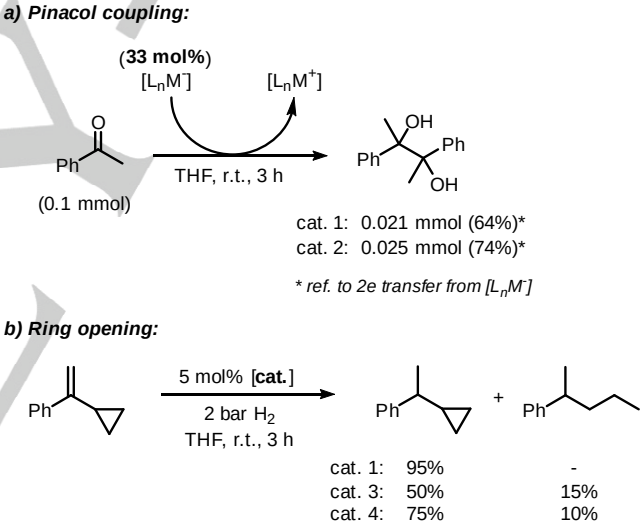
[a] Standard conditions: 0.5 mmol substrate in 2 mL toluene; yields of hydrogenation products determined by quantitative GC vs. internal reference *n*-pentadecane. [b] Solvent: THF [c] 7.5 mol% **1**, 70 °C, 10 bar H_2.



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

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 latter two pathways under the present reaction conditions. The catalytic hydrogenation reaction generates an acidic proton in the resulting alcohol and amine products, both with pK_a values of ~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 a catalyst oxidation after the direct electron transfer to the ketone or after the first hydrogenation catalysis turnover, we postulate the formation of a cobalt(+I) catalyst which displays lower catalytic activity and therefore requires harsher conditions. The formation of dihydrogen was observed by ^{1}H NMR in an equimolar reaction between **1** and 1,3-diphenyl-2-propanol. Furthermore, a transfer hydrogenation experiment between 4-methylstyrene and 4 equiv. of 1,3-diphenyl-2-propanol afforded 18% yield of ethylbenzene in the presence of 5 mol% **1**.[18]

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 the bis(η^4-anthracene)metalates **1** and **2** exhibit good activity in catalytic hydrogenation reactions. The bis(η^4-anthracene)cobaltate **1** is a highly active pre-catalyst for the hydrogenation of a variety of alkenes, ketones and imines at ambient H_2 pressure and temperatures. The iron analogue [K([18]crown-6)][Fe(η^4-anthracene)$_2$] (**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 [K([18]crown-6)][Co(η^4-naphthalene)-(η^4-cod)] (**3**), [K(thf)$_x$][Co(η^4-cod)$_2$] (**4**), [K([18]crown-6)][Co-(η^4-cod)(η^2-styrene)$_2$] (**5**), [K([18]crown-6)]Co(η^4-cod)(η^4-dct)] (**6**),

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$[K(thf)_2][Co(\eta^4\text{-dct})_2]$ (**7**), $[Li(thf)_2][CpFe(\eta^4\text{-naphthalene})]$ (**8**), and [K([18]crown-6)][Cp*Fe-(η^4-naphthalene)] (**9**). **5** – **7** were synthesized for the first time. **1** – **6** as well as **8** and **9** are competent pre-catalysts for the hydrogenation of alkenes under mild conditions. Unlike **1** and **2**, the bis(η^4-styrene) complex **5** rapidly reacts with H_2 (1 bar) with release of ethylbenzene. Kinetic studies and ^{1}H NMR monitoring experiments presented 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. Further, we proved the concept of the release-catch mechanism of catalyst activation by ^{1}H NMR monitoring of π-ligand exchange reactions and by negative-ion mode ESI mass spectrometry investigations. The selective formation of a bis(η^2-monoalkene)cobaltate is believed to be key to a 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 support the hypothesis that the active species have a homogeneous nature. The validity of *Crabtree's* dct test for cobaltate complexes was confirmed by the formation of $[K(thf)_2][Co(\eta^4\text{-dct})_2]$ (**7**) and [K([18]crown-6)][Co(η^4-cod)-(η^4-dct)] (**6**). Bis(η^4-dct) complex **7** is not a competent pre-catalyst, presumably because the dct ligands are not substituted or hydrogenated under the reaction conditions. By contrast, **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 proceed via a different mechanism than 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 glovebox 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 assignments are based on COSY, HSQC and NOESY 2D NMR 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.

Pre-catalysts [K(dme)$_2$][Co(η^4-anthracene)$_2$] (**1**),[19],[21] [K([18]crown-6)]-[Fe(η^4-anthracene)$_2$] (**2**),[20] [K([18]crown-6)][Co(η^4-naphthalene)(η^4-cod)] (**3**),[22] $[K(thf)_x][Co(\eta^4\text{-cod})_2]$ (**4**),[23] $[Li(thf)_2][CpFe(\eta^4\text{-naphthalene})]$ (**8**),[28] and [K([18]crown-6)][Cp*Fe(η^4-naphthalene)] (**9**)[29] were prepared according to literature procedures. The THF content of $[K(thf)_x][Co(\eta^4\text{-cod})_2]$ (**4**) varies according to ^{1}H NMR 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 [K([18]crown-6)][Co(η^4-naphthalene)-(η^4-cod)] (**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, Xray-quality crystals of **5** formed after layering of the THF solution with *n*-hexane (1:2). Yield: 105 mg (62%). M.p. 125 °C (decomp.). Elemental analysis calcd for $C_{36}H_{52}O_6CoK$ (M = 678.84): C 63.70, H 7.72, found C 63.04, H 7.47. ^{1}H NMR (300.13 MHz, THF-d_8), major isomer: δ = –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 (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 (m). ^{13}C{^{1}H} NMR (100.61 MHz, 300 K, THF-d_8): δ = 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 (styrene $C_{quart.}$-Ar); minor isomer: δ = 29.0, 29.4, 38.5, 117.6, 118.0, 124.4, 126.9, 127.5.

*Method 2 (from **4**):* Styrene (2.09 mL, 18.2 mmol, 30.0 equiv.) was added to a solution of $[K(thf)_x][Co(\eta^4\text{-cod})_2]$ (**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. **5** was obtained as orange blocks by storage at room temperature. Yield: 290 mg (70%). The ^{1}H NMR spectrum of the sample prepared by method 2 was identical with those 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 [K([18]crown-6)][Co(η^4-naphthalene)(η^4-cod)] (**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** is contaminated with a varying amount of **7**, which could not be removed by crystallization. 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, THF-d_8): δ = 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 (m, 4H, dct Ar-H); in addition one set of signals assigned to the $[Co(dct)_2]^-$ anion of $[K([18]crown\text{-}6)][Co(\eta^4\text{-dct})_2]$ can be observed.

$[K(thf)_2][Co(\eta^4\text{-dct})_2]$ (**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 (3x from THF/*n*-hexane 1:3) was necessary to remove remaining dct and anthracene. **7** was obtained as bright orange crystals. Yield: 220 mg (19%). M.p. 112 °C (decomp.). Elemental analysis calcd for $C_{40}H_{40}O_2CoK$ (M = 650.79): C 73.82, H 6.20, found C 73.45, H 6.04. ^{1}H NMR (400.13

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MHz, THF-d_8): δ = 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 (m, 8H, dct Ar-H). $^{13}C\{^1H\}$ NMR (100.61 MHz, 300 K, THF-d_8): δ = 26.3 (THF), 68.1 (THF), 87.6 (CH), 122.8 (C-Ar), 124.9 (C-Ar), 152.9 (C_{quart}-Ar).

*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 THF (120 mL) solution of **1** (932 mg, 1.47 mmol, 1.00 equiv.) 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 one hour according to ^1H NMR and elemental analysis. Yield: 512 mg (62%). The ^1H NMR spectrum of samples prepared by this method was identical with those 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 stir bar and a solution of the pre-catalyst (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 removed, and the reaction quenched with saturated aqueous $NaHCO_3$ (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 pre-catalyst was dissolved in 0.5 mL THF before a THF stock solution of the phosphane (0.5 mL, $c = 1.25 \cdot 10^{-2}$ mol/L) was added. For the experiments with dct the catalyst poison was added to the solid pre-catalyst before dissolving both together in THF. When using elementary mercury as the catalyst poison, the liquid metal was added directly to the dissolved pre-catalyst with a syringe before the addition of the substrate solution. For the filtration experiments, the pre-catalyst 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 ^1H NMR monitoring. Reaction monitoring by ^1H NMR was carried out in a sealed J. Young NMR tube. A solution of the pre-catalyst ($5 \cdot 10^{-3}$ mmol, 5 mol%) in THF-d_8 (0.5 mL) was transferred into a NMR tube, and the first ^1H NMR spectrum was measured. In the glovebox, styrene (10 mg, 0.1 mmol, 1.0 equiv.) was added to the pre-catalyst solution. After storing the sample for 90 min, the second ^1H 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 pre-catalyst (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 mass spectrometry. 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 µLmin^{-1}. For the ESI process and the transfer of the 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 *m/z* range of 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 X-ray diffraction 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**, using CuKα radiation for **5** and **6** and MoKα radiation for 7. Empirical multi-scan and analytical absorption corrections were applied to the data.[40],[41] Using Olex2,[42] the structures were solved with SHELXS or SHELXT.[43],[44] Least-square refinements were carried out with SHELXL.[43] CCDC 1513657, 1513658, and 1513659 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.**cam.ac.uk/data_request/cif**.

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Keywords: cobalt • iron • hydrogenations • transition metal catalysis • reaction mechanism

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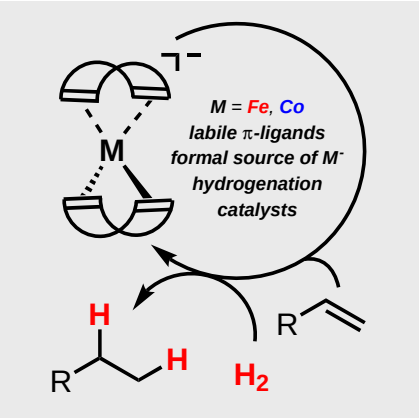
Entry for the Table of Contents

FULL PAPER

A series of nine alkene and arene metalates (M = Fe, Co) were prepared and studied as pre-catalysts in hydrogenation reactions. Excellent catalytic activities in olefin hydrogenations were observed. The catalyst activation mechanism by redox-neutral π-ligand exchange was monitored by NMR and ESI-MS experiments. With carbonyl substrates, catalyst species of higher oxidation states are likely formed by SET and deprotonation reactions.



P. Büschelberger, D. Gärtner, E. Reyes-Rodriguez, F. Kreyenschmidt, K. Koszinowski, A. Jacobi von Wangelin, and R. Wolf**

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Alkene Metalates as Hydrogenation Catalysts

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