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Reactivity of Cyclocobaltated Benzylamine Derivatives toward Terminal Alkynes

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The cyclocobaltated complexes $[(\eta^5\text{-}C_5H_5)Co(4\text{-}RC_6H_3CH_2NMe_2\text{-}C^2,N)I]$ (**1**; R = H, Me, F) reacted with terminal alkynes such as $R'C{\equiv}CH$ (**2**; R′ = ${}^tBu$, $SiMe_3$) to afford a mixture of the two compounds $\{(\eta^5\text{-}C_5H_5)Co[\eta^5\text{-}C_5H_4CH{=}CR'(4\text{-}R\text{-}2\text{-}(CH_2NMe_2)C_6H_3)]\}^+PF_6^-$ (**3**) and (*E*)-$CHR'{=}CH(4\text{-}R\text{-}2\text{-}(CH_2NMe_2)C_6H_3)$ (**4**) in a ca. 1:1 ratio. The reaction is rationalized by assuming that insertion of the alkyne into the Co−C bond of **1** occurred with no regioselectivity, leading to two unstable regioisomers; a selective migration of the less hindered alkenyl−Co derivative to a Cp unit followed by migration of the monosubstituted Cp ring thus obtained to another cobalt center afforded **3**, whereas compound **4** should be obtained via protiodemetalation of the other isomer formed.

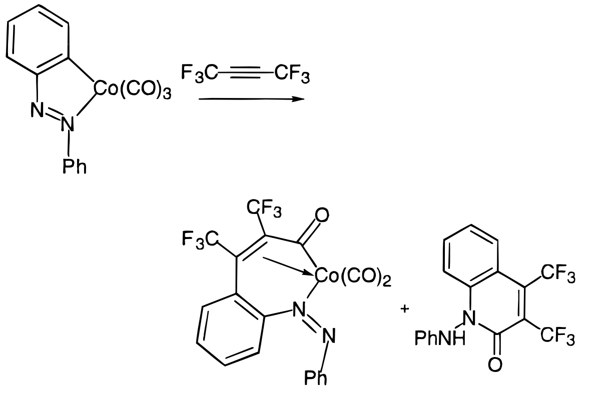
Introduction

Transition-metal-mediated organic synthesis with compounds in which metals take part in a ring system, i.e. metallacycles, is an important line of research of our group.[1] These compounds have indeed proved to be effective in heterocycle synthesis, and among these compounds, palladium derivatives have been shown to display a large variety of processes in both bulk and fine chemicals. We have thus long been interested in the reactions of cyclopalladated amines with internal alkynes, which have afforded important pathways to the syntheses of heterocyclic compounds.

One recent aim of our search was to determine to what extent other transition-metal complexes can display analogous (and perhaps complementary) behavior to their cyclopalladated counterparts. We have already demonstrated that pseudotetrahedral ruthenacycle derivatives of $Ru(C_6H_4CH_2NMe_2)Cl(\eta^6\text{-}C_6H_6)$ react with disubstituted alkynes to afford heterocyclic compounds bound to Ru(0) complexes. The organic product was readily obtained under smooth oxidation conditions, and hence, this method may become useful for the synthesis of 2,3-disubstituted isoquinolinium derivatives.[2]

It has been shown on many occasions that the chemistry of organometallic derivatives of cobalt is very rich, leading, in several instances, to the formation of carbon−carbon and carbon−heteroatom bonds. Of the many examples that may illustrate this point, the synthesis of pyridines via cyclotrimerization of alkynes and nitriles that involves Co(III) metallacyclic intermediates is rather representative of these properties.[3]

In line with our present investigation it was found that cobalt(I) derivatives made with orthometalated azobenzene ligands displayed interesting reactivity when reacted with activated alkynes. Thus, Bruce and co-workers reported the first insertion reaction between [(phenylazo)phenyl-*C*²,*N*]tricarbonylcobalt, containing a C,N-coordinated azobenzene ligand, and hexafluorobutyne, as shown in eq 1.[4] However, this result seemed to be limited to this alkyne, as Pauson et al. failed to extend it to less activated alkynes such as dimethyl acetylenedicarboxylate and phenylacetylene.[5]



(1)

We have recently demonstrated that organometallic compounds of Co(III) containing a metallacyclic unit could be readily synthesized by transmetalation reactions of lithiated tertiary amines. These reactions afforded a large variety of stable pseudotetrahedral

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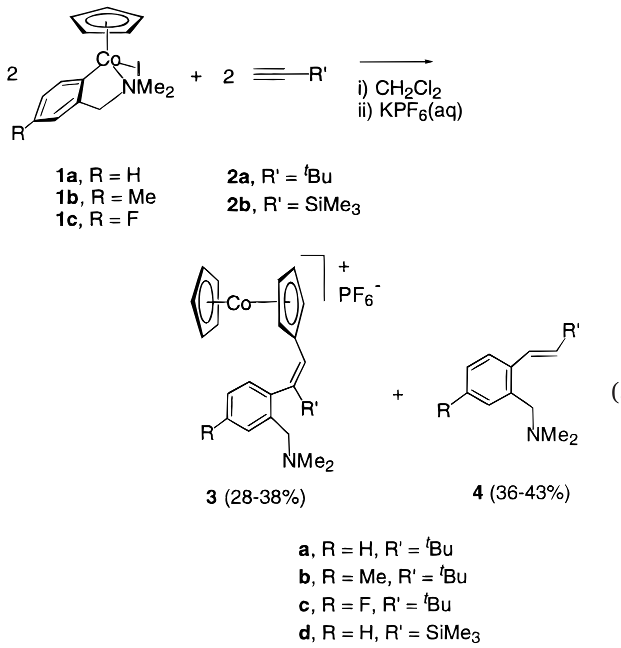
organocobalt compounds, in which the cobalt is a stereogenic center. These compounds are isoelectronic and structurally analogous to the ruthenacycles mentioned above, and therefore these organocobalt compounds were excellent candidates for the research field we are interested in. In this paper we thus describe the result of the reactions between these complexes and terminal alkynes leading to organic and organometallic derivatives that are without precedent in this chemistry.

Results and Discussion

While investigating the reactivity of the new series of organocobalt complexes[6] with alkynes we have observed that neutral cobaltacyclic complexes of type **1** display an amazing reactivity toward alkynes. No reaction at all was observed between **1** and any internal alkynes. However, in marked contrast to what we found in many instances with the corresponding palladium and ruthenium complexes, we have now observed that only terminal alkynes lead to interesting reactions. Terminal alkynes with bulky donor substituents gave the best results, leading to the formation of an organic product together with a cobaltocenium derivative as shown in eq 2.



1a, R = H
1b, R = Me
1c, R = F

2a, R' = ^{t}Bu
2b, R' = SiMe$_3$

3 (28-38%)
4 (36-43%)

(2)

a, R = H, R' = ^{t}Bu
b, R = Me, R' = ^{t}Bu
c, R = F, R' = ^{t}Bu
d, R = H, R' = SiMe$_3$

We have found that such reactions do not depend on the substitution at the *para* position with respect to the Co−C bond for the series of cyclometalated amines used, as neither the yield nor the selectivities of the reaction have been significantly modified.

In a typical experiment **1a** was dissolved in CH$_2$Cl$_2$, and an excess of HC≡C^{t}Bu was added at room temperature. This afforded, after 16 h, a mixture of the two main products **3** and **4**. The latter was extracted in hexane, whereas **3** was dissolved in water, affording a yellow solution which led in the presence of KPF$_6$ to a light yellow powder which was very stable toward hydrolysis and air.

The structures of compounds **4** were easily deduced from their ^{1}H and ^{13}C{^{1}H} NMR spectra and mass spectroscopy. In ^{1}H NMR, the olefinic unit displayed a large $^3J_{H-H}$ coupling constant (16−19 Hz), which is diagnostic of their *trans* geometry, and the CH$_2$NMe$_2$ unit displayed nondiastereisotopic signals typical of a symmetrical molecule.

All of the compounds **3** were characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. The combustion analysis proved, however, to be somewhat frustrating for all these compounds. The amount of carbon found was often lower than the calculated amount, despite all our efforts to crystallize the compounds and/or to dry the obtained crystals in vacuo. However, this is a feature that has been encountered several times for related ruthenium or palladium compounds containing PF$_6$ as a counteranion. Since (i) the N and H analyses were correct, (ii) one compound (**3a**) has been unambiguously characterized by a X-ray diffraction analysis (see below), and (iii) no other species could be seen on the ^{1}H NMR spectra of the compounds, we may consider that these unsatisfactory C analyses do not hamper the characterization of the compounds **3**. The ^{1}H NMR spectra revealed the existence of two Cp rings bonded to the metal in which one of them is monosubstituted. The resulting diastereotopicity of their methylenic groups, evidenced by the presence of well-defined AB spin systems in their ^{1}H NMR spectra, can only occur if important steric effects are present, since the molecules display a formal plane of symmetry. Thus, although there is conjugation between the Cp′ ring, the vinyl group, and the phenyl ring, the most favored conformation must be *clinal*.[7] Steric repulsion between the (dimethylamino)methyl and *tert*-butyl groups is sufficient to offset the energy lost on conjugation and to result in a nonplanar structure.

To establish with assurance which factors are responsible for such atropisomerism, the solid-state structure of **3a** was elucitated via a single-crystal X-ray diffraction study. The molecular structure is represented in Figure 1, together with the adopted numbering scheme. Selected bond distances and angles are shown in Table 1.

According to this study, the molecular structure of **3a** clearly reveals the presence of a cationic fragment typical of a cobaltocene geometry in which the cobalt(III) center is located between two almost parallel Cp rings. In addition, the *Z* stereochemistry of the vinyl group was unambiguously established. Restricted rotation about a single bond must occur around the C17−C12 bond. In the solid state the dihedral angle between C13−C12 and C17−C18 is 101°. Such strong steric effects are present also in solution, thus explaining the presence of a diastereotopic methylene group.

These two classes of products, **3** and **4**, were both isolated in yields close to 50%, which indicates that they probably are the only products of the reaction. In other words, no metalated C,N-coordinated ligands seem to have been lost during the reaction. Considering that in **3** and **4** the R groups are on the carbon atom which is respectively adjacent and remote from the aryl ring, there is probably no regioselectivity in the alkyne insertion reaction leading to the intermediate organocobalt species. Thus, a 1,2-insertion should lead to

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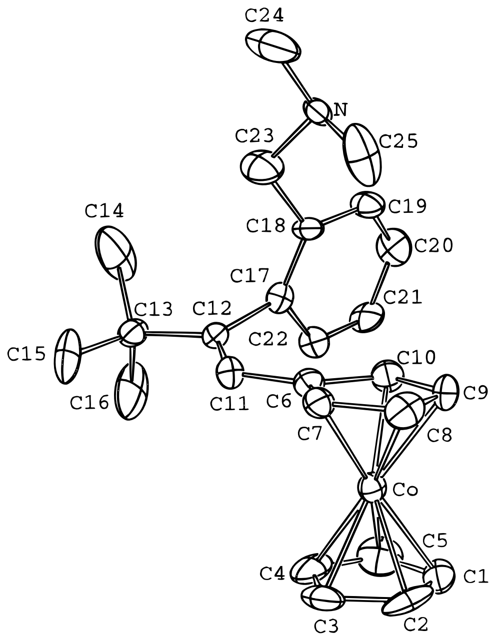


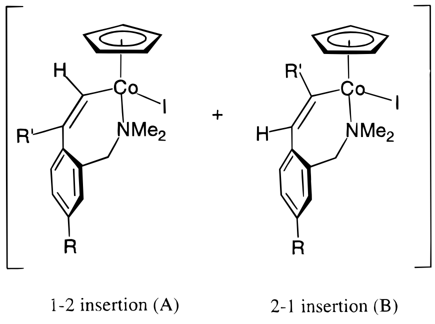
Figure 1. ORTEP view of the cationic part of compound **3a**.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 3a

Co−C(Cp)$_{av}$	2.01(2)	C11−C12	1.33(2)
Co−C(Cp′)$_{av}$	2.01(2)	C12−C17	1.53(2)
Co−Cp^{a} [a]	1.64(2)	C−C(Ph)$_{av}$	1.36(2)
Co−Cp′^{a} [b]	1.62(2)	C18−C23	1.56(2)
C−C(Cp)$_{av}$	1.37(3)	C23−N	1.48(2)
C−C(Cp′)$_{av}$	1.41(2)	N−C24	1.40(2)
C6−C11	1.47(2)		
Cp^{a}−Co−Cp′^{a}	179(2)	C12−C17−C22	116(1)
C7−C6−C11	122(1)	C17−C18−C19	117(1)
C10−C6−C11	131(1)	C17−C18−C23	121(1)
C6−C11−C12	128(1)	C19−C18−C23	119(1)
C11−C12−C13	121(1)	C18−C23−N	111(1)
C11−C12−C17	121(1)	C13−C12−C17−C18	101(2)
C13−C12−C17	117(1)	C11−C12−C18−C18	−80(2)
C12−C17−C18	122(1)		

[a] Cp^{a} is the centroid of Cp. [b] Cp′^{a} is the centroid of Cp′.

Chart 1. Proposed Intermediates for the Formation of 3 and 4



cobaltocenium derivatives **3**, whereas a 2,1-insertion should afford the organic product derivatives **4** (Chart 1). The insertion should occur via either cleavage of the iodide−Co bond or decoordination of the nitrogen atom from Co in order to coordinate the alkyne to the Co center prior to the insertion/migration process. As the use of cationic species did apparently not increase the reactivity of these complexes toward alkynes (including internal ones), we are inclined to believe that the second hypothesis is the one that should be operative.

The two intermediates, which both contained seven-membered cobaltacyclic rings, formed soon after the insertion of the alkyne and are then likely to be unstable, leading to rearrangements. According to the yields of the products **3** and **4**, it is likely that this rearrangement should be somehow concerted: the alkenyl group attached to Co in A should migrate to a Cp ring, a feature that is in line with previous observations made by Maitlis[8] and Werner,[9] whereas the alkenyl−Co bond in B is cleaved by the proton produced during the process. At this stage it is of course not possible to draw any likely reaction path that would explain this rather efficient transfer of a Cp ring from one Co to the other one. We have just checked that the solvent is not the source of proton, as using deuterated solvent and water afforded no evidence of D-labeled products. Further work is obviously necessary to rationalize this reaction sequence.

Conclusion

It appears from the present study that Co(III) species with ortho-chelating arylamine ligands display lower reactivity in reactions with alkynes when compared to their palladated and ruthenated counterparts; however, this is compensated by the fact that terminal alkynes lead to clean reactions with the cobalt derivatives as opposed to the Pd and Ru complexes, which react only with internal alkynes.

Experimental Section

All reactions were performed in Schlenk flasks under oxygen and water-free nitrogen. CH_2Cl_2 was dried over P_2O_5 and distilled under nitrogen. The ^{1}H NMR spectra were recorded at 300.13 MHz and $^{13}C\{^{1}H\}$ NMR spectra at 75.47 MHz on a FT-Bruker instrument (AC-300) and externally referenced to TMS. Chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz, respectively. All mass spectra were performed by the Laboratory of Molecular Catalysis da Universidade Federal do Rio Grande do Sul. Column chromatography was carried out on alumina 90 (activity II−III mesh; 0.063−0.200 mm) from Merck.

Syntheses. [Co(η^5-C_5H_5){η^5-C_5H_4[CH=C(^{t}Bu)($C_6H_4CH_2$-NMe_2)]}]PF_6 (3a) and *trans*-^{t}BuCH=CH$C_6H_4CH_2NMe_2$ (4a). *tert*-Butylacetylene (1.0 mL, 8.0 mmol) was added to a stirred solution of **1a** (0.770 g, 2.00 mmol) in CH_2Cl_2 (20 mL) at room temperature. After 20 h the volatiles were removed in vacuo, affording a light green solid. The crude product was washed with two solvents in order to extract the different products. First, it was washed with hexane (5 × 50 mL). From the combined organic solutions an organic product was isolated after concentration in vacuo. This product was subjected to flash chromatography over alumina using CH_2Cl_2 as eluent, allowing the migration of a red-brown band corresponding to the compound **4a**. After solvent evaporation, the organic product was dried in vacuo, affording **4a** as red-brown oil. Second, the crude product was now washed with water (8 × 25 mL) and, into the combined yellow aqueous solutions, an excess of KPF_6 was added. Immediately, a yellow precipitate was formed. After 15 min the precipitate thus obtained was filtered and washed with water (10 mL) and hexane (30 mL). After recrystallization in CH_2Cl_2/hexane and drying in vacuo,

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3a was isolated as a light yellow powder. Yield: 0.416 g (38% from **1a**) for **3a** and 0.186 g (43% from **1a**) for **4a**.

3a: Anal. Calcd for $C_{25}H_{31}CoF_6NP$ (490.21): C, 54.65; H, 5.69; N, 2.55. Found: C, 49.01; H, 5.16; N, 2.14. ^{1}H NMR ($CDCl_3$): δ 7.60 (m, 1H, Ar); 7.43 (m, 2H, Ar); 7.11 (m, 1H, Ar); 6.42 (s, 1H, HC=); 5.77, 5.70, 5.30, and 4.07 (4 br s, 4H, C_5H_4); 5.50 (s, 5H, C_5H_5); 3.16 and 2.97 (AB spin system, 2H, CH_2N, $^2J_{H-H} = 13.9$); 2.01 (s, 6H, NMe_2); 1.21 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 158.06 and 117.65 (C=CH); 139.52, 133.14, 130.07, 129.35, 128.95, and 128.63 (C_6H_4); 102.85, 85.06, 84.28, and 81.05 (C_5H_4); 86.00 (C_5H_5); 60.55 (CH_2N); 44.59 (NMe_2); 38.47 ($\mathit{C}(CH_3)_3$); 29.79 ($C(\mathit{C}H_3)_3$).

4a: $C_{15}H_{23}N$ (217.18), MS *m*/*z* (M^+) 217. ^{1}H NMR ($CDCl_3$): δ 7.43 (d, 1H, Ar, $^3J_{H-H} = 8.0$); 7.30−7.05 (m, 3H, Ar); 6.73 and 6.08 (2d, 2H, HC=CH, $^3J_{H-H} = 16.1$); 3.38 (s, 2H, CH_2N); 2.23 (s, 6H, NMe_2); 1.15 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 142.91 and 123.28 (HC=CH); 138.65, 136.44, 130.59, 127.64, 126.68, and 125.96 (C_6H_4); 62.45 (CH_2N); 45.13 (NMe_2), 33.68 ($\mathit{C}(CH_3)_3$); 29.61 ($C(\mathit{C}H_3)_3$).

In all cases reported below the cobaltocenium derivative and the organic product were obtained using a workup similar to that used for the synthesis of **3a** and **4a**.

[Co(η^5-C_5H_5){η^5-C_5H_4[CH=C(^{t}Bu)($C_6H_3(CH_3)CH_2NMe_2$)]}]-PF_6 (3b) and *trans*-^{t}BuCH=CHC$_6$H$_3$(CH$_3$)CH$_2$NMe$_2$ (4b). **1b** (0.800 g, 2.00 mmol) reacts with *tert*-butylacetylene (1.0 mL, 8.00 mmol) to give **3b** and **4b** as a light yellow solid and a brown oil, respectively. Yield: 0.320 g of **3b** (28% from **1b**) and 0.210 g of **4b** (45% from **1b**).

3b: Anal. Calcd for $C_{26}H_{33}CoF_6NP$ (563.16): C, 55.42; H, 5.90; N, 2.49. Found: C, 47.56; H, 5.17; N, 1.88. ^{1}H NMR (acetone-d_6): δ 7.55 (s, 1H, Ar); 7.44 (br s, 2H, Ar); 6.73 (s, 1H, HC=); 5.89, 5.72, 5.53, and 4.43 (4 br s, 4H, C_5H_4); 5.74 (s, 5H, C_5H_5); 4.11 and 3.76 (AB spin system, 2H, CH_2N, $^2J_{H-H} = 15.0$); 2.57 (s, 6H, NMe_2); 2.43 (s, 3H, CH_3);1.22 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 157.59 and 118.00 (C=CH); 139.15, 136.40, 131.15, 130.35, 129.82, and 129.32 (C_6H_4); 102.67, 85.28, 85.09, 84.38, and 81.17 (C_5H_4); 85.96 (C_5H_5); 60.12 (CH_2N), 44.35 (NMe_2), 38.56 ($\mathit{C}(CH_3)_3$), 29.73 ($C(\mathit{C}H_3)_3$), 20.87 (CH_3).

4b: $C_{16}H_{25}N$ (231.20), MS *m*/*z* (M^+) = 231. ^{1}H NMR ($CDCl_3$): δ 7.34 (d, 1H, Ar, $^3J_{H-H} = 7.8$); 7.06 (s, 1H, Ar); 7.01 (d, 1H, Ar, $^3J_{H-H} = 7.8$); 6.68 and 6.05 (2d, 2H, HC=CH, $^3J_{H-H} = 16.1$); 3.38 (s, 2H, CH_2N); 2.31 (s, 3H, CH_3); 2.25 (s, 6H, NMe_2); 1.12 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (acetone-d6): δ 141.95 and 123.17 (HC=CH); 136.29, 135.98, 135.80, 131.25, 128.30, and 125.90 (C_6H_3); 62.45 (CH_2N); 45.16 (NMe_2); 33.62 ($\mathit{C}(CH_3)_3$); 29.70 ($C(\mathit{C}H_3)_3$); 20.77 (CH_3).

[Co(η^5-C_5H_5){η^5-C_5H_4[CH=C(^{t}Bu)($C_6H_3(F)CH_2NMe_2$)]}]-PF_6 (3c) and *trans*-^{t}BuCH=CHC$_6$H$_3$(F)CH$_2$NMe$_2$ (4c). 1c (0.806 g, 2.00 mmol) reacts with *tert*-butylacetylene (1.0 mL, 8.00 mmol) to give **3c** and **4c** as a light yellow solid and a brown oil, respectively. Yield: 0.211 g of **3c** (28% from **1c**) and 0.204 g of **4c** (43% from **1c**).

3c: Anal. Calcd for $C_{25}H_{30}CoF_7NP$ (567.13): C, 52.92; H, 5.33 N, 2.47. Found: C, 52.19; H, 5.21; N, 2.22. ^{1}H NMR ($CDCl_3$): δ 7.37 (m, 1H, Ar); 7.14 (m, 2H, Ar); 6.46 (s, 1H, HC=); 5.72, 5.61, 5.36, and 4.23 (4 br s, 4H, C_5H_4); 5.54 (s, 5H, C_5H_5); 3.14 and 2.90 (AB spin system, 2H, CH_2N, $^2J_{H-H} = 14.5$); 2.01 (s, 6H, NMe_2); 1.19 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 157.82 and 117.84 (C=CH); 164.54 (d, $^1J_{C-F} = 244.1$); 139.09, 135.05, 131.44 (d, $^3J_{C-F} = 7.0$); 116.10 (d, $^2J_{C-F} = 23.5$), 114.75 (d, $^2J_{C-F} = 21.1$) (C_6H_4); 102.86, 85.06, 84.91, 84.29, and 81.11 (C_5H_4); 85.90 (C_5H_5); 60.84 (CH_2N); 45.07 (NMe_2); 38.416 ($\mathit{C}(CH_3)_3$); 29.82 ($C(\mathit{C}H_3)_3$).

4c: $C_{15}H_{22}FN$ (235.17), MS *m*/*z* (M^+) = 235. ^{1}H NMR ($CDCl_3$): δ 7.38 (dd, 1H, Ar, $^3J_{H-H} = 8.6$, $^4J_{H-F} = 5.7$); 7.02 (dd, 1H, Ar, $^3J_{H-F} = 9.8$, $^4J_{H-H} = 2.8$); 7.01 (dt, 1H, Ar, $^3J_{H-F} = {}^4J_{H-H} = 8.6$, $^3J_{H-H} = 2.8$); 6.62 and 6.03 (2d, 2H, HC=CH, $^3J_{H-H} = 16.0$); 3.41 (s, 2H, CH_2N); 2.27 (s, 6H, NMe_2); 1.12 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 162.00 (d, $^1J_{C-F} = 241.8$); 139.00 (d, $^3J_{C-F} = 7.0$); 134.70, 127.80 (d, $^2J_{C-F} = 7.0$); 116.43 (d, $^2J_{C-F} = 21.1$), 114.08 (d, $^2J_{C-F} = 21.1$) (C_6H_3), 143.19, 122.04 (HC=CH), 61.61 (CH_2N), 45.09 (NMe_2), 33.64 ($\mathit{C}(CH_3)_3$), 29.39 ($C(\mathit{C}H_3)_3$).

Table 2. X-ray Experimental Data Collection and Structure Refinement Details for 3a

Crystal Data	
formula	$C_{25}H_{31}CoF_6NP$
mol wt	549.43
cryst syst	orthorhombic
space group	$Pca2_1$
a (Å)	13.533(3)
b (Å)	11.858(3)
c (Å)	16.132(3)
V (Å^3)	2588(1)
Z	4
color	yellow
cryst dimens (mm)	0.30 × 0.25 × 0.20
D_{calcd} (g cm^{-3})	1.41
F(000)	1136
μ (mm^{-1})	0.781
min/max transmissn	0.9277/1.0000
Data Collection	
temp (K)	294
wavelength (Å)	0.71073
radiation	Mo Kα (graphite monochromated)
diffractometer	MACH3 Nonius
scan mode	$\theta-2\theta$
hkl limits	−14 to 0/0−16/0−20
θ limits (deg)	2.5−26.28
no. of data measd	2973
no. of data with $I > 3\sigma(I)$	1209
weighting scheme	$4F_o^2/(\sigma^2(F_o^2) + 0.0064F_o^4)$
no. of variables	306
R	0.053
R_w	0.068
GOF	1.403
largest peak in final diff map (e Å^{-3})	0.323

[Co(η^5-C_5H_5){η^5-C_5H_4[CH=C($SiMe_3$)$C_6H_4CH_2NMe_2$)]}]-PF_6 (3d) and *trans*-SiMe$_3$CH=CHC$_6$H$_4$CH$_2$NMe$_2$ (4d). 1a (0.770 g, 2.00 mmol) reacts with (trimethylsilyl)acetylene (1.4 mL, 8.00 mmol) to give **3d** and **4d** as a light yellow solid and a brown oil, respectively. Yield: 0.339 g of **3d** (30% from **1a**) and 0.168 g (36% from **1a**).

3d: Anal. Calcd for $C_{24}H_{31}F_6NPSi$ (506.19): C, 50.98; H, 5.53; N, 2.48. Found: C, 44.66; H, 4.98; N, 1.75. ^{1}H NMR ($CDCl_3$): δ 7.34 (m, 3H, Ar); 6.89 (d, 1H, Ar, $^3J_{H-H} = 7.1$); 6.64 (s, 1H, HC=); 5.67 (br s, 2H, C_5H_4); 5.42 (br s, 1H, C_5H_4); 4.49 (s, 1H, C_5H_4); 5.55 (s, 5H, C_5H_5); 3.03 and 2.97 (AB spin system, 2H, CH_2N, $^2J_{H-H} = 13.2$); 2.02 (s, 6H, NMe_2); 0.17 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 154.98 and 127.95 (C=CH); 142.07, 130.28, 129.97, 129.72 and 129.47, 128.11 (C_6H_4); 100.92, 85.56, 85.46, 84.78, and 81.80 (C_5H_4); 86.09 (C_5H_5); 60.27 (CH_2N); 44.38 (NMe_2); −1.83 ($Si(CH_3)_3$).

4d: $C_{14}H_{23}NSi$ (233.16), MS *m*/*z* (M^+) = 233. ^{1}H NMR ($CDCl_3$): δ 7.56 (d, 1H, Ar, $^3J_{H-H} = 6.2$); 7.36 and 6.38 (2d, 2H, HC=CH, $^3J_{H-H} = 19.2$); 7.30−7.15 (m, 3H, Ar); 3.45 (s, 2H, CH_2N); 2.25 (s, 6H, NMe_2); 0.16 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 142.48 and 127.73 (HC=CH); 138.93, 136.75, 130.78, 130.28, 127.73, and 125.65 (C_6H_4); 62.29 (CH_2N); 44.97 (NMe_2); −1.49 ($Si(CH_3)_3$).

X-ray Determination of 3a and Processing. Crystals suitable for X-ray analysis were grown by slow diffusion of *n*-hexane into a solution of **3a** in dichloromethane as yellow needles. Crystal data and details of data collection for **3a** are given in Table 2. The crystals displayed a low diffracting power, which explains the rather low values of the observed/collected data and of the parameter/data ratios. Data were collected in the $\theta/2\theta$ mode using Mo Kα graphite-monochromated radiation ($\lambda = 0.710\,73$ Å) on a yellow crystal of dimensions 0.20 × 0.25 × 0.30 mm^3 with a Nonius MACH3 automatic diffractometer at room temperature. Three standard reflections measured every 1 h during the entire data collection period showed no significant trend. The raw data were converted to intensities and corrected for Lorentz polarization and absorption factors, the latter coming from the ψ-scan data of seven reflections. The structure was solved by direct methods. After refinement of the non-hydrogen atoms, difference Fourier maps revealed maxima of residual electron density close to positions expected for hydrogen atoms. Hydrogen atoms were refined at calculated positions with a riding model in which the C−H vector was fixed at 0.95 Å with isotropic temperature factors such as $B(\mathrm{H}) = 1.3[B_{\mathrm{eqv}}(\mathrm{C})]$ Å^2. The absolute structure was determined by refining Flack's x parameter. A final Fourier difference map revealed no significant maxima. All calculations were performed on a DEC Alpha 3000 computer using the Nonius OpenMoleN package.[10] Neutral atom scattering factor coefficients and anomalous dispersion coefficients were taken from a standard source.[11]

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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 **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000053P

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(10) OpenMoleN, Interactive Structure Solution; Nonius BV, Delft, The Netherlands, 1997.

(11) (a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; 1974; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.2b. (b) *Ibid*., Table 2.3.1.