Ionic Phosphine Ligands with Cobaltocenium Backbone: Novel Ligands for the Highly Selective, Biphasic, Rhodium-Catalyzed Hydroformylation of 1-Octene in Ionic Liquids†

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The use of electron-poor phosphine-substituted cobaltocenium salts as ligands for the biphasic hydroformylation in ionic liquids has been investigated. Using improved oxidation methods, 1,1′-bis(diphenylphosphino)cobaltocenium nitrate, 1,1′-bis(diphenylphosphino)-cobaltocenium hexafluorophosphate, and 1,1′-bis[1-methyl(1-diphenylphosphino)ethyl]cobaltocenium hexafluorophosphate have been synthesized. 1,1′-Bis(diphenylphosphinocobaltocenium hexafluorophosphate in particular proved to be a very suitable ligand for the biphasic hydroformylation of 1-octene in 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM PF_6), enabling high catalyst activity, high selectivity to the *n*-product, and no detectable catalyst leaching. In contrast to aqueous biphasic systems, the ionic liquid BMIM PF_6 provides for the rhodium catalyst a low-coordinating medium with limited but sufficient solubility for 1-octene to allow high reaction rates.

Introduction

Metallocene derivatives have found widespread use as ligands. Phosphine ligands based on substituted ferrocenes are even used industrially in enantioselective catalytic hydrogenations.[1] Compared to the isoelectronic ferrocenes, cobaltocenium cations show reduced reactivity on the cyclopentadienyl rings due to their electronic properties, thus being inert to electrophilic and radical attack and all but the strongest oxidants.[2] Owing to their ionic character, they show good solubility in polar solvents. These remarkable properties stimulated our interest in synthesizing functionalized cobaltocenium salts and in testing these as ligands in biphasic catalytic reactions.

Biphasic catalysis is a well-established method for effective catalyst separation and recycling. In the case of Rh-catalyzed hydroformylation reactions this principle was technically realized in the Ruhrchemie−Rhône−Poulenc process, where water is used as catalyst phase.[3] Unfortunately, this process is limited to C_2-C_5 olefins due to the low water solubility of higher olefins. As an alternative polar medium for biphasic hydroformylation, Chauvin et al. suggested novel solvents known as ionic liquids (for general reviews about ionic liquids see ref 4). These authors described in detail the biphasic hydroformylation of 1-pentene with [Rh-$(CO)_2$acac]/triarylphosphine in, for example, 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM PF_6).[5] However, with none of the tested ligands was it possible to combine high activity, complete retention of the catalyst in the ionic liquid, and high selectivity for the desired linear hydroformylation product. The use of PPh_3 resulted in significant leaching of the Rh catalyst out of the ionic liquid layer. This could be suppressed by the application of sulfonated triaryl phosphine ligands, but a major decrease in catalyst activity was found with these ligands. All ligands used in Chauvin's work showed poor selectivity to the desired linear hydroformylation product (*n*/*iso*-ratio between 2 and 4). Obviously, the Rh-catalyzed, biphasic hydroformylation of higher olefins in ionic liquids requires the use of ligand systems that are specifically designed for this application.

In the present article, we describe synthesis and characterization of ionic ligands with a cobaltocenium backbone and their successful application in the highly selective, biphasic, rhodium-catalyzed hydroformylation of 1-octene using ionic liquids as catalyst solvent. New

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[†] Dedicated to Prof. Willi Keim on the occasion of his 65th birthday.

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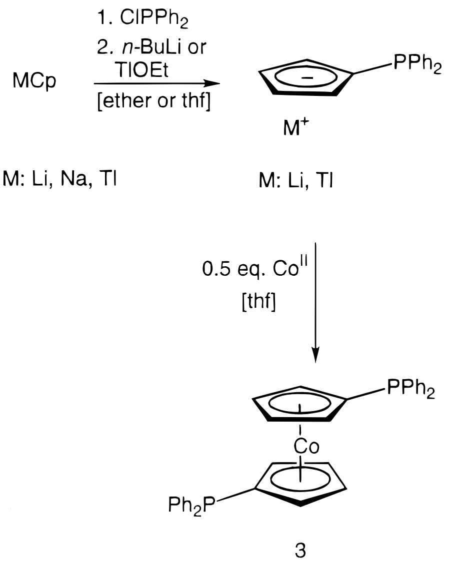
Scheme 1



and optimized syntheses of 1,1′-bis(diphenylphosphino)cobaltocenium nitrate (**1**) and 1,1′-bis(diphenylphosphino)cobaltocenium hexafluorophosphate (**2**) are presented. The preparation of the new compound 1,1′-bis[1-methyl(1-diphenylphosphino)ethylcobaltocenium hexafluorophosphate (**4**) is also described.

Results and Discussion

Synthesis of 1,1′-Bis(diphenylphosphino)cobaltocenium Nitrate (1). Initially, we developed a procedure for the synthesis of the new complex 1,1′-bis(diphenylphosphino)cobaltocenium nitrate (**1**). Our special interest in **1** was based on the idea to use this compound as ligand in the biphasic hydroformylation in aqueous systems.

At first, we synthesized 1,1′-bis(diphenylphosphino)cobaltocene (**3**) following an improved procedure similar to the methods given by Davison[6] and DuBois.[7] The substituted cyclopentadiene $C_5H_5PPh_2$ is obtained quantitatively from NaCp, TlCp, or LiCp. Subsequent quantitative deprotonation with *n*-BuLi generates the anionic ligand, and in situ reaction with Co(acac)$_2$ affords complex **3** in an overall yield of 59% (see Scheme 1). The latter method avoids the use in the deprotonation step of highly toxic thallium reagents, which have been used previously due to their smooth reactivity and high stability.

1,1′-Bis(diphenylphosphino)cobaltocenium nitrate (**1**) could be generated directly by the oxidation of **3** with HNO_3 in propionic anhydride. The compound was characterized by single-crystal X-ray diffraction analysis. Suitable crystals could be obtained by crystallization from hot water. Both cobaltocenium cations and nitrate anions are located on crystallographic inversion centers; this implies a staggered conformation of the cation with phosphine substituents in trans position similar to **3**[7] and orientational disorder for the anion. Crystal data, data collection parameters, and convergence results concerning the structure determination of **1** are presented in Table 1. The PLATON plot of **1** along with selected intramolecular distances and angles is given in Figure 1.

Table 1. Crystal Data, Data Collection Parameters, and Convergence Results for 1

formula	$C_{34}H_{28}CoNO_3P_2$
fw	619.49
system	monoclinic
space group (no.)	$P2_1/c$ (14)
a, Å	13.073(3)
b, Å	9.705(6)
c, Å	11.637(3)
β, deg	101.20(2)
U, Å^3	1448(1)
Z	4
d_{calc}, g cm^{-3}	1.42
μ, cm^{-1}	7.34
$\theta_{\max}$, deg	30
min transmission	0.901
max transmission	0.972
cryst dimens, mm^3	0.58 × 0.15 × 0.04
no. of reflns	4226
indep obs reflns $I > 1.0\ \sigma(I)$	1393
no vars	141
R^a	0.080
$R_w{}^b$	0.069
res electron dens, e Å^{-3}	0.45

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. $w^{-1} = \sigma^2(F_o)$.

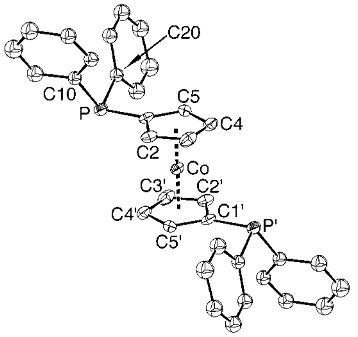


Figure 1. PLATON plot[8] of the 1,1′-bis(diphenylphosphino)cobaltocenium cation. Ellipsoids are scaled to enclose 30% probability. Selected bond distances [Å] and angles [deg]: Co−C(average) 2.038(3), Co−ring 1.644(3), P−C1 1.832(5), P−C10 1.836(6), P−C20 1.813(6); C1−P−C10 101.4(2), C1−P−C20 100.8(3), C10−P − C20 102.4(3).

Improved Synthesis of 1,1′-Bis(diphenylphosphino)cobaltocenium Hexafluorophosphate (2). Davison et al. had described a method to prepare 1,1′-bis(diphenylphosphino)cobaltocenium hexafluorophosphate (**2**) from **3** by in situ oxidation with oxygen in acetic acid. However, using this method, they obtained **2** in only 20% yield.[6] Obviously, their oxidation method favored the oxidation of **3** to the related phosphine oxides. We were able to show by ^{31}P NMR that **2** prepared in this manner indeed contained large amounts of phosphine oxides. Additionally, Davison et al. used a purification method by chromatography over silica. As the polarity of **2** leads to strong interactions with silica, we suggest high losses of the product during this procedure.

Recently, Johnson et al. reported **2** (which they isolated in 5% yield) being an unstable compound, that decomposes even in dry solvents to form a black mud.[9]

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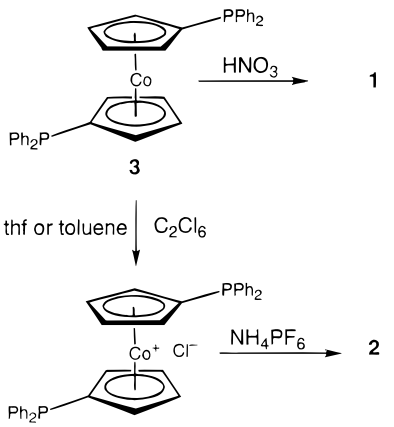
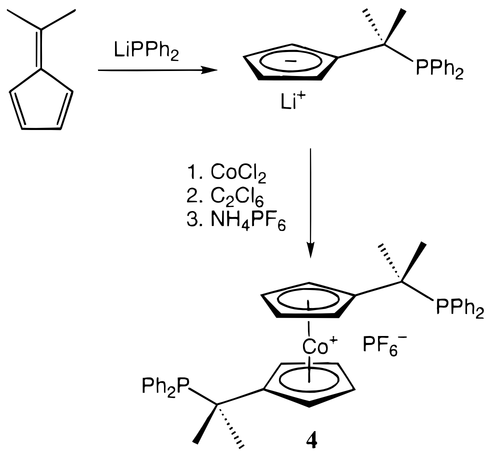
Scheme 2



Scheme 3



In contrast, we observed **2** to be a yellow powder that is easy to handle and indefinitely stable and storable under nitrogen.

Using a new procedure, we were able to obtain **2** in high yields free of phosphine oxides. This was achieved by applying to diphenylphosphinocobaltocene **3** the smooth anaerobic oxidation method developed by Herberich et al.[10] (see Scheme 2). The reaction of **3** with C_2Cl_6 generates the oily 1,1′-bis(diphenylphosphino)-cobaltocenium chloride. The byproduct C_2Cl_4 can be easily removed by evaporation. Anion exchange leads to stable and solid **2**. Using this method, we were able to synthesize **2** without the formation of major amounts of byproducts.

Aiming to apply **2** as chelating ligand in catalytic reactions, we extended the synthesis to a preparative scale (20 g). Even on this large scale an overall yield of 63% based on $CoCl_2$ could be achieved.

Interestingly, it is not possible to synthesize **2** in analogy with the procedure used for the preparation of **1**. The highly exothermic reaction of hexafluorophosphoric acid with propionic anhydride is very difficult to control, and the formation of phosphine oxides becomes a major problem. Additionally, it is not easy to separate **2** from these byproducts. Conventional methods to reduce organic P^V-oxides to P^{III} with trichlorosilane in benzene or toluene[11] are not applicable in this case due to the insolubility of the cobaltocenium salts in nonpolar solvents. Attempts to use dichloromethane instead were also not successful.

Synthesis of 1,1′-Bis[1-methyl(1-diphenylphosphino)ethyl]cobaltocenium Hexafluorophosphate (3). The introduction of an alkyl bridge between the cyclopentadienyl ligand and phosphorus is interesting for two reasons. On one hand, the electronic influence of the electron-withdrawing cobaltocenium fragment on the phosphine is considerably weakened. On the other hand, the introduction of the alkyl bridge enhances the structural flexibility and its ability to adapt to different coordination polyhedra.

Our procedure to synthesize cobaltocene derivatives with this ligand uses in its initial step the nucleophilic addition of lithium diphenylphosphide to 6,6′-dimethylfulvene, which proceeds regioselectively according to a known method for the synthesis of alkyl-substituted cyclopentadienides described by Coville et al.[12] and generates directly the desired monosubstituted lithio[1-methyl-(1-diphenylphosphino)ethyl]cyclopentadienide. Parallel to our work, Erker et al. published a similar procedure for the synthesis of phosphinomethylenecyclopentadienyl ligands.[13]

As shown in Scheme 3, 1,1′-bis[1-methyl(1-diphenylphosphino)ethyl]cobaltocenium chloride is obtained by the in situ reaction of lithium diphenylphosphide and 6,6-dimethylfulvene followed by the reaction with $CoCl_2$ and subsequent oxidation by C_2Cl_6. Using this procedure, a mixture of the phosphine and the related phosphine oxide was obtained in 83% yield. After anion exchange with NH_4PF_6, **4** could be easily isolated in pure form as the PF_6^- salt, making use of the different solubility of phosphine and phosphine oxide in methanol.

Ionic Liquids. First screening experiments already revealed that the water solubility of the phosphinocobaltocenium salts **2** and **4** was not high enough to allow biphasic catalytic reactions in aqueous systems. Even with the nitrate salt **1**, almost complete leaching of the Rh catalyst into the organic layer was observed after the hydroformylation of 1-hexene in a biphasic mixture of water and 1-hexene.

Alternatively, we chose the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM PF_6) as standard solvent for our investigations of the biphasic hydroformylation of 1-octene. Carrying the same anion as the ionic catalyst complexes under investigation, this ionic liquid was particular suitable for our investigations. BMIM PF_6 was prepared using standard methods described by Fuller et al.[14] and de Souza et al.[15] or purchased from Solvent Innovation GmbH, Köln (http://www.solvent-innovation.de).

Catalysis. The catalytic systems were prepared in situ by mixing $[Rh(CO)_2acac]$ with the ligand in BMIM PF_6 at room temperature. The results obtained in the

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Table 2. Comparison of Different Phosphine Ligands in the Rh-Catalyzed Hydroformylation of 1-Octene in 1-Butyl-3-methylimidazolium Hexafluorophosphate (100 °C, 10 bar syngas pressure)[a]

entry	ligand	TOF/h^{-1}	*n*/*iso*	*S* (*n*-Ald)[b]/%
a	PPh_3	426	2.6	72
b	TPPTS	98	2.6	72
c	dppe	35	3.0	75
d	dppf	828	3.8	79
e	4	66	2.6	73
f	2	810	16.2	94

[a] Conditions: ligand/Rh = 2, CO/H_2 = 1:1, $t = 1$ h, $T = 100$ °C, $p = 10$ bar, 1-octene/Rh = 1000, 5 mL of BMIM PF_6. [b] *S* (*n*-Ald) = selectivity to *n*-nonanal in the product.

biphasic hydroformylation of 1-octene using different ligands are summarized in Table 2. To evaluate the properties of the ionic diphosphine ligands with cobaltocenium backbone, we compared the results obtained with the ligands **2** and **4** with those obtained with PPh_3, two common neutral bidentate ligands, and with NaTPPTS as standard anionic ligand.

It is noteworthy that only with ligand **2** was a clear enhancement of the selectivity to the linear hydroformylation product observed (Table 2, entry f). With all other ligands used in our experiments, we found *n*/*iso*-ratios in the range between 2 and 4. While this is in quite good accordance with known results in the case of PPh_3 (Table 2, entry a), dppe (Table 2, entry c), and dppf (in comparison with the monophasic hydroformylation, taking into account slightly different reaction conditions[16]) and also in good accordance with reported results in the case of NaTPPTS (Table 2, entry b; by comparison with the biphasic hydroformylation of 1-pentene in BMIM PF_6[5]), it is more remarkable for the bidentate cobaltocenium ligand **4**. All hydroformylation experiments showed low hydrogenation activity (<2%) and some isomerization activity with nonconverted 1-octene and *iso*-octenes being typically on the same order of magnitude after reaction. However, in all experiments only minor amounts of 3- and 4-nonanales (<1%) were found.

With regard to the ligand influence on the reaction selectivity, a direct comparison of the results obtained with the isoelectronic and isostructural metallocene ligands dppf and **2** is of particular interest (comparison of entries d and f in Table 2). Considering the high structural similarity of both ligands, their different influence on the reaction's selectivity has to be attributed to electronic reasons. The electron density at the phosphorus atoms is significantly lower in the case of ligand **2** due to the electron-withdrawing effect of the formal cobalt(III) central atom in the ligand. This interpretation is supported by former work from Casey et al.[17] and Moser et al.[18] These groups described positive effects of ligands with electron-poor phosphorus atoms in selective hydroformylation reactions which they attribute to their ability to allow back-bonding from the catalytically active metal atom.

The same explanation may help to understand the much lower activity and selectivity found with ligand **4** (comparison of entries c and e, Table 2). Obviously, the alkyl bridge between the cyclopentadienyl and the phosphorus atom of the ligand considerably weakens the electronic influence of the central cobalt atom on the phosphorus atom. The resulting electronic and steric properties of **4** seem more to resemble a bidentate diarylalkylphosphine. Consequently, selectivity and activity of **4** are in the same range as found with dppe.

It has to be pointed out that only with the phosphinocobaltocenium ligands **2** and **4** does the reaction take place exclusively in the ionic liquid phase (clear and colorless organic layer). The quantitative rhodium analysis of the organic layer (by AAS and ICP after evaporation of the organics and treatment with concentrated HNO_3) revealed that the amount of rhodium leaching into the organic layer is less than 0.2%. Moreover, no rhodium or cobalt deposition was found at the reactor walls after reaction using these ligands.

With all other ligands, a significant leaching of the catalyst into the organic layer is observed (deep yellow color of the organic phase). In the latter case, the catalyst is active in both phases, which makes a clear interpretation of solvent effects on the catalyst's reactivity difficult.

In the case of complete retention of the catalyst in the ionic liquid (entries e, f in Table 2), an easy catalyst separation by decantation was possible. Moreover, we could principally demonstrate that the recovered ionic catalyst solution can be reused. The recycling experiment showed the same activity and selectivity as in the original run.

In this context, the high activity obtained with ligand **2** in the biphasic hydroformylation of 1-octene in BMIM PF_6 is very interesting. It clearly indicates the special usefulness of this ionic liquid for the biphasic hydroformylation of 1-octene. BMIM PF_6 provides a polar but weakly coordinating medium for the rhodium catalyst. Moreover, this ionic liquid shows very favorable solubility properties for a biphasic reaction with 1-octene. While the rate of the biphasic hydroformylation of 1-octene in aqueous systems is known to be heavily limited by the low solubility of 1-octene in water (about 0.0001 mol % at 25 °C[19]), BMIM PF_6 combines limited but sufficient solubility for 1-octene (about 2.5 mol % at 25 °C) to allow high rates even in a biphasic reaction.

Conclusion and Outlook

1,1′-Disubstituted cobaltocenium salts bearing phosphine donors have been synthesized using new and improved methods and were successfully used as bidentate chelating ligands in the biphasic, rhodium-catalyzed hydroformylation of 1-octene in 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM PF_6).

For the first time, 1,1′-bis(diphenylphosphino)cobaltocenium nitrate (**1**) was synthesized by direct oxidation of 1,1-bis(diphenylphosphino)cobaltocene with nitric acid. 1,1′-Bis(diphenylphosphino)cobaltocenium hexaflu-

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orophosphate (**2**) and 1,1′-bis[1-methyl(1-diphenylphosphino)ethyl]cobaltocenium hexafluorophosphate (**4**) could be synthesized in good yields using a mild oxidation method with hexachlorethane as oxidizing agent.

Compound **2**, in particular, proved to be a very suitable ligand for the biphasic hydroformylation in ionic liquids combining high solubility in BMIM PF_6 with favorable electronic properties. The latter are ascribed to a decrease of electronic density on the phosphine substituents compared with the analogue ferrocene derivative caused by the influence of the central cobalt atom.

In contrast with aqueous biphasic systems, the ionic liquid BMIM PF_6 provides a weakly coordinating medium for the rhodium with limited but sufficient solubility for 1-octene to allow high reaction rates. Using ligand **2** in BMIM PF_6, it was possible to realize a biphasic hydroformylation with high catalytic activity, high selectivity to the desired *n*-product (selectivity to *n*-nonanal: 94%; *n*/*iso*-ratio: 16.2), and without detectable catalyst leaching. Furthermore, the technical advantage of catalyst separation and recycling by simple phase separation contributes considerably to the benefit of our new concept to immobilize catalyst complexes in ionic liquids using cationic ligands.

Experimental Section

General Procedures. All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and deoxygenated by conventional methods prior to use. Alumina was deactivated with 5% deoxygenated water. 1-Octene for the hydroformylation experiments was used as supplied by Aldrich.

NMR spectra were recorded on a Varian Mercury 200 (200 MHz, ^1H; 50 MHz, ^{13}C; 81 MHz, ^{31}P) at ambient temperature. Chemical shifts (δ) are given in ppm relative to internal $SiMe_4$ (^1H and ^{13}C spectra) or to external H_3PO_4 (^{31}P spectra). Mass spectra were obtained with a Finnegan MAT 95 spectrometer. AAS measurements were obtained using a Perkin-Elmer 1100 spectrometer; ICP analysis were run on a Spectro Instrument System, Spectroflame D.

The catalytic experiments were carried out in 75 mL stainless steel autoclaves equipped with a dropping funnel and a magnetic stirring bar. The hydroformylation products were analyzed by gas chromatography using a Siemens Sichromat 2 with a 50 m Pona HP-FS column.

Syntheses. Diphenylphosphinocyclopentadienyllithium. Freshly prepared NaCp[20] or LiCp, prepared from the reaction of CpH with 1 equiv of *n*-BuLi at −78 °C, is suspended in ether, and 1 equiv of $ClPPh_2$ dissolved in ether is added at −30 °C. The reaction mixture is stirred for 1.5 h at room temperature, then filtered over Celite. The solvent is removed in vacuo, and the residue is dissolved in THF and cooled to −78 °C. One equivalent of *n*-BuLi (1.6 M in hexane) is added dropwise. The mixture is stirred for 1.5 h at room temperature. The product $LiC_5H_4PPh_2$ can be isolated quantitatively from the reaction mixture as a pale yellow powder in quantitative yield or used in situ. ^1H NMR (THF-d_8): δ 7.32−7.28 (m, 8H, Ph-*ortho*); 7.15−7.06 (m, 12H, Ph-*meta*/*para*); 5.9−5.8 (m, 8H, C_5H_4 ppm. $^{13}C\{^1H\}$ NMR (THF-d_8): δ 145.70 (d, $J_{PC} = 12.1$ Hz, Ph-*ipso*); 133.92 (d, $J_{PC} = 18.6$ Hz, Ph-*ortho*); 128.04 (d, $J_{PC} = 6$ Hz, Ph-*meta*); 127.17 (s, Ph-*para*); 113.13 (d, $J_{PC} = 20.8$ Hz, C_2 in C_5H_4P); 107.38 (d, $J_{PC} = 8.8$ Hz, C_3 in C_5H_4P), 105.72 (d, $J_{PC} = 3.3$ Hz, C_1 in C_5H_4P) ppm. $^{31}P\{^1H\}$ NMR (THF-d_8): δ −16.26 ppm.

1,1′-Bis(diphenylphosphino)cobaltocene (3). A solution of $LiC_5H_4PPh_2$ in THF is freshly prepared and cooled to −30 °C. While $Co(acac)_2$ is added in situ, the color of the solution turns immediately from yellow to dark brown. The reaction is stirred overnight, and the solvent is changed to toluene and filtered over Celite. After adding hexane to the concentrated filtrate, a precipitate is formed slowly during storage at −80 °C. The solid is isolated, washed with hexane, and dried in vacuo (isolated yield: 59%).

1,1′-Bis(diphenylphosphino)cobaltocenium Nitrate (1). To a suspension of 0.2 g of bis(diphenylphosphino)cobaltocene **3** (0.36 mmol) in 3 mL of propionic anhydride was added 0.5 mL of concentrated nitric acid. The resulting yellow-orange solution was added dropwise to ether, and an oil was formed. The latter was washed with ether, dissolved in a very small amount of CH_2Cl_2, and again added dropwise to ether. The formation of a pale yellow precipitate was observed, which was filtered, washed with ether, and dried in vacuo (0.13 g, 0.21 mmol, 58%). For further purification, **1** was recrystallized from hot water to obtain suitable crystals for the crystal structure determination. ^1H NMR (CD_3NO_2): δ 7.8−7.35 (m, 20H, Ph); 5.85, 5.52 (m, 8H, Cp) ppm. $^{13}C\{^1H\}$ NMR (CD_3NO_2): δ 136.10 (s, Ph-*ipso*); 135.07 (d, $J_{PC} = 20.7$ Hz, Ph-*ortho*); 131.70 (s, Ph-*para*); 130.58 (s, Ph-*meta*); 90.56 (s, C_1 in C_5H_4P); 89.84 (s, C_3 in C_5H_4P); 89.24 (s, C_2 in C_5H_4P) ppm. IR (KBr): 1475 (w), 1431 (s), 1381 (vs), 1193, 1116, 747, 726 (m), 700, 562 (s) cm^{-1}. Anal. Calcd for $C_{34}H_{28}CoNO_3P_2$: C, 65.92; H, 4.55. Found: C, 65.54; H, 4.46.

1,1′-Bis(diphenylphosphino)cobaltocenium Hexafluorophosphate (2). $LiC_5H_4PPh_2$ is prepared as follows: To a solution of 21.2 g of $LiCpPPh_2$ (83 mmol) in 200 mL of THF was added 5.6 g of $CoCl_2$ (43 mmol), producing a dark brown solution. After stirring this solution overnight under reflux, 5.79 g (24 mmol, 1.22 equiv) of C_2Cl_6 was added. The resulting solution was stirred at room temperature for another 10 min. After evaporation of all volatile substances in vacuo, the residue was dissolved in 100 mL of CH_2Cl_2 and filtered through cotton wool and Celite to remove LiCl. The filtrate was dried in vacuo to obtain an oily, brown residue. The oil was dissolved in 150 mL of acetone, and 6.5 g of NH_4PF_6 (40 mmol) in acetone was added. No precipitate was formed. The solution was added dropwise to 500 mL of water, producing an oil. After extraction with 400 mL of CH_2Cl_2, the solution was added dropwise to ether. The solid was filtered off and washed with ether to obtain 18.82 g (27 mmol, 63%) of crude **2**. For further purification the solid was dissolved in acetone and filtered over alumina, eluted with acetone, and recrystallized from CH_2Cl_2/ether to obtain 15.07 g (21.5 mmol, 50%) of pure **2**. ^1H NMR (CD_3NO_2): δ 7.47 (m, 20H, Ph); 5.83, 5.51 (m, 8H, Cp) ppm. $^{13}C\{^1H\}$ NMR (CD_3NO_2): δ 136.35 (d, Ph-*ortho*, 20.7 Hz); 133.0, 131.88 (Ph-*meta*/*para*); 91.0, 90.45 (Cp-C_{2-5}) ppm. $^{31}P\{^1H\}$ NMR (CD_3NO_2): δ −22.24 (br s, PR_2R'); −145.13 (sept, 707.6 Hz, PF_6) ppm. Anal. Calcd for $C_{34}H_{28}CoF_6P_3$: C, 58.17; H, 4.02; P, 13.24; F, 16.24. Found: C, 57.57; H, 3.53; P, 13.0; F, 16.6. IR (KBr): 3111; 1474; 1431;1381 (w); 831 (vs); 750; 697; 558 (m); 440 (w) cm^{-1}.

1,1′-Bis[1-methyl-1-(diphenylphosphino)ethyl]cobaltocenium Hexafluorophosphate (4). A 4.3 mL sample of diphenylphosphine (25 mmol) was dissolved in 40 mL of diethyl ether, and 15.6 mL of *n*-BuLi (1.6 M, 25 mmol) was added dropwise at −60 °C. The reaction mixture was allowed to warm to room temperature and stirred at this temperature for 3 h. To the resulting solution of $LiPPh_2$, 2.6 g of 6,6-dimethylfulvene (25 mmol) was added at −10 °C. A small amount of THF was added to prevent the formation of a precipitate. The solution was then stirred for another 3 h at room temperature. After cooling the reaction mixture to −40 °C, 1.9 g of $CoCl_2$ (15 mmol) was added. The solution was stirred overnight at room temperature.

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[20] Herrmann, W. A., Salzer, A., Eds.; *Synthetic Methods of Organometallic and Inorganic Chemistry*; G. Thieme Verlag: Stuttgart, 1996; Vol. 1, p 51.

At −50 °C 2.2 g of hexachlorethane (9 mmol, 1.2 equiv) was added, and a greenish-yellow precipitate was formed immediately. The solid was filtered off, washed with diethyl ether and hexane, and dried in vacuo. A total of 8.5 g of solid was isolated in this way. The latter was identified by ^{31}P NMR spectroscopy to be a mixture of phosphine and phosphine oxides.

The isolated solid was dissolved in acetone/water, and a solution of 2.7 g of NH_4PF_6 (16.5 mmol) in water was added at room temperature. The formation of a brownish-yellow solid was observed. The flask was filled with water, and the solid was filtered off. The isolated solid was washed with diethyl ether to yield 4.39 g of **7** (5.6 mmol, 47%). For further purification **3** was washed with 60 mL of methanol to obtain pure **4** in the form of a shiny yellow solid. ^{1}H NMR (CD_3NO_2): δ 7.40 (m, 10H, Ph); 5.56, 5.10 (2m, 4H, Cp-CH); 1.50 (d, 6H, $^3J_{PH} = 14.4$ Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (CD_3NO_2): $\delta = 136.2$ (d, $^4J_{PC} = 22$ Hz, Ph-*meta*); 134.7 (d, $^1J_{PC} = 20.6$ Hz, Ph-*ipso*); 131.31 (s, Ph-*para*); 129.70 (d, $^3J_{PC} = 7.8$ Hz, Ph-*ortho*); 119.21 (s, Cp-1); 83.08, 82.28 (Cp-CH); 37.1 (d, $^1J_{PC} = 25.2$ Hz, C_q-$(CH_3)_2$); 28.1 (d, $^2J_{PC} = 20.1$ Hz, CH_3) ppm. ^{31}P{^{1}H} NMR (CD_3NO_2): δ 30.5; −142.04 (sept, $^1J_{PF}$= 705 Hz, PF_6) ppm. MS (FAB): m/z (I_{rel}): +VE: 641 [M^+], −VE: 145 (100) [PF_6]. Anal. Calcd for $C_{40}H_{40}CoF_6P_2$: C, 60.92; H, 5.36. Found: C, 60.33; H, 5.22.

Catalytic Experiments. In a typical experiment, the ionic catalyst system was prepared in situ by mixing 5.2 mg of [Rh(CO)$_2$acac] (0.02 mmol) with 0.04 mmol of the ligand in 5 mL of 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM PF_6) for 1 h at room temperature. The ionic catalyst solution was transferred to a 75 mL steel autoclave equipped with a dropping funnel and a magnetic stirring bar. A 3.15 mL (20 mmol) sample of 1-octene were placed into the dropping funnel, and the autoclave was heated to 100 °C and pressurized with CO/H_2 (1:1) to the reaction pressure (batch reaction mode). To start the reaction, the dropping funnel was opened and the autoclave was stirred at 1000 rpm. After 1 h reaction time the autoclave was cooled and degassed. The biphasic reaction mixture was separated by simple decantation of the upper phase. The catalyst activity and the *n*/*iso*-selectivity were determined by gas chromatography using di-*n*-butyl ether as internal standard. Using **2** as ligand, the remaining catalytic ionic solution could be reused at least one more time.

Crystallographic Data Collection and Structure Determination of 1. Pale yellow single crystals of **1** obtained as described above were studied on an ENRAF Nonius CAD4 diffractometer equipped with an incident beam monochromator. Crystal data, data collection parameters, and convergence results are compiled in Table 1. Before averaging over symmetry-related reflections a numerical absorption correction based on Gaussian integration[21] was applied. The structure was solved by Patterson and Fourier difference methods and refined on F with the local version of the SDP suite.[22] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-143 975. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, int. +1223/336-033; E-mail, teched@chemcrys.cam.ac.uk).

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Supporting Information Available: Tables with crystal data, atomic coordinates, anisotropic displacement parameters, and listings of interatomic distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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