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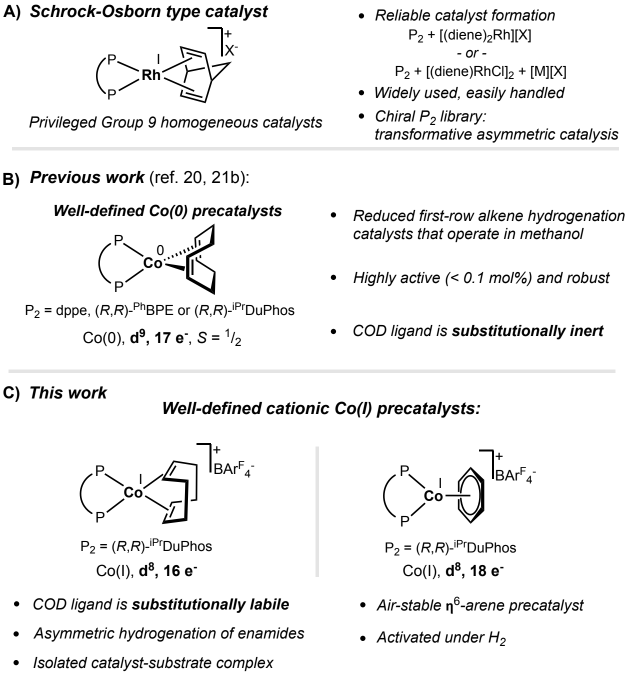
Syntheses and Catalytic Hydrogenation Performance of Cationic Bis(phosphine) Cobalt(I) Diene and Arene Compounds.

Hongyu Zhong,[a] Max R. Friedfeld[a] and Paul J. Chirik*[a]

Abstract: Chloride abstraction from $[(R,R)\text{-}(^{iPr}\text{DuPhos})\text{Co}(\mu\text{-Cl})]_2$ with NaBAr^F_4(BAr^F_4 = $\text{B}[(3,5\text{-}(\text{CF}_3)_2)\text{C}_6\text{H}_3]_4$) in the presence of dienes such as 1,5-cyclooctadiene (COD) or norbornadiene (NBD) yielded long sought-after cationic bis(phosphine) cobalt complexes, $[(R,R)\text{-}(^{iPr}\text{DuPhos})\text{Co}(\eta^2,\eta^2\text{-diene})][\text{BAr}^F_4]$. The COD complex proved substitutionally labile undergoing diene substitution with tetrahydrofuran, NBD or arenes. The resulting 18-electron, cationic cobalt(I) arene complexes, as well as the $[(R,R)\text{-}(^{iPr}\text{DuPhos})\text{Co}(\text{diene})][\text{BAr}^F_4]$ derivatives, proved to be highly active and enantioselective precatalysts for asymmetric alkene hydrogenation. A cobalt-substrate complex, $[(R,R)\text{-}(^{iPr}\text{DuPhos})\text{Co}(\text{MAA})][\text{BAr}^F_4]$ (MAA = methyl 2-acetamidoacrylate) was crystallographically characterized as the opposite diastereomer than expected for productive hydrogenation demonstrating a Curtin-Hammett kinetic regime similar to rhodium catalysis.

Cationic bis(phosphine) rhodium(I) complexes are privileged structures in organometallic chemistry and homogeneous catalysis with applications ranging from alkene hydrogenation,[1] hydroformylation[2] and hydroacylation[3] to a variety of C-C bond-forming reactions.[4] Schrock and Osborn's pioneering synthesis and study of these complexes over four decades ago,[5] coupled with advances in chiral phosphine ligands[6] and high-throughput experimentation,[7] established the transformative nature of asymmetric catalysis in organic synthesis (Scheme 1A). The continuing emphasis on relatively earth abundant, *3*d transition metals as alternatives to precious metals has renewed interest in synthesizing the cobalt analogs of these important rhodium compounds.[8] Indeed, cationic bis(phosphine) cobalt(I) complexes have been implicated as the active species in a host of C-C bond-forming reactions including: [4+2] and [2+2] cycloadditions,[9] the asymmetric synthesis of functionalized cyclobutanes,[10] hydrovinylation of alkene and alkynes[9a,11] and in alkene hydroacylation.[12] Aside from mass spectrometry data from a [4+2] reaction in the gas phase,[9b] observation or definitive characterization of cationic bis(phosphine) Co(I) diene compounds has remained elusive.

Cationic, 18-electron tris(phosphine) cobalt complexes with π-coordinated hydrocarbyl ligands are well-documented and examples with cycloheptatriene[13], norbornadiene[14], cyclopentadiene[15], alkyne[16] and ethylene[17] ligands have been reported. With bidentate $R_2\text{PCH}_2\text{CH}_2\text{P}R_2$ (R = cyclopropyl or isopropyl), Jolly and coworkers reported cationic, 18-electron cobalt(I) arene complexes.[18] By contrast, synthesis of the cobalt analogs of the Schrock-Osborn type η^2,η^2-diene complexes has remained elusive and possibly complicated by 1e$^-$ redox processes and substitutional lability unique to cobalt.[19] We have recently demonstrated the utility of bis(phosphine) cobalt complexes in both diastereo-[20] and enantioselective alkene hydrogenation reactions.[21] Catalysis was successfully initiated from precatalysts over three different oxidation states: Co(0)[20,21b] (Scheme 1B), neutral Co(I)[21b] and Co(II)[20,21a-c]. For the directed hydrogenation of terpinenol,[20] computational studies support formation of metallocycles arising from the Co(II) oxidation state being maintained throughout the catalytic cycle.[22] An alternative pathway involving a more traditional Co(0)-Co(II)[23] cycle was also computed and while energetically reasonable, was higher in energy than the metallocycle pathway and does not explain the observed diastereoselectivity. Despite these advances, cationic bis(phosphine) cobalt(I) complexes have remained elusive and motivated our studies to explore their catalytic performance and compare them to the neutral cobalt examples as well as the well-established rhodium congeners.



Scheme 1. A) Modular (*in situ*) generation of cationic bis(phosphine) Rh(I) diene species, the Schrock-Osborn type catalysts. B) Previously reported neutral bis(phosphine) Co(0) diene compounds. C) Cationic bis(phosphine) Co(I) diene and arene compounds (this work).

A common synthesis of cationic metal complexes relies on halide abstraction from a metal halide precursor with no accompanying oxidation state change at the metal. Our laboratory has recently reported the isolation and characterization of dimeric bis(phosphine)cobalt(I) chloride complexes[21b] that are attractive precursors for targeted cationic

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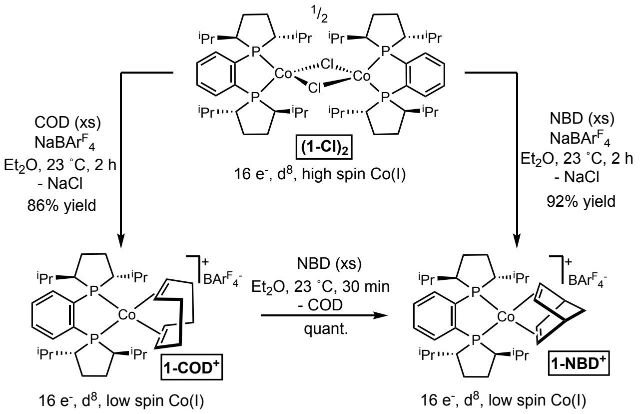
cobalt(I) diene complexes. The bis(phospholane), (*R*,*R*)-^{iPr}DuPhos (1,2-bis((2*R*,5*R*)-2,5-diisopropylphospholano)benzene) was selected for the majority of these studies, owing to its established role in promoting highly enantioselective alkene hydrogenation reactions.[21] Chloride abstraction in the presence of 1,5-cyclooctadiene (COD) was initially explored with $NaBF_4$, $NaPF_6$, NaOTf and $NaClO_4$. In each case, no abstraction reaction was observed. By contrast, addition of $NaBAr^F{}_4$ to a diethyl ether solution containing the S = 1 chloride-bridged dimer, $[(R,R)\text{-}(^{iPr}\text{DuPhos})\text{Co}(\mu\text{-Cl})]_2$ (**(1-Cl)$_2$**) in the presence of excess COD produced a blue-purple solid identified as $[(R,R)\text{-}(^{iPr}\text{DuPhos})\text{Co}(\eta^2,\eta^2\text{-COD})][\text{BAr}^F{}_4]$ (**1-COD$^+$**) in 86 % isolated yield (Scheme 2, left).



Scheme 2. Syntheses of cationic $[(R,R)\text{-}(^{iPr}\text{DuPhos})\text{Co}]^+$ diene complexes from chloride abstraction of $[(R,R)\text{-}(^{iPr}\text{DuPhos})\text{Co}(\mu\text{-Cl})]_2$ or ligand substitution.

The solid-state structure of **1-COD$^+$** was determined by X-ray diffraction and exhibits a distorted planar geometry at cobalt (Figure 1A, 1B). This geometry contrasts the neutral cobalt(0) complex, $(R,R)\text{-}(^{iPr}\text{DuPhos})\text{Co}(\eta^2,\eta^2\text{-COD})$ (**1-COD**)[21b] (Figure 1C) where a distorted tetrahedral environment was observed owing to the d^9, Co(0) electron configuration(Figure 1C). Compared to a related rhodium congener, $[(R,R)\text{-}(^{Et}\text{DuPhos})\text{Rh}(\eta^2,\eta^2\text{-COD})][\text{BF}_4]$,[24] **1-COD$^+$** has more elongated *C*=*C* bonds (1.39(1) vs 1.35(2) Å), demonstrating stronger back-bonding from the first row metal. Despite being isolable in the solid state, **1-COD$^+$** is unstable in solution as the COD ligand is substitutionally labile in the presence of arenes or coordinating solvents. For example, dissolving **1-COD$^+$** in benzene-d_6 resulted in an immediate color change to orange, signaling displacement of the diene and formation of $[(R,R)\text{-}(^{iPr}\text{DuPhos})\text{Co}(\eta^6\text{-C}_6\text{D}_6)][\text{BAr}^F{}_4]$ (*vide infra*). In THF-d_8, a broad $^{31}P\{^1H\}$ signal was observed for **1-COD$^+$** at 87.5 ppm while the ^1H NMR spectrum contained peaks assigned to the diamagnetic **1-COD$^+$** and new paramagnetic compounds. Over time, the mixture irreversibly converts to unidentified paramagnetic compound(s), likely derived from substitution of the COD by THF solvent.

The norbornadiene (NBD) cobalt complex, $[(R,R)\text{-}(^{iPr}\text{DuPhos})\text{Co}(\eta^2,\eta^2\text{-NBD})][\text{BAr}^F{}_4]$ (**1-NBD$^+$**) was prepared in a similar manner to **1-COD$^+$** and also by substitution of **1-COD$^+$** with free NBD (Scheme 2). Red-purple **1-NBD$^+$** proved less substitutionally labile than **1-COD$^+$** as no paramagnetic impurities were observed by ^1H NMR spectroscopy upon standing in THF-d_8 over the course of 4 weeks at 23 ºC.

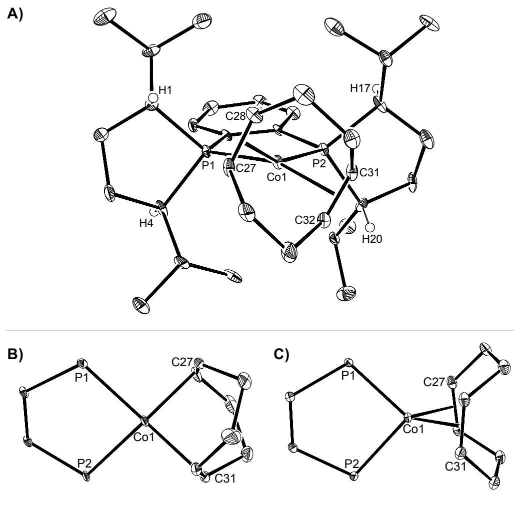
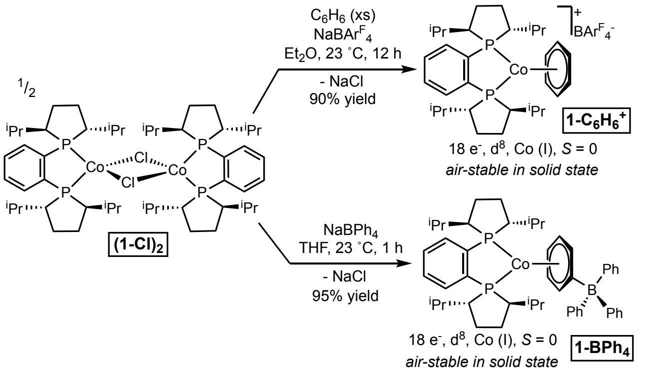


Figure 1. A) Solid-state structures of **1-COD$^+$** at 30% probability ellipsoids with H atoms (except the H atoms on chiral carbon atoms) and $[\text{BArF}_4]^-$ counter-ion omitted for clarity. B) Core of the solid-state structure of cation of **1-COD$^+$** Dihedral angle (Co1, P1, P2); (Co1, C27, C31) = 4.89º). C) Core of the solid-state structure of **1-COD** (Dihedral angle (Co1, P1, P2); (Co1, C27, C31) = 71.17º)

The chloride abstraction protocol was also applied to the direct syntheses of cationic cobalt(I) arene complexes. Addition of one equivalent of $NaBAr^F{}_4$ to a diethyl ether solution of **(1-Cl)$_2$** in excess benzene followed by filtration resulted in isolation of $[(R,\ R)\text{-}(^{iPr}\text{DuPhos})\text{Co}(\eta^6\text{-C}_6\text{H}_6)][\text{BAr}^F{}_4]$ (**1-C$_6$H$_6$$^+$**) as an orange solid in 90% yield (Scheme 3, top) that was also characterized by X-ray diffraction (Figure 2, left). A related compound, $(Me_3P)_2Co(\eta^6\text{-}C_6H_5)BPh_3$ was reported by Beauchamp and coworkers and obtained as a mixture with $(Me_3P)_4Co$ from addition of $NaBPh_4$ to $(Me_3P)_3CoBr$.[25] Use of $NaBPh_4$ as the chloride abstraction reagent produced the $[BPh_4]$-coordinated zwitterionic complex, $(R,R)\text{-}(^{iPr}\text{DuPhos})\text{Co}(\text{BPh}_4)$ (**1-BPh$_4$**) as a dark orange solid in 95% yield (Scheme 3, bottom). Notably attempts to prepare **1-C$_6$H$_6$$^+$** with a $[BPh_4]^-$ anion were unsuccessful even when the chloride abstraction reaction was performed in the presence of excess benzene (3:1 THF:benzene solution). The solid-state structure of **1-BPh$_4$** (Figure 2, right) established η^6-coordination of one of the phenyl groups from the $[BPh_4]^-$ anion with the boron-attached carbon atom(C27) slightly displaced (0.124 Å) from the plane of the remaining five carbons.[26]



Scheme 3. Syntheses of [(*R*,*R*)-(^{iPr}DuPhos)Co(η^6-arene)]$^+$ complexes from chloride abstraction from [(*R*,*R*)-(^{iPr}DuPhos)Co(μ-Cl)]$_2$.

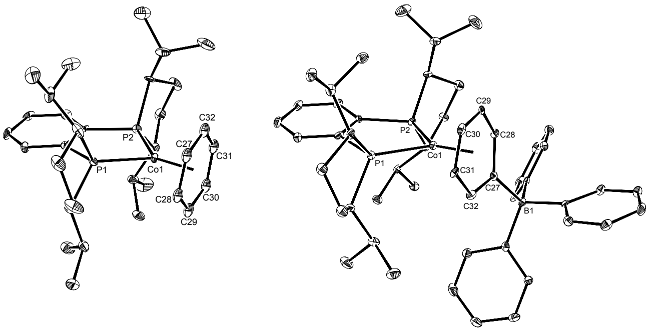
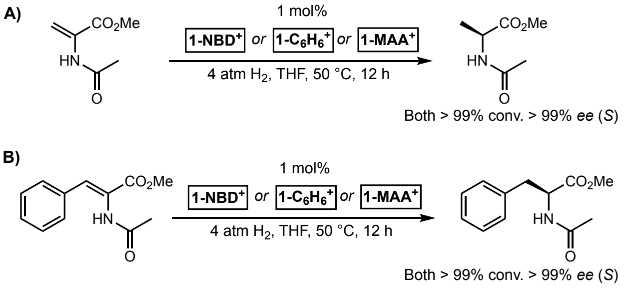


Figure 2. Solid-state structures of [(*R*,*R*)-(^{iPr}DuPhos)Co(η^6-C_6H_6)][BAr$^F_4$] and (*R*,*R*)-(^{iPr}DuPhos)Co(BPh_4) compounds at 30% probability ellipsoids with hydrogen atoms and [BAr$^F_4$$^-$] counter-ion omitted for clarity.

Each of the 16-electron, cationic cobalt complexes is substitutionally labile as the diene ligands were readily displaced by arenes to form the corresponding 18-electron products. This behavior may explain why the cobalt variants of Schrock-Osborn catalysts remained elusive for nearly five decades while the 18 electron, cationic bis(phosphine) Co(I) η^6-arene complexes[18] and cationic tris(phosphine) Co(I) diene complexes are well precedented.[13-17] Fluorobenzene and 1,2-difluorobenzene η^6-arene complexes, **1-$C_6H_5F^+$** and **1-$C_6H_4F_2^+$**, were synthesized by the same protocol and characterized by X-ray diffraction (see Supporting Information, Figure S51, S52). The relative coordination affinity of the π-coordinating ligands for [(*R*,*R*)-(^{iPr}DuPhos)Co(I)]$^+$ is: benzene > NBD > fluorobenzene > 1,2-difluorobenzene > COD. Substitution of the electron-poor η^6-1,2-difluorobenzene by diene and alkenes has been reported for the corresponding rhodium compounds.[27] In stark contrast, the COD ligand in the neutral 17-electron bis(phosphine) Co(0) COD complexes[21b] are inert to substitution by enamide, benzene or methanol, a striking difference in fundamental coordination properties resulting from one-electron reduction.

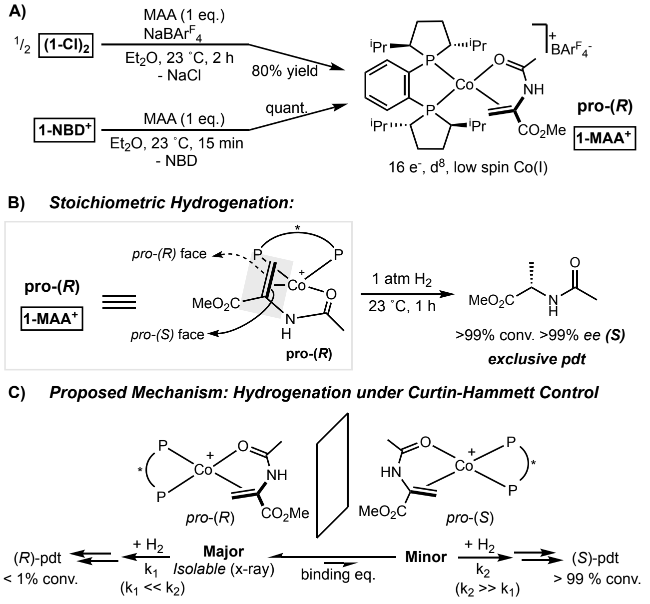
With a family of cationic bis(phosphine) cobalt complexes in hand, their performance in catalytic asymmetric alkene hydrogenation was evaluated. With 1 mol% of **1-NBD$^+$** as the precatalyst, successful hydrogenation of methyl 2-acetamidoacrylate (MAA) was observed in THF solution at 23 ºC with 4 atm of H_2. The (*S*)-hydrogenation product was obtained in >99% conversion and >99% *ee* (Scheme 4A). The arene derivative, **1-$C_6H_6^+$** was also an active precatalyst for the hydrogenation of MAA (>99% conv., >99% *ee*), highlighting that the coordinatively saturated 18e$^-$ Co(I) cation is effectively activated under hydrogenation conditions. This is notable as both **1-$C_6H_6^+$** and **1-BPh_4** proved stable in acetone-d_6 and CD_2Cl_2 solution and upon exposure to air (23 ˚C, 5h as solids), rare but attractive features of first row transition metal alkene hydrogenation catalysts.[8] Both **1-NBD$^+$** and **1-$C_6H_6^+$** were also active for the hydrogenation of the tri-substituted enamide, (*Z*)-2-acetamido-3-phenylacrylate(MAC), and produced the (*S*)-hydrogenation product in excellent yield and enantioselectivity (Scheme 4B). The enantioselectivity for MAC hydrogenation with Co(I)$^+$ is higher than that obtained with the Co(II) dialkyl precatalyst, (*R*,*R*)-(^{iPr}DuPhos)Co(CH_2SiMe_3)$_2$ (92.7% *ee*),[22] suggesting different catalytic pathways and origins of enantioselection for Co(I)$^+$ and Co(II) precatalysts.



Scheme 4. Catalytic asymmetric hydrogenation using well-defined cationic bis(phosphine) cobalt diene and η^6-arene complexes.

Because of the exceptional performance of **1-NBD$^+$** for the asymmetric hydrogenation of MAA and MAC, studies were conducted to gain insight into the substrate-catalyst interaction. Addition of NaBAr$^F_4$ to a diethyl ether solution containing equimolar **(1-Cl)$_2$** and MAA followed by filtration yielded [(*R*,*R*)-(^{iPr}DuPhos)Co(η^2,η^2-MAA)][BAr$^F_4$] (**1-MAA$^+$**) (Scheme 5A). Green **1-MAA$^+$** was also prepared from displacement of the diene from **1-NBD$^+$** by one equivalent of MAA. The solid-state structure of **1-MAA$^+$** was determined by X-ray diffraction (Figure 3) and established an idealized planar geometry about the cobalt. The MAA exhibits familiar two-point coordination through the carbonyl of the amide group and the alkene *C=C* bond, mirroring known rhodium(I) compounds.[28] Of the two π faces of the alkene available for coordination, the cobalt center is bonded exclusively to the pro-(*R*) face. The THF-d_8 ^{31}P{^{1}H} NMR spectrum of **1-MAA$^+$** at 23 ºC exhibited a single resonance at 63.8 ppm. At temperatures below -60 ºC, two ^{31}P resonances were observed with $^2J_{P\text{-}P}$ of 34.3 Hz, consistent with two inequivalent phosphorus atoms in the major diastereomer. The observed dynamic behavior and line broadening likely originates from reversible coordination of the alkene. By comparison, the same synthesis with MAC produced [(*R*,*R*)-(^{iPr}DuPhos)Co(η^6-MAC)][BAr$^F_4$] (**1-MAC$^+$**). Characterization by ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR established its η^6-phenyl coordination to Co(I)$^+$ instead of two-point binding.

The catalytic competency of **1-MAA$^+$** was evaluated by exposure of THF-d_8 solution of the compound to 1 atm of H_2. Analysis of the alkane product by gas chromatography established formation of the (*S*)-hydrogenation product in >99% conversion and >99% *ee* (Scheme 5B), which is the opposite alkane configuration expected from turnover of the pro-(*R*) adduct following H_2 oxidative addition, alkene migratory insertion and C-H reductive elimination. This result supports a Curtin-Hammett kinetic regime (Scheme 5C), where substrate coordination is fast and reversible as compared to the oxidative addition of H_2, analogous to rhodium hydrogenation established in the landmark study by Halpern and coworkers[29] and also independently by Brown[28c,30] and Heller[31]. With a catalytic amount of 1 mol% **1-MAA⁺**, the (*S*)-hydrogenation product was also obtained in >99% conversion and >99% *ee*. Using the same procedure, stoichiometric and catalytic hydrogenation with **1-MAC⁺** both produced the (*S*)-hydrogenation product in >99% conv. and >99% *ee*, which suggests a possible equilibrium between η^6- and η^2,η^2-binding of MAC with the latter being on the catalytic cycle.



Scheme 5. A) Synthesis of (*R*,*R*)-[(^{iPr}DuPhos)Co]⁺–substrate adduct **1-MAA⁺**. B) Stoichiometric hydrogenation of **1-MAA⁺**. C) Proposed mechanism of pro-(*R*) and pro-(*S*) equilibrium and their different rates of reaction with H_2.

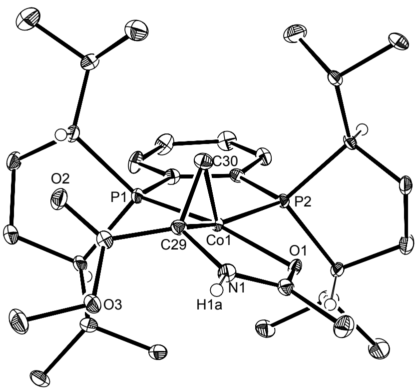


Figure 3. Solid-state structure of **1-MAA⁺** at 30% probability ellipsoids with H atoms(except H atoms on chiral carbon atoms and the amide H atom) and [$BAr^F{}_4{}^-$] counter-ion omitted for clarity. Dihedral angle (Co1, P1, P2); (Co1, C29, O1) = 20.83°.

In summary, syntheses of 16-electron, cationic bis(phosphine)-Co(I) diene complexes among the privileged class of Group 9 homogeneous transition metal catalysts, have been achieved for the first time more than 40 years after Schrock and Osborn's report of the rhodium(I) catalysts. The 18-electron η^6-arene variants are also synthesized and characterized. Catalytic hydrogenation of enamides has been achieved using both precatalysts and provided excellent enantioselectivity. Stoichiometric hydrogenation of a well-defined 16-electron catalyst-substrate adduct revealed hydrogenation initiated from cationic Co(I) to be under Curtin-Hammett control that mimics the classic rhodium system.

Acknowledgements

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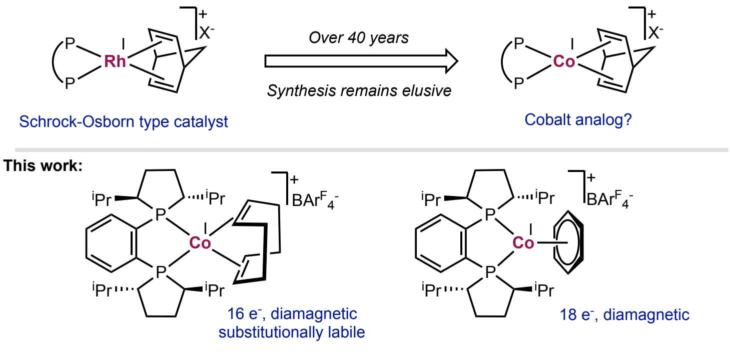
Crystallographic Data

CCDC 1900392, 1900393, 1900394, 1900395, 1900396 and 1900398 contain the supplementary crystallographic data of compounds **1-COD⁺**, **1-MAA⁺**, **1-C_6H_6⁺**, **1-BPh_4**, **1-C_6H_5F⁺**, **1-$C_6H_4F_2$⁺**. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Keywords: cobalt • alkene hydrogenation • asymmetric catalysis • catalyst–substrate complex

Table of Content Graphic



Highly active precatalysts for asymmetric alkene hydrogenation

The cobalt analogs of the Schrock-Osborn type rhodium catalysts have been synthesized and characterized for the first time and showed excellent catalytic asymmetric hydrogenation activity. Study of an isolated catalyst-substrate adduct revealed enantioselection mirroring the classic Rh(I) asymmetric hydrogenation.

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