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Synthesis of Configurationally Stable, Optically Active Organocobalt Compounds

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The transmetalation reaction between a series of ortho-lithiated tertiary amine derivatives (N^C−Li) and $[(\eta^5\text{-}C_5H_5)CoI_2]_2$ affords a series of cobaltacyclic compounds of the general form $(\eta^5\text{-}C_5H_5)Co(C^\wedge N)I$, in which the cobalt center is in a pseudotetrahedral environment. With optically active lithiated compounds, such as those obtained from (*R*)- or (*S*)-1-(dimethylamino)-1-phenylethane, the reaction forms a mixture of two diastereoisomers (R_C,R_{Co})-**12a**, (R_C,S_{Co})-**12a′** and (S_C,R_{Co})-**12b**, (S_C,S_{Co})-**12b′**, respectively, of which the isomers **12a** and **12b′** are predominant, as they are formed with a de of 90%. ^1H NMR studies indicate that the compounds are configurationally stable at the cobalt center. Reaction of these species with neutral ligands such as phosphines, phosphites, or isocyanides led to the formation of cationic complexes via substitution of the iodide ligand, this reaction occurring mainly with retention of configuration for the optically active species.

Introduction

Optically active organometallic compounds have long been fascinating molecules for synthetic chemists interested in the field of metal-mediated synthesis. Part of this interest is due to the fact that they provide valuable tools for the investigation of the stereochemical course of reactions. Moreover, they may provide access to new catalysts that can be used in asymmetric C−C or C−H bond synthesis.[1]

Since the first example of the synthesis and resolution of optically active organometallic complexes containing a stereogenic metal center,[2] related work has been performed mainly with metals such as Ti,[3] Co,[4] Cr,[5] Mo,[6] W,[7] Mn,[8] Re,[9] Fe,[10] Ir,[11] Ru,[12] Rh,[13] etc. Among these examples a burst of activity was devoted to pseudotetrahedral arene or cyclopentadienyl “half-sandwich” transition-metal complexes. Recently we have been involved in the synthesis of related (arene)ruthenium compounds based upon cyclometalated tertiary amino ligands. When synthesizing these starting materials with optically active 1-(dimethylamino)-1-phenylethane derivatives, we isolated the optically active ruthenacycles (R_C,S_{Ru})- and (R_C,R_{Ru})-$[(\eta^6\text{-}C_6H_6)Ru(C_6H_4CH(Me)NMe_2)Cl]$ displaying a configurationally stable Ru center. In each case these compounds were a 20:1 mixture of two diastereoisomers.[14] These results prompted us to investigate the synthesis of related cyclopentadienylcobalt(III) species with the same optically active chelates.

Among the large variety of organocobalt(III) compounds reported in the literature, it appeared that only very few examples of cobalt hydrocarbyls, intramolecularly stabilized by a heteroatom coordinating group, exist.[15] This is rather surprising, as the compound $Co(C_6H_4CH_2NMe_2\text{-}o)_3$[16] was described more than 30 years ago. Recently a new type of this compound was synthe-

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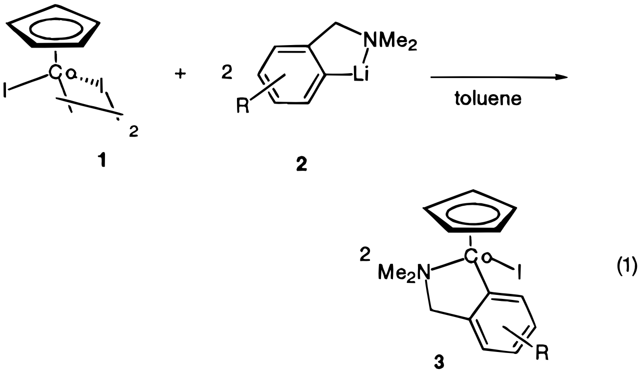
sized by Werner et al. via a (3 + 2) cycloaddition of a terminal alkyne and an iminoacylcobalt(III) derivative.[17]

We report herein the successful transmetalation reaction between a series of ortho-lithiated tertiary amine derivatives and $[CpCoI_2]_2$, which afforded high yields of the expected pseudotetrahedral organocobalt compounds.

Results and Discussion

We recently described the facile synthesis of pseudotetrahedral ruthenium derivatives by means of a transmetalation reaction whereby the [(dimethylamino)methyl]aryl ligand was transferred from $Hg(C_6H_4CH_2NMe_2)_2$ to a ruthenium(II) center, $[(\eta^6\text{-}C_6H_6)RuCl_2)]_2$, affording high yields of $[(\eta^6\text{-}C_6H_6)Ru(C_6H_4CH_2NMe_2)Cl]$. This latter compound displayed an interesting reactivity, as it led to the synthesis of quinolinium derivatives by reactions with internal alkynes.[18] We thus chose $[(\eta^5\text{-}C_5H_5)CoI_2]_2$ (**1**) as the starting material because it could lead to Co(III) derivatives isostructural with the Ru compounds. **1** is readily available through oxidation of $CpCo(CO)_2$ by I_2.[19] This compound was extensively studied by Maitlis et al., and surprisingly it seemed not to have been used as a starting material in transmetalation reactions. Most of the related transmetalation reactions (with alkyllithium or Grignard derivatives) have been performed using $CpCo(L)I_2$ (L = CO, PR_3) instead.[15a,20]

We found that **1** was a much better starting material than $CpCo(CO)I_2$, as it afforded high yields of **3a**[21] when the transmetalation reaction was performed in toluene at room temperature in the presence of **2a** ([2-((dimethylamino)methyl)phenyl]lithium) (eq 1). In a typical reaction **2a** was added to a suspension of **1** in toluene. The solution turned gradually from black to dark green, and after ca. 18 h of stirring the reaction was complete, affording **3a** after workup.[22] We found that the best yield of **3a** was obtained when the reaction was performed in the absence of solvents such as THF and Et_2O. With these solvents, the reaction of **2a** with **1** led to rapid and extensive decomposition and we could not isolate any organocobalt(III) species from the reaction mixture. This phenomenon may be related to a better solubility of **2a** in these solvents and hence to a high reactivity of **2a** toward the Co(III), which might be detrimental to the isolation of the desired half-sandwich cobaltacycle complex **3**.



(1)

Table 1. Yields of Compounds 3 Obtained via Eq 1

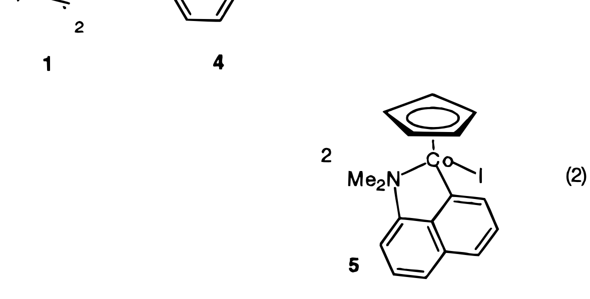
compd **3**	4-R	5-R	6-R	yield (%)
3a	H	H	H	78
3b	Me	H	H	86
3c	H	Me	H	70
3d	F	H	H	70
3e	H	F	H	48
3f	MeO	H	H	59
3g	H	MeO	H	4

$(\eta^5\text{-}$Cyclopentadienyl)[2-((dimethylamino)methyl)phenyl]cobalt iodide (**3a**) was isolated as a green powder. It was both air- and water-stable, this stability being somehow reminiscent to that of $Co(C_6H_4CH_2NMe_2)_3$.[16]

3a was readily characterized through ^1H and ^{13}C NMR spectroscopy. The complex **3a** displayed typical chemical shifts for a diastereotopic CH_2NMe_2 unit. However, combustion analysis proved to be somewhat frustrating, as for **3a** and the related compounds **3** of this series the carbon values were often higher than the theoretical amounts, despite all our efforts to crystallize the compounds and/or to dry the obtained crystals in vacuo. Nevertheless, the ambiguity surrounding the purity of **3a** was practically overcome when studying the corresponding cationic compounds (see below), for which we obtained satisfactory elemental analyses.

Several compounds related to **3a** were synthesized by following the same procedure as for **3a** by reactions of lithiated derivatives of substituted dimethylbenzylamines (**2b**−**g**) according to eq 1. The results are summarized in Table 1. It is clear from this series of compounds that there should be significant interaction between the Cp ring and the second substituent ortho to the cobalt atom (i.e., Me, F, and OMe), thus preventing the formation of the expected aryl−Co compounds with these latter substituents. On the other hand, there seems to be only a marginal difference in the yields for the synthesis of para- and meta-substituted Co−aryl derivatives. We believe, however, that the low yield observed for **3g** might be related to a better solubility of the lithiated ligand as compared to the other reagent, this being in line with the reactions performed in THF or Et_2O (see above).

A transmetalation reaction using **4** ([8-(dimethylamino)-1-naphthyl]lithium) with **1** allowed the synthesis of **5** in good yields (eq 2). The diastereotopicity of



(2)

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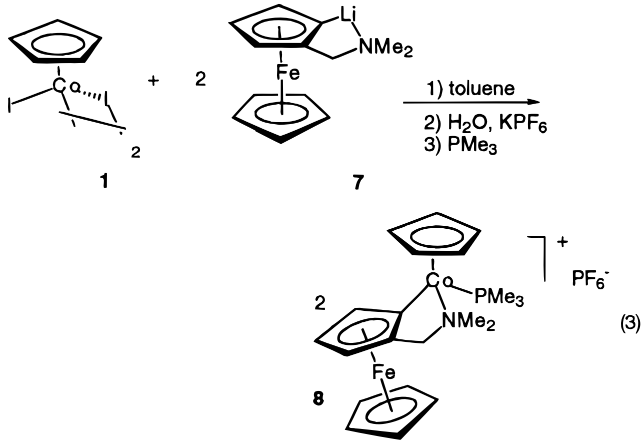
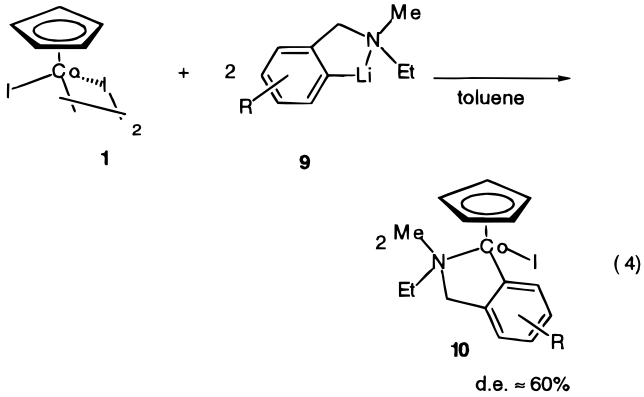
the NMe$_2$ group allowed us to conclude that it is isostructural with the series of complexes of type **3**.

This transmetalation could also be extended to pseudoaromatic rings such as **7** ([(2-((dimethylamino)methyl)ferrocenyl]lithium).[23] This reaction was, however, accompanied by some decomposition products that were difficult to remove from the desired neutral cobalt compound. Nevertheless, it was possible to obtain the cationic derivative **8** as a single pair of enantiomers by adding trimethylphosphine to the transmetalation reaction mixture, analogous to those described below (eq 3).



However, in the absence of a crystal structure analysis of **8** the relative configurations of both the Co and the Fe centers remain uncertain.

To verify the influence of different alkyl substituents on the N atom coordinated to the cobalt center, **1** was allowed to react with **9** ([2-((ethylmethylamino)methyl)phenyl]lithium). This transmetalation reaction yielded a mixture of the two pairs of diastereoisomers **10a** and **10b** in a 4:1 ratio. No difference in this diastereoisomeric ratio was observed when, after 3 days, solutions of **10a**,**b** in CDCl$_3$ and acetone-d_6 were analyzed (eq 4).

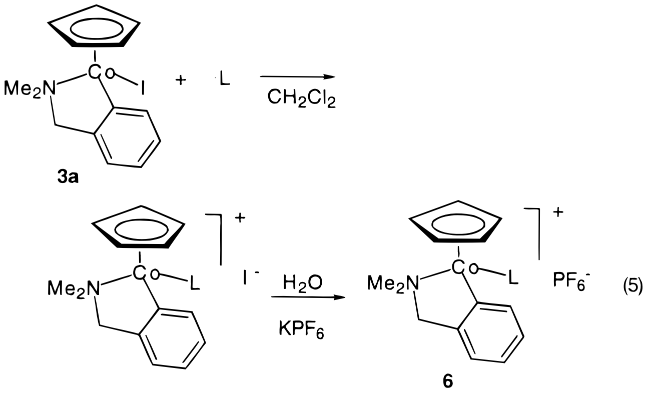


Red cationic complexes could be obtained by allowing **3a** to react with neutral ligands even in solvents such as CH$_2$Cl$_2$ (eq 5). The resulting complexes are soluble in these solvents as well as in water. Pure compounds were thus isolated from the latter solution in the presence of KPF$_6$, affording **6a**–**f** in good to excellent yields (see Table 2). Only phosphines with a small cone angle[24] could be used, as PPh$_3$ proved to be too bulky to coordinate to the cobalt center. Trimethyl phosphite could also react with **3a** to afford **6d**. It is noteworthy that this reaction was rather slow, compared to the previous ones, as it took ca. 7 h to reach completion. When this latter reaction was run for a total reaction time of 18 h, no **6d** was obtained, but we observed instead the quantitative formation of **6e**. The formation of the latter could be rationalized as the result of a typical Arbusov reaction.[25]

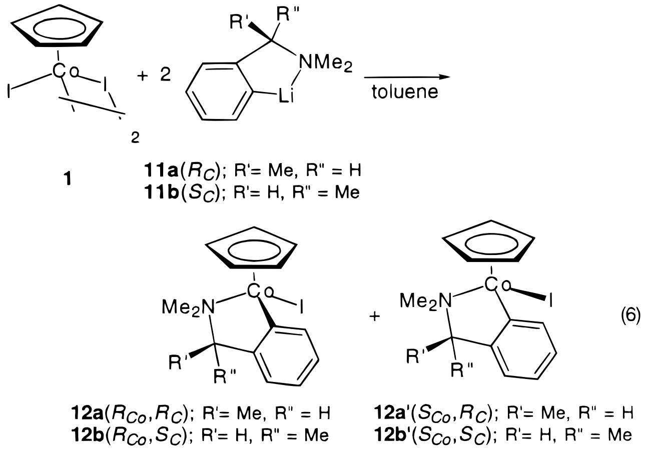
Table 2. Synthesis of Cationic Complexes According to Eq 5

complex	L	reacn time (h)	yield(%)
6a	PMe$_2$Ph	1	86
6b	PPh$_2$Me	1	87
6c	PMe$_3$	1	87
6d	P(OMe)$_3$	7	72
6e[a]	PO(OMe)$_2$	18	87
6f	CN^{t}Bu	3	47

[a] Obtained from P(OMe)$_3$.



Optically Active Organocobalt Compounds. Using the same procedure as for the synthesis of **3a**–**g** with the optically active reagents **11a** and **11b**, we could obtain high yields of the optically active compounds **12a,a′** and **12b,b′** (eq 6).



The transmetalation reactions occurred in very much the same way as for the corresponding ruthenium

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[21] CpCo(CO)I$_2$ led only to "intractable materials" when used under similar conditions.

[22] Alternative approaches to the synthesis of **3** via either C–H activation (of dimethylbenzylamine) in the presence of a base or oxidative addition of 2-I-C$_6$H$_3$CH$_2$NMe$_2$ to CpCo(CO)$_2$ failed.

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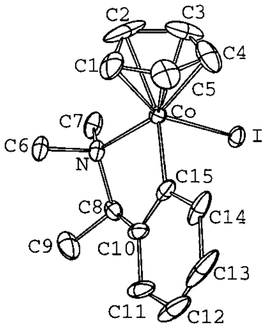


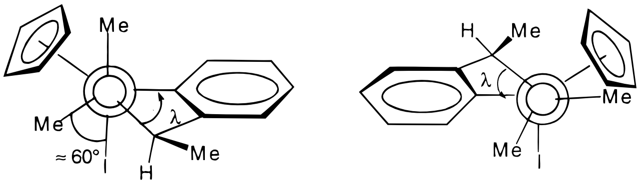
Figure 1. ORTEP view of (R_{Co},R_C)-(η^5-C_5H_5)Co(C_6H_4CH(Me)NMe_2)I (**12a**).

Table 3. Selected Bond Distances (Å) and Angles (deg) for 12a[a]

Co−C(Cp) av	2.073(8)	Co−C(15)	1.924(5)
C−C av (Cp)	1.39(2)	N−C(6)	1.481(6)
C−C av (Ph)	1.39(2)	N−C(7)	1.469(7)
Co−I	2.6291(7)	N−C(8)	1.526(7)
Co−Cp^a	1.70(5)	C(10)−C(15)	1.39(1)
Co−N	2.024(4)	C(8)−C(10)	1.51(1)
N−C(8)−C(9)	114.5(6)	I−Co−C(15)	90.7(1)
N−C(8)−C(10)	106.3(4)	N−Co−C(15)	84.2(2)
C(9)−C(8)−C(10)	115.1(8)	C(6)−N−C(7)	108.6(4)
Cp^a−Co−I	131.3(1)	C(6)−N−C(8)	108.5(4)
Cp^a−Co−C(15)	124.1(3)	C(7)−N−C(8)	110.2(4)
Cp^a−Co−N	131.3(1)	N−C(8)−C(10)	116.1(5)
I−Co−N	95.7(1)	C(7)−N−Co−I	−60(2)

[a] Cp^a represents the centroid of the cyclopentadienyl ring.

Scheme 1. Conformations of the Five-Membered Chelate Ring in 12a and 12a′ [a]



[a] The Newman projections of the organocobalt compounds are viewed along the Co−N axis.

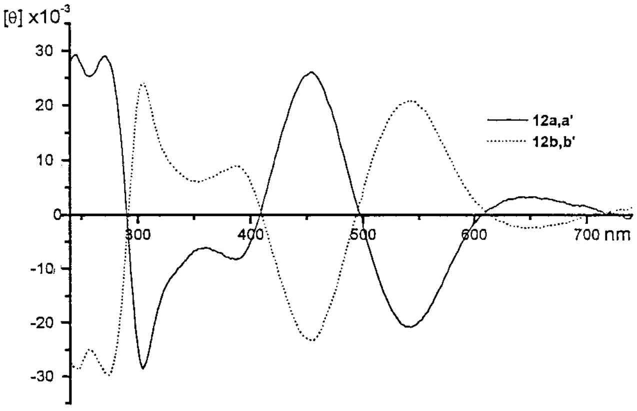


Figure 2. CD spectra of **12a**,**a′** and **12b**,**b′**.

containing compounds described earlier.[14,26] These compounds proved to be stable toward interconversion in solution. No epimerization of **12a** into **12a′** could be observed in solution, for instance, over a period of 7 days at room temperature in either $CDCl_3$ or d_6-acetone. Hence, the stereoselectivity of the transmetalation reaction can be calculated from the ratio of the integrated intensities of the ^{1}H NMR signals. We found that the ratios **12a**:**12a′** and **12b′**:**12b** amount to 19:1 (de = 91%). This de is very close to that determined for the corresponding chloro derivative of the Ru compound (90%), but it is lower than those for the iodo derivatives which were obtained from the latter via a halide metathesis reaction (de = 94%). The ratio **12a**:**12a′** could not be improved by fractional crystallization or column chromatography. The solid-state structure of **12a** was unambiguously determined via a single-crystal X-ray diffraction study (see Figure 1). **12a** and **12a′** displayed comparable crystallization rates so that the bulk sample from which X-ray-quality crystals were obtained contained the same ratio of both diastereoisomers as determined above. Thus, we assume that the crystal structure depicted in Figure 1 is that of the major species, since the crystals of this species have a much higher statistical chance of being isolated from the mixture of diastereoisomers.[27] The molecular structure is represented in Figure 1, together with the adopted numbering scheme. Selected bond distances and angles are shown in Table 3.

The structure of **12a** is that of a "three-legged piano stool" in which the C and the N atoms of the arylamino ligand and the iodide occupy the three "leg" positions. The absolute configuration at cobalt is assigned by assuming the following priority numbers: 1 (I atom), 2 (η^5-cyclopentadienyl ligand), 3 (N atom), and 4 (phenyl C atom). Thus, **12a** is designated as the R_C,R_{Co} diastereoisomer.[28]

The five-membered chelate ring is puckered. This is best visualized in a Newman projection of **12a** (see Scheme 1), which is viewed along the N−Co axis. The ring puckering is related to the torsion angle observed between Co−C(15) and C(8)−N. This puckering is most probably due to some steric repulsion between the Cp ring and the benzylic methyl unit C(9), which forces the latter to be in an equatorial position with respect to the metalated aryl ring. As a consequence of this situation, the methyl C(7) on the nitrogen atom is in a staggered position with the iodide atom (torsion angle C(7)−N and Co−I ~60°, λ conformation for the ring puckering). It is most likely that this ring puckering is very much different in the other diastereoisomer **12a′**, as the benzylic proton and one of the methyls of the NMe_2 group display a remarkable difference in their chemical shift in comparison with those of the diastereoisomer **12a**. The former is deshielded by 0.50 ppm, whereas the methyl is shielded by 0.55 ppm, thus indicating that they are in different magnetic environments. We shall propose later a conformation for the five-membered chelate ring in this isomeric form.

The configuration at the cobalt centers of the other diastereoisomer **12b**,**b′** have been ascertained by the comparison of the CD spectra of **12a**,**a′** and of **12b**,**b′**. As is expected for configurationally rigid diastereoisomers, these CD spectra are mirror images of each other (see Figure 2). Thus, we can assign to the major isomer **12b′** (S_{Co},S_C) a configuration opposite that of **12a**

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(26) Pfeffer, M.; Sutter, J. P.; Urriolabeitia, E. P. *Inorg. Chim. Acta* **1996,** *249*, 63.

(27) Unfortunately, an NOE experiment did not allow the unambiguous identification of the relative positions of the $CH(CH_3)$ group with respect to the Cp ring, as there is no NOE effect between these groups.

(28) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975,** *97*, 6598.

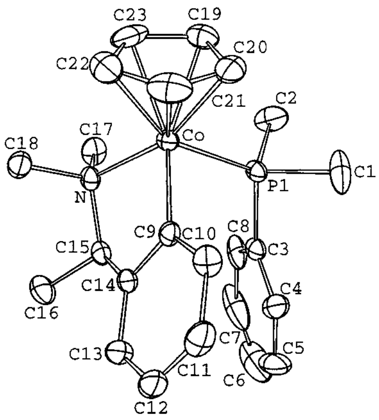
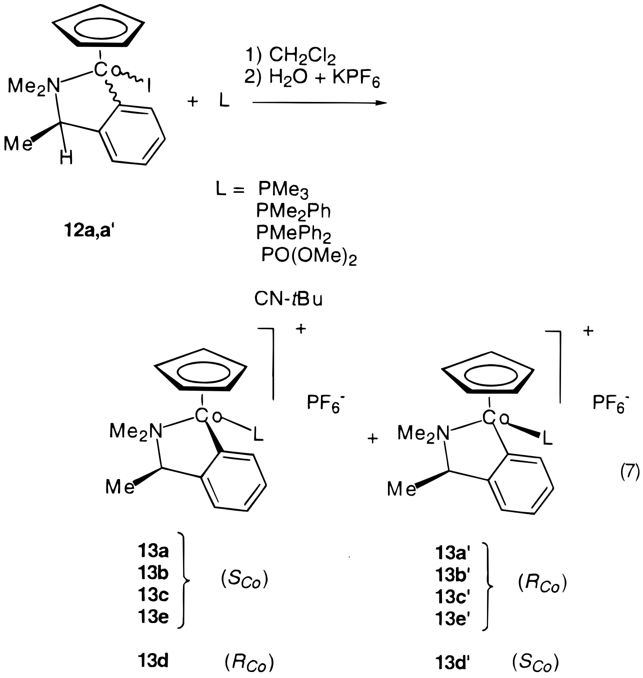


Figure 3. ORTEP view of the cationic part of **13b**.

(R_{Co},R_C) and vice versa for **12b** (R_{Co},S_C) as compared to **12a′** (S_{Co},R_C).

As we have seen earlier, the iodide ligands in these organocobalt compounds are readily substituted by a phosphine ligand in the presence of PF_6^-. Thus, treating **12a**,**a′** with 1 equiv of PMe_2Ph afforded a quantitative yield of **13b**,**b′** (eq 7). The ^1H as well as the ^{31}P NMR spectra (see below) indicate that **13b**:**13b′** has been obtained in a ratio of 19:1 (de = 91%). This result clearly indicated that the reaction proceeds without racemization at the metal center.



(7)

To establish whether the substitution reaction has taken place with retention or inversion of configuration at the Co center, the crystal structure of this compound has been determined (see Figure 3).

Assuming again that the crystal that has been used for the X-ray diffraction is that of the major isomer,[29] it is at once apparent that the configuration at the cobalt atom is the same as in **12a**; i.e., the substitution of the iodide by PMe_2Ph has occurred with retention of configuration. The conformation of the five-membered chelate ring is the same as that found for **12a**. A selection of bond distances and angles is displayed in Table 4.

Table 4. Selected Bond Distances (Å) and Angles (deg) for 13b[a]

Co−C(Cp) av	2.097(4)	P(1)−C(2)	1.830(5)
C−C(Cp) av	1.392(8)	P(1)−C(3)	1.817(4)
C−C(Ph) av	1.389(7)	C(9)−C(14)	1.403(6)
Co−P(1)	2.236(1)	C(14)−C(15)	1.495(6)
Co−C(9)	1.933(4)	C(15)−N	1.523(5)
Co−N	2.038(3)	N−C(17)	1.495(5)
Cp^a−Co	0.93(2)	N−C(18)	1.485(5)
P(1)−C(1)	1.814(5)		
P(1)−Co−C(9)	88.4(1)	Co−C(9)−C(14)	113.6(3)
P(1)−Co−N	101.08(9)	C(9)−C(14)−C(15)	116.3(3)
Cp^a−Co−N	157.8(1)	C(14)−C(15)−C(16)	115.3(3)
Cp^a−Co−C(9)	114.5(5)	C(14)−C(15)−N	107.0(3)
Cp^a−Co−P(1)	91.5(4)	C(16)−C(15)−N	115.2(3)
Co−P(1)−C(1)	112.9(2)	Co−N−C(15)	107.1(2)
Co−P(1)−C(2)	115.7(2)	Co−N−C(17)	111.5(2)
Co−P(1)−C(3)	119.9(1)	Co−N−C(18)	112.0(2)
C(1)−P(1)−C(2)	101.7(3)	C(15)−N−C(17)	109.0(3)
C(1)−P(1)−C(3)	101.7(2)	C(15)−N−C(18)	109.3(3)
C(2)−P(1)−C(3)	102.4(2)	C(17)−N−C(18)	108.0(3)
C(9)−Co−N	84.2(1)	C(17)−N−Co−P(1)	−71(2)

[a] Cp^a represents the centroid of the cyclopentadienyl ring.

The ^1H NMR spectum of the minor isomer **13b′** shows an important downfield chemical shift for the benzylic proton ($\Delta\delta = 2.3$ ppm) and a high-field shift for one of the methyls of the NMe_2 ($\Delta\delta = 1.0$ ppm). The latter signal appeared additionally as a doublet due to $^4J_{H-P}$ coupling with the phosphorus atom. Similar effects have been observed for the minor isomer obtained with other phosphines (see below). This latter result shed light upon the likely conformation of the five-membered chelate ring in **13b′**. In this compound the configuration at Co is opposite that in **13b** and this leads to important steric repulsion between the PMe_2Ph ligand and the benzylic methyl unit which are now closer to each other than in the major isomer **13b** (see Figure 3). Due to this repulsion the methyl is forced into an equatorial position with respect to the aryl ring, and this leads to a ring-puckering conformation inverse to that unambiguously established for **13b**.[30] As a consequence, one methyl group of the NMe_2 unit and the phosphorus atom of PMe_2Ph are in an almost eclipsed situation (see the Newman projection in Scheme 2), and this is the reason for the occurrence of the $^4J_{H-P}$ coupling constant that has been found for one Me of the NMe_2 group. Other phosphine ligands, e.g. PMe_3 and PPh_2Me, may also be used to substitute the iodide ligand in **12a**,**a′**. With PMe_3 we obtained **13a**,**a′** with a de of 75%, whereas with PPh_2Me **13c**,**c′** was formed with a lower de. In this latter case, however, we found that the formation of the minor isomer **13c′** was under kinetic control. Indeed, after 17 h of reaction the formation of **13c**,**c′** occurred with a de of ∼60% but, when **13c**,**c′** was allowed to slowly crystallize, led to a quantitative formation of **13c**, whereas no **13c′** could be detected at all, which is a strong indication that the formation of the major isomer is controlled thermodynamically.

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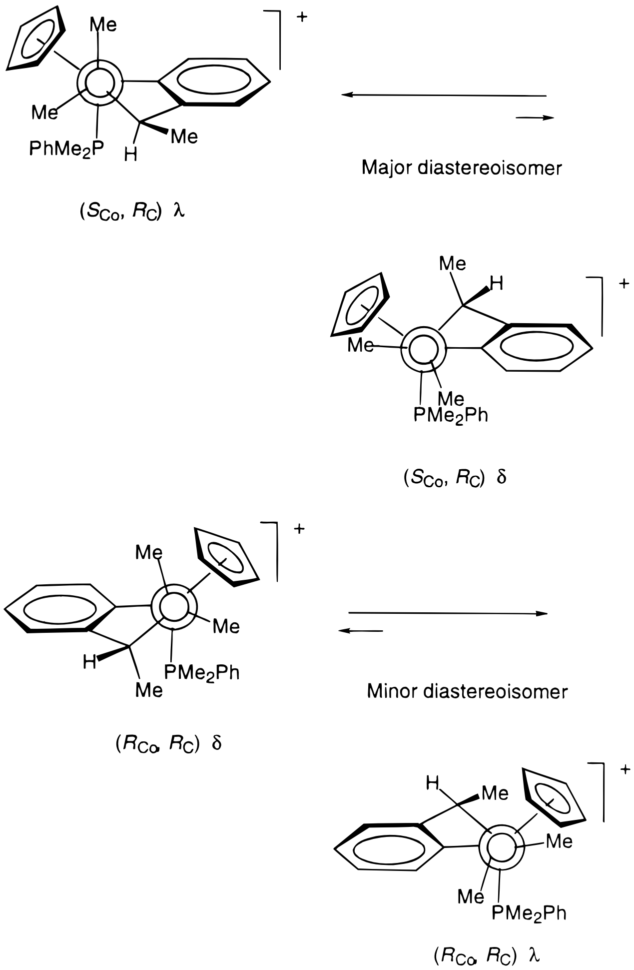
[29] NOESY ^1H NMR of **13b**,**b′** showed that the benzylic hydrogen atom of the major isomer is in close proximity to both the methyl groups and the ortho protons of the phenyl of PMe_2Ph and, hence, the configuration of the major isomer is indeed the same as that of the crystal used for the X-ray structure determination.

[30] According to Figure 4 the major and minor diastereoisomers have different ring puckering; however, they are labeled by the same configuration, λ.

Scheme 2. Conformations of the Five-Membered Chelate Ring in 13b and 13b′ [a]



[a] The Newman projections of the organocobalt compounds are viewed along the Co−N axis.

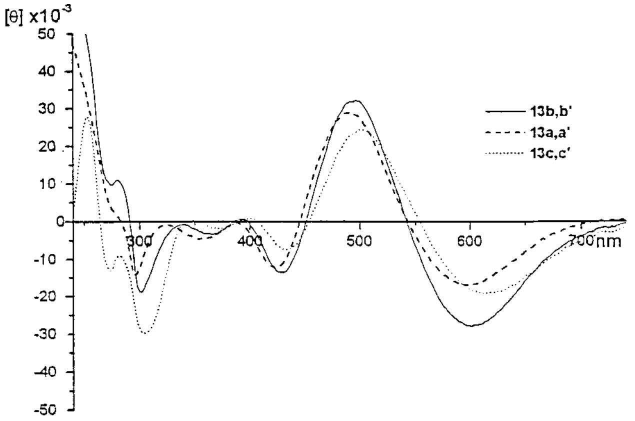


Figure 4. CD spectra of **13a**,**a′**, **13b**,**b′**, and **13c**,**c′**.

The assignment of the same configuration at the Co atom in the isomers **13a**−**c** came from the comparison of their CD spectra. Almost the same approach was observed in their corresponding CD curves (see Figure 4).

The CD spectra of **13d**,**d′** and **13e**,**e′** appear to display related features (see Figure 5). However, as the natures of the ligands L are very different, an accurate analysis based on their CD spectra is not advisable and the determination of the configuration of the metal center can afford erroneous results.[12a]

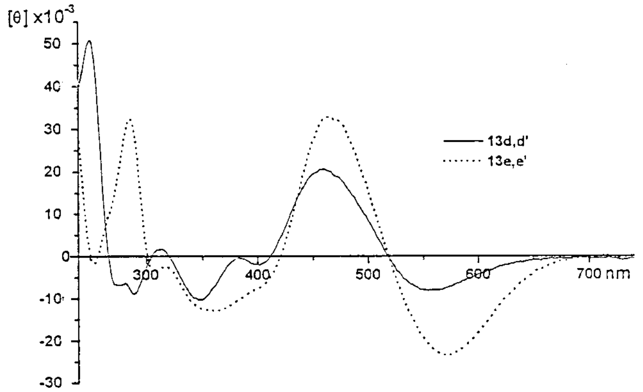


Figure 5. CD spectra of **13d**,**d′** and **13e**,**e′**.

Table 5. Selected ^{1}H NMR Data (in ppm) for Cationic Co Derivatives

complexes	C*H*Me	N(C*H*$_3$)$_2$	Δδ
12a, **12b**	3.42	3.51 and 2.48	1.03
12a′, **12b′**	3.94	3.26 and 1.92	1.34
13a	3.17	3.04 and 2.62	0.42
13a′	4.40	3.12 and 1.75[a]	1.34
13b	1.90	2.81 and 2.40	0.41
13b′	4.17	3.01 and 1.38[a]	1.63
13c	1.98	3.05 and 2.57	0.48
13c′	4.36	3.18 and 1.48[a]	1.7
13d	3.23	2.94 and 2.51	0.43
13d′	4.10	3.03 and 1.84	1.19
13e	4.28	2.84 and 2.42	0.42
13e′	4.06	n.o.[b] and 1.79	n.d.[c]

[a] The high-field diastereotopic Me of the NMe$_2$ unit is a doublet due to $^2J_{H-P}$ coupling. [b] n.o. = not observed. [c] n.d. = not determined.

Nevertheless, the analysis of the ^{1}H NMR spectrum of **13d**,**d′** allowed a rather safe determination of the configuration at the metal center. As described earlier, the ^{1}H NMR spectra of the minor isomers show an important downfield chemical shift for the benzylic proton and a high-field shift for one of the methyls of the NMe$_2$ unit (see Table 5).

The reactions for the synthesis of complexes related to **13** were performed basically by abstraction of the iodo ligand and replacement by the neutral ligands (PR$_3$ and CN*t*Bu). Two basic mechanisms can be proposed for this type of substitution reactions: *dissociative* and *associative*. It is generally accepted[1,3,31−33] that substitution reactions take place via a dissociative mechanism, frequently with retention of the metal configuration. The behavior of compounds **13c** and **13c′** obtained with the PPh$_2$Me ligand suggests a specific behavior of this ligand toward coordination to the cobalt atom with respect to the other phosphines used in this study. It appeared indeed that this ligand led to a mixture of diastereoisomers whose ratio varied as a function of time, evolving from a 60% to a >99% de after ca. 7 days. We checked that this behavior was taking place in solution (CDCl$_3$) over the same period of time; i.e., the isomerization of **13c′** to **13c** was not due only to a solid-state phenomenon whereby, for instance, **13c** would

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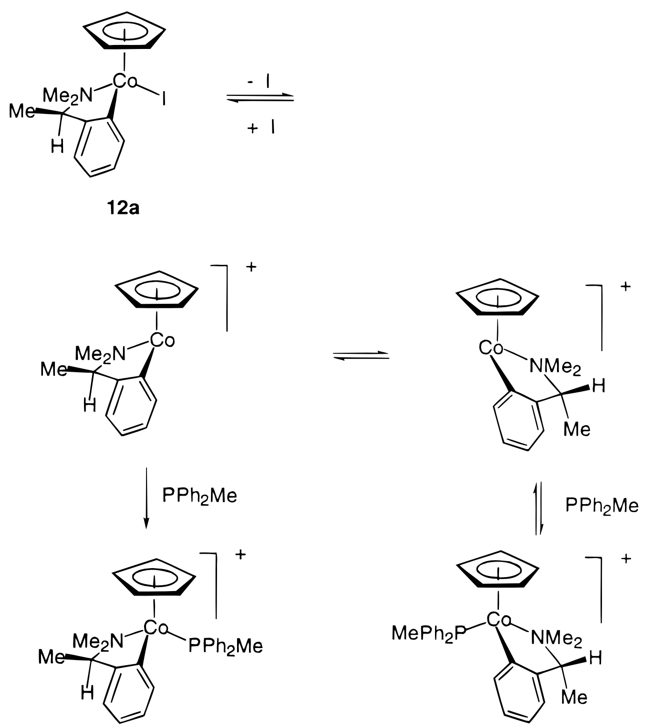
(31) Hofmann, P. *Angew. Chem.* **1977**, *89*, 551.

(32) Bogdanovic, *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 954. Konowles, W. S.; Sabacky, M. J.; Vineyard, B. D.; Weinkauf, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 2567. Trost, B. M.; Runge, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 2485, 7550, 7559.

(33) Dewey, M. A.; Stark, G. A.; Gladysz, J. A. *Organometallics* **1996**, *15*, 4798.

Scheme 3



crystallize faster than **13c′**. The rate of this isomerization was not dependent upon the concentration of free ligand, as the presence of 1 equiv of PPh$_2$Me per **13c** did not accelerate the process. We can therefore exclude a mechanism through which the phosphine in excess would substitute the phosphine already present at Co via a S$_N$2 type reaction. Thus, we can actually assume that, for this particular phosphine, there should exist a reverse reaction for the coordination of the phosphine for the less abundant diastereomer **13c′** leading to a decoordinated Co species. This latter should be in equilibrium with the major isomer, thus leading to the complete epimerization of the minor isomer, this process being controlled thermodynamically. We therefore propose that the substitution reaction with PPh$_2$Me takes place according to the reaction pathway depicted in Scheme 3.

Accordingly we can also assume that the other optically active cationic species studied here should not epimerize once they have been formed. This particular behavior might well be related to the large cone angle of PPh$_2$Me compared to that of the other phosphine used, which would have as a consequence a rather weak interaction of the phosphine with Co (note that the bulkier PPh$_3$ did not coordinate to Co). This should occur especially in the minor isomer, for which there should be much steric hindrance at the Co center because of the presence of the benzylic methyl group in proximity to the site of coordination of the phosphine, a situation that is dramatically different in the other diastereomer.

Conclusions

Several conclusions may be drawn from this investigation. It is now clear that a large number of anionic N-containing ligands can be transferred to Co(III), forming a wealth of pseudotetrahedral compounds having a cobalt atom as a stereogenic center. A very close analogy exists between the structure of the resulting cobalt(III) complexes and that of related ruthenium(II) derivatives.[14,34] This striking analogy is best emphasized when studying the transmetalation of optically active ligands, as this reaction afforded the same diastereoisomers with almost the same de. Moreover, both compounds display the same configurational stability at the Co and Ru center, as no epimerization could be evidenced, with the important exception however of the compound **13c′**, derived from the coordination of PPh$_2$Me on **12a**. Some important differences exist, however, between these two families of organometallic compounds. Among these is the extraordinary chemical stability in protic solvents of the cobalt derivatives, whereas their ruthenium counterparts are markedly less stable, as they usually lead rapidly to decomposition products under these conditions.[35]

Experimental Section

All reactions were performed in Schlenk flasks under oxygen- and water-free nitrogen. Solvents were dried and distilled under nitrogen: toluene over sodium and CH$_2$Cl$_2$ over P$_2$O$_5$. IR spectra were recorded in KBr on a Bruker IFS-66. The Service Central d'Analyse of Université Louis Pasteur and of Institut Charles Sadron (Strasbourg, France) performed the elemental analyses. The ^{1}H NMR spectra were recorded at 300.13 MHz, ^{13}C NMR spectra at 75.47 MHz, and ^{31}P NMR at 121.51 MHz on a FT-Bruker instruments (AC-300) and were externally referenced to TMS. Chemical shifts (δ) and coupling constant (J) are expressed in ppm and Hz, respectively. Circular dichroism spectra were recorded in CH$_2$Cl$_2$ on an ISA Jobin-Yvon CD6 instrument. UV–vis spectra were recorded on a Perkin-Elmer Lambda 11 UV–vis spectrometer and are reported over the range of ca. 200–800 nm. $[\alpha]_D$ values were measured at 20 °C on a Perkin-Elmer 341 polarimeter.

The starting materials [CpCoI$_2$]$_2$ (**1**)[20] and lithiated tertiary arylamines derivatives (N^C–Li) were prepared according to published methods.[36,38]

Syntheses. (η^5-C$_5$H$_5$)Co(C$_6$H$_4$CH$_2$NMe$_2$)I (3a). [2-((Dimethylamino)methyl)phenyl]lithium (**2a**; 0.282 g, 2.00 mmol) was slowly added to a stirred suspension of [CpCoI$_2$]$_2$ (**1**; 0.756 g, 1.00 mmol) in toluene (50 mL). The resulting green suspension was stirred for 16 h at room temperature, and all the volatiles were removed in vacuo. The residue was extracted with CH$_2$Cl$_2$ (100 mL) and filtered. The filtrate was washed with water (5 × 10 mL). The organic phase was dried with MgSO$_4$, filtered, and concentrated in vacuo, giving **3a** as a green solid. Yield: 0.60 g (78%). Anal. Calcd for C$_{14}$H$_{17}$CoIN (385.14): C, 43.66; H, 4.45; N, 3.64. Found: C, 43.87; H, 4.50; N, 3.64. ^{1}H NMR (CDCl$_3$): δ 8.35 (d, Ar, $^3J_{H-H} = 7.58$), 7.19 (t, 1H, Ar, $^3J_{H-H} = 7.12$), 6.90 (t, 1H, Ar, $^3J_{H-H} = 7.58$), 6.82 (d, 1H, Ar, $^3J_{H-H} = 7.12$), 5.03 (s, 5H, C$_5$H$_5$), 3.52 and 2.96 (AB spin system, 2H, CH$_2$N, $^2J_{H-H} = 13.20$), 3.36 and 2.74 (2s, 6H, NMe$_2$). ^{13}C{^{1}H}NMR (CDCl$_3$): δ 153.53, 149.38, 142.38, 126.23, 123.36, 121.98 (C$_6$H$_4$), 72.76 (CH$_2$N), 57.57, 56.44 (NMe$_2$).

All the compounds **3b–g** were obtained by following a similar procedure and workup.

(η^5-C$_5$H$_5$)Co(4-CH$_3$-C$_6$H$_3$CH$_2$NMe$_2$)I (3b). Compound **1** (0.756 g, 1.00 mmol) reacted with [2-((dimethylamino)methyl)-4-methylphenyl]lithium (**2b**; 0.310 g, 2.00 mmol) to give **3b**

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(36) Jastrzebski, J. T. B. H.; van Koten, G. *Inorg. Synth.* **1988**, *26*, 150.

(37) Arlen, C.; Pfeffer, M.; Bars, O.; Grandjean, P. *J. Chem. Soc., Dalton Trans.* **1983**, 1535.

(38) Lednicer, D.; Hauser, C. R. *Org. Synth.* **1960**, *40*, 31.

as a green solid. Yield: 0.69 g (86%). Anal. Calcd for $C_{15}H_{19}CoIN$ (399.16): C, 45.14; H, 4.80; N, 3.51. Found: C, 46.71; H, 5.03; N, 3.51. ^1H NMR ($CDCl_3$): δ 8.23 (d, 1H, Ar, $^3J_{H-H} = 7.67$), 7.06 (d, 1H, Ar, $^3J_{H-H} = 7.67$), 6.69 (s, 1H, Ar), 5.02 (s, 5H, C_5H_5), 3.48 and 2.91 (AB spin system, 2H, CH_2N, $^2J_{H-H} = 13.35$), 3.37 and 2.73 (2 s, 6H, NMe_2), 2.36 (s, 3H, Ar$-CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 149.18, 148.10, 141.97, 132.66, 127.38, 123.09, (C_6H_3), 85.46 (C_5H_5), 72.67 (CH_2N), 57.56, 56.38 (NMe_2), 20.65 (Ar$-CH_3$).

(η^5-C_5H_5)Co(5-CH_3-$C_6H_3CH_2NMe_2$)I (3c). Compound **1** (0.756 g, 1.00 mmol) reacted with [2-((dimethylamino)methyl)-5-methylphenyl]lithium (**2c**; 0.310 g, 2.00 mmol) to give **3c** as a green solid. Yield: 0.56 g (70%). Anal. Calcd for $C_{15}H_{19}CoIN$ (399.16): C, 45.14; H, 4.80; N, 3.51. Found: C, 46.40; H, 4.99; N, 3.52. ^1H NMR ($CDCl_3$): δ 8.17 (s, 1H, Ar), 6.72 (s, 2H, Ar), 5.03 (s, 5H, C_5H_5), 3.47 and 2.93 (AB spin system, 2H, CH_2N, $^2J_{H-H} = 13.34$), 3.36 and 2.73 (2s, 6H, NMe_2), 2.43 (s, 3H, Ar$-CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.30, 143.15, 141.77, 135.45, 124.47, 121.61 (C_6H_3), 85.65 (C_5H_5), 72.54 (CH_2N), 57.56, 56.38 (NMe_2), 21.86 (Ar$-CH_3$).

(η^5-C_5H_5)Co(4-F-$C_6H_3CH_2NMe_2$)I (3d). Compound **1** (0.756 g, 1.00 mmol) reacted with [2-((dimethylamino)methyl)-4-fluorophenyl]lithium (**2d**; 0.318 g, 2.00 mmol) to give **3d** as a green solid. Yield: 0.56 g (70%).Anal. Calcd for $C_{14}H_{16}CoFIN$ (403.13): C, 41.71; H, 4.00; N, 3.47. Found: C, 41.98; H, 3.99; N, 3.56. ^1H NMR ($CDCl_3$): δ 8.22 (dd, 1H, Ar, $^3J_{H-F} = 8.30$, $^3J_{H-H} = 6.00$), 6.97 (apparent ddd, 1H, Ar, $^3J_{H-F} = 8.80$, $^3J_{H-H} = 6.00$, $^4J_{H-H} = 2.70$), 6.61 (dd, 1H, Ar, $^3J_{H-F} = 9.51$, $^4J_{H-H} = 2.70$), 5.03 (s, 5H, C_5H_5), 3.47 and 2.94 (AB spin system, 2H, CH_2N, $^2J_{H-H} = 13.53$), 3.37 and 2.73 (2s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 161.49 (d, $^1J_{C-F} = 239.42$), 149.60 (d, $^3J_{C-F} = 7.04$), 144.49, 142.01 (d, $^3J_{C-F} = 7.04$), 112.98 (d, $^2J_{C-F} = 18.78$), 109.25 (d, $^2J_{C-F} = 18.78$) (C_6H_3), 85.36 (C_5H_5), 72.23 (CH_2N), 57.36, 56.27 (NMe_2).

(η^5-C_5H_5)Co(5-F-$C_6H_3CH_2NMe_2$)I (3e). Compound **1** (0.756 g, 1.00 mmol) reacted with [2-((dimethylamino)methyl)-5-fluorophenyl]lithium (**2e**; 0.318 g, 2.00 mmol) to give **3e** as a green solid. Yield: 0.39 g (48%). Anal. Calcd for $C_{14}H_{16}CoFIN$ (403.13): C, 41.71; H, 4.00; N, 3.47. Found: C, 41.98; H, 3.99; N, 3.56. ^1H NMR ($CDCl_3$): δ 8.01 (dd, 1H, Ar, $^3J_{H-F} = 9.30$, $^4J_{H-H} = 2.19$), 6.75 (t, 1H, Ar, $^3J_{H-H} = 7.68$), 6.58 (dt, 1H, Ar, $^3J_{H-F} = 8.90$, $^4J_{H-F} = 2.37$), 5.04 (s, 5H, C_5H_5) 3.48 and 2.94 (AB spin system, 2H, CH_2N, $^2J_{H-H} = 13.17$), 3.34 and 2.73 (2s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 161.70, (d, $^1J_{C-F} = 248.06$), 156.46, 144.59, 128.24 (d, $^2J_{C-F} = 17.72$), 122.01 (d, $^3J_{C-F} = 7.88$), 109.96 (d, $^2J_{C-F} = 21.66$) (C_6H_3), 85.76 (s, 5H, C_5H_5), 72.17 (CH_2N), 57.49, 56.36 (NMe_2).

(η^5-C_5H_5)Co(4-CH_3O-$C_6H_3CH_2NMe_2$)I (3f). Compound **1** (0.756 g, 1.00 mmol) reacted with [2-((dimethylamino)methyl)-4-methoxyphenyl]lithium (**2f**; 0.318 g, 2.00 mmol) to give **3f** as a green solid. Yield: 0.49 g (59%). Anal. Calcd for $C_{15}H_{19}CoINO$ (415.16): C, 43.40; H, 4.61; N, 3.37. Found: C, 43.43; H, 4.67; N, 3.36. ^1H NMR ($CDCl_3$): δ 8.19 (d, 1H, Ar, $^3J_{H-H} = 8.40$), 6.88 (dd, 1H, Ar, $^3J_{H-H} = 8.40$, $^4J_{H-H} = 2.76$), 6.50 (d, 1H, Ar), 5.01 (s, 5H, C_5H_5), 3.77 (s, 3H, CH_3O), 3.48 and 2.90 (AB spin system, 2H, CH_2N, $^2J_{H-H} = 13.35$), 3.38 and 2.74 (2s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 157.30, 149.42, 141.80, 139.48, 112.25, 108.86, (C_6H_3), 85.19 (C_5H_5), 72.52 (CH_2N), 57.41 and 56.26 (NMe_2), 55.12 (CH_3O).

(η^5-C_5H_5)Co(5-CH_3O-$C_6H_3CH_2NMe_2$)I (3g). Compound **1** (0.756 g, 1.00 mmol) reacted with [2-((dimethylamino)methyl)-5-methoxyphenyl]lithium (**2g**; 0.318 g, 2.00 mmol) to give **3g** as a green solid. Yield: 0.03 g (4%). Anal. Calcd for $C_{15}H_{19}CoINO$ (415.16): C, 43.40; H, 4.61; N, 3.37. Found: C, 43.48; H, 4.72; N, 3.46. ^1H NMR ($CDCl_3$): δ 7.90 (d, 1H, Ar, $^4J_{H-H} = 2.37$), 6.73 (d, 1H, Ar, $^3J_{H-H} = 8.04$), 6.46 (dd, 1H, Ar, $^3J_{H-H} = 8.04$, $^4J_{H-H} = 2.37$), 5.02 (s, 5H, C_5H_5), 3.89 (s, 3H, CH_3O), 3.46 and 2.92 (AB spin system, 2H, CH_2N, $^2J_{H-H} = 12.96$), 3.34 and 2.72 (2s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 156.77, 155.12, 141.59, 128.33, 121.77, 107.89 (C_6H_3), 85.67 (C_5H_5), 72.11 (CH_2N), 57.46, 56.33 (NMe_2), 55.26 (CH_3O).

(η^5-C_5H_5)Co($C_{10}H_7NMe_2$)I (5). This complex was obtained using a workup similar to that used for **3a**. **1** (0.756 g, 1.00 mmol) reacts with [8-((dimethylamino)naphthyl]lithium[34] (**4**; 0.318 g, 2.00 mmol) to give **5** as a green solid. Yield: 0.68 g (81%). Anal. Calcd for $C_{17}H_{17}CoIN$ (421.17): C, 48.48; H, 4.07; N, 3.33. Found: C, 48.30; H, 4.10; N, 3.27. ^1H NMR ($CDCl_3$): δ 8.40 (d, 1H, Ar, $^3J_{H-H} = 10.35$), 7.55$-$7.37 (m, 3H, Ar), 7.21 (t, 1H, Ar, $^3J_{H-H} = 11.79$), 7.00 (d, 1H, Ar, $^3J_{H-H} = 11.43$), 5.21 (s, 5H, C_5H_5), 3.97 and 3.17 (2s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 156.77, 144.38, 139.82, 134.39, 132.77, 127.14, 126.37, 125.04, 121.16, 114.50 ($C_{10}H_6$), 86.26 (C_5H_5), 63.71 and 57.47 (NMe_2).

[(η^5-C_5H_5)Co($C_6H_4CH_2NMe_2$)(PMe_2Ph)]$^+$$PF_6^-$ (6a). Dimethylphenylphosphine (0.17 mL, 1.20 mmol) was added to a stirred solution of **3a** (0.385 g, 1.00 mmol) in CH_2Cl_2 (10 mL) at room temperature. The color of the solution turned from green to red-brown. After 1 h the volatiles were removed in vacuo, affording a red-brown solid. This crude product was dissolved with water (50 mL) and filtered. To the red aqueous solution was added KPF_6(aq) in excess, affording a red precipitate. After 15 min the precipitate thus obtained was filtered and washed with water (10 mL) and hexane (30 mL). **6a** was isolated as a red powder after crystallization in acetone/hexane and drying in vacuo. Yield: 0.46 g (86%). Anal. Calcd for $C_{22}H_{28}CoF_6NP_2$ (541.35): C, 48.81; H, 5.21; N, 2.59. Found: C, 47.95; H, 5.25; N, 2.50. ^1H NMR (AcD_6): δ 7.95 (d, 1H, Ar, $^3J_{H-H} = 7.65$) 7.48 (t, 1H, Ar, $^3J_{H-H} = 7.32$), 7.35$-$7.05 (m, 6H, P(C_6H_5)), 6.70 (d, 1H, Ar, $^3J_{H-H} = 7.32$), 5.55 (s, 5H, C_5H_5), 2.82 and 2.15 (AB spin system, 2H, CH_2N, $J_{H-H} = 15.00$), 2.81 and 2.79 (2s, 6H, NMe_2), 2.35 and 1.79 (2d, 6H, PMe_2, $^2J_{H-P} = 10.41$). $^{31}P\{^1H\}$ NMR (AcD_6): δ 11.69, (s, PMe_2-Ph), $-$143.57 (septet, PF_6, $^1J_{P-F} = 707.00$). $^{13}C\{^1H\}$ NMR (AcD_6): δ 150.52 (d, $^2J_{C-P} = 43.31$), 150.24, 143.79, 127.20, 124.72, 124.07 (C_6H_4), 134.51 (d, C_i, $^1J_{C-P} = 39.37$), 131.30 (d, C_m, $^3J_{P-C} = 7.87$) 131.01, 129.05 (d, C_o, $^2J_{C-P} = 9.85$) (PC_6H_5), 90.08 (C_5H_5), 71.85 (CH_2N), 60.86 and 56.98 (NMe_2), 17.53 (d, $^2J_{C-P} = 27.56$) and 16.97 (d, $^2J_{C-P} = 37.40$) (PMe_2).

[(η^5-C_5H_5)Co($C_6H_4CH_2NMe_2$)(PPh_2Me)]$^+$ PF_6^- (6b). Compound **3a** (0.385 g, 1.00 mmol) reacted with PPh_2Me (0.17 mL, 1.20 mmol) to give **6b** as a red solid. Yield: 0.52 g (87%). Anal. Calcd for $C_{27}H_{30}CoF_6NP_2$ (603.42): C, 53.74; H, 5.01; N, 2.32. Found: C, 51.28; H, 4.85; N, 2.16. ^1H NMR (AcD_6): δ 8.12 (m, 3H, PPh_2 and Ar), 7.71 (app br s, PPh_2, 3H), 7.44 (t, 1H, Ar, $^3J_{H-H} = 7.68$), 7.34 (t, 1H, Ar, $^3J_{H-H} = 7.68$), 7.28$-$7.08 (m, 3H, PPh_2), 6.79 (m, 2H, PPh_2), 6.70 (d, 1H, Ar, $^3J_{H-H} = 7.32$), 5.57 (s, 5H, C_5H_5), 2.88 (app s, 6H, NMe_2), 2.81 and 2.16 (AB spin system, 2H, CH_2N, $^2J_{H-H} = 14.80$), 2.14 (d, 3H, PMe, $^2J_{H-P} = 9.69$). $^{31}P\{^1H\}$ NMR (AcD_6): δ 24.79 (s, PPh_2Me), $-$143.53 (septet, PF_6, $^1J_{P-F} = 707.00$). $^{13}C\{^1H\}$ NMR (AcD_6): δ 150.62, 150.02 (d, $^2J_{C-P} = 34.17$), 143.95, 145.82, 129.48, 126.89, 126.33 (C_6H_4), 92.23 (C_5H_5), 74.18 (CH_2N), 63.34 and 60.24 (NMe_2), 17.89 (d, PMe, $^2J_{C-P} = 37.38$).

[(η^5-C_5H_5)Co($C_6H_4CH_2NMe_2$)(PMe_3)]$^+$ PF_6^- (6c). Compound **3a** (0.385 g, 1.00 mmol) reacted with PMe_3 (1 M in toluene, 1.2 mL, 1.20 mmol) to give **6c** as a red solid. Yield: 0.42 g (87%). Anal. Calcd for $C_{17}H_{26}CoF_6NP_2$ (479.27): C, 42.60; H, 5.47; N, 2.92. Found: C, 43.69; H, 5.51; N, 2.90. ^1H NMR (AcD_6): δ 7.76 (apparent ddd, 1H, Ar, $^3J_{H-H} = 7.47$, $^4J_{H-P} = 2.37$, $^4J_{H-H} = 1.11$), 7.14 (td, 1H, Ar, $^3J_{H-H} = 7.47$, $^4J_{H-H} = 1.47$), 7.06 (tt, 1H, Ar, $^3J_{H-H} = 7.32$, $^4J_{H-H} = 1.11$), 6.99 (dd, 1H, Ar, $^3J_{H-H} = 7.32$, $^4J_{H-H} = 1.47$), 5.48 (d, 5H, C_5H_5, $^3J_{H-P} = 0.90$), 3.40 and 3.35 (AB spin system, 2H, CH_2N, $^2J_{H-H} = 16.26$), 2.90 and 2.88 (2s, 6H, NMe_2), 1.56 (d, 9H, PMe_3, $^2J_{H-P} = 10.59$). $^{31}P\{^1H\}$ NMR (AcD_6): δ 8.80 (s, PMe_3), $-$143.53 (septet, PF_6, $^1J_{P-F} = 707.00$). $^{13}C\{^1H\}$ NMR (AcD_6): δ 151.27 (d, $^2J_{C-P} = 39.38$), 149.64, 142.89, 127.34, 124.63, 123.50 (C_6H_4), 89.91 (C_5H_5), 73.21 (CH_2N), 61.05, 57.77 (NMe_2), 17.20 (d, PMe, $^2J_{C-P} = 29.53$).

[(η^5-C_5H_5)Co($C_6H_4CH_2NMe_2$)[P(OMe)$_3$]]$^+$ PF_6^- (6d). This complex was obtained using a workup similar to that used for **6a**; however, the reaction time was 7 h. **3a** (0.385 g, 1.00 mmol) reacts with $P(OMe)_3$ (0.14 mL, 1.20 mmol) to give **6d** as a red solid. Yield: 0.38 g (72%). Anal. Calcd for $C_{17}H_{26}CoF_6NO_3P_2$ (527.27): C, 38.73; H, 4.97; N, 2.66. Found: C, 39.04; H, 5.04; N, 2.66. ^1H NMR (AcD_6): δ 7.75 (d, 1H, Ar, $^3J_{H-H} = 6.39$), 7.13−7.00 (m, 3H, Ar), 5.53 (s, 5H, C_5H_5), 3.77 (d, 9H, OMe, $^3J_{H-P} = 10.59$), 3.65 (A part of an AB spin system, 1H, $C\mathbf{H_a}H_b$, $^2J_{H-H} = 13.11$), 3.30 (B part of the AB spin system, $CH_a\mathbf{H_b}N$, $^3J_{H-P} = 1.26$), 2.88 and 2.82 (2s, 6H, NMe_2). $^{31}P\{^1H\}$ NMR (AcD_6): δ 135.00 (s, $P(OMe)_3$), −143.80 (septet, PF_6, $^1J_{P-F} = 712.08$). $^{13}C\{^1H\}$ NMR (AcD_6): δ 150.45, 146.35 (d, $^2J_{C-P} = 21.62$), 144.57, 126.69, 124.91, 123.65 (C_6H_4), 90.63 (C_5H_5), 73.12 (CH_2N), 60.52 ($P(OMe)_3$), 57.15 and 55.35 (NMe_2).

[(η^5-C_5H_5)Co($C_6H_4CH_2NMe_2$)[PO(OMe)$_2$] (6e). $P(OMe)_3$ (0.14 mL, 1.20 mmol) was added to a stirred solution of **3a** (0.385 g, 1.00 mmol) in CH_2Cl_2 (10 mL) at room temperature. After 6 h the solution turned from green to red. After 17 h the volatiles were removed in vacuo, affording a red oily solid. This crude product was recrystallized in CH_2Cl_2/hexane and dried in vacuo; **6e** was isolated as a light red powder. Yield: 0.25 g (87%). Anal. Calcd for $C_{16}H_{23}CoF_6NO_3P_2$ (512.25): C, 52.33; H, 6.31; N, 3.81. Found: C, 52.33; H, 6.32; N, 3.78. IR (KBr): 1151 cm^{-1} (vs, $\nu_{P=O}$) and 1040 and 993 cm^{-1} (doublet vs, ν_{P-O}). ^1H NMR (AcD_6): δ 7.60 (d, 1H,Ar, $^3J_{H-H} = 7.50$), 7.00 (td, 1H, Ar, $^3J_{H-H} = 7.50$, $^4J_{H-H} = 1.26$), 6.94 (td, 1H, Ar, $^3J_{H-H} = 7.11$, $^4J_{H-H} = 1.29$), 6.82 (d, 1H, Ar, $^3J_{H-H} = 7.11$), 4.98 (s, 5H, C_5H_5), 4.28 (A part of an AB spin system, 1H, $C\mathbf{H_a}H_b$, $^2J_{H-H} = 13.50$), 2.71 (B part of the AB spin system, 1H, $CH_a\mathbf{H_b}N$, $^3J_{H-P} = 1.83$), 3.41 and 3.30 (2d, 6H, $PO(OMe)_2$, $^2J_{H-P} = 10.23$), 2.76 and 2.67 (2s, 6H, NMe_2). $^{31}P\{^1H\}$ NMR (AcD_6): δ 0.94.85 (s, $PO(OMe)_2$), −143.80 (septet, PF_6, $^1J_{P-F} = 712.08$). $^{13}C\{^1H\}$ NMR (AcD_6): δ 152.129 (d, 1H, Ar, $^2J_{C-P} = 49.29$), 149.84, 143.93, 125.34, 123.07, 121.76 (C_6H_4), 88.45 (C_5H_5), 72.05 (CH_2N), 60.61 and 56.48 (NMe_2), 51.65 and 50.54 (2d, $PO(OMe)_2$, $^2J_{C-P} = 9.39$).

[(η^5-C_5H_5)Co($C_6H_4CH_2NMe_2$)(CN*t*Bu)]$^+$$PF_6^-$ (6f). This complex was obtained using a workup similar to that used for **6a**; however, the reaction time was 3 h. **3a** (0.385 g, 1.00 mmol) reacts with CN*t*Bu (0.14 mL, 1.20 mmol), giving **6f** as a red solid. Yield: 0.230 g (47%). Anal. Calcd for $C_{19}H_{26}CoF_6N_2P$ (486.34): C, 46.93; H, 5.39; N, 5.76. Found: C, 46.78; H, 5.34; N, 5.50. IR (Nujol): 2188 cm^{-1} (vs, $\nu_{C\equiv N}$). ^1H NMR ($CDCl_3$): δ 7.50 (d, 1H, Ar), 7.26−6.98 (m, 3H, Ar), 5.33 (s, 5H, C_5H_5), 3.65 and 3.36 (AB spin system, 2H, CH_2N, $^2J_{H-H} = 14.08$), 2.82 and 2.53 (2s, 6H, NMe_2), 1.43 (s, 9H, *t*Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 149.75, 147.23, 141.40, 127.56, 124.68 (C_6H_4), 91.62 ($C\equiv N$), 89.65 (C_5H_5), 74.31 (CH_2N), 60.31 ($\mathbf{C}(CH_3)_3$), 57.78 and 56.98 (NMe_2), 29.71 ($C(\mathbf{C}H_3)_3$).

[(η^5-C_5H_5)Co(η^5-C_5H_5)Fe(η^5-C_5H_3)CH_2NMe_2(PMe_3)]$^+$$PF_6^-$ (8). *n*-Butyllithium (l.5 M in hexane; 3.6 mL, 5.5 mmol) was slowly added to a stirred suspension of $CpFeCpCH_2NMe_2$[35] (1.0 mL, 5.0 mmol) in Et_2O (10 mL). After 1 h the volatiles were removed in vacuo and an orange oily solid was isolated. The residue was dissolved in toluene (40 mL) and cooled to −78 °C, and **1** (1.511 g, 2.00 mmol) was added. The reaction temperature was increased to room temperature and left for 30 min. Trimethylphosphine (1 M in toluene; 4.2 mL, 4.2 mmol) was added. After 2 h the volatiles were removed in vacuo, water (50 mL) was added, and the mixture was stirred for 30 min. The red-brown mixture was filtered, and the residue was washed with water (2 × 20 mL). To the combined aqueous solutions was added KPF_6 in excess. The red precipitate thus formed was filtered and washed with water (10 mL) and hexane. The crude product was purified by chromatography on silica gel CH_2Cl_2/MeOH (95:5), recrystallized in acetone/hexane, and dried in vacuo, giving **8** as a red solid. Yield: 0.30 g (13%); de > 99%. Anal. Calcd for $C_{21}H_{30}CoF_6FeNP_2$ (587.20): C, 42.92; H, 5.15; N, 2.39. Found: C, 39.96; H, 4.67; N, 2.12. ^1H NMR (AcD_6): δ 5.53 (s, 5H, C_5H_5−Co), 4.66 (app s, 1H, C_5H_3), 4.51 (t, 1H, C_5H_3, $^3J_{H-H} = 2.19$), 4.36 (s, 5H, C_5H_5−Fe), 4.11 (d, 1H, C_5H_3, $^3J_{H-H} = 1.83$), 3.51 and 2.90 (2 s, 6H, NMe_2), 2.82 (AB spin system, 2H, CH_2N, $^2J_{H-H} = 15.18$), 1.41 (d, 9H, PMe_3, $^2J_{H-H} = 10.77$). $^{31}P\{^1H\}$ NMR (AcD_6): major isomer, δ 11.64 (s, PMe_3), −143.57 (septet, PF_6, $^1J_{P-F} = 706.99$). $^{13}C\{^1H\}$ NMR (AcD_6): major isomer, δ 99.75, 95.99, 73.65, 68.88, 65.81 (C_5H_3), 89.05 (C_5H_5−Co), 70.28 (C_5H_5−Fe), 62.75 (CH_2NMe_2), 60.98 ($NCH_3{}^a$), 59.75 (d, $NCH_3{}^b$, $^3J_{C-P} = 4.20$), 17.07 (d, PMe_3, $^1J_{C-P} = 29.46$).

(η^5-C_5H_5)Co[$C_6H_4CH_2NMe(Et)$]I (10). [2-((Ethylmethylamino)methyl)phenyl]lithium (**9**; 0.310 g, 2.00 mmol) was slowly added to a stirred suspension of **1** (0.756 g, 1.00 mmol) in toluene (50 mL). The resulting green suspension was stirred for 16 h at room temperature, and all the volatiles were removed in vacuo. The residue was extracted with CH_2Cl_2 (100 mL) and filtered. The filtrate was washed with water (5 × 10 mL). The organic phase was dried with $MgSO_4$, filtered, and concentrated in vacuo, giving **10** as a green solid. Yield: 0.17 g (21%). de = 63%. Anal. Calcd for $C_{15}H_{19}CoIN$ (399.16): C, 45.14; H, 4.80; N, 3.51. Found: C, 45.99; H, 4.77; N, 3.57. ^1H NMR ($CDCl_3$): major isomer, δ 8.37 (d, Ar, $^3J_{H-H} = 7.68$), 7.20 (t, 1H, Ar, $^3J_{H-H} = 7.11$), 6.90 (t, 1H, Ar, $^3J_{H-H} = 7.32$), 6.82 (d, 1H, Ar, $^3J_{H-H} = 7.14$), 5.03 (s, 5H, C_5H_5), 4.27 and 2.86 (ABX_3 spin system, 2 dt, 2H, $N\mathbf{CH_2}CH_3$, $^2J_{H-H} = 13.71$, $^3J_{H-H} = 7.11$), 3.35 and 3.08 (AB spin system, 2H, $ArCH_2N$, $^2J_{H-H} = 13.17$), 2.70 (s, 3H, NMe), 1.22 (t, 3H, $NCH_2\mathbf{CH_3}$); minor isomer, δ 8.44 (d, Ar, $^3J_{H-H} = 7.68$), 5.02 (s, 5H, C_5H_5), 3.45 and 3.29 (AB spin system, 2H, $ArCH_2N$, $^2J_{H-H} = 13.68$), 3.12 (s, 3H, NMe), 1.13 (t, 3H, $NCH_2\mathbf{CH_3}$, $^3J_{H-H} = 7.11$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): major isomer, δ 154.09, 150.69, 142.57, 125.69, 122.95, 121.89 (C_6H_4), 86.00 (C_5H_5), 68.39 ($ArCH_2N$), 61.86 ($N\mathbf{C}H_2CH_3$), 50.35 (NMe), 9.14 ($NCH_2\mathbf{C}H_3$); minor isomer, δ 143.23, 121.30 (C_6H_4), 86.00 (C_5H_5), 66.40 ($ArCH_2N$), 59.44 ($N\mathbf{C}H_2CH_3$), 52.69 (NMe), 10.20 ($NCH_2\mathbf{C}H_3$).

(R_{Co},R_C)-(η^5-C_5H_5)Co($C_6H_4CH(Me)NMe_2$)I (12a,a′). [(*R*)-2-(1-(Dimethylamino)ethyl)phenyl]lithium (**11a**; 0.310 g, 2.00 mmol) was slowly added to a stirred suspension of **1** (0.756 g, 1.00 mmol) in toluene (50 mL). The resulting green suspension was stirred for 16 h at room temperature, and all the volatiles were removed in vacuo. The residue was extracted with CH_2Cl_2 (100 mL) and the extract filtered. The filtrate was washed with water (5 × 10 mL). The organic phase was dried with $MgSO_4$, filtered, and concentrated in vacuo, giving **12a**,**a′** as a green solid. Yield: 0.32 g (79%). de = 91%. Anal. Calcd for $C_{15}H_{19}CoIN$ (399.16): C, 45.14; H, 4.80; N, 3.51. Found: C, 45.83; H, 4.89; N, 3.47. UV−vis (CH_2Cl_2): λ_{max} 242 nm (log ϵ_{max} 0.94). ^1H NMR ($CDCl_3$): major isomer, δ 8.44 (d, Ar, $^3J_{H-H} = 7.47$), 7.22 (t, 1H, Ar, $^3J_{H-H} = 7.50$), 6.90 (t, 1H, Ar, $^3J_{H-H} = 7.47$), 6.67 (d, 1H, Ar, $^3J_{H-H} = 7.50$), 5.05 (s, 5H, C_5H_5), 3.51 and 2.48 (2s, 6H, NMe_2), 3.42 (q, 1H, $C\mathbf{H}(Me)N$, $^3J_{H-H} = 6.75$), 1.12 (d, 3H, $CH(\mathbf{Me})N$); minor isomer, δ 8.53 (d, Ar, $^3J_{H-H} = 7.32$), 7.35 (t, 1H, Ar, $^3J_{H-H} = 7.36$), 7.03 (t, 1H, Ar, $^3J_{H-H} = 7.35$), 6.74 (d, 1H, Ar, $^3J_{H-H} = 7.47$), 5.05 (s, 5H, C_5H_5), 3.94 (q, 1H, $C\mathbf{H}(Me)N$, $^3J_{H-H} = 6.57$), 3.26 and 1.92 (2s, 6H, NMe_2), 1.12 (d, 3H, $CH(\mathbf{Me})N$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): major isomer, δ 153.07, 152.81, 142.06, 126.39, 123.44, 123.05 (C_6H_4), 86.24-(C_5H_5), 69.40 ($\mathbf{C}H(Me)N$), 54.34, 47.95 (NMe_2), 9.50($CH(\mathbf{Me})N$); minor isomer, δ 86.99 (C_5H_5).

All the compounds **13** were obtained following a similar procedure and workup.

(S_{Co},R_C)-[(η^5-C_5H_5)Co($C_6H_4CH(Me)NMe_2$)(PMe_3)]$^+$$PF_6^-$ (13a,a′). Trimethylphosphine (1 M in toluene; 1.2 mL, 1.2 mmol) reacted with **12a**,**a′** (0.399 g, 1.00 mmol) to give **13a**,**a′** as a red solid. Yield: 0.42 g (86%). de = 75%. Anal. Calcd for $C_{18}H_{28}CoF_6NP_2$ (493.31): C, 43.83; H, 5.72; N, 2.84. Found: C, 43.97; H, 5.79; N, 2.76. UV−vis (CH_2Cl_2): λ_{max} 241 nm (log ϵ_{max} 0.58). ^1H NMR ($CDCl_3$): major isomer, δ 7.85 (ddd, 1H, Ar, $^3J_{H-H} = 7.29$, $^4J_{H-P} = 2.37$, $^4J_{H-H} = 1.44$), 7.21−7.07 (m, 2H, Ar), 6.87 (ddd, $^3J_{H-H} = 7.32$, $^5J_{H-P} = 2.73$, $^4J_{H-H} = 1.30$), 5.50 (d, 5H, C_5H_5, $^3J_{H-P} = 0.72$), 3.17 (q, 1H, $C\mathbf{H}(Me)N$, $^3J_{H-H} = 6.57$), 3.04 and 2.62 (2s, 6H, NMe_2), 1.53 (d, 9H, PMe_3, $^2J_{H-P} = 10.59$), 1.28 (d, 3H, $CH(\mathbf{Me})N$); minor isomer, δ 7.61 (app d, 1H, Ar, $^3J_{H-H} = 7.11$), 6.95 (app d, 1H, Ar, $^3J_{H-H} = 6.93$), 5.43 (d, 5H, C_5H_5, $^3J_{H-P} = 0.90$), 4.40 (q, 1H, $C\mathbf{H}(Me)N$, $^3J_{H-H} = 6.75$), 3.12 and 1.75 (s and d, 6H, NMe_2, $^4J_{H-P} = 3.09$), 1.66 (d, 9H, PMe$_3$, $^{2}J_{H-P}$ = 10.41), 1.30 (d, 3H, CH(**Me**)N). ^{31}P{^{1}H} NMR (CDCl$_3$): major isomer, δ 6.40 (s, PMe$_3$), −143.57 (septet, PF$_6$, $^{1}J_{P-F}$ = 707.00); minor isomer, δ 10.00 (s, PMe$_3$), −143.57 (septet, PF$_6$, $^{1}J_{P-F}$ = 707.00). ^{13}C{^{1}H} NMR (CDCl$_3$): major isomer, δ 152.97, 152.27 (d, $^{2}J_{C-P}$ = 24.03), 142.62, 127.53, 124.77, 124.77 (C$_6$H$_4$), 90.50 (C$_5$H$_5$), 71.59 (**C**H(Me)N), 55.03, 51.34 (NMe$_2$), 17.50 (d, PMe$_3$, $^{1}J_{C-P}$ = 50.82), 10.44 (CH(**Me**)N); minor isomer, δ 152.54, 141.40, 127.95 (C$_6$H$_4$), 89.05 (C$_5$H$_5$), 75.22 (**C**H(Me)N), 55.31, 47.36 (NMe$_2$), 16.80 (d, $^{1}J_{C-P}$ = 50.80), 9.68 (NMe$_2$).

(S_{Co},R_C)-[(η^5-C$_5$H$_5$)Co(C$_6$H$_4$CH(Me)NMe$_2$)(PMe$_2$Ph)]$^+$PF$_6^-$ (13b,b′). Dimethylphenylphosphine (0.17 mL, 1.20 mmol) was added to a stirred solution of **12a**,**a′** (0.399 g, 1.00 mmol) in CH$_2$Cl$_2$ (10 mL) at room temperature. The solution turned from green to red-brown. After 1 h the volatiles were removed in vacuo, affording a red-brown solid. This crude product was dissolved in water (50 mL) and filtered. To the red aqueous solution was added KPF$_6$(aq) in excess, affording a red precipitate. After 15 min the precipitate thus obtained was filtered and washed with water (10 mL) and hexane (30 mL). After recrystallization in acetone/hexane and drying in vacuo, **13b**,**b′** was isolated as a red powder. Yield: 0.43 g (77%). de = 91%. Anal. Calcd for C$_{23}$H$_{30}$CoF$_6$NP$_2$ (555.37): C, 49.74; H, 5.44; N, 2.52. Found: C, 49.85; H, 5.46; N, 2.52. UV−vis (CH$_2$Cl$_2$): λ_{max} 246 nm (log ϵ_{max} 0.62). ^{1}H NMR (CDCl$_3$): major isomer, δ 7.78 (app ddd, 1H, Ar, $^{3}J_{H-H}$ = 8.58, $^{4}J_{H-P}$ = 2.37, $^{4}J_{H-H}$ = 1.11), 7.35 (tdd, 1H, Ar, $^{3}J_{H-H}$ = 6.86, $^{5}J_{H-P}$ = 1.83, $^{4}J_{H-H}$ = 1.11), 7.31−7.19 (m, 3H, P(C$_6$H$_5$)), 7.12 (t, 1H, Ar, $^{3}J_{H-H}$ = 7.29), 6.84 (m, 2H, P(C$_6$H$_5$)), 6.51 (dd, 1H, $^{3}J_{H-H}$ = 7.47, $^{4}J_{H-H}$ = 1.08), 5.22 (d, 5H, C$_5$H$_5$, $^{3}J_{H-P}$ = 0.75), 2.81 and 2.40 (2s, 6H, NMe$_2$), 2.13 and 1.74 (2d, 6H, PMe$_2$, $^{2}J_{H-P}$ = 9.66), 1.90 (q, 1H, C**H**(Me)N, $^{3}J_{H-H}$ = 6.57), 0.81 (d, 3H, CH(**Me**)N); minor isomer, δ 5.24 (d, 5H, C$_5$H$_5$, $^{3}J_{H-P}$ = 0.54), 4.17 (q, 1H, C**H**(Me)N, $^{3}J_{H-H}$ = 6.57), 3.01 and 1.38 (s and d, 6H, NMe$_2$, $^{4}J_{H-P}$ = 3.15), 1.23 (d, 3H, CH(**Me**)N). ^{31}P{^{1}H} NMR (CDCl$_3$): major isomer, δ 7.99 (s, PMe$_2$Ph), −144.29 (septet, PF$_6$, $^{1}J_{P-F}$ = 712.08); minor isomer, δ 18.29 (s, PMe$_2$Ph), −144.29 (septet, PF$_6$, $^{1}J_{P-F}$ = 712.08). ^{13}C{^{1}H} NMR (CDCl$_3$): major isomer, δ 152.64, 150.38 (d, $^{2}J_{C-P}$ = 56.90), 143.07, 130.70, 127.57, 124.94 (C$_6$H$_4$), 134.94 (d, C$_i$, $^{1}J_{C-P}$ = 61.84), 130.64, 130.39 (d, C$_m$, $^{3}J_{C-P}$ = 9.90), 128.88 (d, C$_o$, $^{2}J_{C-P}$ = 14.84) (PC$_6$H$_5$), 90.14 (C$_5$H$_5$), 69.74 (**C**H(Me)N), 54.40 (d, $^{3}J_{C-P}$ = 4.95) 54.40 and 51.35 (NMe$_2$), 17.69 (d, $^{2}J_{C-P}$ = 54.43) and 17.60 (d, $^{2}J_{C-P}$ = 42.06) (PMe$_2$), 9.85 (CH(**Me**)N); minor isomer, δ 88.85 (C$_5$H$_5$).

(S_{Co},R_C)-[(η^5-C$_5$H$_5$)Co(C$_6$H$_4$CH(Me)NMe$_2$)(PPh$_2$Me)]$^+$PF$_6^-$ (13c,c′). Diphenylmethylphosphine (0.17 mL, 1.2 mmol) reacts with **12a**,**a′** (0.399 g, 1.00 mmol) to give **13c**,**c′** as a red solid. Yield: 0.34 g (55%). de = 60% and de > 99% after slow recrystallization in acetone/hexane. Anal. Calcd for C$_{28}$H$_{32}$CoF$_6$NP$_2$ (617.45): C, 54.47; H, 5.22; N, 2.27. Found: C, 54.26; H, 5.00; N, 2.25. UV−vis (CH$_2$Cl$_2$): λ_{max} 223 nm (log ϵ_{max} 0.70). ^{1}H NMR (AcD$_6$): major isomer, δ 8.23 (ddd, 1H, Ar, $^{3}J_{H-H}$ = 7.65, $^{4}J_{H-P}$ = 2.58, $^{4}J_{H-H}$ = 1.11), 8.14−6.75 (m, 12H, Ar and PPh$_2$), 6.58 (dd, 1H, Ar, $^{3}J_{H-H}$ =7.47, $^{4}J_{H-H}$ = 1.29) 5.56 (d, 5H, C$_5$H$_5$, $^{3}J_{P-H}$ = 0.54) 3.05 and 2.57 (2s, 6H, NMe$_2$), 1.98 (q, 1H, C**H**(Me)N, $^{3}J_{H-H}$ = 6.75) 2.10 (d, 3H, PMe, $^{2}J_{H-P}$ = 9.66) 0.85 (d, 3H, CH(**Me**)N); minor isomer, δ 7.97 (d, 1H, Ar, $^{3}J_{H-H}$ = 6.78), 7.00 (d, 1H, Ar, $^{3}J_{H-H}$ = 7.47), 5.31 (d, 5H, C$_5$H$_5$, $^{3}J_{H-P}$ = 0.57), 4.36 (q, 1H, C**H**(Me)N, $^{3}J_{H-H}$ = 6.7z), 3.18 (s, 3H, NMe), 1.82 (d, 3H, PMe, $^{2}J_{H-P}$ = 9.87), 1.48 (d, 3H, NMe, $^{4}J_{H-P}$ = 3.30), 1.28 (d, 3H, CH(**Me**)N). ^{31}P{^{1}H} NMR (AcD$_6$): major isomer, δ 22.27 (s, PPh$_2$Me), −143.48 (septet, PF$_6$, $^{1}J_{P-F}$ = 701.91); minor isomer, δ 30.60 (s, PPh$_2$Me), −143.48 (septet, PF$_6$, $^{1}J_{P-F}$ = 701.91). ^{13}C{^{1}H} NMR (AcD$_6$): major isomer, δ 153.80, 151.19 (d, $^{2}J_{C-P}$ = 35.78), 143.71, 127.81, 125.64, 125.19 (C$_6$H$_4$), 134.30 (d, $^{1}J_{C-P}$ = 39.99), 133.60 (d, $^{2}J_{C-P}$ = 10.52), 133.57 (d, $^{1}J_{C-P}$ = 40.00), 132.80 (d, $^{3}J_{C-P}$ = 8.41), 131.97, 131.10, 129.61 (d, $^{2}J_{C-P}$ = 10.52), 128.85 (d, $^{3}J_{C-P}$ = 10.52) (PPh$_2$), 90.86 (C$_5$H$_5$), 70.34 (**C**H(Me)N), 55.70, 51.52 (NMe$_2$), 15.98 (d, $^{2}J_{C-P}$ = 37.88) (PMe), 5.46 (CH(**Me**)N); minor isomer (CDCl$_3$), δ 152.51, 142.10, 128.39, 125.15 (C$_6$H$_4$), 89.46 (C$_5$H$_5$), 75.72 (**C**H(Me)N), 55.60, 46.42 (NMe$_2$), 13.44 (d, $^{1}J_{C-P}$ = 31.50) (PMe), 10.08 (CH(**Me**)N).

(S_{Co},R_C)-[(η^5-C$_5$H$_5$)Co(C$_6$H$_4$CH(Me)NMe$_2$)(CN*t*-Bu)]$^+$PF$_6^-$ (13d,d′). *tert*-Butyl isocyanide (0.14 mL, 1.20 mmol) was added to a stirred solution of **12a**,**a′** (0.399 g, 1.00 mmol) in CH$_2$Cl$_2$ (10 mL) at room temperature. The solution turned from green to light red. After 4 h the volatiles were removed in vacuo, affording a light red solid. This crude product was dissolved in water (50 mL) and filtered. To the red aqueous solution was added KPF$_6$(aq) in excess, affording a red precipitate. After 15 min the product thus obtained was filtered and washed with water (10 mL) and hexane (30 mL). After recrystallization in acetone/hexane and drying in vacuo **13d**,**d′** was isolated as a red powder. Yield: 0.41 g (82%). de = 55%. Anal. Calcd for C$_{20}$H$_{28}$CoF$_6$N$_2$P (500.36): C, 48.01; H, 5.64; N, 5.60. Found: C, 47.88; H, 5.79; N, 5.48. UV−vis (CH$_2$Cl$_2$): λ_{max} 225 nm (log ϵ_{max} 0.60). IR (KBr): 2194 cm^{-1} ($\nu_{s\ C\equiv N}$). ^{1}H NMR (CDCl$_3$): major isomer, δ 7.58 (dd, 1H, Ar, $^{3}J_{H-H}$ = 7.32, $^{4}J_{H-H}$ = 1.47), 7.12 (m, 2H, Ar), 6.85 (dd, 1H, Ar, $^{3}J_{H-H}$ = 7.05, $^{4}J_{H-H}$ = 0.99), 5.37 (s, 5H, C$_5$H$_5$), 3.23 (q, 1H, C**H**(Me)N, $^{3}J_{H-H}$ = 6.84), 2.94 and 2.51 (2s, 6H, NMe$_2$), 1.30 (s, 9H, CN*t*Bu), 1.29 (d, 3H, CH(**Me**)N); minor isomer, δ 7.47 (dd, 1H, Ar, $^{3}J_{H-H}$ = 7.08, $^{4}J_{H-H}$ = 1.98), 6.88 (app d, 1H, Ar, $^{3}J_{H-H}$ = 7.08), 5.30 (s, 5H, C$_5$H$_5$), 4.10 (q, 1H, C**H**(Me)N, $^{3}J_{H-H}$ = 6.84), 3.03 and 1.84 (2 s, 6H, NMe$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): major isomer, δ 151.24, 149.34, 141.25, 127.92, 125.16, 124.42 (C$_6$H$_4$), 90.64 (C$_5$H$_5$), 73.27 (**C**H(Me)N), 60.67 (**C**(CH$_3$)$_3$), 56.08, 49.94 (NMe$_2$), 29.91 (C(**C**H$_3$)$_3$), 12.32 (CH(**Me**)N); minor isomer (CDCl$_3$), δ 152.63, 141.49, 128.05, 124.76 (C$_6$H$_4$), 89.52 (C$_5$H$_5$), 75.75 (**C**H(Me)N), 60.15 (**C**(CH$_3$)$_3$), 55.29, 47.62 (NMe$_2$), 30.41 (C(**C**H$_3$)$_3$), 10.35 (CH(**Me**)N).

(S_{Co},R_C)-[(η^5-C$_5$H$_5$)Co(C$_6$H$_4$CH(Me)NMe$_2$)(PO(OMe)$_2$)] (13e,e′). Trimethyl phosphite (0.14 mL, 1.2 mmol) was added to a stirred solution of **12a**,**a′** (0.399 g, 1.00 mmol) in CH$_2$Cl$_2$ (10 mL) at room temperature. The solution turned from green to red-brown. After 18 h the volatiles were removed in vacuo, affording a red solid. This crude product was dissolved with CH$_2$Cl$_2$ (5.0 mL), recrystallized with hexane, and dried in vacuo, affording **13e**,**e′** as a red powder. Yield: 0.21 g (55%). de = 91%. Anal. Calcd for C$_{17}$H$_{25}$CoNO$_3$P (381.30): C, 53.55; H, 6.61; N, 3.67. Found: C, 52.81; H, 6.49; N, 3.51. UV−vis (CH$_2$Cl$_2$): λ_{max} 225 nm (log ϵ_{max} 0.80). IR (KBr): 1154 and 1124 cm^{-1} ($\nu_{s,P=O}$), 1042 and 997 cm^{-1} ($\nu_{s,P-O}$). ^{1}H NMR (CDCl$_3$): major isomer, δ 7.65 (d, 1H, Ar, $^{3}J_{H-H}$ = 6.75), 7.10−6.95 (m, 2H, Ar), 6.67 (d, 1H, Ar, $^{3}J_{H-H}$ = 6.75), 4.99 (s, 5H, C$_5$H$_5$), 4.28 (q, 1H, C**H**(Me)N, $^{3}J_{H-H}$ = 6.93), 3.45 and 2.25 (2d, 6H, P(OMe)$_2$, $^{3}J_{H-P}$ = 10.23), 2.84 and 2.42 (2s, 6H, NMe$_2$), 1.11 (d, 3H, CH(**Me**)N); minor isomer, δ 7.71 (d, 1H, Ar, $^{3}J_{H-H}$ = 7.14), 4.93 (s, 5H, C$_5$H$_5$), 4.06 (q, 1H, C**H**(Me)N, $^{3}J_{H-H}$ = 6.75), 1.79 (s, 3H, NMe), 1.20 (d, 3H, CH(**Me**)N). ^{31}P{^{1}H} NMR (CDCl$_3$): major isomer, δ 65.64 (s, PO(OMe)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): major isomer, δ 153.20, 152.80 (d, $^{2}J_{C-P}$ = 53.16), 143.52, 125.26, 123.02, 122.55 (C$_6$H$_4$), 88.87 (C$_5$H$_5$), 67.87 (**C**H(Me)N), 53.02, 51.18 (NMe$_2$), 51.52 and 50.09 (2 d, 6H, P(OMe)$_2$, $^{2}J_{C-P}$ = 7.88 and $^{2}J_{C-P}$ = 9.84), 9.41 (CH(**Me**)N); minor isomer, δ 143.16, 125.89 (C$_6$H$_4$), 87.67 (C$_5$H$_5$), 74.71 (**C**H(Me)N), 55.12, 45.83 (NMe$_2$), 9.85 (CH(**Me**)N).

X-ray Experiments. Collection of the X-ray Data and Structure Determination for 12a and 13b. For both structures, data were collected on a Nonius KappaCCD diffractometer using Mo Kα graphite-monochromated radiation (λ = 0.7107 Å). The structures were solved using direct methods and refined against |*F*|. Hydrogen atoms were introduced as fixed contributors at their calculated positions (d_{C-H} = 0.95 Å, B_H = 1.3B_{equiv} for the carbon to which it was attached). For both structures, all non-hydrogen atoms were refined anisotropically. Absorption corrections are integrated in the scaling procedure. For all computations the Nonius

OpenMoleN package[39] was used. The absolute structures were determined by refining Flack's *x* parameters. Table 4 contains X-ray data collection partameters and final results.

Crystal data for 12a: dark green crystals, data collected at −100 °C (crystal dimensions 0.20 × 0.20 × 0.20 mm^3); $C_{15}H_{19}NCoI$, $M_r = 399.16$, orthorhombic, space group $P2_12_12_1$, $a = 7.0212(1)$ Å, $b = 14.2383(3)$ Å, $c = 14.7569(3)$ Å, $V = 1475.25(8)$ Å^3, $Z = 4$, $D_c = 1.80$ g cm^{-3}, μ(Mo Kα) = 3.215 mm^{-1}; total of 12 992 reflections, $2.5° < \theta < 29.58°$; 3203 unique parameters. Final results: $R(F) = 0.046$, $R_w(F) = 0.064$, GOF = 1.370, maximum residual electronic density 0.962 e Å^{-3}.

Crystal Data for 13b: red crystals, data collected at −100 °C (crystal dimensions 0.20 × 0.14 × 0.11 mm^3); $C_{26}H_{36}NOF_6P_2Co$, $M_r = 613.45$, orthorhombic, space group $P2_12_12_1$, $a = 8.2523(1)$ Å, $b = 12.4052(3)$ Å, $c = 27.5552(6)$ Å, $V = 2820.9(2)$ Å^3, $Z = 4$, $D_c = 1.44$ g cm^{-3}, μ(Mo Kα) = 0.776 mm^{-1}; total of 15 575 reflections was collected, $2.5° < \theta < 26.29°$; 3916 unique reflections having $I > 3\sigma(I)$; 334 parameters. Final results: $R(F) = 0.037$, $R_w(F) = 0.055$, GOF = 1.187, maximum residual electronic density 0.674 e Å^{-3}.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **12a** and **13b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[39] OpenMoleN, Interactive Structure Solution; Nonius BV, Delft, The Netherlands, 1997.