

Hydrogenations

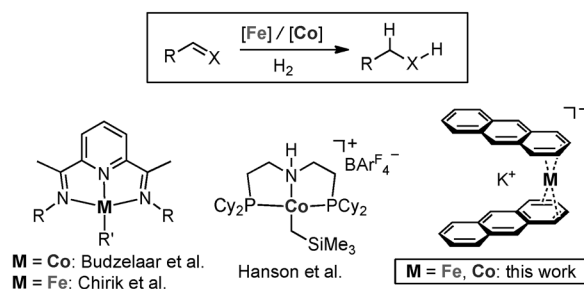
Heteroatom-Free Arene-Cobalt and Arene-Iron Catalysts for Hydrogenations

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Abstract: 75 years after the discovery of hydroformylation, cobalt catalysts are now undergoing a renaissance in hydrogenation reactions. We have evaluated arene metalates in which the low-valent metal species is—conceptually different from heteroatom-based ligands—stabilized by π coordination to hydrocarbons. Potassium bis(anthracene)cobaltate **1** and ferrate **2** can be viewed as synthetic precursors of quasi-“naked” anionic metal species; their aggregation is effectively impeded by (labile) coordination to the various π acceptors present in the hydrogenation reactions of unsaturated molecules (alkenes, arenes, carbonyl compounds). Kinetic studies, NMR spectroscopy, and poisoning studies of alkene hydrogenations support the formation of a homogeneous catalyst derived from **1** which is stabilized by the coordination of alkenes. This catalyst concept complements the use of complexes with heteroatom donor ligands for reductive processes.

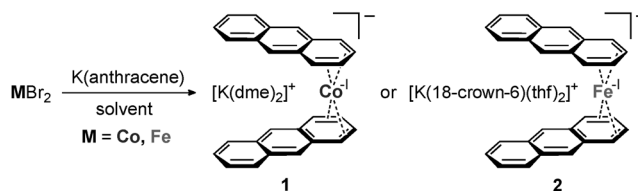
Catalytic hydrogenations constitute one of the most important operations for the conversion of chemical raw materials and in the synthesis of fine chemicals and pharmaceuticals.^[1] Noble metal catalysts display the widest substrate scope and functional group tolerance.^[2] However, economic and environmental concerns have prompted an ever increasing demand for sustainable processes, including efficient hydrogenation methods with base-metal catalysts. Significant progress has only recently been made with the use of first-row transition-metal catalysts for the mild hydrogenation of olefins and carbonyl compounds.^[3] Iron-catalyzed hydrogenations have only played a major role in bulk-scale reductions (Haber–Bosch, gas-to-liquid).^[4] Early cobalt-catalyzed hydroformylations also included hydrogenation studies.^[5] Careful ligand design has recently allowed the use of well-defined low-valent iron and cobalt catalysts.^[6] Cobalt catalysts with redox-active bis(imino)pyridine ligands were applied to olefin hydrogenations by Budzelaar and co-workers.^[6b,c] A PNP pincer ligand was recently used by Hanson and co-workers to stabilize a cobalt catalyst with 15 valence electrons that allowed hydrogenation of alkenes, ketones, and imines after activation by Brookhart’s acid.^[7] Cobalt-catalyzed hydrogenations of styrenes were also developed by Chirik

and co-workers.^[8] The same research group reported high activities of bis(imino)pyridine- and bis(arylimidazol-2-ylidene)pyridine–iron and –cobalt catalysts bearing two labile N₂ ligands (Scheme 1).^[9] We envisioned capitalizing on the



Scheme 1. Iron- and cobalt-based hydrogenation catalysts with an odd number of electrons.

presence of the labile arene ligands in potassium bis(anthracene)cobaltate **1** and ferrate **2** which render these complexes synthetic precursors quasi-“naked” anionic metal species (Scheme 2).^[10,11] Unlike many catalytic reactions where this



Scheme 2. Synthesis of bis(anthracene)metalates(–I) **1** and **2**.^[14]

scenario would entail catalyst aggregation and deactivation, the presence of a large excess of π -acidic ligands in hydrogenations (of unsaturated molecules such as alkenes, arenes, and carbonyl compounds) can effect rapid ligand exchange between π ligands and thus assure prolonged catalyst activity in the homogeneous phase.^[12] We tested this catalyst concept for the first time in hydrogenations.^[13,14]

Initially, hydrogenations of styrenes—which are prone to competing polymerization^[15] by anionic, redox-active catalysts—were studied under mild conditions (1 bar H₂, 20 °C, Table 1).^[16] Cobaltate **1** exhibited far higher activity than the related ferrate **2**. This is likely a consequence of the higher propensity for oxidation of the latter, which has been shown to release the anthracenyl anion in ligand-exchange reactions.^[10c] Excellent yields were obtained in hydrogenations of

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Table 1: Hydrogenations of alkenes, alkynes, and arenes.

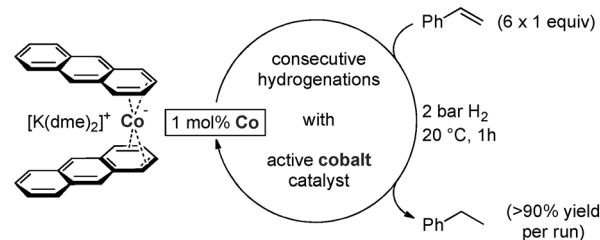
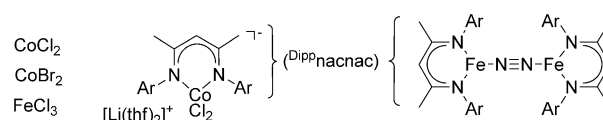
Entry	Olefin	R	Yield [%] Cat. 1	Cat. 2
1		H	95 (89) ^[a]	89
2		4-OMe	98	100 ^[b]
3		4-F	100	100
4		4-NH ₂	27	0
5		4-CO ₂ Me	89	2
6		2-OMe	95	50
7		2-CF ₃	100	75 ^[c]
8		2-Cl (2-Br)	0 (0)	0 (0)
9		3-Me	96	27
10		2-Me	100 ^[d]	–
11		4-Me	100 ^[d]	–
12		H	100 ^[d]	–
13		OMe	97 ^[d]	58
14		OAc	69	–
15		Me	100 ^[b]	–
16		Ph	100 ^[e]	–
17		Me	100 ^[b]	–
18		Ph	100 ^[b]	–
19		CO ₂ Et	76 ^[e]	–
20		Me	99 ^[e]	–
21		CO ₂ Et	86 ^[e]	–
22		n = 4	88 ^[e,f]	73 ^[e,f]
23		n = 8	92 ^[e,f]	72 ^[e,f]
24			92 ^[e]	–
25			89 ^[b]	–
26			100 ^[b]	–
27			60 ^[e,g]	–
28			78 (d.r. 1:1) ^[e]	–
29			63 ^[e,h]	–
30		H	99 ^[e] (2:1) ^[i]	–
31		Cl	0 ^[e]	–
32			79 ^[e]	< 5 ^[e]
33			99 ^[e,i]	< 5 ^[e,k]

[a] With 150 equiv Hg/[Co]. [b] 60 °C, 2 bar, 24 h. [c] 2 mol % cat. [d] 2 bar. [e] 5 mol % cat., 60 °C, 10 bar, 24 h. [f] < 8 % 2-alkene. [g] 80 °C. [h] 1-menthene. [i] 9,10-dihydro-/1,2,3,4-tetrahydroanthracene. [j] bibenzyl. [k] (*E*)-stilbene.

styrenes and alkenes with catalyst **1** at a H₂ pressure of 1–10 bar. Polymerization was observed only to a minor extent (< 5 %). Aryl halides (Br, Cl) led to oxidation of the catalyst,

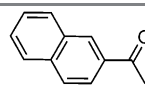
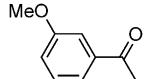
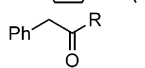
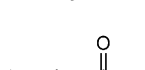
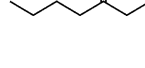
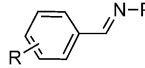
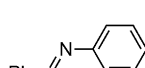
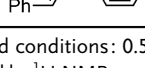
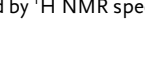
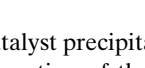
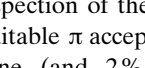
as observed in cross-coupling reactions.^[13,17] A comparative study of initial reaction rates revealed no significant electronic effect of the *para* substituent of different styrene derivatives (F, H, Me, OMe). The isomerization of alkenes was largely suppressed (entries 22, 23, and 28);^[18] tri-substituted olefins reacted slower (entries 27 and 29). The hydrogenation of anthracene gave 9,10-dihydroanthracene and 1,2,3,4-tetrahydroanthracene (2:1, entry 30). Exchange of the cation by using [K(18-crown-6){Co(C₁₄H₁₀)₂}]^[10] instead of **1** afforded identical yields in reactions of various styrenes. The different activity of **1** and **2** was also reflected in hydrogenations of 1,2-diphenylacetylene. Catalyst **1** gave full conversion into bibenzyl (10 bar H₂, 60 °C), whereas **2** led to low conversion to (*Z*)-stilbene.^[16b] The reactions are chemoselective despite the presence of anionic catalyst species: the C–O bonds of esters and activated ethers were tolerated (entries 5, 14, 19, 21, and 32).

It is important to note that this protocol does not require pretreatment or activation of the precatalyst and operates under essentially ligand-free conditions.^[6,7,9] The standard conditions allowed consecutive catalyses of **1** by addition of another equivalent of styrene after each run (6 × 1 equiv, see Scheme 3). The higher valent precursors FeCl₃, CoCl₂, CoBr₂, [Li(thf)₂][Co(Dippnacnac)Cl₂]^[19] and [Fe₂(μ-N₂)-(Dippnacnac)₂]^[20] exhibited no catalytic activity at 2 bar H₂ (Scheme 4).


Scheme 3. Consecutive hydrogenations with precatalyst **1**.

Scheme 4. Inactive precatalysts. Ar = 2,6-*i*Pr₂C₆H₃ (Dipp).

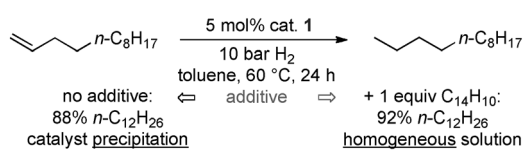
Aiming at a broader substrate scope, we wondered whether anionic **1** would selectively catalyze hydrogenations of carbonyl compounds or instead engage in undesired nucleophilic addition or oligomerization with these electrophiles. Gratifyingly, **1** displayed excellent activity in the hydrogenation of various aromatic and aliphatic ketones and imines at 10 bar H₂ and 60 °C (Table 2). No pinacol products were detected. The high chemoselectivity of cobaltate **1** also resides in its poor nucleophilicity: no direct reactions with styrenes and the more electrophilic cinnamyl ethers, ketones, and imines were observed. Aldehydes engaged in oligomerizations and condensations.

Table 2: Hydrogenations of ketones and imines with cobaltate **1**.^[a]

Entry	Carbonyl compound	Yield [%]
1		88
2		71
3		R = Me 99
4		R = Bn 96 (36, ^[b] 14) ^[c]
5		100
6		R = H 96
7		R = 2-Me 98
8		R = 3-Me 100
9		R = 4-OMe 100
10		R = CO ₂ Et 79 ^[d]
11		R = Br 0

[a] Standard conditions: 0.5 mmol substrate in 2 mL toluene; yields determined by ¹H NMR spectroscopy. [b] RT. [c] 2 bar H₂. [d] 7.5 mol % **1**, 70 °C.

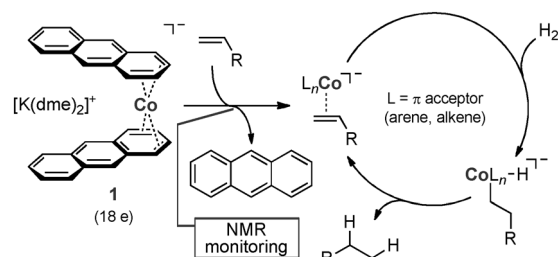
No catalyst precipitation or color change was observed by visual inspection of the olefin hydrogenation reactions. The loss of suitable π acceptors after complete hydrogenation of 1-dodecene (and 2% anthracene from the precatalyst) resulted in catalyst precipitation. Under identical conditions, crude reactions containing an equimolar amount of anthracene remained homogeneous as a result of the slow hydrogenation of anthracene (Scheme 5). This is consistent with the assumption that π acceptors other than anthracene are also capable of stabilizing reactive low-valent homogeneous metal species.^[10–12]



Scheme 5. Hydrogenation in the presence of anthracene.

Unambiguous distinction between homogeneous and heterogeneous catalysts is intricate,^[21] yet our observations are consistent with a homogeneous mechanism. Hg poisoning (addition of 150 equiv Hg per [Co] at the start of the reaction and at 25% conversion, respectively) showed no loss of activity (Table 1, entry 1, and see Figure S4 in the Supporting Information). The homogeneity of the catalyst was further indicated by experiments carried out in the presence of dibenzo[*a,e*]cyclooctatetraene (dct).^[22] Dct selectively binds homogeneous metal species as a consequence of its rigid tublike structure and π -acceptor ability, and it is resistant to hydrogenation. Complete inhibition of the catalytic activity

was observed when adding 2 equiv dct per [Co] to styrene hydrogenations at 20% conversion (see Figure S1 in the Supporting Information). We postulate a mechanism initiated by the substitution of the labile anthracene molecules by π -acceptor substrates (Scheme 6). Similar stoichiometric reac-



Scheme 6. Proposed mechanism of the hydrogenations catalyzed by **1**. The active catalyst is generated by ligand exchange and stabilized by π coordination of the substrate.

tions were previously reported for cyclooctadiene and butadiene.^[10] Reaction progress analyses (GC-FID) fully support the notion of an initial anthracene substitution which is hydrogenated only after the stoichiometric substrate (styrene) is entirely consumed (Figure 1). Quantitative analysis of the early reaction phase (<20 min) showed neither an induction period nor a sigmoidal kinetic curve (see Figure S2 in the Supporting Information), which could indicate a nano-cluster nucleation step en route to particle formation (Figure S2).^[21a]

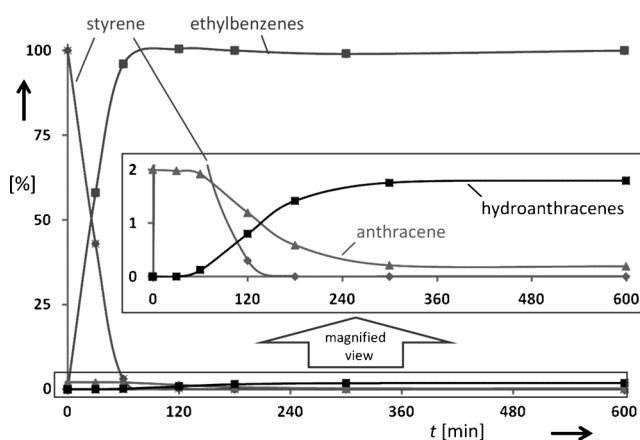
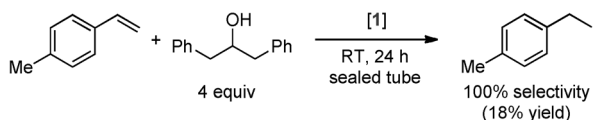


Figure 1. Ligand exchange followed by ligand hydrogenation.

Monitoring a mixture of **1** with 20 equiv styrene by ¹H NMR spectroscopy revealed that anthracene is indeed rapidly exchanged by styrene (see Figure S3 in the Supporting Information). No direct reaction between **1** and H₂ was observed under these conditions. The activation of H₂ at the catalyst species followed by alkene insertion into a hydridocobaltate gives an alkylcobalt(I) hydride.^[23] Substitution of the hydrogenated product occurs by coordination of another olefin. The catalytic intermediates are apparently stabilized by π accep-

tors which are present in large excess (arenes, olefins). Cobalt-catalyzed hydrogenations of styrene and 1,3-diphenylacetone followed by work-up with D₂O afforded no deuterated products (¹H, ²H NMR). The reaction of styrene under 2 bar D₂ gave α,β-[D₂]-ethylbenzene. Treatment of **1** with alcohols (ethanol, 1,3-diphenylpropan-2-ol) at room temperature resulted in oxidation of the catalyst to another catalytic species, a color change (dark red to dark green), and H₂ evolution.^[24] Transfer hydrogenation between 1,3-diphenylpropan-2-ol (4 equiv) and 4-methylstyrene in the presence of **1** indeed afforded 1-ethyl-4-methylbenzene with 100% selectivity (18% yield) in the absence of an H₂ atmosphere (Scheme 7). NMR studies confirmed the exchange of anthra-



Scheme 7. Initial result of a transfer hydrogenation with secondary alcohols.

cene ligands with ketones in the coordination sphere of **1** (see Figure S5 in the Supporting Information). No direct reduction of diphenylacetone by an equimolar amount of **1** was observed. We thus postulate the initiation of carbonyl hydrogenation by cobaltate **1** and the operation of a cobalt(I) catalyst after the first turnover at elevated temperature and H₂ pressure.^[24,25]

For the first time, homoleptic arene complexes were applied to catalytic hydrogenations. Catalysts **1** and **2** are readily accessible by reduction of metal halides with potassium-anthracene.^[10] Bis(anthracene)cobaltate **1** was highly active in the hydrogenation of alkenes, ketones, and imines (1–5 mol% cat., 1–10 bar H₂, 20–60 °C). It displays comparable activity to Hanson's ternary catalyst system PNP ligand/cobalt/HB(Ar^F)₄,^[7] but does not require sophisticated ligands or further additives (e.g. Brookhart's acid). Olefin hydrogenation catalysis with **1** is initiated by anthracene dissociation to release an active species which is homogeneous and stable in the presence of suitable π acceptors. Consecutive reactions were performed without loss of activity. Current studies aim at the spectroscopic characterization of the intermediate cobalt species with labile π-acceptor ligands and applications of this new catalyst concept to other transformations with alkenes, carbonyl compounds, and arenes, including transfer hydrogenation.^[26]

Experimental Section

Representative procedure for the hydrogenation of styrenes: In an argon-filled glove box, a dry 5 mL vial with a screw cap and PTFE septum was charged with a magnetic stir bar and a solution of catalyst **1** (0.005 mmol, 3.2 mg) and 2-methoxy-6-vinylnaphthalene (0.5 mmol, 92.1 mg) in toluene (2 mL). The vial was placed into a high-pressure reactor (Parr Instr.) and the septum punctured with a short needle (Braun). The reactor was sealed, removed from the glove box, placed on a magnetic stirrer plate, and purged with hydrogen. After 3 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 NaHCO₃ (1 mL). The mixture was extracted (diethyl ether) and the organic phases dried (Na₂SO₄). For quantitative GC-FID analysis, *n*-pentadecane was added as an internal standard. For preparative work-up, the solvents were removed in vacuum and the residue was purified by flash-chromatography (SiO₂, pentane/ethyl acetate). 2-Methoxy-6-ethylnaphthalene: ¹H NMR (400 MHz, CDCl₃): δ = 7.63 (m, 3H), 7.56 (s, 1H), 7.32 (m, 1H), 7.10 (m, 2H), 3.91 (s, 3H), 2.78 (q, 7.6 Hz, 2H), 1.31 ppm (t, 7.6 Hz, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ = 157.1, 139.47, 132.9, 129.2, 128.9, 127.6, 126.7, 125.4, 118.6, 105.7, 55.3, 28.8, 15.6 ppm. MS (EI, 70 eV, *m/z*): 186 [*M*⁺].

Representative procedure for the hydrogenation of ketones/imines: In an argon-filled glove box, a dry 5 mL vial with a screw cap and PTFE septum was charged with a magnetic stir bar and a solution of catalyst **1** (15.1 mg, 0.025 mmol) and 1-phenylpropan-2-one (67.1 mg, 0.5 mmol) in toluene (2 mL). The vial was placed into a high-pressure reactor (Parr Instr.) and the septum punctured with a short needle (Braun). The reactor was sealed, removed from the glove box, placed on a magnetic stirrer plate, and purged with hydrogen. After 20 h at 60 °C under an atmosphere of hydrogen (10 bar), the pressure was released, the vial removed, and the reaction quenched with saturated aqueous NaHCO₃ (1 mL). The mixture was extracted (diethyl ether) and the organic phases dried (Na₂SO₄). For quantitative GC-FID analysis, *n*-pentadecane was added as an internal standard. For preparative work-up, the solvents were removed in vacuum and the residue was purified by flash-chromatography (SiO₂, pentane/ethyl acetate). 1-Phenylpropan-2-ol: ¹H NMR (300 MHz, CDCl₃): δ = 7.33–7.19 (m, 4H), 4.00 (m, 1H), 2.80–2.64 (m, 2H), 1.70 (m, 1H), 1.23 ppm (d, 6.1 Hz, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 138.6, 129.4, 128.6, 126.5, 68.9, 45.8 ppm, 22.8. MS (EI, 70 eV, *m/z*): 121 [*M*–O]⁺.

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