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Transmetalation of Aryl Units from Gold(I) to Cobalt(III): A Clean Route to the Synthesis of Anion Cobaltoreceptors

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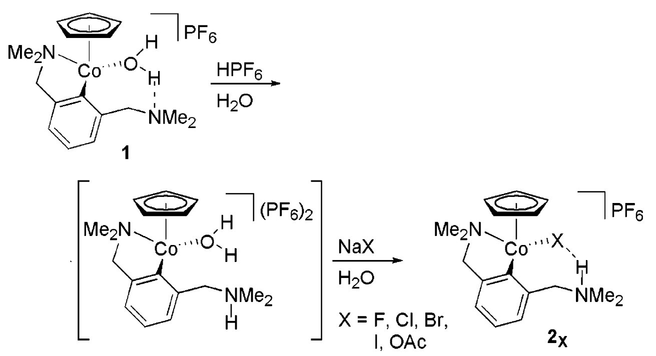
New organocobalt complexes were synthesized through the transmetalation reaction of lithium derivatives of several N,C,N pincer ligands, $\mathrm{Li(2,6\text{-}(NR^2R^1CH_2)_2C_6H_2R')}$, with $[(\eta^5\text{-}\mathrm{Cp})\mathrm{CoI_2}]_2$. Changing one or both methyl groups on the nitrogen atoms for ethyl, *tert*-butyl, or a $\mathrm{(CH_2)_4}$ group led to rather unstable aquo or HX derivatives of the form $[(\eta^5\text{-}\mathrm{Cp})\mathrm{Co\{2,6\text{-}(NR^1R^2CH_2)_2C_6H_3\}HY]PF_6}$ (where $\mathrm{R^1}$, $\mathrm{R^2}$ = Me, Et, *t*-Bu, $\mathrm{(CH_2)_4}$ and Y = OH, Cl, I), which were characterized by ^{1}H NMR spectroscopy and a crystal structure analysis for the compound in which $\mathrm{R^1 = R^2}$ = Et. Related organocobalt derivatives could, however, be prepared more readily by using a transauration reaction. Thus, the transmetalation reaction between $\mathrm{Ph_3PAu(2,6\text{-}(Me_2NCH_2)_2C_6H_3)}$ and $[(\eta^5\text{-}\mathrm{Cp})\mathrm{CoI_2}]_2$ afforded the known $[(\eta^5\text{-}\mathrm{Cp})\mathrm{Co\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}H_2O]PF_6}$ in good yield. Two organocobalt complexes containing pincer ligands substituted at the para position by either an electron-withdrawing group, −COMe (**5a**), or an electron-donating group, −OMe (**5b**), were thus prepared by the transauration with gold(I) derivatives: $\mathrm{Ph_3PAu(2,6\text{-}(Me_2NCH_2)_2(4\text{-}COMeC_6H_2)}$ and $\mathrm{Ph_3PAu(2,6\text{-}(Me_2NCH_2)_2\text{-}(4\text{-}MeOC_6H_2)}$ and $[(\eta^5\text{-}\mathrm{Cp})\mathrm{CoI_2}]_2$. The thermodynamic study of these latter compounds indicated that they display high selectivity for acetate versus chloride anion in water. We found for **5b** that the acetate versus chloride selectivity reaches a factor of 40. Such results are without precedent in the literature, if one does not take into account the selectivities found for oxyanions in nonprotic solvents such as acetonitrile, dimethyl sulfoxide, and chloroform.

Introduction

We have recently described the synthesis of the novel organocobalt compound **1**,[1] which resulted from the coupling between a cyclopentadienyl−cobalt(III) complex and the monoanionic terdentate pincer ligand (NCN).[2,3] A structural analysis performed by X-ray diffraction studies showed, however, that in compound **1** the NCN ligand was coordinated to the cobalt center in a bidentate fashion via the aryl carbon and one nitrogen atom, the second N atom interacting with a metal−aquo unit through a hydrogen bond. We have also observed that Brønsted acids could be coordinated to the NCN−metal fragment with no hydrolysis of the Co−C bond being observed. The pK_a determinations[4] of the aquo derivative **1** demonstrated that the proton was acting as an allosteric effector and that the complexes $\mathbf{2_X}$, derived from the reaction of **1** with Brønsted acids (HX), are better described as anion supercomplexes (Scheme 1).[5,6]

Scheme 1



In these latter compounds, the anions are coordinated both to the cobalt center and to an ammonium unit contained in the same receiving molecule. Modification of the cobaltoreceptor was attempted to determine if modulation of the binding properties was feasible by changing, for instance, the nature of the nitrogen substituents or the electronic properties of the organocobalt center. This was envisioned as a route to possibly tuning the selectivity of the anion receptor, which is a property of paramount interest in molecular receptors.[7−13] In addition, anchoring facilities introduced at the para

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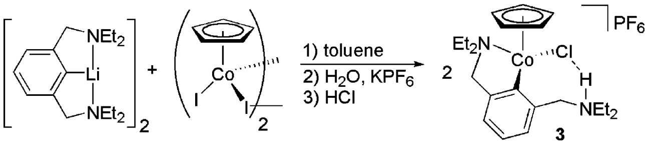
10.1021/om0490482 CCC: $30.25

Scheme 2



position of the aryl ring of the pincer would allow the possibility of integrating the organocobalt receptor into larger structures such as polymers[14,15] and dendrimers.[16–18]

Results and Discussion

Synthesis. The attempted syntheses of pincer complexes of cobalt(III) related to **1** or $\mathbf{2_X}$, in which the substituents have been changed from methyl to ethyl, *tert*-butyl, or $(CH_2)_4$, have led to rather disappointing results, as the complexes obtained were unstable and difficult to purify. In this respect, the only remotely acceptable results were obtained in the synthesis of the tetraethyl derivative **3**.

The transmetalation with 2-lithio-1,3-bis[(diethylamino)methyl]benzene[19] and $[CpCoI_2]_2$ was followed by treatment of the resulting compound with HCl to afford **3** as a green solid (Scheme 2). Its ^1H NMR spectrum was in line with that of the corresponding *N*-methyl complexes. It is worth mentioning, however, that the methylene protons of the diethylamino unit coordinated to the cobalt center did not appear as the expected AB spin system but as a singlet. On the other hand, the protons of the methylene group linking the aryl ring and the protonated diethylamino group were indeed diastereotopic and coupled with the proton on the nitrogen atom. Despite the fact that the compound was difficult to purify (we could not get an acceptable analysis), we succeeded in obtaining a few crystals, one of which among them was amenable to an X-ray diffraction study. An ORTEP diagram of the structure is depicted in Figure 1.

When the geometry around the cobalt center in the related complex $\mathbf{2_{Cl}}$ [1] is compared with that of **3** (Table 3), the main differences arose from the position of the chloride ion, which was located at longer distances from both the cobalt atom and the nitrogen N1 in **3** than was the case in $\mathbf{2_{Cl}}$. The angle C16–Co–Cl is indeed larger in **3** than in $\mathbf{2_{Cl}}$, reflecting the increased steric effects of the ethyl groups as compared to those of the methyl.

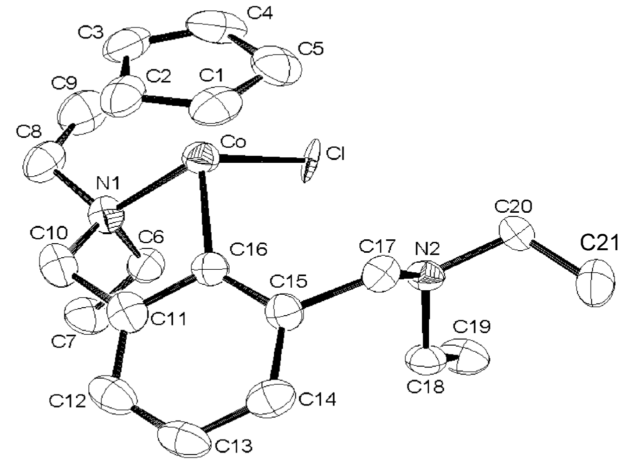


Figure 1. ORTEP representation of **3**.

In addition to the difficulty in synthesizing the aforementioned compounds via Li–halogen exchange, we also found that the transmetalation of lithiated derivatives of para-substituted pincer ligands such as 4-R-2-bromo-1,3-bis[(dimethylamino)methyl] benzene (R = Me, Cl, NMe_2, COMe, O-$SiMe_2$tBu) with $(CpCoI_2)_2$ did not lead to clean syntheses of compounds related to **1**. In most of these cases not only was the yield of the product rather low but also the compounds were difficult to purify, as some paramagnetic byproducts were formed that could not be easily removed. We were thus looking for an alternate method that would avoid these inconveniences. Organogold(I) complexes were shown to be good starting materials for transmetalation reactions toward mercury, gold, and rhenium complexes.[20a–c] Moreover, it was shown recently that the gold(I) complex of the pincer ligand **4** was an interesting starting material to transmetalate the latter ligand on Ni(II), Pd(II), Pt(II), Ti(IV), or Fe(III).[20d] In addition, this reagent obviated the reduction of the Ti(IV) and Fe(III) complexes observed with the corresponding lithium synthon. As such, this method could afford the desired Co(III) compounds without the previously observed difficulties. To test reaction conditions, we repeated the reaction between **4** and $(CpCoI_2)_2$, which gave **1** in a yield (60%) after workup similar to that of the original synthesis (Scheme 3).

This method proved to be synthetically simpler than the corresponding method using lithiated pincer derivatives, as the gold complex is air stable and can be manipulated without need for inert conditions. Moreover, no redox side reactions were observed between the cobalt complex and the gold(I). Also, the gold(I) byproduct $IAuPPh_3$ could be recovered almost quantitatively and was subsequently reused.

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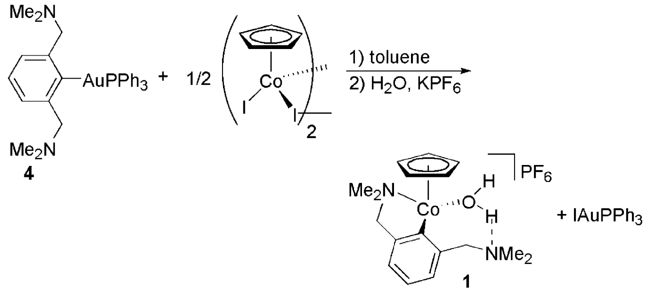
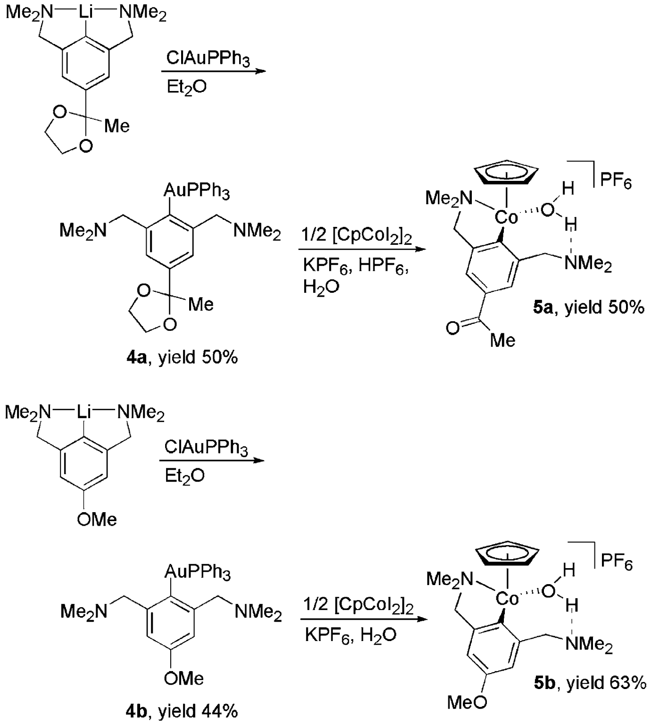
Scheme 3



Scheme 4



Scheme 5

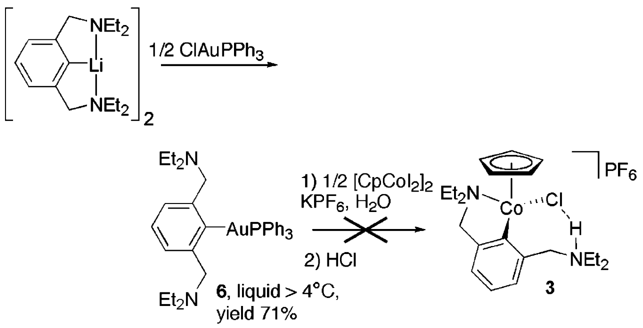


Table 1. Association and Selectivity Data for 5a and 5b Obtained in Water

		log K_{ass} in water			selectivity	
complex	pK_a	Cl^-	AcO^-	$H_2PO_4^-$	$S(AcO^-/Cl^-)$	$S(H_2PO_4^-/Cl^-)$
1	6.1	1.8	3.0	3.1	16	20
5a	5.6	1.8	2.5	2.4	5	4
5b	6.2	1.8	3.4	2.9	40	13

Using this procedure, two new cobaltoreceptors have been prepared having either an electron-withdrawing group (COMe, **5a**) or an electron-releasing group (OMe, **5b**), at the para position, giving the compounds in 50% and 60% yield, respectively (Scheme 4). The synthesis of **5b** was straightforward, but the synthesis of **5a** required protection of the carbonyl function prior to generation of the lithium reagent for the synthesis of **4a**, which was obtained in 50% yield.

Cleavage of the C−Au bond was observed in attempts to deprotect the acetal in **4a**, but fortunately, in situ deprotection after the transmetalation was successful by addition of HPF_6 to the reaction mixture (MeOH/H_2O) until pH 1. Extraction of the cobalt compound **5a** with chloroform afforded a red solution. Concentration and dilution with water followed by addition of KPF_6 led to the precipitation of the expected compound as red-brown crystals in reasonable yield. No further purification was required. It is likely, on the basis of the distinct color of the solutions (see Experimental Section), that the chloroform- and water-soluble compound was the aqua complex having the iodide as a counteranion.

On the basis of the success of the transauration method for the generation of para-substituted complexes, attempts were made to determine if the synthesis of **3** was amenable with this route. We thus synthesized the corresponding Au-pincer complex (**6**) and performed its transmetalation reaction with $[CpCoI_2]_2$.

Complex **6** was obtained in 71% yield (Scheme 5) after purification via a route analogous to that for **4a**, **4b**, and the related dimethyl pincer **4**.[20d] Of note is that **6** is obtained as a highly viscous, clear, colorless oil at room temperature, which solidifies to a white solid upon cooling to 4 °C. Interrogation of the oil under polarized light indicated no liquid crystalline properties. Reaction of **6** with $^1/_2$ equiv of $[CpCoI_2]_2$ in methanol under conditions identical with those used for compounds **5a** and **5b** resulted in the generation of a light yellow solution. Workup and further reaction with HCl gave a product in low yield (5%) that contained, by ^1H NMR spectroscopy, the pincer fragment. There was no indication of CpCo resonances. In line with previous observations during the synthesis of **3** via translithiation, the product is unstable and difficult to isolate. The slightly elevated temperatures needed to effect transauration appear to result in decomposition of the product. Likely due to steric effects, the NEt_2 cannot effectively support the Co center and, thus, the thermodynamic stability of the tetraethyl pincer cobalt species is much lower than that of the tetramethyl compound. To synthesize **3**, lower temperatures are required; therefore, comparatively unreactive reagents, such as **6**, are not compatible.

Thermodynamics. We have studied the thermodynamic properties of the new compounds **5a** and **5b**. The pK_a of the pendant amine and the association constants for selected anions (oxyanions and chloride) have been determined as previously described.[4] A general reaction for both processes is found in Scheme 1. When the pH of the medium was decreased by adding HPF_6 to the reaction medium, the ^1H NMR signals of the complex were shifted to high field. Therefore, variation of the chemical shifts allowed us to measure the pK_a of the ionizable function. We have also measured the association constants of the supercomplexes for the anions Cl^-, AcO^-, and $H_2PO_4^-$ in water solutions buffered at pH 5.5. The results are gathered and compared to those of the original cobaltoreceptor **1** in Table 1.

Figures 2 and 3 show the titration curves for **5a** and **5b**, respectively. The consequence of para substitution of the aryl unit by a COMe or OMe group results in a

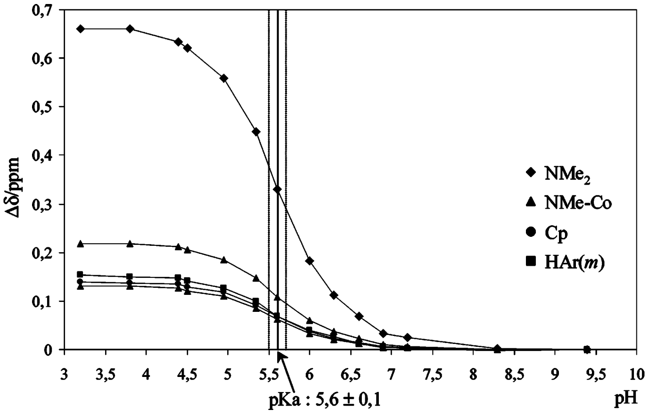


Figure 2. Evolution of Δδ versus pH for compound **5a**.

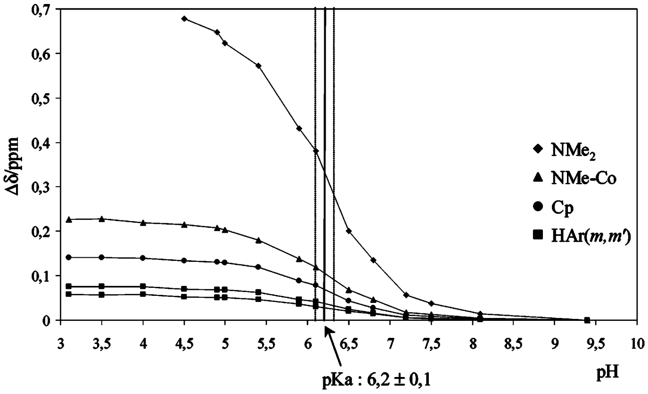


Figure 3. Evolution of Δδ versus pH for compound **5b**.

slight modulation of the pK_a of the amino unit. On comparison of the original receptor **1** (pK_a = 6.1) to the −COMe-substituted **5a** (pK_a = 5.6), the pK_a of the amino fragment decreased by 0.5. The pK_a of **5b** (6.2) is almost identical with that of **1**. This decrease in the basicity of the amino fragment for **5a** reflects a better bonding of the OH$_2$ molecule to the receptor. The stronger association of the water molecule to the receptor might be directly correlated with the electron-withdrawing effect of the para substituent, conferring more electrophilic character to the cobalt center and thus strengthening the HOH- - -N interaction. This results in a more difficult displacement of the water molecule by the incoming substrate. As the association process is measured at pH 5.5, half of the water molecules are still bound to the amino unit. As a consequence the association constants for OAc$^-$ and H$_2$PO$_4$$^-$ are lowered by a factor of 3 to 5.

On the basis of the pK_a values, the behavior of the −OMe-substituted receptor **5b** is expected to be approximately the same as that of the original receptor **1**. In fact, the result is a stronger complexation of acetate anion (2.5 times) and a weaker interaction with dihydrogenophosphate anion (1.5 times). The remarkable consequence is that the acetate versus chloride selectivity reaches a factor of 40. Such results are without precedent in the literature, if one does not take into account the selectivities found for oxyanions in nonprotic solvents such as acetonitrile, dimethyl sulfoxide, and chloroform.[21−24]

Conclusion

Our goal to modify the original structure of an organometallic anion receptor has been only partly fulfilled. The modification of the alkyl substituents on the nitrogens (NMe$_2$ to NEt$_2$) proved to be unfruitful, as steric effects render the resulting tetraethyl molecule less stable. This result leaves modification of the Cp ring, for example, as the remaining potential site for tuning receptor properties. The transauration reaction was demonstrated to be the cleanest method for preparing series of related para-functionalized compounds. Para substitution of the aryl ring of the pincer group offers an excellent route to further functionalize such structures. High selectivity of the *p*-methoxy-substituted receptor toward acetate over chloride (S(AcO$^-$/Cl$^-$) = 40) has been highlighted. Further work is in progress to investigate the use of chiral pincer cobalt receptors to achieve the enantiomeric recognition of oxyanions.[25,26]

Experimental Section

All reactions affording the aryl bromides, the lithium salts, and the cobalt complexes were carried out in freshly distilled solvents, under a dry argon atmosphere using Schlenk techniques. Commercial reagents have been used without further purification. [η^5-CpCoI$_2$]$_2$,[27] AuClPPh$_3$,[28] and 1-Br-2,6(Et$_2$NCH$_2$)$_2$C$_6$H$_4$ [29] were prepared by published methods, All the salts used for K_{ass} measurements were dried in vacuo. Buffer solutions were prepared from 2-(*N*-morpholino)ethanesulfonic acid (MES, 2 equiv of the hemisodium salt and 3 equiv of the acid, [C] = 0.125 M). Elemental analyses were performed by the Service Central d'Analyse de l'Institut de Chimie (Strasbourg, France). ^{1}H NMR spectra were recorded at 300.13 MHz, ^{31}P{^{1}H} NMR spectra at 121.49 MHz, and ^{13}C{^{1}H} NMR spectra at 75.47 MHz on a Bruker FT instrument (AV-300). Chemical shifts (δ) were referenced to the residual solvent peak as internal standard,[30] except for pK_a determinations, for which a small amount of Et$_2$O was added as internal standard. δ and coupling constant values (J) are expressed in ppm and Hz, respectively. pH was measured with a PHN78 pH meter (Tacussel electronique) with an ECS electrode. Absorption spectra were recorded on a Uvikon XL spectrometer. Association constants were determined via the graphical representation of Scatchard. Reproducibility of multiple experiments afforded the same values for a determined anion within a 10% variation. All the selected values have $R^2 > 0.90$, and uncertainty was estimated between 5 and 10%.

[Co{2,6-(Et$_2$NCH$_2$)$_2$C$_6$H$_3$}(η^5-C$_5$H$_5$)(HCl)]PF$_6$ (3). A 1.8 mL portion of a 1.6 M solution of *n*-BuLi in *n*-hexane (2.88 mmol) was added to a solution of 1-bromo-2,6-bis[(diethylamino)methyl]benzene (0.9 g, 2.75 mmol) in 20 mL of Et$_2$O cooled to −78 °C. The solution was then heated to 30 °C and stirred for 2 h. This solution was added dropwise to a stirred suspension of [η^5-CpCoI$_2$]$_2$ (0.98 g, 1.3 mmol) in toluene (100 mL) at −25 °C. The reaction mixture was heated to 20 °C and

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stirred for 16 h, during which time it turned green. The solvent was then removed in vacuo, and the product was extracted by dissolving it in CH_2Cl_2 (3 × 50 mL). Filtration of this solution over Celite and addition of *n*-hexane to it afforded a powder that was dried in vacuo. The powder was then dissolved in MeOH (10 mL), and a solution of HCl in water (36%; 0.1 mL, 1.2 mmol) was added to it, affording a purple solution. A large excess of NaCl and KPF_6 (10 equiv each) were added and the mixture was filtered after 30 min of stirring. The residue was washed with MeOH (2 × 15 mL). The product was redissolved in acetone (3 × 30 mL), and the solvent was removed in vacuo to afford **3** as a purple solid. Crystals were obtained from a solution in acetone layered with *n*-hexane.

^{1}H NMR (AcD$_6$): δ 9.36 (br s, 1H, NH^+), 7.45 (dd, ^3J = 5.1, ^3J = 3.9, 1H, Ar), 7.18 (d, ^3J = 5.1, 1H, Ar), 7.17 (d, ^3J = 3.9, 1H, Ar), 5.39 (s, 5H, Cp), 4.97 and 4.67 (AB system, ^2J = 12.9, 2H, CH$_2$N−Co), 4.2 (s, 2H, CH$_2$NH$^+$), 3.74 (qd, 1H, ^2J = 13.6, ^3J = 7.1, Co−NCH_2CH$_3$), 3.54 (qd, 2H, ^2J = 7.3, ^3J = 4.9, NH$^+$CH_2CH$_3$), 3.00 (qd, 1H, ^2J = 13.6, ^3J = 7.1, Co−NCH_2CH$_3$), 2.98−2.88 (m, 2H, Co−NCH_2CH$_3$), 2.27 (qd, 1H, ^2J = 14.6, ^3J = 7.3, NH$^+$CH_2CH$_3$), 1.86 (t, 3H, ^3J = 7.1, Co−NCH$_2$CH_3), 1.50 (t, 3H, ^3J = 7.3, NH$^+$CH$_2$CH_3), 1.10 (t, 3H, ^3J = 7.3, Co−NCH$_2$CH_3), 0.84 (qd, 1H, ^2J = 14.6, ^3J = 7.3, NH$^+$CH_2CH$_3$), 0.68 (t, 3H, ^3J = 7.1, NH$^+$CH$_2$CH_3).

Au{2,6-(Me$_2$NCH$_2$)$_2$-4-MeC(OCH$_2$CH$_2$O)-C$_6$H$_2$}(PPh$_3$) (4a). A 4.35 mL portion of a 2.3 M solution of *n*-BuLi in *n*-hexane (10 mmol) was added to a solution of 2-[4-bromo-3,5-bis[(dimethylamino)methyl]phenyl-2-methyl-1,3-dioxolane (3.51 g, 9.82 mmol) in 20 mL of hexane that was cooled to −80 °C. The solution was then heated to 25 °C and stirred for 16 h. This solution was then added dropwise to a slurry of AuClPPh$_3$ (4.95 g, 9.82 mmol) in Et$_2$O (70 mL) at −30 °C. The reaction mixture was heated (35 °C) for 6 h and the solution became brownish. A 50 mL portion of water was then added, and the mixture was stirred for 30 min. After filtration over Celite, the aqueous phase was extracted with 2 × 50 mL of Et$_2$O. The organic phases were recovered, dried over MgSO$_4$, and filtered on a G4 glass frit. The crude product was obtained as a white powder through removal of the solvent in vacuo. **4a** was obtained as white crystals via crystallization from CH$_2$Cl$_2$/hexane. Yield: 3.60 g (50%).

^{1}H NMR (CDCl$_3$): δ 7.67−7.61 (m, 6H, H$_m$ PPh$_3$), 7.50−7.42 (m, 9H, H$_{o,p}$ PPh$_3$), 7.37 (s, 2H, Ar), 4.00−3.92 (m, 2H, OCH$_2$), 3.79 (s, 4H, NCH$_2$), 3.79−3.71 (m, 2H, OCH$_2$), 2.24 (s, 12H, NMe$_2$), 1.66 (s, 3H, CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 175.5 (COO), 147.1 (C, Ar), 139.7 (C, Ar), 134.2 (d, $^2J_{C-P}$ = 14.3, C$_o$, PPh$_3$), 131.7 (C, Ar), 131.0 (C$_p$, PPh$_3$), 128.9 (d, $^3J_{C-P}$ = 11.2, C$_m$, PPh$_3$), 124.1 (CH, Ar), 109.3 (C, Ar), 70.0 (CH$_2$N), 64.2 (2C, OCH$_2$), 45.8 (NCH$_3$), 27.6 (CCH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 45.56 (s, PPh$_3$). Anal. Calcd for C$_{34}$H$_{40}$AuN$_2$O$_2$P (736.25): C, 55.44; H, 5.47; N, 3.80. Found: C, 55.67; H, 5.51; N, 3.70.

[Co{2,6-(Me$_2$NCH$_2$)$_2$-4-MeCO-C$_6$H$_2$}(η^5-C$_5$H$_5$)(H$_2$O)]PF$_6$ (5a). Compound **4a** (1.10 g, 1.50 mmol) and (CpCoI$_2$)$_2$ (0.57 g, 0.75 mmol) were mixed in 15 mL of methanol. The black-green solution was heated to 35 °C for 6 h and became heterogeneous (purple solution and brown precipitate). The crude product was filtered over Celite (recovering of gold) and extracted with 2 × 30 mL of methanol. The dark red solution was concentrated to ca. 25 mL. A 50 mL portion of water was added, and HPF$_6$ (60% in H$_2$O) was added dropwise until the pH of the solution was equal to 1. The green solution was stirred for 10 min; thereafter the product was extracted with 3 × 40 mL of CHCl$_3$. The red organic phase was concentrated to ca. 10 mL, and 150 mL of water was added (pH 7). CHCl$_3$ was removed, and the product was totally soluble in water. Filtration over Celite removed all residual solids (further recovery of gold). KPF$_6$ (10 equiv) was added to the aqueous solution, and after 15 min of stirring, a precipitate could be isolated by filtration over a G4 glass frit. It was washed with 2 × 50 mL of water, 2 × 50 mL of hexane, and 2 × 50 mL of Et$_2$O. **5a** was isolated as a brown solid. Yield: 0.39 g (50%).

^{1}H NMR (AcD$_6$): δ 7.84 (s, 1H, Ar), 7.66 (s, 1H, Ar), 5.53 (s, 5H, C$_5$H$_5$), 4.71 and 3.81 (AB system, ^2J = 12.4, 2H, CH$_2$N), 4.49 and 3.80 (AB system, ^2J = 14.0, 2H, CH$_2$N−Co), 3.50 and 1.33 (2s, 6H, Co−NMe$_2$), 2.59 (s, 3H, COCH$_3$), 2.25 (s, 6H, NMe$_2$). ^{13}C{^{1}H} NMR (AcD$_6$): δ 197.9 (CO), 172.0 (C−Co), 153.1 (Ar), 149.2 (Ar), 136.0 (C−CO), 129.1 (CH, Ar), 121.5 (CH, Ar), 86.3 (5C, Cp), 77.0 (CH$_2$N−Co), 68.0 (CH$_2$NMe$_2$), 58.9 (NCH$_3$−Co), 49.7 (NCH$_3$−Co), 43.2 (Ls, NCH$_3$), 26.6 (CH$_3$). ^{31}P{^{1}H} NMR (AcD$_6$): δ −143.0 (sept, $^1J_{P-F}$ = 707.6, PF$_6$). Anal. Calcd for C$_{19}$H$_{28}$CoF$_6$N$_2$O$_2$P (520.34): C, 43.86; H, 5.42; N, 5.38. Found: C, 43.19; H, 5.21; N, 5.37. The lower value found for C is due to the presence of ca. 7% of CH$_2$Cl$_2$ (checked by ^{1}H NMR), which could not be removed even after treatment of **5a** for several hours in vacuo. MS (FAB+): 375.2 (24%) (**5a** − PF$_6$, calcd 375.15), 357.1 (100%) (**5a** − PF$_6$ − H$_2$O, calcd 357.1).

Au{2,6-(Me$_2$NCH$_2$)$_2$-4-MeO-C$_6$H$_2$}(PPh$_3$) (4b). A 5.6 mL portion of a 2.3 M solution of *n*-BuLi in *n*-hexane (12.9 mmol) was added to a solution of 4-bromo-3,5-bis[(dimethylamino)-methyl]anisole (3.9 g, 12.9 mmol) in 25 mL of hexane that was cooled to −80 °C. The solution was then heated to 25 °C and stirred for 16 h. This solution was then added dropwise to a slurry of AuClPPh$_3$ (4.95 g, 9.82 mmol) in Et$_2$O (70 mL) at −30 °C. The medium was heated (35 °C) for 6 h, and the solution became brownish. A 60 mL portion of water was then added, and the mixture was stirred for 30 min. After filtration over Celite, the aqueous phase was extracted with Et$_2$O (2 × 50 mL). The organic phases were recovered, dried over MgSO$_4$, and filtered on a G4 glass frit. The crude product was obtained as a white powder through removal of the solvent in vacuo. **4b** was obtained as white crystals via crystallization from CH$_2$Cl$_2$/hexane. Yield: 3.84 g (44%).

^{1}H NMR (CDCl$_3$): δ 7.70−7.61 (m, 6H, H$_m$ PPh$_3$), 7.50−7.44 (m, 9H, H$_{o,p}$ PPh$_3$), 6.91 (s, 2H, Ar), 3.81 (s, 3H, CH$_3$), 3.80 (s, 4H, CH$_2$), 2.26 (s, 12H, NMe$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 158.2 (CO), 148.6 (Ar), 140.0 (C−Au), 134.4 (s, C$_o$, PPh$_3$), 131.2 (C$_p$, PPh$_3$), 129.1 (s, C$_m$, PPh$_3$), 113.2 (CH, Ar), 70.2 (CH$_2$N), 55.3 (OCH$_3$), 46.0 (NCH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 45.85 (s, PPh$_3$). Anal. Calcd for C$_{31}$H$_{36}$AuN$_2$OP (680.22): C, 54.71; H, 5.33; N, 4.12. Found: C, 54.70; H, 5.31; N, 4.14.

[Co{2,6-(Me$_2$NCH$_2$)$_2$-4-MeO-C$_6$H$_2$}(η^5-C$_5$H$_5$)(H$_2$O)]PF$_6$ (5b). Compound **4b** (2.8 g, 4.1 mmol) and (CpCoI$_2$)$_2$ (1.56 g, 2.05 mmol) were mixed in 25 mL of methanol. The black-green solution was heated at 35 °C for 6 h and became green-brown. The crude product was filtered over Celite (recovering of gold) and extracted with 2 × 30 mL of methanol. The red-brown solution was concentrated to ca. 15 mL, and then 20 mL of water was added and the solution was filtered over Celite (further recovery of gold). The solution was concentrated again on a rotary evaporator ($T \approx 40$ °C), and the methanol removed. An additional 50 mL of water and 10 equiv of KPF$_6$ were added with stirring. After 15 min, a precipitate could be isolated by filtration over a G4 glass frit. It was washed with 2 × 50 mL of water, 2 × 50 mL of hexane and 2 × 50 mL of Et$_2$O. **5b** was isolated as a violet solid. Yield: 1.30 g (63%).

^{1}H NMR (AcD$_6$): δ 6.96 (d, ^4J = 2.3, 1H, Ar), 6.80 (d, ^4J = 2.3, 1H, Ar), 5.44 (s, 5H, C$_5$H$_5$), 4.58 and 3.59 (AB system, ^2J = 12.2, 2H, CH$_2$N), 4.32 and 3.60 (AB system, ^2J = 13.8, 2H, CH$_2$N−Co), 3.81 (s, 3H, OCH$_3$), 3.46 and 1.32 (2s, 6H, Co−NMe$_2$), 2.19 (s, 6H, NMe$_2$). ^{13}C{^{1}H} NMR (AcD$_6$): δ 159.6 (Ar), 152.4 (Ar), 148.8 (Ar), 143.0 (C−Co), 117.2 (CH, Ar), 109.6 (CH, Ar), 85.6 (Cp), 77.1 (CH$_2$N−Co), 68.0 (CH$_2$N), 58.8 (NCH$_3$−Co), 55.6 (OCH$_3$), 49.7 (NCH$_3$−Co), 43.3 (Ls, NCH$_3$). ^{31}P{^{1}H} NMR (AcD$_6$): δ −143.0 (sept, $^1J_{P-F}$ = 707.6, PF$_6$). Anal. Calcd for C$_{18}$H$_{28}$CoF$_6$N$_2$O$_2$P (508.32): C, 42.53; H, 5.55; N, 5.51. Found: C, 41.74; H, 5.55; N, 5.55. The lower value found for C is due to the presence of ca. 8% of CH$_2$Cl$_2$ (checked by ^{1}H NMR), which could not be removed even after treatment of **5a** for several hours in vacuo. MS (FAB+): 363.1 (35%) (**5b** − PF$_6$, calcd 363.15), 345.1 (100%) (**5b** − PF$_6$ − H$_2$O, calcd 345.14).

Table 2. X-ray Diffraction Data for 3

formula	$C_{21}H_{33}CoN_2Cl{\cdot}PF_6$
mol wt	552.86
cryst syst	orthorhombic
space group	*Pbca*
a (Å)	14.2005(3)
b (Å)	20.7594(5)
c (Å)	16.4489(6)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	4849.0(4)
Z	8
color	violet
cryst dimens (mm)	0.20 × 0.20 × 0.05
ρ_{calcd} (g cm^{-3})	1.51
F_{000}	2288
μ (mm^{-1})	0.942
T (K)	173
λ (Å)	0.710 73
radiation	Mo Kα
diffractometer	KappaCCD
scan mode	*ϕ* scans
h, k, l limits	0−18, 0− 21, 0−26
θ limits (deg)	2.5−27.49
no. of data measd	6153
no. of data with $I > 3\sigma(I)$	3008
no. of variables	298
R	0.082
R_w	0.099
GOF	1.071
largest peak in final diff map (e Å^{-3})	2.517

Table 3. Comparison of the Structural Data of Supercomplexes 3 and 2_{Cl}

bond length (Å)			bond angle (deg)		
	3	**2_{Cl}**		**3**	**2_{Cl}**
Co−Cp$^{\#a}$	1.718(2)	1.71(1)	Cl−Co−N_1	97.7(2)	96.8(1)
Co−C(Cp)$_m^{b}$	2.10(5)	2.089(4)	Cl−Co−C_{16}	103.3(2)	95.9(1)
Co−Cl	2.429(2)	2.283(2)	Cl−Co−Cp$^{\#a}$	116.8(4)	120.9(2)
Co−N_1	2.094(8)	2.074(3)	N_1−Co−C_{16}	81.8(3)	82.8(3)
Co−C_{16}	1.968(9)	1.964(3)	N_1−Co−Cp$^{\#a}$	128.5(5)	125.5(8)
N_1−C_{10}	1.49(1)	1.487(5)	C_{16}−Co−Cp$^{\#a}$	121.4(4)	128.7(6)
C_{10}−C_{11}	1.50(1)	1.490(5)	Co−N_1−C_{16}	100.7(6)	
C_{11}−C_{16}	1.41(1)	1.406(5)	N_1−C_{10}−C_{11}	107.6(8)	107.5(3)
N_2−Cl	3.201(5)	3.02(8)	C_{10}−C_{11}−C_{16}	114.7(8)	116.4(3)
			C_{11}−C_{16}−Co	111.0(2)	
			C_6−N_1−Co−Cl	27.0(8)	14.6(6)
			C_{16}−C_{15}−C_{17}−N_2	−75.5(4)	

[a] Cp# = cyclopentadienyl centroïd. [b] $(Cp)_m$ = mean value.

Au{2,6-($Et_2NCH_2)_2$-C_6H_4}(PPh_3) (6). Solid 2-lithio-1,3-bis-[(diethylamino)methyl] benzene (0.259 g, 1.02 mmol) was dissolved in dry Et_2O (15 mL) and cannula-transferred onto a slurry of $ClAuPPh_3$ (0.504 g, 1.02 mmol) in dry Et_2O at 0 °C. The flask was rinsed with dry Et_2O (1 × 10 mL), and the reaction mixture was stirred for 16 h. The reaction was quenched with water (90 mL), and the layers were separated. The aqueous layer was washed with Et_2O (3 × 50 mL), and the combined organics were dried over $MgSO_4$, filtered, and dried in vacuo to obtain a sticky, clear, colorless oil. The oil was dissolved in hot pentane and placed in the freezer (−30 °C). The cold solution was quickly decanted from the white solid, which liquefies at room temperature (melting point ~10 °C), and the oil was dried in vacuo. Yield: 0.510 g, 71%.

^{1}H NMR (C_6D_6): δ 7.74 (d, 2H, ^3J = 7.8, Ar), 7.57 (m, 6H, H_m PPh_3), 7.35 (t, 1H, ^3J = 7.7, Ar), 6.92 (br m, 9H, $H_{o,p}$ PPh_3), 4.18 (s, 4H, ArCH_2N), 2.61 (q, 8H, ^3J = 7.2, NCH_2CH$_3$), 0.92 (t, 12H, ^3J = 7.1, NCH$_2$CH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 148.8 (*Ar*CH$_2$N), 134.7 (d, $^2J_{C-P}$ = 14, C_o PPh_3), 132.4 (d, $^1J_{C-P}$ = 45, C_{ipso} PPh_3, 131.0 (d, $^5J_{C-P}$ = 0.2, C_p PPh_3), 129.1 (d, $^4J_{C-P}$ = 10, C_m PPh_3), 127.5 (AuC), 127.4 (C_pH, Ar), 126.0 (C_mH, Ar), 64.6 (Ar*C*H$_2$N), 47.1 (N*C*H$_2$CH$_3$), 12.1 (NCH$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ 45.1. Anal. Calcd for $C_{34}H_{42}AuN_2P$ (706.65): C, 57.79; H, 5.99; N, 3.96. Found: C, 57.92; H, 5.96; N, 3.99.

X-ray Crystallographic Study. Single crystals suitable for X-ray diffraction analysis were obtained as described above. These crystals were poorly formed, which explains the low quality of the crystal structure determination. Data were collected on a Nonius KappaCCD diffractometer, using Mo Kα graphite-monochromated radiation (λ = 0.7107 Å) and φ and ω scans. Absorption corrections were partially included in the data reduction procedure. The structures were solved using direct methods and refined against |*F*|. Hydrogen atoms were introduced in structure factor calculations as fixed contributors by their computed coordinates (d(C−H) = 0.95 Å, B(H) = 1.3B_{eqv} (Å^2) of the attached carbon atom). For all computations, the Nonius OpenMoLeN package[31] was used. Further experimental details are given in Table 2.

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Supporting Information Available: CIF files giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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