Cyclopentadienone-like Behavior of Fluorenone and 4,5-Diazafluoren-9-one

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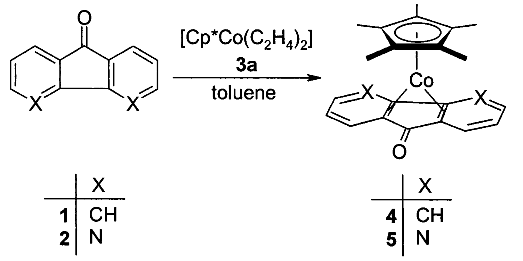
*Summary: The aromatic compounds fluorenone (**1**) and 4,5-diazafluoren-9-one (**2**) behave like cyclopentadienones in their reaction with [Cp*Co(C_2H_4)$_2$] (**3a**), affording the sandwich-type complexes [Cp*Co(η^4-**1**)] (**4**) and [Cp*Co(η^4-**2**)] (**5**), respectively, whose structures have been determined by X-ray diffraction. Both complexes show double-bond fixation in their η^2-coordinated six-membered rings and belong to a new structure type of mononuclear organometallics. The cobalt-coordinated ligands **1** and **2** present in **4** and **5**, respectively, may be replaced by two molecules of carbon monoxide. In accord with their cyclopentadienone-like nature, they are nucleophilic and undergo O-acylation with acetyl chloride, affording cobaltocenium species.*

The six-membered rings in fluorenone (**1**) are aromatic and do not show any significant bond length alternation.[1] The same holds true for 4,5-diazafluoren-9-one (**2**).[2] Not unexpectedly, therefore, **1** acts as an η^6-arene ligand, forming organometallic complexes such as, for example, [(η^6-**1**)Cr(CO)$_3$][3] and [(η^6-**1**)FeCp]$^+$.[4] For **2**, only Werner type N,N-chelates, but no π-complexes, have been described to date.[5]

In contrast to expectations based on their structures, the reactions of **1** and **2** with [Cp*Co(C_2H_4)$_2$] (**3a**) afforded the air-stable complexes [Cp*Co(η^4-**1**)] (**4**) and [Cp*Co(η^4-**2**)] (**5**), respectively, where **1** and **2** show cyclopentadienone-like behavior, containing two η^2-coordinated six-membered rings (Scheme 1).[6]

Scheme 1. Synthesis of Compounds 4 and 5



The structures of both complexes have been determined by single-crystal X-ray diffraction and are rather similar to one another (Figure 1).[7] The six-membered rings show a pronounced Kekulé bond localization (Δd_{C-C} = 7 pm), the respective C−C bond orders being ca. 1.3 and 1.7.[8] Metal coordination leads to a lengthening of the C−O bond (**1** at 1.217(4) Å[1] and **4** at 1.2466(18) Å; **2** at 1.213(1) Å[2] and **5** at 1.275(2) Å), as is commonly observed for η^4-cyclopentadienone complexes.[9] The weakening of this bond upon metal coor-

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[1] Luss, H. R.; Smith, D. L. *Acta Crystallogr., Sect. B: Struct. Sci.* **1972**, *28*, 884−889.

[2] Fun, H.-K.; Sivakumar, K. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1995**, *51*, 2076−2078.

[3] Merlic, C. A.; Walsh, J. C. *J. Org. Chem.* **2001**, *66*, 2265−2274.

[4] Pierre, F.; Moinet, C.; Toupet, L. *J. Organomet. Chem.* **1997**, *527*, 51−64.

[5] Selected examples: (a) Kulkarni, P.; Padhye, S.; Sinn, E.; Anson, C. E.; Powell, A. K. *Inorg. Chim. Acta* **2002**, *332*, 167−175. (b) Wang, Y.; Perez, W.; Zheng, G. Y.; Rillema, D. P. *Inorg. Chem.* **1998**, *37*, 2051−2059. (c) Menon, S.; Rajasekharan, M. V. *Inorg. Chem.* **1997**, *36*, 4983−4987. (d) Anderson, P. A.; Deacon, G. B.; Haarmann, K. H.; Keene, F. R.; Meyer, T. J.; Reitsma, D. A.; Skelton, B. W.; Strouse, G. F.; Thomas, N. C.; Treadway, J. A.; White, A. H. *Inorg. Chem.* **1995**, *34*, 6145−6157. (e) Henderson, L. J., Jr.; Fronczek, F. R.; Cherry, W. R. *J. Am. Chem. Soc.* **1984**, *106*, 5876−5879. (f) Dickeson, J. E.; Summers, L. A. *Aust. J. Chem.* **1970**, *23*, 1023−1027.

[6] Synthesis of **4**: a stirred solution of **1** (1.08 g, 6.00 mmol) and **3a** (1.50 g, 6.00 mmol) in toluene (60 mL) was heated to 60 °C for 4 h. The mixture was cooled to room temperature. Volatile components were removed in vacuo, and the solid residue was washed with hexane (2 × 5 mL). The resulting brown microcrystalline solid was dried in vacuo. Yield: 1.18 g (53%). ^{1}H NMR (CDCl$_3$, 500 MHz): δ 1.14 (s, 15 H, Cp*), 7.24 (m, 2 H), 7.37 (m, 2 H), 7.59 (m, 4 H). ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz): δ 6.7 (C_5Me_5), 83.3 (quat C), 83.8 (quat C), 88.0 (C_5Me$_5$), 122.3 (CH), 124.9 (CH), 125.9 (CH), 127.4 (CH), 143.0 (C=O). Anal. Calcd for $C_{23}H_{23}CoO$ (374.37): C, 73.79; H, 6.19. Found: C, 73.44; H, 6.20. Synthesis of **5**: a stirred solution of **2** (3.64 g, 20.0 mmol) and **3a** (5.00 g, 20.0 mmol) in toluene (100 mL) was heated to 50 °C for 7 h. The mixture was cooled to room temperature. The precipitate was filtered off and washed with hexane (2 × 20 mL). The resulting brown microcrystalline solid was dried in vacuo. Yield: 6.88 g (91%). Anal. Calcd for $C_{21}H_{21}N_2CoO$ (376.35): C, 67.02; H, 5.62; N, 7.44. Found: C, 66.96; H, 5.41; N, 7.80. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 1.12 (s, 15 H, Cp*), 7.14 (m, 2 H), 7.95 (m, 2 H), 8.91 (m, 2 H). ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz): δ 6.9 (C_5Me_5), 89.5 (C_5Me$_5$), 101.7 (quart. C), 121.4 (CH), 135.0 (CH), 137.6 (C=O), 155.6 (CH).

[7] Single crystals were obtained by slow evaporation of an ethanol solution. Data were collected at 100 K on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation (0.710 73 Å). Crystal data for **4**: $C_{23}H_{23}CoO$, M_r = 374.34, monoclinic, space group $P2_1/c$, a = 6.9000(4) Å, b = 15.5450(14) Å, c = 15.9470(14) Å, β = 94.207(6)°, V = 1705.9(2) Å^3, Z = 4, ρ_{calcd} = 1.458 g cm^{-3}, $2\theta_{max}$ = 60°, μ = 1.013 mm^{-1}, F(000) = 784, 40 774 reflections collected, 4977 independent reflections, 4105 reflections with $I > 2\sigma(I)$, 236 parameters, GOF = 1.041, R1 = 0.0298 ($I > 2\sigma(I)$), wR2 = 0.0718 (all data), minimum/maximum residual electron density −0.316/0.405 e Å^{-3}. Crystal data for **5**·6H$_2$O: $C_{21}H_{21}N_2CoO \cdot 6H_2O$, M_r = 484.42, orthorhombic, space group $Pmn2_1$, a = 18.7670(1) Å, b = 9.1110(1) Å, c = 6.7660(2) Å, V = 1156.89(4) Å^3, Z = 2, ρ_{calcd} = 1.391 g cm^{-3}, $2\theta_{max}$ = 60°, μ = 0.785 mm^{-1}, F(000) = 512, 17 475 reflections, 3229 independent reflections, 3097 reflections with $I > 2\sigma(I)$, 183 parameters, GOF = 1.048, R1 = 0.0258 ($I > 2\sigma(I)$), wR2 = 0.0663 (all data), minimum/maximum residual electron density −0.323/0.335 e Å^{-3}.

[8] Review: Hubig, S. M.; Lindeman, S. V.; Kochi, J. K. *Coord. Chem. Rev.* **2000**, *200−202*, 831−873.

10.1021/om030615f CCC: $27.50

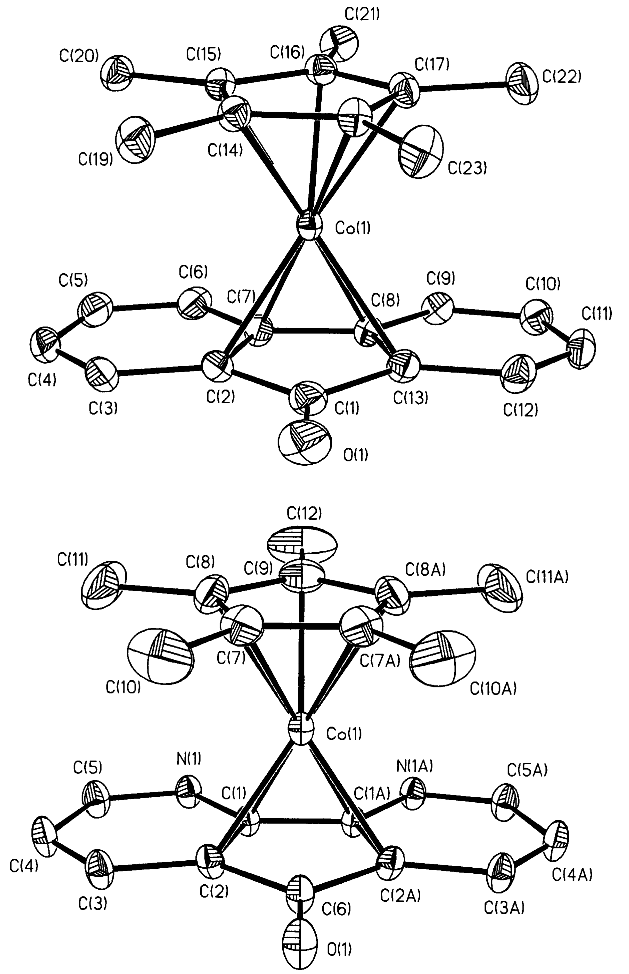

Figure 1. Molecular structures of **4** (top) and **5** (bottom). Selected atomic distances (Å): for **4**, Co(1)−C(1) = 2.2326(14), Co(1)−C(2) = 2.0916(14), Co(1)−C(7) = 2.0335(14), Co(1)−C(8) = 2.0468(14), Co(1)−C(13) = 2.0918(14), Co(1)−C(14) = 2.0442(14), Co(1)−C(15) = 2.0555(14), Co(1)−C(16) = 2.0744(14), Co(1)−C(17) = 2.0326(14), Co(1)−C(18) = 2.0427(14), C(1)−C(2) = 1.471(2), C(1)−C(13) = 1.4723(19), C(2)−C(3) = 1.427(2), C(2)−C(7) = 1.440(2), C(3)−C(4) = 1.356(3), C(4)−C(5) = 1.424(3), C(5)−C(6) = 1.361(2), C(6)−C(7) = 1.422(2), C(7)−C(8) = 1.4434(19), C(8)−C(9) = 1.4268(19), C(8)−C(13) = 1.4372(19), C(9)−C(10) = 1.363(2), C(10)−C(11) = 1.424(2), C(11)−C(12) = 1.361(2), C(12)−C(13) = 1.423(2); for **5**, Co(1)−C(1) = 2.0319(15), Co(1)−C(2) = 2.0783(15), Co(1)−C(6) = 2.170(2), Co(1)−C(7) = 2.0574(16), Co(1)−C(8) = 2.0526(17), Co(1)−C(9) = 2.081(2), C(1)−N(1) = 1.3776(15), C(1)−C(2) = 1.4441(16), C(2)−C(3) = 1.4203(17), C(3)−C(4) = 1.3667(18), C(4)−C(5) = 1.4368(17), C(5)−N(1) = 1.3142(17).

dination is also consistent with IR spectroscopic data (ν_{CO} (cm^{-1}): **1** at 1715 and **4** at 1564; **2** at 1716 and **5** at 1546). At the same time, the interannular C−C bond length decreases (**1** at 1.475(5) Å[1] and **4** at 1.4434(19) Å; **2** at 1.485(1) Å[2] and **5** at 1.441(2) Å). The keto group in cyclopentadienone complexes is always pointing away from the metal, the fold angle of the five-membered ring usually being larger than 10°.[9] In the case of **4** and **5**, this angle is considerably smaller than that (**4**, 4.8°; **5**, 2.2°), which is primarily due to the ring annelation.

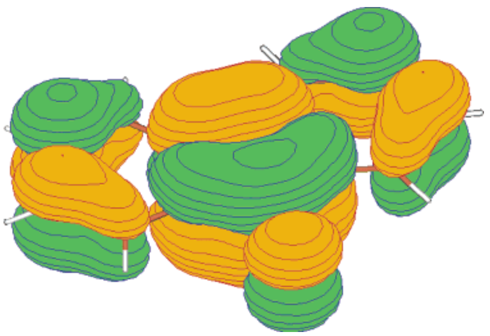

Figure 2. Structure of the LUMO of fluorenone (**1**).

These experimental findings are in accord with the results of DFT calculations (B3LYP/ECP-31g(d)),[10,11] which show that metal coordination severely affects the delocalized π-bonds of fluorenone, resulting in a double-bond fixation in the η^2-coordinated six-membered rings. This bond localization is evident from the LUMO structure of fluorenone (Figure 2). Similar to the related cyclopentadienone complexes, electron density is delocalized from the electron-rich cyclopentadienylcobalt moiety into the LUMO of the respective ligand.[9a]

The coordination of the Cp*Co fragment, η^2 to each six-membered ring,[12] is interesting for several reasons. First, the counterintuitive cyclopentadienone-like coordination of **1** and **2** is unprecedented, with η^6-fluorenone species being the only class of π-complexes of these ligands known to date. Second, in the case of **5**, π-coordination, instead of the formation of an N,N-chelate, takes place, although such a chelate has been observed for the closely related [Cp*Co(bpy)],[13] which was obtained from the reaction of [Cp*Co(CH$_2$CHSiMe$_3$)$_2$] (**3b**) with 2,2′-bipyridine (bpy). Third, only very few examples of cyclopentadienylcobalt(I) arene complexes have been described to date.

It is worth addressing the last point in more detail, since it turns out that **4** and **5** are quite unique in this context. All cyclopentadienylcobalt(I) arene complexes known so far belong to one of the following four categories: (A) mononuclear complexes of the electron-poor arenes C$_6$(CF$_3$)$_6$[14] and C$_6$(COOMe)$_6$[15] (although crystal structure determinations have not been reported for these types of compounds, there is no doubt that the arene shows η^4 coordination in each case); (B) mononuclear complexes of the electron-rich arene C$_6$Me$_6$[16] (it is generally accepted that this ligand is always η^6 coordinated, although no reliable structural data have been reported); (C) mononuclear complexes of polycyclic

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[9] (a) Gleiter, R.; Roers, R.; Rominger, F.; Nuber, B.; Hyla-Kryspin, I. *J. Organomet. Chem.* **2000**, *610*, 80−87. (b) Chinn, J. W., Jr.; Hall, M. B. *Organometallics* **1984**, *3*, 284−288. (c) Hoffmann, R.; Hoffmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 598−604.

[10] The GAMESS program system was used for the calculations: Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsanuga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347−1363.

[11] ECP according to: (a) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026−6033. (b) Stevens, W. J.; Krauss, M.; Basch, H.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 612−630. (c) Cundari, T. R.; Stevens, W. J. *J. Chem. Phys.* **1993**, *98*, 5555−5565.

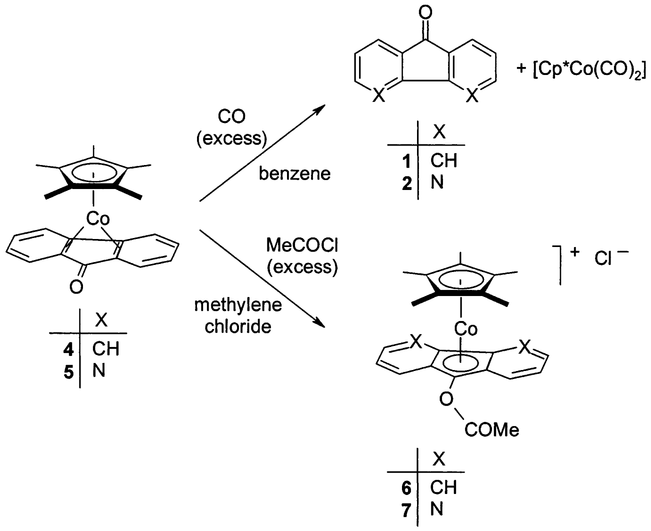
[12] Review on η^2-arene complexes: Brooks, B. C.; Gunnoe, T. B.; Harman, W. D. *Coord. Chem. Rev.* **2000**, *206−207*, 3−61.

[13] Lenges, C. P.; White, P. S.; Marshall, W. J.; Brookhart, M. *Organometallics* **2000**, *19*, 1247−1254.

[14] (a) Dickson, R. S.; Evans, G. S.; Fallon, G. D. *Aust. J. Chem.* **1985**, *38*, 273−291. (b) Corrigan, P. A.; Dickson, R. S.; Fallon, G. D.; Michel, L. J.; Mok, C. *Aust. J. Chem.* **1978**, *31*, 1937−1951.

[15] (a) Koelle, U.; Fuss, B. *Chem. Ber.* **1986**, *119*, 116−128. (b) Beevor, R. G.; Frith, S. A.; Spencer, J. L. *J. Organomet. Chem.* **1981**, *221*, C25−C27. (c) King, R. B.; Efraty, A.; Douglas, W. M. *J. Organomet. Chem.* **1973**, *56*, 345−355.

Scheme 2. Reactions of Compounds 4 and 5



aromatic hydrocarbons such as, for example, anthracene,[16e] decacyclene,[17] and angular [3]phenylene[18] (an η^4 coordination of a single six-membered ring is observed in each case); (D) oligonuclear complexes with bridging arene ligands (an antifacial η^4:η^4 coordination[19] of an arene ring is commonly observed here).[20] In view of these facts, an η^4 coordination of a single six-membered ring might have been expected for **4** and **5**.

Metal coordination affects the aromaticity of the coordinated arenes. In the cyclopentadienylcobalt(I) arene complexes known so far, at least one metal−ligand fragment is necessary for the partial dearomatization of a single arene ring.[21] In contrast to this, in the case of **4** and **5** coordination of a single metal−ligand fragment is sufficient for a *multiple* dearomatization of this kind, affecting two arene rings. A comparable coordinative situation has only been described so far for Ag^{I}, where, however, only negligible bond length alternations ($\Delta d_{C-C} \leq 1$ pm) have been observed.[8,22] Not only, therefore, do compounds **4** and **5** belong to none of the four categories mentioned above, they also constitute a new structure type altogether of mononuclear organometallics.

The results of preliminary experiments addressing the chemical behavior of **4** and **5** are also in accord with their similarity to cyclopentadienone complexes (Scheme 2).[23] **4** and **5** in C_6D_6 solution were reacted in a pressure NMR tube with an excess of carbon monoxide (2 atm). The reaction was sluggish at room temperature. After 2 days at 50 °C, however, quantitative formation of Cp*Co(CO)$_2$ and the respective arene was observed by ^{1}H NMR spectroscopy by comparison with authentic samples of **1**, **2**, and [Cp*Co(CO)$_2$] in the same solvent. Delocalization of electron density into the LUMO of cyclopentadienones leads to an increase in nucleophilicity of the oxygen atom, which is reflected by reactions with suitable electrophiles, furnishing cobaltocenium species in the case of cyclopentadienylcobalt(I) complexes.[9a] In analogy to this, **4** and **5** reacted cleanly and swiftly with acetyl chloride in methylene chloride, forming **6** and **7** as brownish yellow solids, whereas **1** and **2** show no reaction with acetyl chloride.

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Supporting Information Available: Tables containing full X-ray crystallographic data and computational results. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) (a) Schneider, J. J.; Hagen, J.; Heinemann, O.; Krüger, C.; Fabrizi de Biani, F.; Zanello, P. *Inorg. Chim. Acta* **1998**, *281*, 53−59. (b) Schneider, J. J. *Z. Naturforsch., B, Chem. Sci.* **1995**, *50*, 1055−1060. (c) Nehl, H. *Chem. Ber.* **1993**, *126*, 1519−1527. (d) Jonas, K.; Deffense, E.; Habermann, D. *Angew. Chem.* **1983**, *95*, 729; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 716. (e) Jonas, K.; Deffense, E.; Habermann, D. *Angew. Chem. Suppl.* **1983**, 1005−1016.

(17) Schneider, J. J.; Spickermann, D.; Labahn, T.; Magull, J.; Fontani, M.; Laschi, F.; Zanello, P. *Chem. Eur. J.* **2000**, *6*, 3686−3691.

(18) Diercks, R.; Eaton, B. E.; Gürtzgen, S.; Jalisatgi, S.; Matzger, A. J.; Radde, R. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1998**, *120*, 8247−8248.

(19) (a) Schneider, J. J.; Wolf, D.; Bläser, D.; Boese, R. *Eur. J. Inorg. Chem.* **2000**, 713−718. (b) Schneider, J. J.; Wolf, D.; Janiak, C.; Heinemann, O.; Rust, J.; Krüger, C. *Chem. Eur. J.* **1998**, *4*, 1982−1991. (c) Schneider, J. J.; Wolf, D. *Z. Naturforsch., B, Chem. Sci.* **1998**, *53*, 1267−1272. (d) Schneider, J. J.; Denninger, U.; Heinemann, O.; Krüger, C. *Angew. Chem.* **1995**, *107*, 631−634; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 592−595.

(20) An antifacial η^4:η^2 coordination of each six-membered ring is observed for the trinuclear biphenyl complex [(Cp*Co)$_3$C$_{12}$H$_{10}$]: (a) Lehmkuhl, H.; Nehl, H.; Benn, R.; Mynott, R. *Angew. Chem.* **1986**, *98*, 628−629; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 646. Trinuclear clusters of the type [(CpCo)$_3$(η^2:η^2:η^2-arene)] have also been described: (b) Wadepohl, H.; Büchner, K.; Hermann, M.; Metz, A.; Pritzkow, H. *J. Organomet. Chem.* **1998**, *571*, 267−278.

(21) For compounds belonging to category C, the aromaticity of the free arenes is already notably diminished with respect to benzene. See, for example: Zander, M. *Polycyclische Aromaten*; Teubner: Stuttgart, Germany, 1995.

(22) Lindeman, S. V.; Rathore, R.; Kochi, J. K. *Inorg. Chem.* **2000**, *39*, 5707−5716.

(23) Reactions with CO: a sample of **4** and **5**, respectively, in C_6D_6 (ca. 5 mg in ca. 0.5 mL) was prepared in a pressure NMR tube, and CO (2 atm) was introduced via the vacuum line. The mixture was heated at 50 °C for 2 days in an oil bath, leading to quantitative formation of [Cp*Co(CO)$_2$] as well as **1** and **2**, respectively. ^{1}H NMR for [Cp*Co(CO)$_2$] (C_6D_6, 500 MHz): δ 1.59. ^{1}H NMR for **1** (C_6D_6, 500 MHz): δ 6.77 (m, 2 H), 6.95 (m, 4 H), 7.55 (m, 2 H). ^{1}H NMR for **2** (C_6D_6, 500 MHz): δ 6.33 (m, 2 H), 7.33 (m, 2 H), 8.33 (m, 2 H). Reactions with acetyl chloride: a sample of **4** and **5**, respectively, in CD_2Cl_2 (ca. 8 mg in ca. 0.5 mL) was prepared in an NMR tube. An excess of acetyl chloride (ca. 0.05 mL) was added. Quantitative formation of **6** and **7**, respectively, was observed at room temperature over the course of ca. 5 min. Both compounds were isolated in analytically pure form by removal of volatile components in vacuo. ^{1}H NMR for **6** (CD_2Cl_2, 250 MHz): δ 1.23 (s, 15 H, Cp*), 2.59 (s, 3 H, COMe), 7.41 (d, J = 8.5 Hz, 2 H), 7.71 (m, 2 H), 7.87 (m, 4 H). Anal. Calcd for $C_{25}H_{26}ClCoO_2$ (452.87): C, 66.31; H, 5.79. Found: C, 66.70; H, 5.83. ^{1}H NMR for **7** (CD_2Cl_2, 250 MHz): δ 1.31 (s, 15 H, Cp*), 2.69 (s, 3 H, COMe), 7.73 ("d", apparent J = 4.8 Hz, 2 H), 8.23 ("d", apparent J = 8.2 Hz, 2 H), 9.34 ("d", apparent J = 2.9 Hz, 2 H). Anal. Calcd for $C_{23}H_{24}N_2ClCoO_2$ (454.84): C, 60.74; H, 5.32; N, 6.16. Found: C, 60.99; H, 5.66; N, 6.25.