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Communication

A Highly Reduced Magnesium Dicobalt Complex for the Hydrogenation of Tri- and Tetra-Substituted Alkenes

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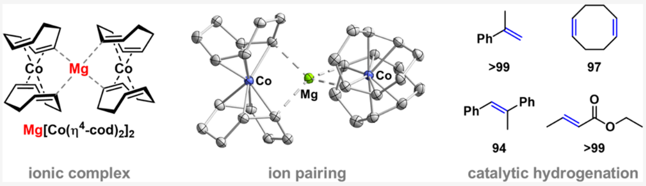
ABSTRACT: The reaction of $[K(thf)_{0.33}][Co(\eta^4\text{-}cod)_2]$ (**E**; cod = 1,5-cyclooctadiene) with 0.5 equiv of $MgCl_2$ led to the isolation of the magnesium dicobalt complex $Mg[Co(\eta^4\text{-}cod)_2]_2$ (**1**). Complex **1** forms a tight ionic complex in the solid state and in toluene solution due to electrostatic interactions between the Mg^{2+} cation and the $[Co(\eta^4\text{-}cod)_2]^-$ anions. The complex is a successful precatalyst for the hydrogenation of sterically challenging tri- and tetra-substituted alkenes, surpassing the catalytic capabilities of related alkali metal and β-diketiminate magnesium complexes.



Low-oxidation state alkali metal cobaltate salts, such as $[M(thf)_n][Co(\eta^2\text{-}C_2H_4)_4]$ (M = Li, donor = TMEDA, **A**; M = K, donor = thf, **B**; C_2H_4 = ethylene), $[M(thf)_n][Co(\eta^4\text{-}cod)_2]$ (**C**: M = Li; **D**: M = Na; **E**: M = K; cod = 1,5-cyclooctadiene), and $[K([2.2.2]crypt.)][Co(\eta^4\text{-}C_{14}H_{10})_2]$ (**F**; $C_{14}H_{10}$ = anthracene, crypt. = cryptand), are versatile synthetic equivalents for the “Co^-” anion in organometallic chemistry (Figure 1, top).[1] These complexes also display promising reactivities in processes such as small molecule activation,[2] alkene hydrogenation,[1e,3] and other catalytic reactions.[4] The reactivity and catalytic properties of the cobaltate anions can be manipulated by heteroatomic ligands (e.g., phosphines, bipyridines, or α-diimines).[1c,5,6] However, the effect of the countercations on their reactivity has not been thoroughly understood. Only a few alkaline earth metal cobaltates are known, including the “inorganic Grignard reagent” $[MgBr(thf)_2][CpCo(\eta^3\text{-}C_3H_5)]$ (**G**) reported by Jonas, and the carbonyl complexes $[AE(thf)_n][Co(CO)_x(PCy_3)]_2$ reported by Mountford (where x = 1−3 and AE = Mg−Ba; see, for example, complex **H** in Figure 1, bottom).[7] Furthermore, there are few structurally related cobaltate compounds with counterions beyond groups 1 and 2, with $Hg[Co(CO)_4]$ and $Zn[Co(\eta^4\text{-}C_4H_6)_2]_2$ (C_4H_6 = 1,3-butadiene) being scarce examples.[1c,8] Recently, we discovered that countercations have a significant impact on the catalytic properties of anionic cobaltates **C**-**E** and $[(^{Dep}nacnac)Mg][Co(\eta^4\text{-}cod)_2]$ (**J**; Dep = 2,6-diethylphenyl) during alkene hydrogenations.[1e] Our studies suggest that the counterion plays an active cocatalytic role in the hydrogenation reaction by coordinating to cobalt hydride intermediates. To investigate the enhanced reactivity of magnesium cobaltates compared to their alkali metal salts, we have now prepared the Mg^{2+} complex, $Mg[Co(\eta^4\text{-}cod)_2]_2$ (**1**, Figure 2), which lacks any additional ligands on the magnesium cation. In this report, we describe the synthesis and molecular structure of **1**, which features a linear Co−Mg−Co arrangement. We analyze the bonding situation in **1** and

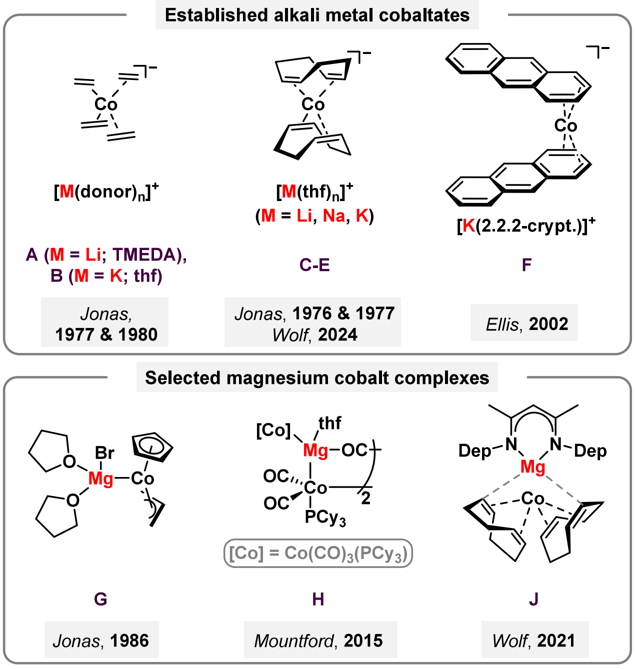


Figure 1. Established alkali metal cobaltates used as synthetic precursors, precatalysts or in the activation of small molecules (top) and selected examples of magnesium cobalt complexes (bottom). Dep = 2,6-diethylphenyl. crypt. = cryptand.

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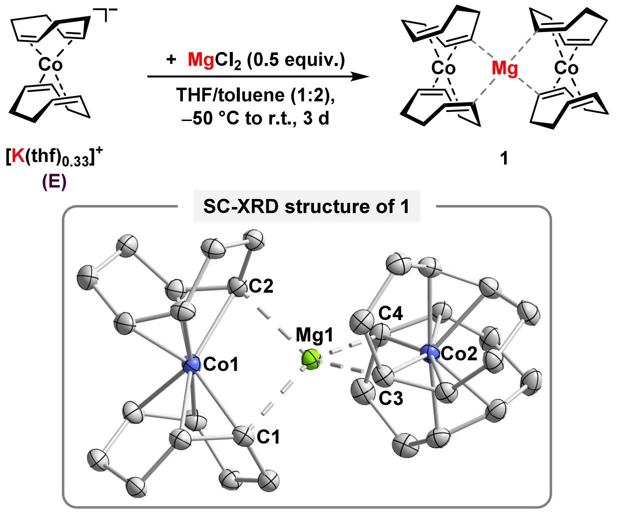

Figure 2. Top: Synthesis of Mg[Co(η^4-cod)$_2$]$_2$ (**1**). Bottom: Solid-state molecular structure of **1**. Thermal ellipsoids are drawn at 40% probability level. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Co1−Mg1 2.631(6), Co2−Mg1 2.615(6), Mg1−C1 2.411(2), Mg1−C2 2.362(2), Mg1−C3 2.363(2), Mg1−C4 2.415(2), Co1−Mg1−Co2 179.36(4).

demonstrate that this complex catalyzes the hydrogenation of tri- and tetra-substituted alkenes with a remarkable efficiency.[1e]

Complex **1** was prepared by treating anhydrous MgCl$_2$ with [K(thf)$_{0.33}$][Co(η^4-cod)$_2$] (**E**) in THF/toluene. The compound was isolated as an orange-yellow powder in 63% yield. Crystals grown from a saturated toluene solution were analyzed by single crystal X-ray diffraction. In the solid state, **1** forms an ion triple with a Mg^{2+} cation sandwiched by two [Co(η^4-cod)$_2$]$^-$ units (Figure 2, bottom; Co1−Mg1−Co2 179.36(4)°).[9] The two [Co(η^4-cod)$_2$]$^-$ anions are rotated toward each other at 50.42(6)° along the Co−Mg−Co axis (plane[C1−Co1−C2]-to-plane[C3−Co2−C4]). The Co−Mg distances (2.631(6) and 2.615(6) Å) are similar to those in complex **J**.[2d] Close contacts of the Mg^{2+} cation with four carbon atoms of the cod ligands (C1, C2, C3 and C4; Mg−C 2.362(8)-2.415(8) Å) arise from an interaction with the π-bonds of the cod ligand. Similar Mg···alkene interactions have been reported by Harder and co-workers.[10] An analysis of the C−C distances reveals that the interaction with Mg results only a very minor elongation of the C=C double bonds (e.g., C4−C8 1.427(3) Å vs C12−C16 1.407(3) Å); Table S6, SI). Note that the C=C bond distances in **1** are nearly identical to those of the ion-separated *tetra-n*-butylammonium salt [N(^{n}Bu)$_4$][Co(η^4-cod)$_2$].[1e]

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **1** show two species in a ratio of approximately 1.0:0.25, which is explained by the presence of different isomers with similar NMR spectra. ^{1}H NMR resonances between 1.2 and 4.5 ppm are assigned to the (chemically) inequivalent H atoms of the cod ligands (Figure S14, SI). The cod ligands give rise to eight ^{13}C{^{1}H} NMR resonances between 27.0 and 83.0 ppm (Figure S15, SI). This agrees with the structure of the ionic complex observed in the solid state, for which chemically inequivalent carbon atoms are expected.[2d] Broadening of the resonances is observed at elevated temperature (60 °C), which possibly indicates chemical exchange between diastereomeric species showing D_2 and C_2 symmetry (Figures S19 and S20, SI). Such species have different configurations of the C atoms interacting with the cobalt and magnesium atoms (see Figure S21, SI). Further confirmation of the intimate ion pair character in solution was provided by DOSY NMR studies of **1** and the lithium salt [Li(thf)$_{1.92}$][Co(η^4-cod)$_2$] (**C**) (see the Supporting Information for details). For **1**, similar diffusion coefficients ($D \approx 9.1 \times 10^{-10}$ m^2 s^{-1}) were obtained for all suitable cod ligand signals, which correspond to a hydrodynamic volume $V_H \approx 754$ Å^3; for comparison, the diffusion coefficients for the 1,5-cod ligand signals ($D \approx 1.0 \times 10^{-9}$ m^2 s^{-1}) and the Li$^+$ cation (D $\approx 9.9 \times 10^{-10}$ m^2 s^{-1}; ^{7}Li NMR) of **C** give volumes $V_H \approx 566$ Å^3 and $V_H \approx 448$ Å^3, respectively. The larger hydrodynamic volume V_H of **1** strongly supports the presence of the magnesium salt as an ionic complex in solution. NMR spectroscopic evidence of this alkene···Mg^{2+} interaction can be found in the ^{13}C{^{1}H} NMR spectrum of **1**, which features one of four olefinic signals at an unusual chemical shift of 40.8 ppm, significantly upfield shifted compared to the other resonances at approximately 80.0 ppm (Figures S15 and S16, SI). The ^{13}C{^{1}H} NMR chemical shifts calculated at the PBE0/def2-TZVPP level of theory show that this resonance can be assigned to the four inward-facing C$_\pi$ atoms (δ_{calc} = 44.9 ppm for C1/2/3/4; Table S8, SI). The ^{1}H NMR spectrum of **1** does not change significantly upon the addition of THF (Figure S8, SI). However, much simpler ^{1}H and ^{13}C{^{1}H} NMR spectra are observed with 4-(dimethylamino)pyridine (DMAP), which indicate the formation of the ion-separated complex [Mg(DMAP)$_6$][Co(η^4-cod)$_2$]$_2$ (**2**; Figures S9 and S10, SI). In

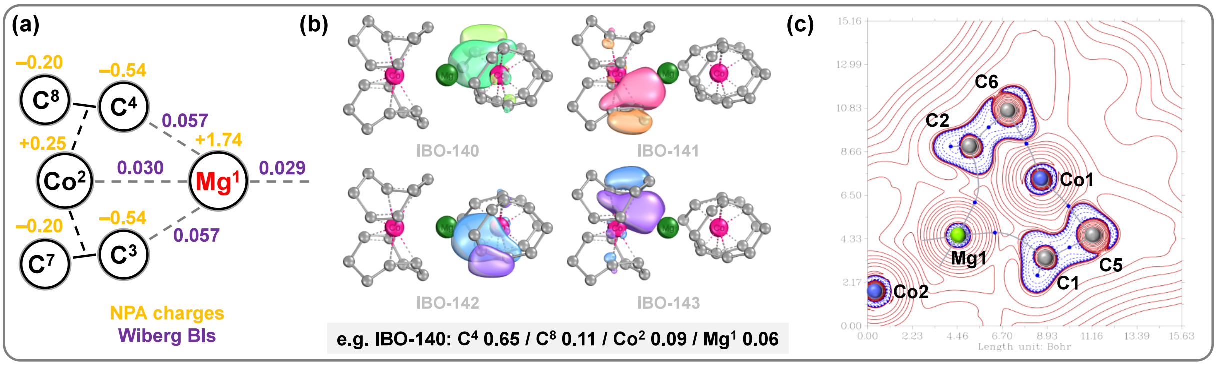

Figure 3. (a) NBO analysis including NPA charges and Wiberg bond indices of **1**. (b) Selected IBOs of **1**. The interaction type and percentage of the electron density on C, Co and Mg are given exemplarily for IBO-140. (c) Plot of the Laplacian of the electron density on the C5−Mg1−C6 plane of **1** displaying two of the four bond critical points between C$_\pi$ and Mg (blue dots: bond critical points; gray lines: bond paths).

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contrast to complex **J**, **1** does not react with styrene and dibenzo[*a*,*e*]cyclooctene even at elevated temperatures (see the Supporting Information for details).[1e] This indicates that the tight ion-pairing in **1** significantly slows down ligand exchange.

Quantum chemical calculations confirm that the bonding in the Co−Mg−Co core of **1** is highly ionic, while weak donor−acceptor interactions between the Mg^{2+} center and four alkene C atoms contribute to the overall stabilization of the complex. Natural bond order (NBO) and second-order perturbation theory analyses show that any donor−acceptor interactions between the cobalt and magnesium atoms are negligible (<1 kcal mol^{-1}; Table S9, SI). The Wiberg bond index for the Co−Mg bond is 0.029 (0.030), and the QTAIM analysis displays no bond critical point (BCP) along the Co−Mg−Co motif (Figure 3a,c). The charges from the natural population analysis (NPA) are positive for the Mg^{2+} cation (+1.74) and overall negative for the [Co(η^4-cod)$_2$]$^-$ anions (−0.87), while the formal Co(−I) center itself has a positive charge (+0.25/+0.26), indicative of significant π-backbonding to the C═C double bonds (see Table S9, SI). The C═C double bonds interacting with the Mg^{2+} cation are polarized (e.g., NPA charge (C4) of − 0.54 vs NPA charge (C8) of − 0.20). QTAIM analysis identifies four BCPs between the inward-facing C$_\pi$ atoms and Mg^{2+}, indicating a stabilizing alkene···Mg^{2+} interaction with donor−acceptor character (Figure 3c and Figure S25, SI). Based on the descriptors at these BCPs, together with NBO and IBO analyses, we classify the interactions as predominantly electrostatic with minor covalent contributions (Tables S9 and S10, SI). Notably, no BCPs are detected between the alkene C atoms (C1−C4) and Co, whereas C═C double bonds not coordinated to Mg display BCPs between both carbon atoms and Co (Figure S25, SI). NBO analysis of the orbital contributions indicates a minor rehybridization from sp^2 to sp^3 in the C═C double bonds close to Mg, which is reflected by a reduced s-character compared to the C═C double bonds distant from Mg (e.g., C$_4$═C$_8$ vs C$_{12}$═C$_{16}$; Table S9, SI).

To assess the influence of the Mg^{2+} cation, we compared the properties of **1** with **J** in alkene hydrogenation reactions (Figure 4).[1e] Various mono- to tetra-substituted alkenes were hydrogenated quantitatively using **1** under mild H$_2$ pressures (1.5 mol %, 2−12 bar H$_2$, 30−60 °C). Catalyst **1** surpasses **J** in terms of yield and reaction rate for most of these substrates (Figure 4, top and Table S1, SI). The sterically most hindered substrate 1,1,2,2-tetraphenylethylene was converted to the corresponding alkane with **1** in 88% yield, while a modest conversion of only 8% was achieved with **J**. This shows that the β-diketiminate motif is not an essential counterion component for the effective hydrogenation of alkenes. To gain initial information on the topicity of the catalyst, we conducted mercury poisoning and NMR spectroscopic reaction monitoring experiments.[11] The hydrogenation of α-methylstyrene was not inhibited by the addition of mercury, while varying product formation was recorded for 1,1,2-triphenylethylene (52−89% yield), and significant inhibition was found for 1,1,2,2-tetraphenylethylene (35% vs 88% yield; Table S2, SI).

These data suggest a homotopic catalyst predominantly operates at mild temperature and H$_2$ pressure, while heterotopic catalyst species are likely to contribute at higher temperatures and pressure required for challenging substrates such as 1,1,2,2-tetraphenylethylene. The ^{1}H NMR spectroscopic monitoring of the hydrogenation of α-methylstyrene with **1** (2 mol %, 2 bar H$_2$, ambient temperature) revealed the complete formation of cumene in <71 min (Figure S13, SI). Moderate line broadening after H$_2$ addition may indicate the formation of a minor amount of cobalt particles. In previous monitoring studies with **E** and **J**, such broadening coincided with catalyst deactivation,[1e] whereas with **1** the hydrogenation reaction did not cease when spectral broadening appeared. Considering that mercury poisoning had also no effect on the catalytic reaction (see above), we presume that the initially formed particles are inactive in hydrogenation and that a molecular species is responsible for catalysis at ambient temperature. However, the possibility of catalytically active heterotopic species or a combination of homotopic and heterotopic species, as demonstrated in recent studies on solid Fe(0) with soluble s-block metal or aluminum species,[12] cannot be ruled out and requires further investigation beyond the scope of this work.

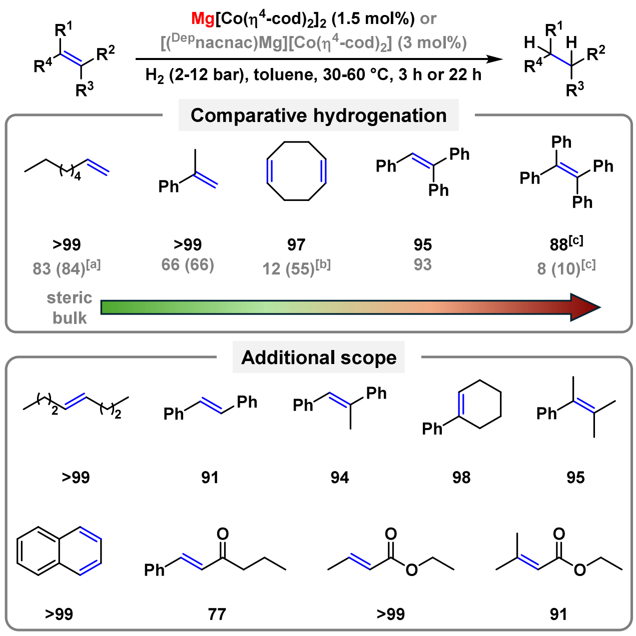

Figure 4. Hydrogenation of alkenes using Mg[Co(η^4-cod)$_2$]$_2$ (**1**) and [($^{\text{Dep}}$nacnac)Mg][Co(η^4-cod)$_2$] (**J**). Standard conditions: 0.2 mmol substrate (0.4 mol/L in toluene). 2−12 bar H$_2$, 30−60 °C, 3 or 22 h (see the Supporting Information for the individual reaction conditions). Yields and conversions in [%] were determined by quantitative GC-FID analysis vs internal n-pentadecane. Conversions are given in parentheses if <90%. [a] Isomerization to internal double bonds. [b] Formation of cis-cyclooctene as the major product. [c] c = 0.1 mol/L; V = 2.0 mL.

In summary, the complex Mg[Co(η^4-cod)$_2$]$_2$ (**1**) features an unsupported linear Co−Mg−Co unit and can be synthesized through a simple salt metathesis reaction. Single crystal X-ray diffraction, DOSY NMR spectroscopy, and quantum chemical studies indicate that complex **1** exists as an intact ion triple in the solid state, characterized by an ionic magnesium−cobalt interaction and predominantly electrostatic bonds between the 1,5-cyclooctadiene ligands and Mg^{2+}. This molecular structure is preserved in toluene solution. Complex **1** effectively catalyzes the hydrogenation of sterically demanding alkenes, surpassing the performance of the magnesium β-diketiminate salt **J**. These findings highlight a significant counterion effect on catalytic activity that is intrinsic to the Mg^{2+} cation.

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■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.5c00246.

> Experimental details and synthetic procedures, further spectroscopic and analytical data, crystallographic information, and details of DFT calculations (PDF)
>
> Optimized structures in xyz format (XYZ)

Accession Codes

Deposition Number 2469391 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Jonas, K.; Mynott, R.; Krüger, C.; Sekutowski, J. C.; Tsay, Y.-H. Bis(η-1,5-cyclooctadiene)cobaltlithium. *Angew. Chem., Int. Ed.* **1976**, *15*, 767−768. (b) Jonas, K. (Studiengesellschaft Kohle mbH), Method of Preparing Transition Metal-Olefin Complex Compounds and Alkali Metal-Transition Metal-Olefin Complex Compounds. U.S. Patent US4169845A, 1977. (c) Habermann, D. Organocobaltverbindungen aus (η-Cyclopentadienyl)cobalt-Komplexen durch reduktive C_5H_5-Ablösung. Ph.D. Dissertation, Ruhr-Universität Bochum, 1980. (d) Brennessel, W. W.; Young, V. G., Jr.; Ellis, J. E. Bis(1,2,3,4-η^4-anthracene)cobaltate(1−). *Angew. Chem., Int. Ed.* **2002**, *41*, 1211−1215. (e) Gawron, M.; Gilch, F.; Schmidhuber, D.; Kelly, J. A.; Horsley Downie, T. M.; Jacobi von Wangelin, A.; Rehbein, J.; Wolf, R. Counterion Effect in Cobaltate-Catalyzed Alkene Hydrogenation. *Angew. Chem., Int. Ed.* **2024**, *63*, No. e202315381.

(2) (a) Wolf, R.; Ehlers, A. W.; Slootweg, J. C.; Lutz, M.; Gudat, D.; Hunger, M.; Spek, A. L.; Lammertsma, K. The Homoleptic Sandwich Anion $[Co(P_2C_2tBu_2)_2]^-$: A Versatile Building Block for Phosphaorganometallic Chemistry. *Angew. Chem., Int. Ed.* **2008**, *47*, 4584−4587. (b) Ziegler, C. G. P.; Hennersdorf, F.; Weigand, J. J.; Wolf, R. Iron-Gallium and Cobalt-Gallium Tetraphosphido Complexes. *Z. Anorg. Allg. Chem.* **2020**, *646*, 552−557. (c) Hierlmeier, G.; Coburger, P.; Scott, D. J.; Maier, T. M.; Pelties, S.; Wolf, R.; Pividori, D. M.; Meyer, K.; van Leest, N. P.; de Bruin, B. Di-*tert*-butyldiphosphatetrahedrane as a Source of 1,2-Diphosphacyclobutadiene Ligands. *Chem.—Eur. J.* **2021**, *27*, 14936−14946. (d) Kelly, J. A.; Gramüller, J.; Gschwind, R. M.; Wolf, R. Low-Oxidation State Cobalt−Magnesium Complexes: Ion-Pairing and Reactivity. *Dalton Trans.* **2021**, *50*, 13985−13992.

(3) (a) Gärtner, D.; Welther, A.; Rad, B. R.; Wolf, R.; Jacobi von Wangelin, A. Heteroatom-Free Arene-Cobalt and Arene-Iron Catalysts for Hydrogenations. *Angew. Chem., Int. Ed.* **2014**, *53*, 3722−3726. (b) Büschelberger, P.; Gärtner, D.; Reyes-Rodriguez, E.; Kreyenschmidt, F.; Koszinowski, K.; Jacobi von Wangelin, A.; Wolf, R. Alkene Metalates as Hydrogenation Catalysts. *Chem.—Eur. J.* **2017**, *23*, 3139−3151.

(4) Baumann, B. N.; Lange, H.; Seeberger, F.; Büschelberger, P.; Wolf, R.; Hapke, M. Cobalt and Iron Metallates as Catalysts for Cyclization Reactions of Diynes and Triynes: [2 + 2+2] Cycloaddition vs. Garratt-Braverman Reaction. *Mol. Catal.* **2023**, *550*, No. 113482.

(5) Brennessel, W. W.; Ellis, J. E. Naphthalene and Anthracene Cobaltates(1−): Useful Storable Sources of an Atomic Cobalt Anion. *Inorg. Chem.* **2012**, *51*, 9076−9094.

(6) (a) Pelties, S.; Maier, T. M.; Herrmann, D.; de Bruin, B.; Rebreyend, C.; Gärtner, S.; Shenderovich, I. G.; Wolf, R. Selective P_4 Activation by a Highly Reduced Cobaltate: Synthesis of Dicobalt Tetraphosphido Complexes. *Chem.—Eur. J.* **2017**, *23*, 6094−6102. (b) Maier, T. M.; Sandl, S.; Shenderovich, I. G.; Jacobi von Wangelin, A.; Weigand, J. J.; Wolf, R. Amine−Borane Dehydrogenation and Transfer Hydrogenation Catalyzed by α-Diimine Cobaltates. *Chem.—Eur. J.* **2019**, *25*, 238−245. (c) Sandl, S.; Maier, T. M.; van Leest, N. P.; Kröncke, S.; Chakraborty, U.; Demeshko, S.; Koszinowski, K.; de Bruin, B.; Meyer, F.; Bodensteiner, M.; Herrmann, C.; Wolf, R.; Jacobi von Wangelin, A. Cobalt-Catalyzed Hydrogenations via Olefin Cobaltate and Hydride Intermediates. *ACS Catal.* **2019**, *9*, 7596−7606. (d) Hoidn, C. M.; Maier, T. M.; Trabitsch, K.; Weigand, J. J.; Wolf, R. [3 + 2] Fragmentation of a Pentaphosphido Ligand by Cyanide. *Angew. Chem., Int. Ed.* **2019**, *58*, 18931−18936. (e) Hauer, S.; Horsley Downie, T. M.; Balázs, G.; Schwedtmann, K.; Weigand, J. J.; Wolf, R. Cobalt-Mediated [3 + 1] Fragmentation of White Phosphorus: Access to Acylcyanophosphanides. *Angew. Chem., Int. Ed.* **2024**, *63*, No. e202317170.

(7) (a) Jonas, K.; Koepe, G.; Krüger, C. Heterometallic Dinuclear Complexes by Ethene Displacement with Grignard Compounds or Diorganomagnesium Compounds. *Angew. Chem., Int. Ed.* **1986**, *25*, 923−925. (b) Blake, M. P.; Kaltsoyannis, N.; Mountford, P. Probing the Limits of Alkaline Earth−Transition Metal Bonding: An Experimental and Computational Study. *J. Am. Chem. Soc.* **2015**, *137*, 12352−12368. (c) Green, R.; Walker, A. C.; Blake, M. P.; Mountford, P. Synthesis, Characterisation and Structural Studies of Amidinate and Guanidinate Alkaline Earth−Transition Metal Bonded Complexes. *Polyhedron* **2016**, *116*, 64−75.

(8) (a) Sheldrick, G. M.; Simpson, R. N. F. The Crystal Molecular Structure of Mercury Cobalt Carbonyl. *Chem. Commun.* **1967**, *19*, 1015a. (b) Sheldrick, G. M.; Simpson, R. N. F. The Crystal and Molecular Structure of Bis(tetracarbonylcobalt)mercury, $Hg(Co(CO)_4)_2$. *J. Chem. Soc. A* **1968**, 1005−1009.

(9) To the best of our knowledge, the only structurally related complex is $Zn[Co(\eta^4\text{-}C_4H_6)_2]_2$, which was already reported in 1980

(ref 1c) but only subjected to a small reactivity study with nucleophiles.

(10) Thum, K.; Friedrich, A.; Pahl, J.; Elsen, H.; Langer, J.; Harder, S. Unsupported Mg−Alkene Bonding. *Chem.—Eur. J.* **2021**, *27*, 2513−2522.

(11) (a) Widegren, J. A.; Finke, R. G. A Review of the Problem of Distinguishing True Homogeneous Catalysis from Soluble or Other Metal-Particle Heterogeneous Catalysis under Reducing Conditions. *J. Mol. Catal. A* **2003**, *198*, 317−341. (b) Jaska, C. A.; Manners, I. Heterogeneous or Homogeneous Catalysis? Mechanistic Studies of the Rhodium-Catalyzed Dehydrocoupling of Amine-Borane and Phosphine-Borane Adducts. *J. Am. Chem. Soc.* **2004**, *126*, 9776−9785. (c) Crabtree, R. H. Resolving Heterogeneity Problems and Impurity Artifacts in Operationally Homogeneous Transition Metal Catalysts. *Chem. Rev.* **2012**, *112*, 1536−1554. (d) Gärtner, D.; Sandl, S.; Jacobi von Wangelin, A. Homogeneous vs. Heterogeneous: Mechanistic Insights into Iron Group Metal-Catalyzed Reductions from Poisoning Experiments. *Catal. Sci. Technol.* **2020**, *10*, 3502−3514.

(12) (a) Färber, C.; Stegner, P.; Zenneck, U.; Knüpfer, C.; Bendt, G.; Schulz, S.; Harder, S. Teaming up Main Group Metals with Metallic Iron to Boost Hydrogenation Catalysis. *Nat. Commun.* **2022**, *13*, 3210. (b) Knüpfer, C.; Färber, C.; Langer, J.; Harder, S. Lithium Aluminium Hydride and Metallic Iron: A Powerful Team in Alkene and Arene Hydrogenation Catalysis. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202219016.

https://doi.org/10.1021/acs.organomet.5c00246