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Synthesis, Structure, and Reactivity of [C_5Me_5CoLL'] Complexes with L = Pyridine and L′ = Olefin or L−L′ = Bipyridine

Christian P. Lenges,[†] Peter S. White,[†] Will J. Marshall,[‡] and
Maurice Brookhart*[,†]

Department of Chemistry, Venable and Kenan Laboratories, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, and DuPont Central Research & Development, Experimental Station, Wilmington, Delaware 19880

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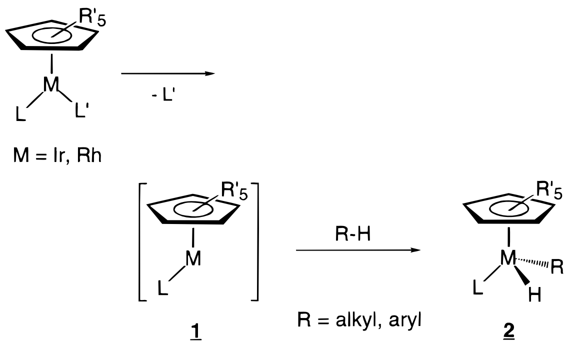
The bis(olefin) complex [$C_5Me_5Co(C_2H_3SiMe_3)_2$] (**6**) reacts with pyridine at 22 °C to give the pyridine olefin complex [$C_5Me_5Co(C_2H_3SiMe_3)(C_5H_5N)$] (**7**). The addition of excess pyridine does not result in the formation of a bis(pyridine) adduct. Thermolysis of solutions of **7** in benzene-d_6 results in catalytic H/D exchange which incorporates deuterium from the solvent into coordinated olefin. Pyridine dissociation generates a 16-electron intermediate which is formulated as the reactive species. At long times deuteration of the coordinated pyridine is also observed via shuttling of deuterium from the solvent to the olefin ligand and then to the pyridine. The reaction of **6** with pyridine-d_5 results in the analogue **7**-d_5. Thermolysis of **7**-d_5 shows preference for H/D exchange at the *ortho* positions of coordinated pyridine, which has been explained by the formation of η^2-coordinated intermediates. Reaction of 4-phenylpyridine with **6** yields the analogous pyridine adduct [$C_5Me_5Co(C_2H_3SiMe_3)(4\text{-}C_6H_5\text{-}C_5H_4N)$] (**12**), which was characterized by X-ray structural analysis. H/D exchange catalysis is also observed using this pyridine derivative. In a reaction of bipyridine with **6** clean olefin substitution is observed at 22 °C to generate violet, highly air sensitive [$C_5Me_5Co(bipy)$] (**13**). Complex **13** has been characterized by X-ray structural analysis.

Introduction

Half-sandwich complexes of the type [C_5R_5MLL'] (M = Rh, Ir) have been investigated in detail as model systems for C−H bond activation reactions. The extrusion of the small molecule L′ (L′ = H_2, C_2H_4, CO) generates the 16-electron fragment **1**, which reacts via oxidative addition with C−H bonds to generate alkyl hydride species **2** (eq 1). The second ligand, L, is usually a phosphine, CO, or CNR ligand, which does not participate in further reactions of these complexes.[1−5]



(1)

We have used precursors of the type [$C_5Me_5M(C_2H_3R)_2$] (M = Co, Rh) in our investigations of catalytic reactions based on C−H bond activation.[6−8] Dissociative loss of 1 equiv of olefin generates a 16-electron species of type **1** which can incorporate a second equivalent of olefin after an insertion reaction to close a catalytic cycle. Cobalt complexes of the type [$C_5R_5Co(olefin)_2$] have been used extensively as precursors to the 14-electron fragment [C_5R_5Co] in organometallic and cluster synthesis. These types of complexes serve as catalyst precursors for the trimerization of alkynes to generate substituted arenes and in the synthesis of pyridines from alkynes and nitriles.[9−24]

[†] The University of North Carolina at Chapel Hill.
[‡] DuPont Central Research and Development.
(1) Bergman, R. G.; Janowicz, A. H. *J. Am. Chem. Soc.* **1982**, *104*, 352.
(2) Bergman, R. G. *Science* **1984**, *223*, 902.
(3) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91.
(4) Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 686.
(5) Graham, W. A. G.; Hoyano, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 3723.
(6) Lenges, C. P.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 6965.
(7) Lenges, C. P.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **1999**, *121*, 4385.
(8) Lenges, C. P.; Brookhart, M. *J. Am. Chem. Soc.* **1999**, *121*, 6616.
(9) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1.
(10) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539 and references therein.
(11) Bönnemann, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248.
(12) Vollhardt, K. P. C.; Naiman, A. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 708.
(13) Vollhardt, K. P. C.; Hirthammer, M. *J. Am. Chem. Soc.* **1986**, *108*, 2481.
(14) For recent reviews, see: Frühauf, H.-W. *Chem. Rev.* **1997**, *97*, 523.
(15) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49.
(16) Wakatsuki, Y.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1978**, 1278 and references therein.
(17) Bönnemann, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 505.
(18) Heller, B.; Oehme, G. *J. Chem. Soc., Chem. Commun.* **1995**, 179.

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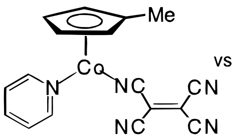
[C_5R_5CoLL'] complexes normally incorporate ligands L, L′ that stabilize the electron-rich low-oxidation-state cobalt(I) system (L, L′ = olefins, phosphines, phosphites, CO, CNR,[21,25−27] heterocyclic carbenes[28]). Ligands such as amines and pyridines have been extensively studied in classic cobalt coordination chemistry, but these ligands usually do not stabilize the low oxidation state in complexes of the electron-rich 14-electron fragment [C_5R_5Co]. In support of this apparent trend, no [C_5R_5Co] pyridine adducts have been isolated during investigations of cobalt-catalyzed pyridine syntheses. The coordination chemistry of α-diimine ligands with the [C_5R_5Co] fragment has been reported by tom Dieck and co-workers; these chelating α-diimine ligands are able to stabilize the cobalt(I) oxidation state[29] due to their increased π-acceptor character in comparison to the aromatic pyridine analogues. The cobalt(III) complex [$C_5Me_5Co(C_5H_5N)Cl_2$] has been reported,[30−32] but entry into simple cobalt(I) pyridine derivatives using this precursor was not possible. A rare example of such a cobalt(I) pyridine complex also incorporates the tetracyanoethylene (TCNE) ligand. The characterization of this complex, **3**, is not conclusive and indicates that TCNE may function as an electron acceptor for the electron-rich cobalt(I) center (an alternative structure is **3′**, in which the cobalt oxidation state could be regarded as +3).[33] The homoleptic cationic pyridine complex [$Co(py)_6$][BPh_4] has been reported[34] and used as a precursor for catalytic hydrosilylations.[35] In recent years, Cp*-type ligands functionalized with a dangling nitrogen donor group were introduced and utilized to prepare novel cobalt complexes. As expected, the donor group can coordinate to a Co(III) center (complex **4**), while no interaction is observed in the Co(I) oxidation state[36] (complex **5**).



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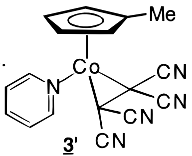
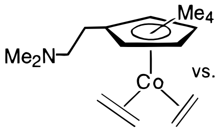
vs.



3′



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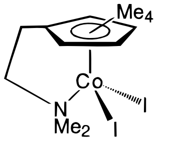

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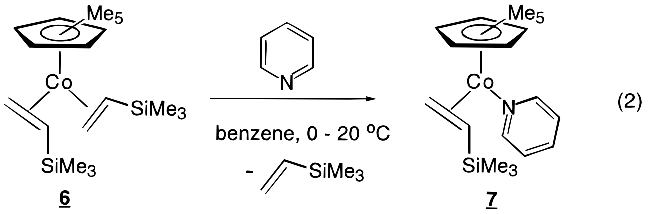
We report here the use of the labile cobalt(I) bis(olefin) complex [$C_5Me_5Co(C_2H_3SiMe_3)_2$] (**6**) for the synthesis of the [$C_5Me_5Co(C_2H_3SiMe_3)$(pyridine)] complex and the reactivity of this complex in catalytic H/D exchange reactions. Using 4-phenylpyridine, a cobalt(I) olefin pyridine complex was prepared from **6** and structurally characterized. In addition, the reaction of **6** with bipyridine was investigated and a [$C_5Me_5Co^I$]−bipyridine complex was isolated and structurally characterized.

Results and Discussion

A. [$C_5Me_5Co(C_5H_5N)(C_2H_3SiMe_3)$]. A solution of **6** in benzene-d_6 was treated with 5 equiv of pyridine at 20 °C, and an immediate color change from the red-orange of **6** to dark green was observed. Analysis of this reaction mixture by ^1H NMR spectroscopy revealed the formation of a new cobalt species with a [C_5Me_5] resonance at 1.46 ppm (15 H) and resonances for one coordinated vinyltrimethylsilane at 2.68 (d, 1H), 1.62 (d, 1H), and 0.80 (dd, 1H) ppm and at −0.04 ppm (−$SiMe_3$, 9H). In addition, the resonances for 1 equiv of coordinated pyridine are observed at 8.58 (2H, m), 6.42 (m, 1H), and 5.95 (m, 2H), significantly shifted from the signals for free pyridine. Analysis by ^{13}C NMR spectroscopy confirms the coordination of pyridine to the cobalt center, with resonances for coordinated olefin (28.9 and 42.1 ppm) and three broadened resonances for coordinated pyridine at 157.5, 133.7, and 122.9 ppm. The removal of all volatiles results in the isolation of complex **7** as an air- and heat-sensitive dark green solid which can be stored for extended periods of time at −25 °C. On the basis of the NMR evidence, elemental analysis, and reactivity studies, complex **7** is assigned as [$C_5Me_5Co(C_2H_3SiMe_3)(C_5H_5N)$], which is a rare example of a low-valent cobalt olefin pyridine complex[37] (eq 2). The pyridine ligand is proposed to coordinate in a σ-fashion[38,39] as opposed to the η^2-π-coordination mode



(2)

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(19) Varela, J. A.; Castedo, L.; Saa, C. *J. Am. Chem. Soc.* **1998**, *120*, 12147.

(20) The reactivity of complexes such as [C_5R_5CoLL'] with L, L′ = phosphines, phosphites, CO, CNR toward electrophiles has been extensively investigated. For example, see: Werner, H.; Juthani, B. *J. Organomet. Chem.* **1981**, *209*, 211−218.

(21) Werner, H.; Hofmann, W. *Chem. Ber.* **1977**, *110*, 3481.

(22) Werner, H.; Neukomm, H.; Kläui, W. *Helv. Chim. Acta* **1977**, *60*, 326.

(23) The activation of C−S bonds was observed using [$C_5Me_5Co(C_2H_4)_2$]: Jones, W. D.; Chin, R. M. *J. Organomet. Chem.* **1994**, *472*, 311.

(24) Jones, W. D.; Chin, R. M. *Organometallics* **1992**, *11*, 2698.

(25) Green, M. L. H.; Pardy, R. B. A. *J. Chem. Soc., Dalton Trans.* **1979**, 355.

(26) Werner, H.; Heiser, B.; Klingert, B.; Döfel, R. *J. Organomet. Chem.* **1982**, *240*, 179.

(27) Werner, H.; Juthani, B. *J. Organomet. Chem.* **1981**, *209*, 211.

(28) Macomber, D. W.; Rogers, R. D. *Organometallics* **1985**, *4*, 1485.

(29) tom Dieck, H.; Haarich, M. *J. Organomet. Chem.* **1985**, *291*, 71.

(30) Kölle, U.; Fuss, B. *Chem. Ber.* **1984**, *117*, 743.

(31) Kölle, U.; Fuss, B.; Belting, M.; Raabe, E. *Organometallics* **1986**, *5*, 980.

(32) For a Cp derivative, see: Kuhn, N.; Brüggemann, H.; Winter, M. *J. Organomet. Chem.* **1987**, *320*, 391−400.

(33) Macazaga, M. J.; Delgado, M. S.; Masaguer, J. R. *J. Organomet. Chem.* **1986**, *310*, 249−254.

(34) Fachinetti, G.; Funaioli, T.; Zanazzi, P. F. *J. Chem. Soc., Chem. Commun.* **1988**, 1100.

(35) Brunner, H.; Amberger, K. *J. Organomet. Chem.* **1991**, *417*, C63−C65.

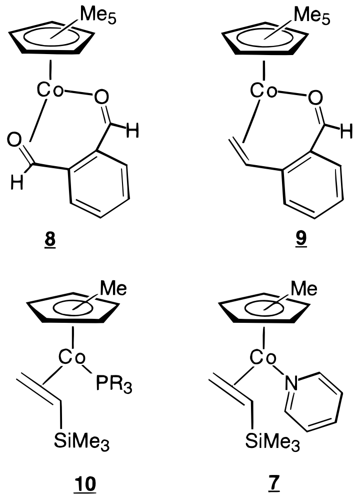
(36) Jutzi, P.; Kristen, M. O.; Dahlhaus, J.; Neumann, B.; Stammler, H. G. *Organometallics* **1993**, *12*, 2980.

(37) The proposed σ-coordination of the pyridine is supported by the local C_2 symmetry observed by NMR spectroscopy. Complex **7** shows no dynamic behavior on the NMR time scale in the temperature range of −80 to 40 °C. Fast rotation around the pyridine axis is assumed.

(38) Tomasik, P.; Ratajewicz, Z. *Pyridine Metal Complexes*; Wiley-Interscience: New York, 1985; Vol. 14.

(39) Reedijk, J. In *Comprehensive Coordination Chemistry*; Pergamon Press: New York, 1987; Vol. 2.

Chart 1. [C_5Me_5Co] Complexes Coordinated to an Acceptor/Donor Ligand Pair



8 **9** **10** **7**

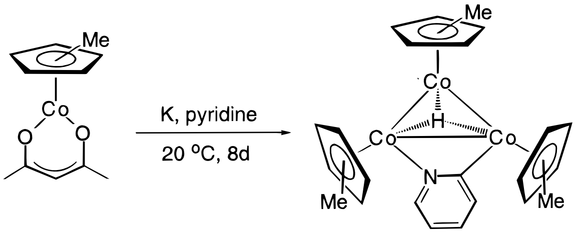
which is observed in other low-valent, electron-rich pyridine complexes.

Using **6** as a precursor, we have recently reported the synthesis of a cobalt phthalaldehyde complex in which both aldehyde coordination modes, σ and π, are observed[40] (complex **8** in Chart 1). In comparison with other cobalt(I) complexes, it appears that the presence of a π-acceptor ligand such as an olefin (or an aldehyde in **8**) is required to accommodate a σ-donor ligand such as an aldehyde (**8** and **9**) or a ligand as basic as pyridine in **7** (Scheme 1).

The reactivity of complex **7** supports this analysis. Increasing the ratio of pyridine to **6** to 20:1 does not result in the displacement of coordinated olefin to generate a bis(pyridine) adduct, nor are further reaction products originating from such an intermediate observed. Complex **7** is the only species observed after extended reaction times (24 h, 50 °C). When complex **6** is treated with $P(OMe)_3$ under analogous reaction conditions, rapid ligand substitution to form a species of type **10** (Chart 1) is observed. The second equivalent of vinyltrimethylsilane is displaced at a convenient rate at 50 °C ($k = 1.4 \times 10^{-4}$ s^{-1})[41] to yield [$C_5Me_5Co(P(OMe)_3)_2$].

Complex **6** was dissolved in pyridine-d_5 to form a dark green solution. NMR analysis confirms the formation of a single product, complex **7**-d_5 in addition to 1 equiv of free vinyltrimethylsilane. The thermolysis of **7** in pyridine-d_5 was followed for extended periods of time. Further reactivity was observed as detailed below, but the formation of a bis(pyridine) adduct was never observed. This result indicates the strong preference of the [C_5Me_5Co] moiety to bind the appropriate combination of ligands to stabilize the cobalt(I) oxidation state. This also suggests that under these conditions pyridine does not function as a π-acceptor type ligand as observed in, for example, other low-valent π-coordinated pyridine−metal complexes.

Attempts to prepare a cobalt(I) olefin pyridine complex using procedures based on the reduction of cobalt(II) precursors were not successful. The reduction of Kölle's cobalt(II) pyridine complex **11**, [$C_5Me_5Co(C_5H_5N)Cl$],[31] with sodium amalgam in the presence of ethylene gave a mixture of inseparable cobalt complexes which contained approximately 30% of the desired pyridine ethylene complex. The reduction of cobalt(II) precursors in neat pyridine was also unsuccessful. Schneider has shown that [$C_5Me_5Co(acac)$] can be used as a precursor to cobalt(I) pyridine complexes in a potassium reduction in neat pyridine (20 °C, 8 days). A M_3-cluster unit coordinated to one molecule of pyridine was isolated (eq 3).[42]



(3)

These results indicate that the presence of a π-acceptor ligand, such as an olefin, is required to prevent aggregation to polynuclear systems. The presence of the highly basic pyridine ligand is not sufficient to stabilize the electron-rich low oxidation state. Oxidative addition is observed in an orthometalation reaction in Schneider's example.

B. Participation of 7 in C−H Bond Activation Reactions. Solutions of **6** in benzene-d_6 catalyze H/D exchange reactions at 22 °C, which result in the selective incorporation of deuterium into the α-positions of the coordinated olefin.[41] Olefin dissociation is followed by the oxidative addition of benzene-d_6, which is followed by reversible olefin insertion. Similarly, thermolysis of **7** in benzene-d_6 at 22 °C also results in selective deuteration of the α-position of the coordinated olefin. The formation of **7**-*d* is evident on the basis of the change of the resonances for coordinated olefin (the resonances at 2.68 and 1.62 ppm are reduced to singlets, while the resonance at 0.80 ppm disappears). This reaction is considerably slower than deuterium incorporation into **6**, and complete deuteration is only observed after 5 h. These results support pyridine dissociation as the initial step to generate the 16-electron intermediate [$C_5Me_5Co(C_2H_3SiMe_3)$], which is common for catalytic H/D exchange in both **6** and **7** (Scheme 1).[43] Pyridine seems to be more tightly bound in **7** in comparison to the olefin in **6** for the initial dissociation reactions. The steric crowding in **6** is most likely responsible for the high reactivity. The pyridine ligand in **7** is expected to be more labile toward ligand substitution reactions than vinyltrimethylsilane on the basis of the above analysis of the combination of ligands found in stable cobalt(I) complexes. Olefin dissociation from **7** can generate a [$C_5Me_5Co(C_5H_5N)$] fragment, but the reactivity of this species in bond activation reactions cannot be ascertained using H/D exchange experiments.[44]

Thermolysis of **7** in the presence of excess pyridine (20 equiv) in benzene-d_6 at 22−50 °C results in a

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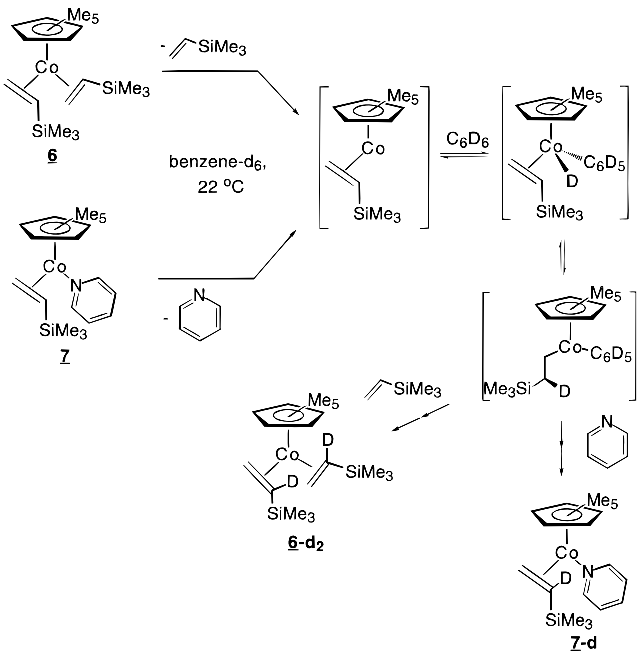
(40) Lenges, C. P.; White, P. S.; Brookhart, M. S. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 552.

(41) Lenges, C. P.; Brookhart, M.; Grant, B. E. *J. Organomet. Chem.* **1997**, *528*, 199.

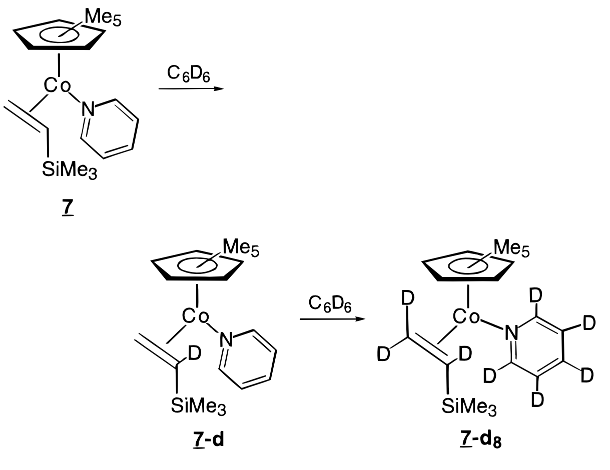
(42) Schneider, J. J. *Chem. Ber.* **1995**, *128*, 321.

(43) Poli, R.; Smith, K. M. *Eur. J. Inorg. Chem.* **1999**, 877.

Scheme 1. H/D Exchange Catalyzed by 6 or 7



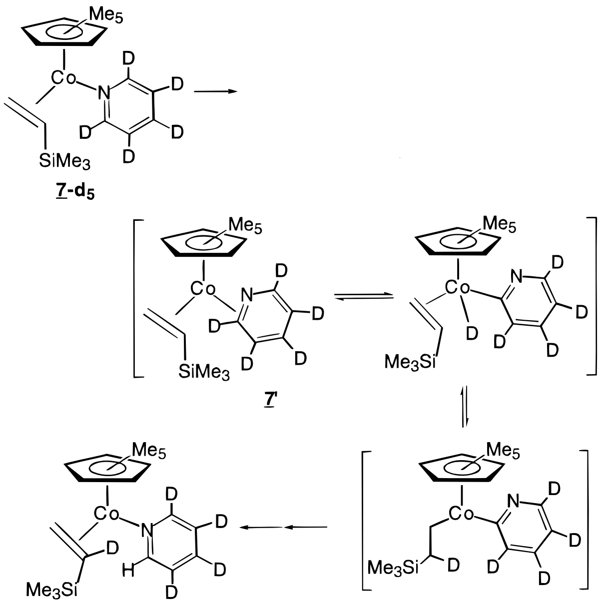
reduced rate for the H/D exchange process, as expected on the basis of the dissociative reversible first step in this reaction. If the thermolysis of **7** in benzene-d_6 is continued (40−80 °C, 8−12 h), deuterium incorporation into coordinated pyridine is observed as well. After 5 h at 45 °C the olefinic resonance for the α-position of **7** has vanished while the resonance at 2.68 ppm (β-hydrogen) has been reduced to 80% of the original value (50% after 11 h; similar D incorporation is observed at the other β-position). The formation of deuterated **7**-d_8 was confirmed in a ligand substitution reaction in which protiopyridine was added to a reaction mixture undergoing thermolysis. Ligand exchange occurs and pyridine-d_5 is substituted for protiopyridine, as indicated by the appearance of resonances for coordinated pyridine in the ^{1}H NMR spectrum. The coordinated olefin shows considerable deuterium incorporation at this point. Equation 4 summarizes the discussed kinetically distinguished deuteration sequence; the α-position of vinyltrimethylsilane exhibits more rapid exchange than the β-positions and the pyridine C−H positions.[44]



(4)

Deuteration of the coordinated pyridine originates from C−H activation of pyridine and H/D exchange from deuterated olefin. Vinyltrimethylsilane functions in this process as a shuttle for the deuterium label. The cobalt-mediated bond activation of the solvent (benzene-d_6) first incorporates the deuterium label into the coordinated olefin. From there it is delivered into pyridine via a series of reversible bond activation and insertion processes.

In a different experiment, complex **6** was treated with pyridine-d_5 (4 equiv) in cyclohexane-d_{12} (complex **6** exhibits no H/D exchange with cyclohexane). After mixing, complex **7** is generated exclusively; the residual resonances for pyridine-d_5 are integrated in a ratio of 1:1:1 at this point (this reflects the degree of deuteration of commercial pyridine-d_5). After thermolysis at 60 °C for 40 h a significant increase is observed for the residual resonances of pyridine-d_5 (the combined normalized resonances accounted for 0.25 proton prior to thermolysis; an increase to 2.1 protons was observed), while the resonances of free vinyltrimethylsilane show considerable deuterium incorporation.[45] Significantly, the residual resonance for the 2,6-positions is increased 3-fold in comparison to the resonance for the 3,5-positions; the 4-position is increased to half of the intensity compared to the 3,5-positions. On the basis of the preference for 2,6-deuteration it seems plausible that initial isomerization of the σ-coordinated pyridine to the π-coordinated isomer **7′** directs the C−H(D) bond activation step (eq 5). The isomerization to other sites of the coordinated pyridine is possible, which results in roughly equal H/D exchange reactivity for the 3,5-positions and the 4-position (eq 5). Jones and co-workers have clear evidence for the intervention of a dynamic



(5)

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[44] Scheme 1 is a condensed version of this H/D exchange mechanism which has been detailed in ref 41 for **6**. The deuteration of the α-position is significantly preferred in this exchange process, as discussed in ref 41, where well-behaved pseudo-first-order kinetics are observed. The deuteration of the β-position of vinyltrimethylsilane in **6** occurs at higher temperatures, not without some decomposition. H/D exchange into the β-site of the coordinated olefin in **7** occurs as described without decomposition.

[45] A reviewer suggested that decomposition products might also be responsible for H/D exchange. The controlled thermolysis at 60 °C in cyclohexane did not generate significant decomposition products (<2%) during the course of this H/D exchange experiment; the only species present was **7**.

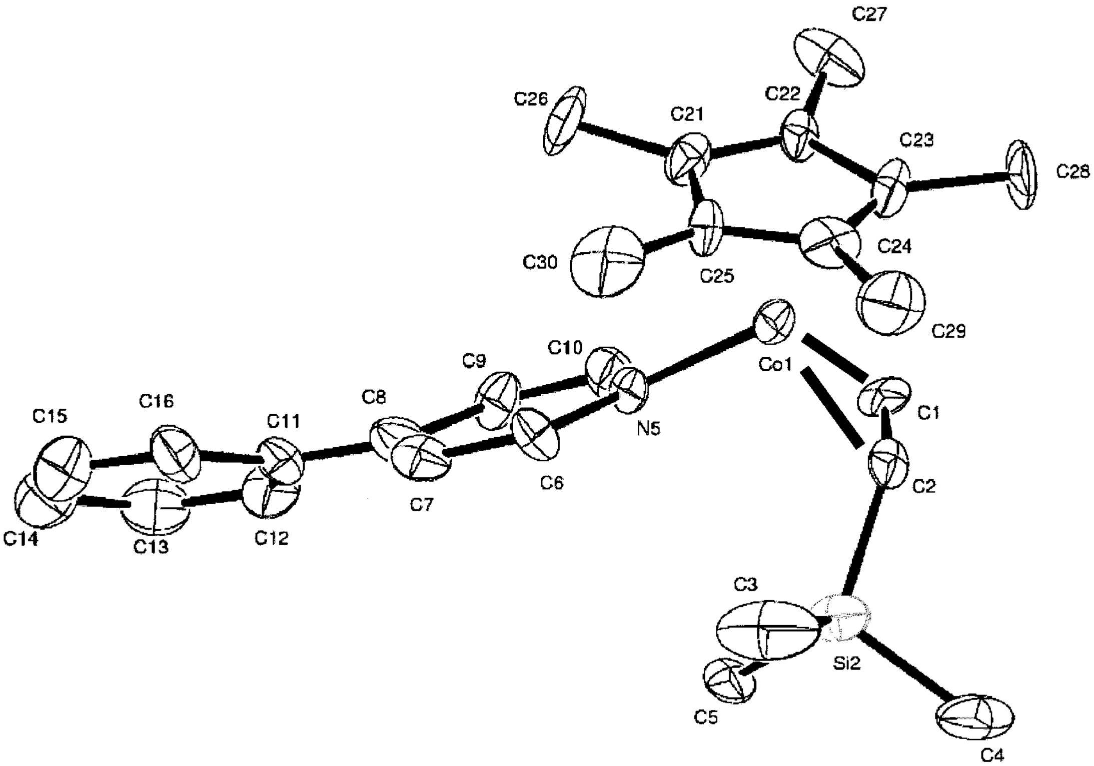

Figure 1. ORTEP diagram of complex **12**. Ellipsoids are drawn with 50% probability. Selected bond distances (Å) and angles (deg): Co−N = 1.947(3), Co−C1 = 1.975(3), Co−C2 = 2.025(3), C1−C2 = 1.425(4), Si−C2 = 1.824(4), N−C6 = 1.346(4), N−C10 = 1.345(3), C6−C7 = 1.384(4), C7−C8 = 1.393(4), C8−C9 = 1.377(4), C9−C10 = 1.368(4), C8−C11 = 1.485(4); Co−N−C6 = 123.9(2), C6−N−C10 = 115.1(3), Co−C2−Si = 120.9(2), Co−C2−C1 = 67.3(2), Si−C2−C1 = 128.3(2).

η^2-coordinated arene intermediate similar to **7′** in Rh-mediated bond activation reactions.[3] Extended heating of these reaction mixtures did not result in olefin−pyridine coupling; decomposition to uncharacterized products was observed.[46,47]

Analogous H/D exchange reactions are observed if pyridine-d_5 is used as a solvent. Deuterium incorporation into coordinated olefin is observed during thermolysis; extended heating results in decomposition products. While the olefinic ^{1}H resonances of **7** decrease during the exchange process, the corresponding resonances for coordinated pyridine do not significantly increase. Fast ligand exchange of coordinated pyridine with the pyridine-d_5 solvent results in an overall increase of the residual ^{1}H solvent resonances due to protio incorporation.[48]

C. Reaction of 4-Phenylpyridine with 6. Attempts to characterize **7** by X-ray crystallographic analysis were not successful. Using 4-phenylpyridine in place of pyridine allowed the synthesis of the analogous cobalt(I) olefin pyridine complex **12**. Spectroscopic features similar to those of **7** are observed: a ^{1}H NMR Cp* resonance at 1.48 ppm (15 H) along with olefinic resonances at 3.72 (d, 1H), 1.72 (d, 1H), and 0.75 (dd, 1H) ppm and a $-SiMe_3$ resonance at 0.01 (s, 9H) ppm. Two broad resonances at 6.34 (2H) and 8.68 (2H) ppm correspond to the substituted pyridine. The resonances assigned to the phenyl group are at 6.92−7.15 (m, 5H) ppm.

Complex **12** shows reactivity similar to that of **7**. Thermolysis of a reaction mixture of **12** (5 mol %) and a 1:1 ratio of vinyltrimethylsilane and 4-phenylpyridine in benzene-d_6 at 65 °C for 24 h results in complete deuteration of the coordinated olefin of **12**. ^{1}H NMR resonances for excess 4-phenylpyridine are reduced by 90% due to deuteration. The residual resonance of benzene-d_6 has been significantly increased in intensity during this process. The free vinyltrimethylsilane has also been deuterated; the α-position shows a roughly 3:1 preference for deuteration relative to the β-positions based on the reduction in integration intensity. The phenyl substituent has been deuterated to a lesser extent; however, clear evidence for this is observed. Coupling products based on olefin addition are not observed.[47] It was possible to obtain single crystals of **12** from pentane which were suitable for a X-ray structure determination. The ORTEP diagram for complex **12** is shown in Figure 1.

The 4-phenylpyridine ligand of **12** is essentially parallel to the two olefinic carbons. A possible perpendicular arrangement is not likely, on the basis of unfavorable steric interactions with the [C_5Me_5] group. The 4-phenyl substituent is twisted roughly 40° out of the pyridine plane. The distance C8−C11 of 1.485 Å is characteristic for a biphenyl fragment. This suggests

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[46] Extended thermolysis experiments were conducted in the temperature range of 60−100 °C for 24−72 h, where some decomposition occurs. We cannot rule out some role for decomposition products in H/D exchange at higher temperatures.

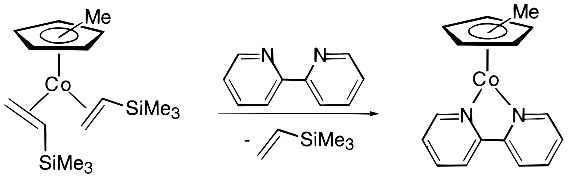
[47] This is in contrast to the unique coupling chemistry observed by Jordan and co-workers using zirconocene systems: Jordan, R.; Taylor, D. *J. Am. Chem. Soc.* **1989**, *111*, 778.

[48] If thermolysis is extended to 48 h at 65 °C, further reactivity is observed to generate unassigned organometallic cobalt complexes. During this process a significant decrease is observed in the $-SiMe_3$ resonance intensity, indicating deuteration of this group. This result suggests that the low-valent cobalt species is capable of activating sp^3 C−H bonds of a Si−Me group.

that the 4-phenyl substituent experiences little steric distortion caused by the coordination to the transition metal. The Co−C1 distance is shorter (1.975 Å) than the Co−C2 distance (2.025 Å), consistent with the fact that C2 bears the bulky $SiMe_3$ group. In comparison to the Co−C distances of **6** (Co−C1 = 2.002 Å and Co−C2 = 2.058 Å)[6] an overall reduction in bond length is noted which might be due to the reduced steric impact of the coordinated pyridine ligand compared to a second vinyltrimethylsilane ligand.[49] The C1−C2 bond length of 1.425 Å is longer than the corresponding distance in **6** of 1.404 Å, which suggests that back-bonding from filled d orbitals has increased in **12** compared to **6**, as expected with an ancillary σ-donor type ligand such as pyridine. The Co−N distance in **12** of 1.947 Å is long compared to the Co−N distance of 1.917 Å in the cobalt(II) complex $[C_5Me_5Co(C_5H_5N)Cl]$ (**11**). The lower oxidation state in **12** and the increased steric crowding at cobalt might explain this difference.

D. Reaction of 6 with 2,2′-Bipyridine. An alternative strategy for assembling two pyridine type ligands in the coordination sphere of the $[C_5Me_5Co]$ moiety was investigated in the reaction of 2,2′-bipyridine with **6**. Kölle and co-workers reported[31] the valence disproportionation of $[C_5Me_5CoBr]_2$ with bipyridine to generate $[C_5Me_5CoBr(bipy)]Br$ and $[C_5Me_5Co(bipy)]$ (**13**). Complex **13** was described as a dark violet, air-sensitive crystalline solid, but no detailed spectroscopic characterization was reported. In a different approach, Kaim and co-workers[50] reported the synthesis of **13** by potassium reduction of $[C_5Me_5CoCl(bipy)]Cl$. Severely broadened ^1H NMR features were reported for this complex which were ascribed to thermally accessible spin states above the singlet ground state, as observed in other examples of 3d organometallic complexes.[51]

Complex **6** seemed to be the ideal precursor to attempt a more controlled synthesis of the $[C_5Me_5Co(bipy)]$ complex. Treatment of **6** in acetone-d_6 with 1 equiv of 2.2′-bipyridine at 20 °C resulted in an immediate color change of the reaction mixture to deep purple. Analysis by ^1H NMR spectroscopy showed the displacement of both equivalents of vinyltrimethylsilane and the formation of one new cobalt complex with a single $[C_5Me_5]$ resonance at 1.92 ppm (s, 15H). In addition, four sharp resonances were observed for 1 equiv of coordinated bipyridine (eq 6). Notably, the resonance for the protons in the 3,3′-positions of bipyridine at 9.94 ppm (d, 2H) is shifted by roughly 1.4 ppm from those in uncoordinated bipyridine (8.59 ppm). Additional resonances are observed at 7.48 (d, 2H), 7.26 (t, 2H), and 6.82 (t, 2H) ppm.



6 **13** (6)

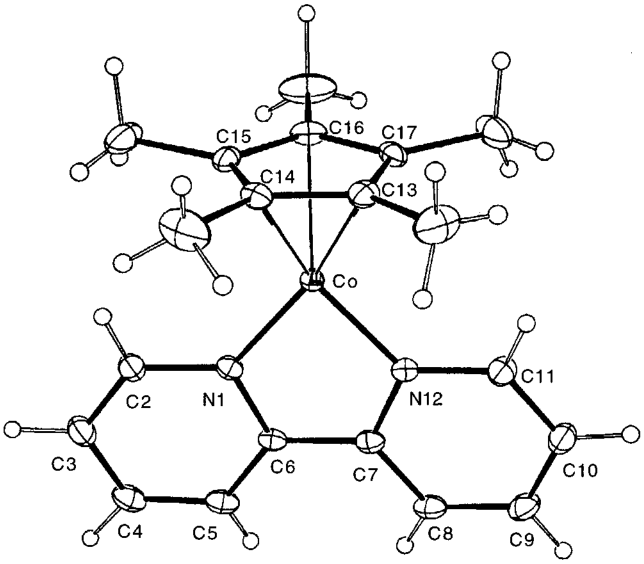


Figure 2. ORTEP diagram of complex **13**. Ellipsoids are drawn with 50% probability. Selected bond distances (Å) and angles (deg): Co−N1 = 1.8750(17), Co−N12 = 1.8766(17), Co−C13 = 2.0699(22), Co−C14 = 2.0916(22), Co−C15 = 2.0762(22), Co−C16 = 2.1074(18), Co−C17 = 2.0776(21), N1−C2 = 1.376(3), N1−C6 = 1.385(3), C2−C3 = 1.366(3), C3−C4 = 1.401(4), C4−C5 = 1.364(4), C5−C6 = 1.410(3), C6−C7 = 1.419(3), C7−C8 = 1.410(3), C7−N12 = 1.389(3), C8−C9 = 1.371(3), C9−C10 = 1.404(4), C10−C11 = 1.374(3), C11−N12 = 1.366(3); N1−Co−N12 = 83.13(8), Co−N1−C2 = 128.33(16), Co−N1−C6 = 115.61(13), N1−C6−C7 = 112.45(18); N12−Co−N1−C2 = 171.3(3), N1−Co−N12−C7 = 7.66(2), Co−N1−C2−C3 = 178.6 (4), C6−C7−N12−Co = 6.10(15), N1−C6−C7−N12 = 0.20(2).

The ^{13}C NMR spectrum also suggests the symmetric coordination of bipyridine to the $[C_5Me_5Co]$ fragment, since only five signals are observed, which compare well to the data reported by Kaim and co-workers.[49,52−54] These results indicate that complex **13** shows no unusual NMR behavior and suggests that the diamagnetic ground state is essentially completely populated in this 18-electron complex. In accord with prior reports, **13** is extremely air-sensitive and a solution of **13** generated as described shows a significant degree of decomposition after 24 h at 20 °C. NMR features are broadened during this process, which indicates the formation of paramagnetic complexes. Ultimately, no resonances are observed in the ^1H NMR spectrum in the $[C_5Me_5]$ region for the deep purple solution. Dynamic processes are not observed on the NMR time scale in the presence of excess bipyridine, which suggests that the exchange of free with coordinated bipyridine is slow. Complex **13** is quite insoluble and precipitates from solution during the course of several hours. Redissolving this purple precipitate generates solutions of **13** with sharp NMR features as described above.

Cooling these reaction mixtures in acetone-d_6 to −25 °C for 2 days results in the deposition of a purple crystalline material that was suitable for X-ray structural analysis. The ORTEP diagram of **13** is shown in

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(49) The increased back-bonding caused by the basic pyridine ligand could also be the reason for the reduced bond length.

(50) Kaim, W.; Reinhardt, R.; Waldhoer, E.; Fiedler, J. *J. Organomet. Chem.* **1996**, *524*, 195.

(51) Kaim, W.; Roth, B.; Olbrich-Deussner, R.; Gross-Lannert, J.; Jordanov, J.; Roth, E. K. H. *J. Am. Chem. Soc.* **1992**, *114*, 5693.

(52) Kaim and co-workers have investigated analogous Rh and Ir complexes in detail as catalysts for hydride transfer reactions: Kaim, W.; Reinhardt, R.; Sieger, M. *Inorg. Chem.* **1994**, *33*, 4453.

(53) Ladwig, M.; Kaim, W. *J. Organomet. Chem.* **1991**, *419*, 233.

(54) Ladwig, M.; Kaim, W. *J. Organomet. Chem.* **1992**, *439*, 79.

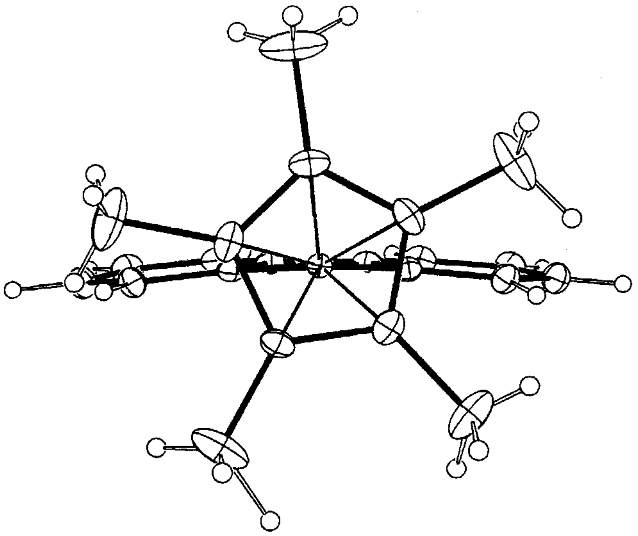
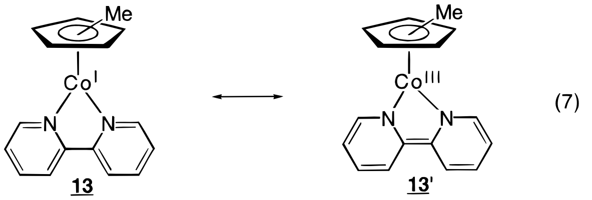


Figure 3. ORTEP diagram of complex **13**. Ellipsoids are drawn with 50% probability.

Figure 2. As suggested by the NMR data, complex **13** shows the coordination of 1 equiv of 2,2′-bipyridine to the [C_5Me_5Co] fragment. Both cobalt−nitrogen distances are similar (1.876 Å) and significantly shorter than the Co−N distance of **12** (1.947 Å). The torsion angle N1−C6−C7−N12 = 0.20° indicates the planar coordination of the bipyridine unit. The molecule possesses a mirror plane bisecting the bipyridine moiety (see Figure 3). In line with this observation are the torsion angles defining each pyridine ring, which are close to either 180 or 0°, supporting the planar ring system. The N1−Co−N12 angle is 83°, while the C6−C7 bond that connects both pyridine rings has a length of 1.419 Å. It is interesting to compare this with the structural data for uncomplexed 2,2′-bipyridine.[55] The C−C bond connecting both pyridine rings in uncomplexed bipyridine is 1.50 Å, considerably longer than C6−C7 in **13**. This suggests that the coordination of the [C_5Me_5Co] fragment contributes to an increased olefinic character for C6−C7 and supports a contribution of a bis(amido) Co(III) resonance form to the structure of **13**. A comparison of the C6−N1 bond distance in **13** (1.385 Å) with the corresponding distance in the uncomplexed bipyridine (1.35 Å) is in accord with a contribution from **13′** (eq 7).[56]



(7)

In the series of [C_5R_5Co] complexes with unsaturated chelating dinitrogen ligands a cobalt(III) resonance structure (similar to **13′**) is most relevant in systems bearing ligands with an increased π-acceptor character. In Trogler's tetraazadiene complex[57,58] this effect is especially prevalent. The cobalt(I) α-diimine complexes described by tom Dieck also show this feature. On the basis of the reduced acceptor ability and increased basicity of bipyridine in comparison to these more π-acidic systems, a description of **13** as a cobalt(I) complex is supported.[59]

The Co−C distances for the C_5Me_5 ligand show a variation of 0.0375 Å. The C−C distances vary from 1.404 Å for C13−C14 to 1.430 Å for C13−C17 and 1.416 Å for C17−C16. The pattern in the C−C distances is indicative of only a slight ene-allyl distortion in the C_5Me_5 fragment. This is in contrast to the cobalt(II) complex [$C_5Me_5Co(acac)$] and the nickel complex [$C_5Me_5Ni(acac)$],[60] which clearly show this distortion and approach an extreme 16-electron allyl resonance form. Complex **13**, however, is better described as an 18-electron complex, which is in agreement with the diamagnetic nature of the ^1H NMR spectrum.

Summary. The high reactivity of the bis(olefin) complex **6** in dissociative ligand substitution reactions has allowed entry into a new class of low-valent [$C_5Me_5Co^I$] complexes supported by pyridine and bipyridine ligands. Cobalt(I) pyridine complexes have been formulated as intermediates in the cobalt-catalyzed pyridine synthesis using alkynes and nitriles. However, well-defined examples for this class of compounds have not been isolated. The labile character of the new [C_5Me_5Co(pyridine)(olefin)] complexes **7** and **12** in substitution reactions has been illustrated in catalytic H/D exchange reactions based on C−H/D bond activation reactions mediated by a reactive 16-electron cobalt species. Even in the presence of a large excess of pyridine the second olefin is not displaced to generate a cobalt(I) bis(pyridine) species. On the basis of the structural analysis of **12** and the reactivity studies of **7** and **12**, a possible rationale for this behavior is the preference of the Co(I) center for binding a strong σ-donor ligand in combination with a π-acceptor ligand such as an olefin. Using bipyridine as a bidentate chelating ligand enables substitution of both olefinic ligands and generation of a cobalt(I) bipyridine complex, **13**.

Experimental Section

General Considerations. All manipulations of air- and/or water-sensitive compounds were performed using standard high-vacuum or Schlenk techniques. Argon and nitrogen were purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. Solid organometallic compounds were transferred in an argon-filled Vacuum Atmospheres drybox. ^1H and ^{13}C NMR chemical shifts were referenced to residual ^1H NMR signals and to the ^{13}C NMR signals of the deuterated solvents, respectively. Elemental analyses were performed by Atlantic Microlabs, Inc., of Norcross, GA.

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(55) In the structure of bipyridine the rings are coplanar; however, the N atoms are "trans" to one another, which generates a structure with inversion symmetry: Cagle, F. W. *Acta Crystallogr.* **1948**, *1*, 158. Merritt, L. L.; Schroeder, E. O. *Acta Crystallogr.* **1956**, *9*, 801.

(56) Kaim and co-workers have described the α-diimine Ir complex [$C_5Me_5Ir(ArN{=}CH{-}CH{=}NAr)$], which also shows a considerable ene-1,2-diamide Ir(III) resonance form, as suggested by the short C−C bond length of 1.33 Å: Greulich, S.; Kaim, W.; Stange, A. F.; Stoll, H.; Fiedler, J.; Zalis, S. *Inorg. Chem.* **1996**, *35*, 3998.

(57) Gross, M. E.; Trogler, W. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 192.

(58) Gross, M. E.; Trogler, W. C.; Ibers, J. A. *Organometallics* **1982**, *1*, 732.

(59) Kölle and co-workers have generated [CpCo(bipy)] electrochemically. In comparison to [CpCo(dad)] (dad = α-diimine) oxidation of the bipy complex is more favored: Kölle, U. *J. Organomet. Chem.* **1980**, *184*, 379.

(60) Smith, M. E.; Andersen, R. A. *J. Am. Chem. Soc.* **1996**, *118*, 11119.

Materials. All solvents used for synthesis were deoxygenated and dried via passage over a column of activated alumina.[61] Complex **6**, [$C_5Me_5Co(C_2H_3SiMe_3)_2$], was prepared by following the literature procedure.[6] Tetrahydrofuran was distilled from sodium benzophenone−ketyl prior to use. Benzene-d_6, toluene-d_8, and cyclohexane-d_{12} were dried over potassium benzophenone−ketyl, and acetone-d_6 was dried over CaH_2; all were vacuum-transferred and degassed by repeated freeze−pump−thaw cycles. Pyridine (Sure-Seal bottle) and bipyridine are commercial grade (Aldrich) and were used as received.

Synthesis of [$C_5Me_5Co(C_2H_3SiMe_3)(C_5H_5N)$] (7). Complex **6** (0.2 g, 5.04 × 10^{-4} mol) was dissolved in benzene at 20 °C. Pyridine (5 equiv, 0.2 g) was added to the stirred solution. An immediate color change to dark green (olive green) was observed. The reaction mixture was stirred for an additional 20 min at 20 °C. All volatiles were removed in vacuo to leave a green solid which was pure by NMR spectroscopy and elemental analysis. Complex **7** is best stored at −20 °C in an inert atmosphere. Spectroscopic data for **7** are as follows. ^1H NMR (300 MHz, benzene-d_6, 20 °C): δ (ppm) 1.46 (s, 15 H, C_5Me_5); 2.68 (d, 10.5 Hz, 1H); 1.62 (d, 8.3 Hz, 1H); 0.80 (dd, 10.5, 8.3 Hz, 1H); −0.04 (s, 9H, $SiMe_3$); 8.58 (m, 2H), 6.42 (m, 1H) and 5.95 (m, 2H). $^{13}C\{^1H\}$ NMR: δ (ppm) 9.63, 87.3 (C_5Me_5); 0.71 ($-SiMe_3$); 28.86 (d, $=CH$); 42.06 (t, $=CH_2$); 157.5 (br, 2C-py); 133.7 (br, py); 122.9 (br, py). Anal. Calcd: C, 64.31; H, 8.63; N, 3.75. Anal. Found: C, 64.50; H, 8.62; N, 3.69.

Synthesis of [$C_5Me_5Co(C_2H_3SiMe_3)(4\text{-}Ph-C_5H_4N)$] (12). Complex **6** (0.2 g, 5.04 × 10^{-4} mol) was dissolved in pentane at 20 °C. 4-Phenylpyridine (1.1 equiv) was added to the stirred solution. An immediate color change to brown was observed. The reaction mixture was stirred for an additional 20 min at 20 °C. The solution was cooled to −30 °C for 36 h and decanted to leave **12** as black-brown crystals. This material was used for the structural analysis. Complex **12** is best stored at −20 °C in an inert atmosphere. Spectroscopic data for **12** are as follows. ^1H NMR (300 MHz, benzene-d_6, 20 °C): δ (ppm) 1.48 (s, 15 H); 3.72 (d, 1H); 1.72 (d, 1H); 0.75 (dd, 1H); 0.01 (s, 9H); 6.34 (br, 2H); 8.68 (br, 2H); 6.92−7.15 (m, 5H). $^{13}C\{^1H\}$ NMR: δ (ppm) 8.90, 86.7 (C_5Me_5); 41.4, 28.6 ($CH_2{=}CH$); −0.3 ($SiMe_3$); 157.0 (br, 2C-py); 147.1, 145.2, 139.5, 130.5, 128.5, 125.9, 119.7 ($C_6H_5\text{-}C_4H_4N$).

Synthesis of [$C_5Me_5Co(bipy)$]. Complex **6** was dissolved in acetone and the solution cooled to 0 °C. To this was added a solution of 2,2′-bipyridine (1.1 equiv) in acetone; an immediate color change to deep purple was observed. The reaction mixture was stirred for 30 min. If the solution remains at this temperature for a longer period of time, purple material precipitates. Cooling the reaction mixture to −78 °C results in increased precipitation of **13**. After filtration **13** can be isolated and stored for a short time at −20 °C under an inert atmosphere. Complex **13** will decompose rapidly if not handled under an inert atmosphere. The storage of the purple material under an inert atmosphere at 20 °C over time results in material which shows broadened NMR features (eventually the loss of all NMR features is observed).

To confirm the identity of the initial reaction products with complex **13**, bipyridine (1 equiv) was added to an acetone-d_6 solution of **6**. Quantitative formation of **13** was observed after 15 min at 20 °C. After 30 min considerable precipitation of purple crystalline solids was observed. Decanting the solvent and redissolving these solids identifies that material as **13**. Aging (12−24 h) the sealed NMR tube at 20 °C results in a loss of all NMR features in the normal ^1H NMR range, while no assignable resonances are observed from 100 to −100 ppm. Spectroscopic data for **10** are as follows. ^1H NMR (300 MHz, acetone-d_6, 20 °C): δ (ppm) 1.92 (s, 15 H); 9.94 (d, 2H); 7.48 (d, 2H); 7.26 (t, 2H); 6.82 (t, 2H). $^{13}C\{^1H\}$ NMR: δ (ppm) 9.16, 84.3 (C_5Me_5); 115.5, 119.5, 122.4, 141.5, 152.3 (aromatic).

Table 1. Crystallographic Data and Refinement Details for 12 and 13

	12	13
mol formula	$CoNSiC_{26}H_{36}$	$CoN_2C_{20}H_{23}$
fw	449.60	350.35
cryst dimens (mm)	0.08 × 0.34 × 0.35	0.20 × 0.20 × 0.10
no. of rflns for cell determn	5078	8192
a (Å)	19.613(1)	7.6254(3)
b (Å)	8.018(1)	13.5145(6)
c (Å)	15.818(1)	16.5949(7)
V (Å^3)	2479.9	1710.16(12)
space group	$P2_1/c$ (No. 14)	$P2_12_12_1$
Z	4	4
μ(Mo Kα) (mm^{-1})	0.75	1.00
T (°C)	−90	−100
no. of rflns	15468	16195
no. of unique rflns	2480	4874
no. of observns ($I > 3.0\sigma(I)$)	2439	4019
R; R_w	0.032, 0.030	0.032, 0.032
GOF	0.92	1.15

X-ray Structural Analysis for 12. Data were collected in a Bruker SMART 1K CCD system. The structure was solved by direct methods using teXsan (SIR-92). Refinement was done using the Z program suite, by full-matrix least squares on F; scattering factors were obtained from ref 63. Crystallographic data and refinement details are given in Table 1. **X-ray Structural Analysis for 13.** Data were collected on a Siemens SMART diffractometer, using the ω-scan method. The structure was solved by direct methods. Refinement was by full-matrix least squares with weights based on counter statistics. Hydrogen atoms were included in the final refinement using a riding model with thermal parameters derived from the atom to which they are bonded. All computations were performed using the NRCVAX suite of programs.[62]Crystallographic data and refinement details are given in Table 1.

Acknowledgment is made to the National Institutes of Health (Grant GM 28938) for financial support. C.P.L. thanks the *Fonds der Chemischen Industrie* of Germany for a Kekulé fellowship.

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

OM990860S

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(61) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(62) Gabe, E. J.; LePage, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

(63) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.