Notes

Novel Phosphine- and Phosphite-Induced Imido Migration to a Cyclopentadienyl Ring in an Imido-Bridged Cobaltadithiolene Complex

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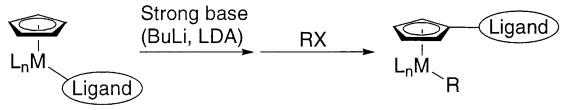
Summary: The mechanism of phosphine- and phosphite-induced migration of the imido group from sulfur to a Cp ring in a tosylimido-bridged cobaltadithiolene complex was investigated, and a probable intermediate was isolated and characterized. The presence of a large excess of PPh_3 causes the formation of the imido- and phosphine-substituted Cp complex.

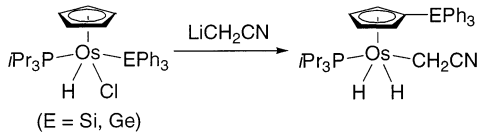
Introduction

The migrations of monodentate ligands from the central transition metal to the Cp ring of η^5-cyclopentadienyl (Cp) complexes are well-known (Scheme 1). This unique reaction is induced by a strong base. The migrating ligands include acyl,[1] alkoxycarbonyl,[1d] formyl,[1e,g] acetylide,[2] silyl,[3] germyl,[3k,4] stannyl,[4b] plumbyl,[4b] hydride,[5] and phosphorus ligands.[6] In addition,

Scheme 1



Scheme 2



polysilane migration to the Cp ring with alkyl rearrangement[3f] has been reported. The proposed mechanism of these base-induced migrations involves the deprotonation of the Cp ring by a strong base followed by the migration of the ligand from the metal center to the Cp ring. In addition, base-induced migration of silyl ligands from iron to the η^5-indenyl ligand has been also reported.[7] Quite recently, Esteruelas et al. reported other migration reactions to the Cp ring (Scheme 2).[8] The reactions of $[CpOs(H)(Cl)(EPh_3)(P\mathit{i}Pr_3)]$ (E = Si, Ge) with $LiCH_2CN$ lead to EPh_3 migration to the Cp ring by EPh_3(Os)/H(Cp) exchange. Furthermore, in this cyclopentadienyl osmium(IV) chemistry, various ligand migration reactions to the Cp ring have been observed by ligand(Os)/H(Cp) exchange reaction (ligand = Me, *n*-Bu, *s*-Bu, NEt_2, $N(allyl)_2$, PPh_2). An interesting migration reaction of the cyclopentadienyl rhodium carbene complex $[CpRh(=CPh_2)(P\mathit{i}Pr_3)]$ with PF_3 has been reported (Scheme 3). The carbene ligand underwent a migratory insertion from the metal center into the C−H bond of the Cp ring.[9a] A similar migratory insertion has

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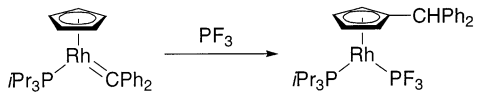
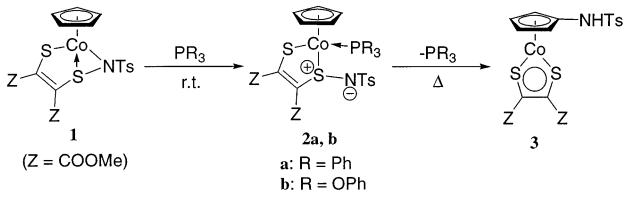
Scheme 3



Scheme 4



also been described in the reaction of the η^5-indenyl rhodium carbene complex $[(C_9H_7)Rh(=CPh_2)(PiPr_3)]$ with CO.[9b]

We have also reported the migration of an imido group in the tosylimido-bridged cobaltadithiolene complex $[CpCo\{S_2C_2(COOMe)_2\}(NTs)]$ (**1**). Complex **1** reacted with 2 equiv of PPh_3 to give the amide-substituted Cp complex $[(C_5H_4NHTs)Co\{S_2C_2(COOMe)_2\}]$ (**3**), in which the tosylimido group was inserted into the C−H of the Cp ring.[10] This has been reported as the first example of nitrogen migration to the Cp ring in organometallic complexes. An amide is a useful group, because this group can be easily converted to other nitrogen groups. Therefore, amide-substituted Cp complexes are very important precursors of novel nitrogen-substituted Cp complexes. Here we report on the migration intermediate and plausible mechanism of the reaction. Furthermore, we also describe an unexpected formation of a disubstituted Cp complex in complex **1** when treated with a large excess of PPh_3.

Results and Discussion

Complex **1** was prepared from $[CpCo\{S_2C_2(COOMe)_2\}]$ using a procedure developed in our laboratory. The reaction of complex **1** with 2 equiv of PPh_3 in refluxing benzene yielded complex **3**. However, when the same reaction is done at room temperature, it gives complex **2a**.[10] A similar migration reaction occurred in the reaction of complex **1** with 5 equiv of $P(OPh)_3$, forming complex **2b** at room temperature and complex **3** under heating (refluxing benzene), respectively. When complexes **2a** and **2b** were reacted under heating (refluxing benzene), complex **3** was formed. Therefore, complexes **2a** and **2b** seem to be the intermediate of the imido migration reaction (Scheme 4). It is supported that the first attack is to the cobalt atom of phosphine or phosphite as a nucleophile, and then the Co−N bond is cleaved. Although spectroscopic and elemental analysis data of complex **2a** have already been reported,[10] the X-ray structure of complex **2a** was not clear because crystallization of complex **2a** was difficult. However, crystallization of analogous complex **2b** was successful in the presence of excess $P(OPh)_3$. The ORTEP drawing of complex **2b** shows a sulfilimine structure (S^+-N^-). The bond length of 1.65 Å between S1 and N1 is in close agreement with a literature value of 1.636 Å for the S^+-N^- bond length of $Me_2S^+-N^-Ts$.[11] This is further

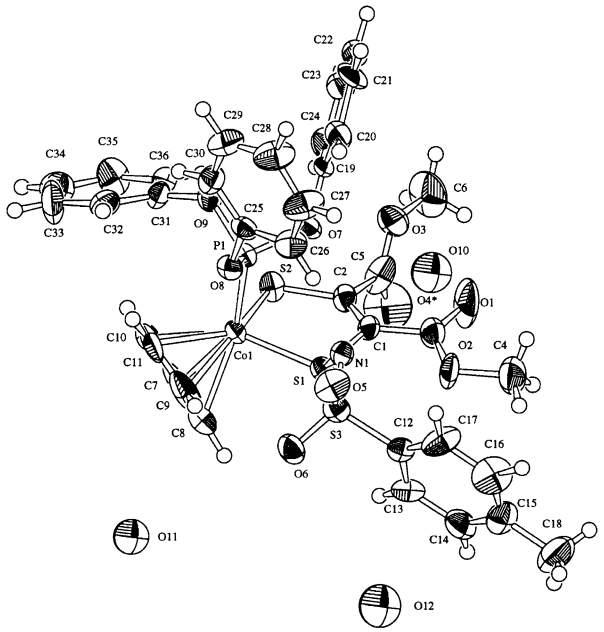


Figure 1. ORTEP drawing of **2b**·$3H_2O$. Selected bond lengths (Å): Co1−S1 2.230(4), Co1−S2 2.206(4), S1−C1 1.77(1), S2−C2 1.71(1), C1−C2 1.37(2), Co1−P1 2.144(4), S1−N1 1.65(1). Selected bond angles (deg): S1−Co1−S2 90.8(2), Co1−S1−C1 102.6(5), Co1−S2−C2 102.9(5), S1−C1−C2 117(1), S2−C2−C1 123(1), S1−Co1−P1 95.4(1), Co1−S1−N1 112.2(4).

supported by an IR absorption band at 932 cm^{-1}, which corresponds to a S^+-N^- stretching vibration. The imido group bonded to the sulfur atom and the phosphite ligand is located at the same side of the cobaltadithiolene ring (Figure 1). This syn arrangement is contrary to the corresponding alkylidene complex $[CpCo\{S_2C_2(COOMe)_2\}\{C(COOMe)_2\}\{P(OMe)_3\}]$, which was reported to have the sulfonium ylide (S^+-C^-) in anti form.[12]

This novel migration reaction may proceed by two possible mechanisms: through either intramolecular migration or intermolecular migration via a nitrene. To exclude one of those possibilities, we performed the reaction shown in Scheme 4 in the presence of cyclohexene. If the migration of the imido group is intermolecular, then the formation of the corresponding aziridine and allylamine compounds due to addition and C−H insertion, respectively, should be observed. However, no aziridine or allylamine could be detected. In addition, a crossover experiment was performed as illustrated in Scheme 5. In this experiment, a mixture of the tosylimido-bridged complex having a methylated Cp ligand $[(C_5H_4-Me)Co\{S_2C_2(COOMe)_2\}(NTs)]$ and the mesylimido-bridged complex having the unsubstituted Cp ligand $[CpCo\{S_2C_2(COOMe)_2\}(NMs)]$[10] was made to react with PPh_3. The only products were the intramolecular migrated ones, and no crossover products were found. These results suggest that the imido group migration to the Cp ring is an intramolecular process.

The effect of a large excess of PPh_3 in this migration reaction was also investigated. Complex **1** was treated

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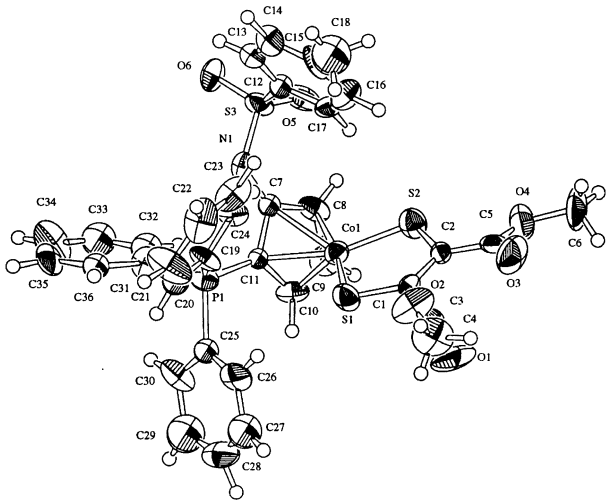
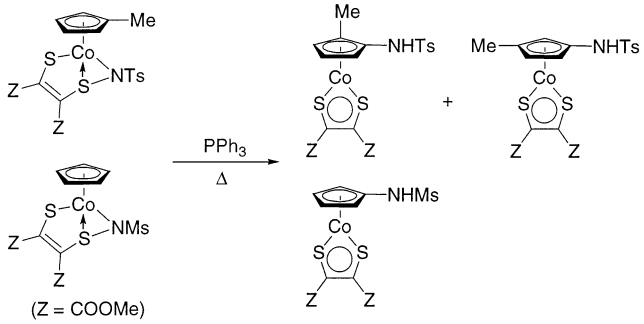
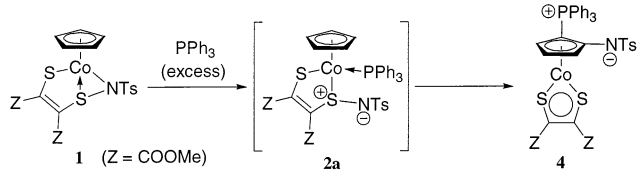


Figure 2. ORTEP drawing of **4**. Selected bond lengths (Å): Co1−S1 2.124(8), Co1−S2 2.107(8), S1−C1 1.72(3), S2−C2 1.74(2), C1−C2 1.37(3), P1−C11, 1.76(2), P1−C19, 1.78(3), N1−C7 1.32(3). Selected bond angles (deg): S1−Co1−S2 90.7(3), Co1−S1−C1 105(1), Co1−S2−C2 107(1), S1−C1−C2 120(2), S2−C2−C1 116(2), S3−N1−C7 121(1).

Scheme 5



Scheme 6



with 10 equiv of PPh_3 in refluxing benzene. The reaction yielded the disubstituted cyclopentadienyl complex $[(C_5H_3{-}NTs{-}PPh_3)Co\{S_2C_2(COOMe)_2\}]$ (**4**) in 17% yield (Scheme 6). Complex **3** and the corresponding precursor of complex **1**, $[CpCo\{S_2C_2(COOMe)_2\}]$, were also formed in 25% and 34% yields, respectively. X-ray diffraction data reveal that complex **4** has the imido and the phosphine group in the 1,2-position of the Cp ligand (Figure 2). None of the 1,3-isomer was found.[13] The bond length of the P1−C11(Cp) was 1.76 Å, which was almost the same as that of the P1−C19(Ph) (1.78 Å). Thus, the P1−C11(Cp) is a single bond. The bond length of the N1−C7(Cp) was 1.32 Å, which was shorter than the N−C bond of the corresponding complex **3** (1.38 Å).[10] However, its bond length was quite longer than that of a typical N−C double bond (1.24 Å).[14] According to the planar structure of the Cp ring of complex **4** (Figure 2), it is concluded that the N1−C7(Cp) is a single bond. The ^{31}P NMR spectrum of complex **4** (δ 23.4 ppm, singlet) is similar to that of a typical phosphonium salt such as $PPh_4^+I^-$ (δ 22.0). This suggests that a triphenylphosphonium-substituted Cp ligand is present in complex **4**. This type of ligand is also observed from $[(C_5H_4{-}P^+Ph_3)Rh(CO)_2]$[15] and $[(\eta^5\text{-Cp})Ru(\mu_2\text{-}\eta\text{:}^5\eta^5\text{-}C_{10}H_8)Ru(\eta^5\text{-}C_5H_4{-}P^+Ph_3)]$.[16] In another reaction, complex **3** was treated with PPh_3. However, complex **4** was not obtained. This result suggests that complex **4** is not formed via intermediate **3**. The formation mechanism of complex **4** is currently under investigation.

Experimental Section

All reactions were carried out under argon atmosphere by means of standard Schlenk techniques. Solvents were dried by known procedures and distilled before use. PPh_3 and $P(OPh)_3$ were used without further treatment. Silica gel, Wakogel C-300, was obtained from Wako Pure Chemical Industries, Ltd. A thin-layer chromatography plate filled with silica gel 60 (20 × 20 cm, 0.25 mm thick) was obtained from Merck Japan Ltd. HPLC was model LC-908 produced by Japan Analytical Industry Co. Mass and IR spectra were recorded on a JEOL JMS-D300 and Shimadzu model FTIR 8600PC, respectively. NMR spectra were measured with a JEOL LA500 spectrometer. UV−vis were recorded on Hitachi model UV-2500PC. Elemental analyses were determined by using a Shimadzu PE2400-II instrument. Melting points were measured by a Yanaco model micromelting point apparatus.

Reaction of Complex 1 with $P(OPh)_3$ at Room Temperature. A solution of complex **1** (50 mg, 0.1 mmol) and $P(OPh)_3$ (131 μL, 0.5 mmol) in dichloromethane (10 mL) was stirred at room temperature for 5 min. After the reaction, hexane was added and the mixture was recrystallized at −30 °C. Product **2b** was obtained as a brown crystalline solid in 80% yield.

Reaction of Complex 1 with $P(OPh)_3$ under Heating. A solution of complex **1** (50 mg, 0.1 mmol) and $P(OPh)_3$ (131 μL, 0.5 mmol) in benzene (10 mL) was refluxed for 5 h. After the solvent was removed under reduced pressure, the residue was separated by thin-layer chromatography (silica gel 60, eluent dichloromethane/ethyl acetate, 10:1). Product **3** was obtained as a purple solid in 40% yield.

Preparation of $[(Me{-}C_5H_4)Co\{S_2C_2(COOMe)_2\}(NTs)]$. A solution of $[(C_5H_4{-}Me)Co\{S_2C_2(COOMe)_2\}]$ (344 mg, 1.0 mmol) and TsN_3 (153 μL, 1.0 mmol) in benzene (10 mL) was refluxed for 2 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (silica gel 60, eluent *n*-hexane/ethyl acetate, 1:1). The product was obtained as a dark green solid in 84% yield.

Crossover Experiment. A solution of $[(C_5H_4{-}Me)Co\{S_2C_2(COOMe)_2\}(NTs)]$ (26 mg, 0.05 mmol), $[CpCo\{S_2C_2(COOMe)_2\}(NMs)]$ (21 mg, 0.05 mmol), and PPh_3 (52 mg, 0.2 mmol) in benzene (10 mL) was refluxed for 5 h. After the solvent was removed under reduced pressure, the residue was separated by thin-layer chromatography (silica gel 60, eluent dichloromethane/ethyl acetate, 1:1). The products $[(C_5H_3{-}Me\text{-}NHTs)Co\{S_2C_2(COOMe)_2\}]$ (mixture of 1,2- and 1,3-substituted Cp isomers) and $[(C_5H_4{-}NHMs)Co\{S_2C_2(COOMe)_2\}]$ were obtained as a purple solid in 50% and 48% yield, respectively. The mixture of 1,2- and 1,3-isomers of $[(C_5H_3{-}Me{-}NHTs)Co\{S_2C_2(COOMe)_2\}]$ was further separated by HPLC.

Reaction of Complex 1 with Excess PPh_3. A benzene solution (30 mL) of complex **1** (50 mg, 0.1 mmol) was poured

(13) NMR analysis of the reaction solution indicated only the presence of the 1,2-isomer.

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into a refluxed benzene (10 mL) solution of PPh_3 (262 mg, 1.0 mmol), and then the reaction mixture was heated for 5 h under refluxed benzene. After the solvent was removed under reduced pressure, the residue was separated by thin-layer chromatography (silica gel 60, eluent ethyl acetate), and then the product was further separated by HPLC. Product **4** was obtained as a blue crystalline solid in 17% yield.

X-ray Diffraction Study. Measurements of complex **2b** and **4** were made on a Rigaku AFC 5S diffractometer with graphite-monochromated Mo Kα radiation. Each structure was solved by direct methods and expanded Fourier techniques. The non-hydrogen atoms were refined anisotropically. Complexes **2b** and **4** of idealized positions were used for the teXsan crystallographic software package of Molecular Structure Corp.

[CpCo{$S_2C_2(COOMe)_2$}(NTs)($P(OPh)_3$)], 2b. Mp: 102−104 °C (dec). Mass (FAB^+, 70 eV): *m*/*z* 810 ($M^+ + 1$), 500 ($M^+ - P(OPh)_3 + 1$). ^1H NMR (500 MHz, $CDCl_3$, vs TMS): δ 7.86 (d, $J = 8.24$ Hz, 2H, Ar), 7.44 (d, $J = 8.24$ Hz, 2H, Ar), 7.29−7.39 (m, 15H, OPh), 5.07 (s, 5H, Cp), 3.86 (s, 3H, OMe), 3.00 (s, 3H, OMe), 2.37 (s, 3H, Me). ^{31}P NMR (200 MHz, $CDCl_3$): δ 126.6 ($P(OPh)_3$). IR (KBr disk): 1732, 1691, 1252, 1182, 932 cm^{-1}.

Crystal Data of 2b·3H_2O ($C_{36}H_{39}NO_{12}S_3PCo$): $M = 863.79$, triclinic, $a = 11.884(1)$ Å, $b = 16.359(2)$ Å, $c = 11.725(1)$ Å, $\alpha = 108.390(10)°$, $\beta = 101.01(1)°$, $\gamma = 69.427(9)°$, $V = 2016.9(5)$ Å^3, $T = 296$ K, space group $P\bar{1}$(#2), $Z = 2$, μ(Mo Kα) = 6.81 cm^{-1}, 9716 reflections measured, 9272 unique ($R_{int} = 0.034$), $R(I > 3\sigma(I)) = 0.094$ and $R_w = 0.127$.

[(C_5H_4−Me)Co{$S_2C_2(COOMe)_2$}(NTs)]. Mp: 180−181 °C. Mass (EI^+, 70 eV) *m*/*z* (rel intensity): 513 (M^+, 2.0), 344 (M^+ − NTs, 77.3), 202 ((C_5H_4−Me)CoS_2^+, 100), 138 ((C_5H_4−Me)Co^+, 18.4). ^1H NMR (500 MHz, $CDCl_3$, vs TMS): δ 7.73 (d, $J = 8.24$ Hz, 2H, Ar), 7.22 (d, $J = 8.24$ Hz, 2H, Ar), 5.83 (m, 1H, Cp), 5.70 (m, 2H, Cp), 5.19 (s, 1H, Cp), 3.80 (s, 3H, OMe), 3.55 (s, 3H, OMe), 2.38 (s, 3H, Me), 2.13 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$, vs TMS): δ 184.5, 166.1, 161.5, 143.2, 137.8, 129.3, 127.2, 114.6, 104.6, 85.1, 83.1, 82.1, 81.4, 53.3, 52.0, 21.5, 13.5. UV−vis (CH_2Cl_2): λ_{max} (ϵ) 638 (1000), 390 (3300), 295 (28000). Anal. Calcd for $C_{19}H_{20}NO_6S_3Co$: C, 44.44; H, 3.93; N, 2.73. Found: C, 44.43; H, 3.87; N, 2.65.

[(C_5H_3−Me−NHTs)Co{$S_2C_2(COOMe)_2$}] (1,2-substituted Cp isomer). Mp: 209−210 °C (dec). Mass (EI^+, 70 eV) *m*/*z* (rel intensity): 513 (M^+, 95.4), 371 ((NHTs−Me−C_5H_3)CoS_2^+, 11.4), 91 ($C_6H_4Me^+$, 100). ^1H NMR (500 MHz, $CDCl_3$, vs TMS): δ 7.35 (d, $J = 8.34$, 2H, Ar), 6.98 (d, $J = 8.34$, 2H, Ar), 6.53 (br, 1H, NH), 5.65 (m, 1H, Cp), 5.16 (m, 1H, Cp), 4.70 (m, 1H, Cp), 3.88 (s, 6H, OMe), 2.41 (s, 3H, Me), 2.25 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$, vs TMS): δ 165.3, 158.3, 145.2, 130.5, 129.6, 127.4, 107.8, 86.9, 76.2, 73.5, 66.3, 52.8, 21.3, 10.5. UV−vis (CH_2Cl_2): λ_{max} (ϵ) 574 (6600), 364 (3700), 297 (21000).

[(C_5H_3−Me−NHTs)Co{$S_2C_2(COOMe)_2$}] (1,3-substituted Cp isomer). Mp: 224−225 °C (dec). Mass (EI^+, 70 eV) *m*/*z* (rel intensity): 513 (M^+, 14.2), 371 ((NHTs−Me−C_5H_3)CoS_2^+, 3.3), 155 (Ts^+, 19.9), 91 ($C_6H_4Me^+$, 100). ^1H NMR (500 MHz, $CDCl_3$, vs TMS): δ 7.37 (d, $J = 8.19$, 2H, Ar), 6.98 (d, $J = 8.19$, 2H, Ar), 5.63 (s, 1H, Cp), 5.52 (t, $J = 2.17$, 1H, Cp), 4.88 (t, $J = 2.17$, 1H, Cp), 3.88 (s, 6H, OMe), 2.25 (s, 3H, Me), 1.88 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$, vs TMS): δ 165.3, 157.5, 145.0, 130.7, 129.5, 127.3, 108.5, 94.8, 73.8, 70.7, 67.7, 52.8, 21.3, 14.2. UV−vis (CH_2Cl_2): λ_{max} (ϵ) 577 (6300), 365 (3900), 296 (20000).

[(C_5H_3−NTs−PPh_3)Co{$S_2C_2(COOMe)_2$}], 4. Mp: 173−174 °C. Mass (FAB^+, 70 eV): *m*/*z* 760 ($M^+ + 1$). ^1H NMR (500 MHz, $CDCl_3$, vs TMS): δ 7.58−7.90 (m, 15H, Ph), 7.41 (d, $J = 8.24$ Hz, 2H, Ar), 6.94 (d, $J = 8.24$ Hz, 2H, Ar), 6.24 (1H, Cp), 5.31 (1H, Cp), 4.83 (1H, Cp), 3.80 (s, 6H, OMe), 2.23 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$, vs TMS): δ 165.5, 154.0, 141.3, 138.6, 136.5, 134.82, 134.79, 134.73, 129.9, 129.8, 128.6, 126.5, 119.1, 118.3, 78.7, 78.6, 78.4, 78.3, 77.2, 67.0, 66.9, 58.6, 57.8, 52.6, 30.9. ^{31}P NMR (200 MHz, $CDCl_3$, vs 85% H_3PO_4): δ 23.4 (PPh_3). UV−vis (CH_2Cl_2): λ_{max} (ϵ) 758 (1500), 586 (5900), 294 (23000). IR (KBr disk): 1705, 1489, 1236 cm^{-1}. Anal. Calcd for $C_{37}H_{33}NO_6PS_3Cl_2Co$: C, 52.61; H, 3.94; N, 1.66. Found: C, 52.47; H, 3.84; N, 1.59.

Crystal Data of 4 ($C_{36}H_{31}NO_6S_3PCo$): $M = 759.73$, triclinic, $a = 11.477(3)$ Å, $b = 16.066(3)$ Å, $c = 9.803(3)$ Å, $\alpha = 95.70(2)°$, $\beta = 96.72(2)°$, $\gamma = 76.91(2)°$, $V = 1743.6(8)$ Å^3, $T = 296$ K, space group $P\bar{1}$(#2), $Z = 2$, μ(Mo Kα) = 7.64 cm^{-1}, 5639 reflections measured, 5317 unique ($R_{int} = 0.027$), $R(I > 3\sigma(I)) = 0.070$ and $R_w = 0.081$.

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Supporting Information Available: Table of atomic coordinates, isotropic and anisotropic displacement parameters, and all bond length and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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