Hydrocarbon-Bridged Metal Complexes, XLI[1]

Addition of Aniline Tricarbonyl Chromium Complexes to the Cyclohexadienyl Ligand of $[(\eta^5\text{-}C_6H_7)M(CO)_3]^+$ (M = Fe, Ru)☆

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The addition of aniline tricarbonyl chromium complexes $(\eta^6\text{-}C_6H_4(R)NHR^1)Cr(CO)_3$ (R = H, CH_3; R^1 = H, CH_3) to $[(\eta^5\text{-}C_6H_7)M(CO)_3]^+$ (M = Fe, Ru) gives the heterobimetallic ligand-bridged complexes $(OC)_3Cr(\eta^6\text{-}C_6H_4(R)N(R^1)C_6H_7\text{-}\eta^4)M(CO)_3$. The structure of $(OC)_3Cr(\eta^6\text{-}C_6H_4(CH_3)N(H)\text{-}C_6H_7\text{-}\eta^4)Ru(CO)_3$ has been determined by X-ray diffraction.

Introduction

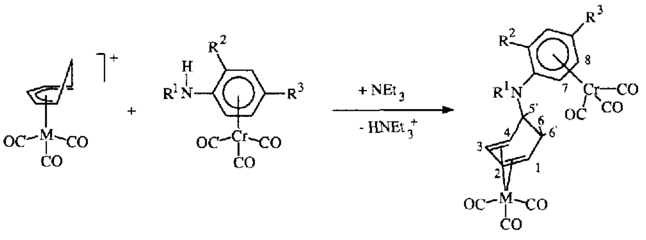
The nucleophilic addition of amines to $[(\eta^5\text{-}C_6H_7)M(CO)_3]^+$ (M = Fe, Ru) is a very well-studied reaction.[3][4] Kane-Maguire et al. found that the first step of the process is attack of the amine at the cyclohexadienyl ligand, to yield an ammonium cation. The second step is deprotonation by a second equivalent of the amine, giving the neutral amino-substituted cyclohexadiene complex.[5][6] It was shown by Kane-Maguire that both steps are reversible. Various amines, even amino acid esters[7], have been employed in this reaction. As part of our studies on the directed synthesis of hydrocarbon-bridged metal complexes by reaction between electrophilic and nucleophilic complexes[8], we now report the synthesis of heterobimetallic hydrocarbon-bridged complexes by the addition of aniline tricarbonyl chromium complexes to $[(\eta^5\text{-}C_6H_7)M(CO)_3]^+[BF_4^-]$ (M = Fe, Ru).

Results and Discussion

The compounds **1**–**8** were obtained by the reaction of various aniline tricarbonyl chromium complexes with $[(\eta^5\text{-}C_6H_7)M(CO)_3]^+[BF_4^-]$ (M = Fe, Ru) using triethylamine as a base (eq. 1). For comparison, complex **9** was prepared from $[(\eta^5\text{-}C_6H_7)Ru(CO)_3]^+[BF_4^-]$ and $p\text{-}H_3CC_6H_4NH_2$.

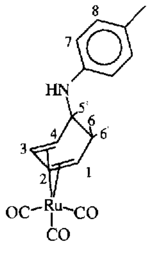
The reaction appears to follow a reversible two-step mechanism, in accordance with the findings of Kane-Maguire et al.[5][6] If **1** is dissolved in acetone and two equivalents of HBF_4 (54% in ether) are added, $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]^+$ and $[(H_3NC_6H_5)Cr(CO)_3]^+$ are obtained. By addition of excess triethylamine, the reaction can be forced back, yielding complex **1** once more after a period of several hours (eq. 2).

These reactions can easily be followed by IR spectroscopy. The ν(CO) bands of the products **1**–**9** prove that addition to the cationic species $[(\eta^5\text{-}C_6H_7)M(CO)_3]^+$ (M = Fe,Ru) occurs, resulting in neutral diene complexes. In the ^{1}H-NMR spectra, the typical signals of a neutral cyclohexa-



1-8

	M	R¹	R²	R³
1	Fe	H	H	H
2	Fe	H	H	CH_3
3	Fe	H	CH_3	H
4	Fe	CH_3	H	H
5	Ru	H	H	H
6	Ru	H	H	CH_3
7	Ru	H	CH_3	H
8	Ru	CH_3	H	H



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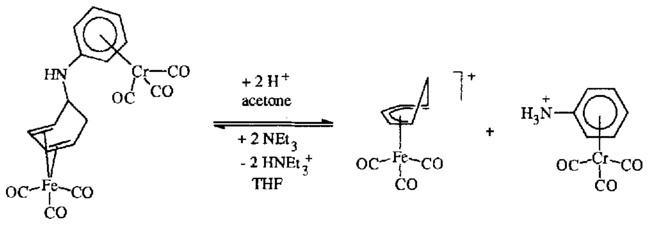
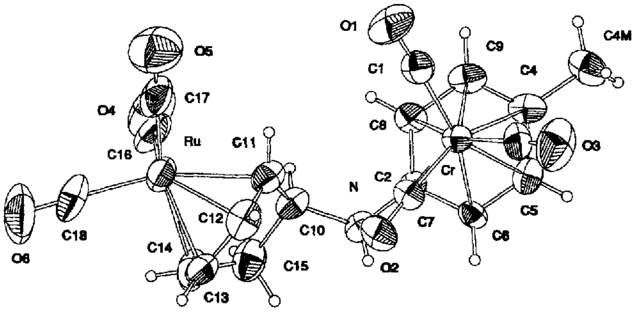


diene tricarbonyl complex are observed. In comparison to non-coordinated anilines, the ^{1}H-resonances of the aniline tricarbonyl chromium fragment are shifted upfield, as expected. The actual set of signals strongly depends on the substitution pattern of the aniline.

Addition of the aniline complexes to the cyclohexadienyl ligand leads to the *exo*-product. This can be ascertained from the coupling constants between 6-H, 6′-H and 5′-H in the ^{1}H-NMR spectra.[7] The $^3J_{6,5'}$- and the $^3J_{6',5'}$-coupling constants show 5′-H to reside in an *endo*-position. The *exo*-addition of the amino group at C-5 is confirmed by X-ray analysis of **6**. The addition of the planar chiral (o-$CH_3C_6H_4NH_2$)$Cr(CO)_3$[9] to $[(\eta^5\text{-}C_6H_7)M(CO)_3]^+$ creates a new asymmetric centre at the C-5 position, hence compounds **3** and **7** are formed as a mixture of diastereoisomers. Indeed, two sets of signals are detected in the ^{1}H-NMR spectrum.

In the ^{1}H-NMR spectrum of **9** an AA′BB′-spin system for the 1,4-substituted benzene and for **2** and **6** an ABCD-spin system is observed. This can be explained by the local symmetry of the arene. **9** has a local C_2-axis for the aromatic system along the C−N bond. In **2** and **6**, this symmetry element is not present due to the coordinated $Cr(CO)_3$ group. The 7-H/7′-H as well as 8-H/8′-H atoms are non-equivalent and thus one signal for each H-atom should be observed in the NMR spectrum. For 7-H and 7′-H, two separate resonances are found, while a multiplet is seen for 8-H and 8′-H.

Figure 1. Molecular Structure of **6** in the crystal. Selected bond lengths [Å] and angles [°]: N−C7 1.373(12), N−C10 1.480(12); C7−N−C10 124.5(8)



X-ray analysis of **6** reveals two different CN bond lengths. The N−C-arene bond [1.373(12) Å] is shorter than the N−C−cyclohexadiene bond [1.480(12) Å], which can be attributed to the electron-withdrawing effect of the $Cr(CO)_3$ group.[10] According to the literature[11], a CNC angle between 109° and 120° could be expected, if the nitrogen is part of the delocalized aromatic system. The observed CNC angle of 124.5(8)° indicates that steric effects lead to an expansion of the CNC bond.

Experimental Section

$[(\eta^5\text{-}C_6H_7)M(CO)_3]BF_4$ (M = Fe, Ru) and the chromium complexes were prepared and purified following published procedures.[12][13] Triethylamine was purchased from Fluka and used without further purification. All operations were carried out under argon using Schlenk techniques. Solvents were dried by distillation from sodium/benzophenone. The ^{1}H-NMR spectra were recorded with a Jeol GSX 270 (270.17 MHz) or a Jeol EX 400 (399.78 MHz). The observed coupling constants are absolute values only. − IR: Perkin-Elmer 841.

General Procedure for the Synthesis of **1**−**9**: The aniline tricarbonyl chromium complex and triethylamine were dissolved in 7 ml of THF. This solution was added to the solid cationic tricarbonyl dienyl complex at room temp. with rapid stirring. The resulting suspension was stirred for 12 h. Then, THF was removed in vacuo, affording a yellow oil, which was dissolved in 10 ml of diethyl ether and filtered through Celite. Diethyl ether was removed under reduced pressure and the precipitate was recrystallized from *n*-pentane, giving a pale-yellow powder. Because of their low solubility, *p*-methylaniline derivatives were merely washed with pentane. The IR and ^{1}H-NMR spectra of **1**-**5** and **7**-**8** are very similar to those of **6**.

1: 60.2 mg (0.197 mmol) of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$, 22.0 mg (0.096 mmol) of $(H_2NC_6H_5)Cr(CO)_3$, 100 µl (0.717 mmol) of $N(C_2H_5)_3$; yield: 34.2 mg (0.076 mmol). − $C_{18}H_{13}CrFeNO_6$ (447.1): calcd. C 48.35, H 2.93, N 3.13; found C 48.21, H 3.27, N 3.05.

2: 56.0 mg (0.183 mmol) of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$, 23.1 mg (0.095 mmol) of (p-$CH_3C_6H_4NH_2$)$Cr(CO)_3$, 80 µl (0.574 mmol) of $N(C_2H_5)_3$; yield: 35.6 mg (0.077 mmol). − $C_{19}H_{15}CrFeNO_6$ (461.2): calcd. C 49.48, H 3.28, N 3.04; found C 49.28, H 3.51, N 2.99.

3: 63.3 mg (0.214 mmol) of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$, 30.2 mg (0.124 mmol) of (o-$CH_3C_6H_4NH_2$)$Cr(CO)_3$, 150 µl (1.076 mmol) of $N(C_2H_5)_3$; yield: 31.8 mg (0.069 mmol). − $C_{19}H_{15}CrNO_6Fe$ (461.2): calcd. C 49.48, H 3.28, N 3.04; found C 48.92, H 4.04, N 2.99.

4: 112.3 mg (0.367 mmol) of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$, 27.2 mg (0.112 mmol) of $(C_6H_5NHCH_3)Cr(CO)_3$, 200 µl (1.434 mmol) of $N(C_2H_5)_3$; yield: 25.8 mg (0.056 mmol). − $C_{19}H_{15}CrNO_6Fe$ (461.2): calcd. C 49.48, H 3.28, N 3.04; found C 48.61, H 3.19, N 3.01.

5: 68.4 mg (0.195 mmol) of $[(\eta^5\text{-}C_6H_7)Ru(CO)_3]BF_4$, 21.0 mg (0.095 mmol) of $(H_2NC_6H_5)Cr(CO)_3$, 100 µl (0.717 mmol) of $N(C_2H_5)_3$; yield: 36.0 mg (0.073 mmol). − $C_{18}H_{13}CrNO_6Ru \bullet 1.1\ H_2O$ (512.2): calcd. C 42.21, H 2.99, N 2.73; found C 42.28, H 3.02, N 2.55.

6: 67.8 mg (0.193 mmol) of $[(\eta^5\text{-}C_6H_7)Ru(CO)_3]BF_4$, 25.5 mg (0.105 mmol) of (p-$CH_3C_6H_4NH_2$)$Cr(CO)_3$, 100 µl (0.717 mmol) of $N(C_2H_5)_3$; yield: 42.0 mg (0.083 mmol). Crystals were grown from diethyl ether solution. − IR (nujol): $\tilde{\nu}$ = 3369 cm^{-1} (m, NH), 2067 (s, RuCO), 1984 (vs, RuCO), 1941 (s, CrCO), 1882 (s, CrCO), 1829 (s, CrCO), 1562 (m, NH), 1512 (m, C=C). − ^{1}H-NMR (400 MHz, [D$_6$]acetone): δ = 5.88 (t, 1 H, 7-H or 7′-H, J = 5.0 Hz), 5.71 (t, 1 H, 7-H or 7′-H, J = 5.0 Hz), 5.66 (d, 2 H, 8′-H, 8-H, $^3J_{8,7} = {}^3J_{8',7'}$ = 5.4 Hz), 5.44 (m, 1 H, NH), 5.02 (dd, 1 H, 2-H or 3-H, $^3J_{2,3} = {}^3J_{3,2}$ = 2.4 Hz, $^3J_{2,1}$ or $^3J_{3,4}$ = 7.2 Hz), 4.95 (dd, 1 H, 3-H or 2-H, $^3J_{3,2} = {}^3J_{2,3}$ = 2.4 Hz, $^3J_{3,4}$ or $^3J_{2,1}$ = 7.2 Hz), 3.81 (m, 1 H, 5′-H), 3.38 (m, 1 H, 1-H), 3.18 (m, 1 H, 4-H), 2.39 (ddd, 1 H, 6′-H, $^3J_{6',1}$ = 3.8 Hz, $^3J_{6',5'}$ = 10.2 Hz, $^2J_{6',6}$ = 13.8 Hz), 2.02 (s, 3 H, p-CH_3), 1.73 (dt, 1 H, 6-H, $^3J_{6,1} = {}^3J_{6,5'}$ = 2.4 Hz, $^2J_{6,6'}$ = 14.8 Hz). − $C_{19}H_{15}CrNO_6Ru \bullet 1\ H_2O$ (524.4): calcd. C 43.51, H 3.27, N 2.67; found C 43.21, H 3.03, N 2.51.

7: 73.6 mg (0.210 mmol) of $[(\eta^5\text{-}C_6H_7)Ru(CO)_3]BF_4$, 26.2 mg (0.108 mmol) of (o-$CH_3C_6H_4NH_2$)$Cr(CO)_3$, 150 µl (1.076 mmol) of $N(C_2H_5)_3$; yield: 33.9 mg (0.067 mmol). − $C_{19}H_{15}CrNO_6Ru \bullet$

1.2 H_2O (528.0): calcd. C 43.22, H 3.32, N 2.65; found C 43.26, H 3.53, N 2.54.

8: 114.4 mg (0.326 mmol) of $[(\eta^5\text{-}C_6H_7)Ru(CO)_3]BF_4$, 28.5 mg (0.117 mmol) of $(C_6H_5NHCH_3)Cr(CO)_3$, 200 µl (1.434 mmol) of $N(C_2H_5)_3$; yield: 38.2 mg (0.075 mmol). – $C_{19}H_{15}NO_6CrRu$ • 2 H_2O (542.4): calcd. C 42.07, H 3.53, N 2.58; found C 41.64, H 3.33, N 2.66.

9: 72.5 mg (0.207 mmol) of $[(\eta^5\text{-}C_6H_7)Ru(CO)_3]BF_4$, 15.8 mg (0.147 mmol) of $p\text{-}CH_3C_6H_4NH_2$, 100 µl (0.717 mmol) of $N(C_2H_5)_3$; yield: 50.1 mg (0.135 mmol). – IR (nujol): $\tilde{\nu}$ = 3386 cm^{-1} (m, NH), 2065 (vs, RuCO), 1996 (vs, RuCO), 1613 (m, NH), 1515 (m, C=C). – ^1H-NMR (270 MHz, $[D_6]$acetone): δ = 6.88 (m, 2 H, 7-H or 8-H), 6.45 (m, 2 H, 8-H or 7-H), 5.89 (t, 1 H, 2-H or 3-H, $^3J_{2,1} = {}^3J_{2,3}$ or $^3J_{3,2} = {}^3J_{3,4}$ = 5.3 Hz), 5.71 (t, 1 H, 3-H or 2-H, $^3J_{3,2} = {}^3J_{3,4}$ or $^3J_{2,1} = {}^3J_{2,3}$ = 5.3 Hz), 4.62 (m, 1 H, NH), 3.93 (m, 1 H, 5′-H), 3.42 (m, 1 H, 1-H), 3.15 (m, 1 H, 4-H), 2.37 (ddd, 1 H, 6′-H, $^3J_{6',1}$ = 3.8 Hz, $^3J_{6',5'}$ = 10.3 Hz, $^2J_{6',6}$ = 14.3 Hz), 2.15 (s, 3 H, $p\text{-}CH_3$), 1.64 (dt, 1 H, 6-H, $^3J_{6,1} = {}^3J_{6,5'}$ = 2.7 Hz, $^2J_{6,6'}$ = 14.6 Hz). – $C_{16}H_{15}NO_3Ru$ (370.4): calcd. C 51.89, H 4.08, N 3.78; found C 51.59, H 4.06, N 3.81.

X-ray Structure Determination of **6**[14]: $C_{19}H_{15}CrNO_6Ru$, M = 506.39, T = 291(2) K, Siemens $P4$ diffractometer, λ = 0.71073 Å, triclinic, P1bar, crystal size 0.25 × 0.06 × 0.03 mm, a = 6.596(1), b = 12.982(2), c = 13.196(2) Å, α = 117.3(1), β = 96.48(1), γ = 96.16(1)°, V = 981.7(3) Å^3, Z = 2, d(calcd.) = 1.713 g/cm^3, μ = 1.357 mm^{-1}, $F(000)$ = 504, Θ range 3.06–22.99°, index ranges $-1 \le h \le 5$; $-12 \le k \le 12$; $-14 \le l \le 14$, 2990 collected reflections, 2193 independent reflections (R_{int} = 0.0540), max./min. transmission 0.743 and 0.654, data/restraints/parameters: 2193/0/256, program: SHELXL 93, SHELXS 86, GOF = 1.053, $R1$ = 0.0581, $wR2$ = 0.0826; $R1$ = 0.1255, $wR2$ = 0.1019 (all data), largest diff. peak/hole = 0.461/–0.372 Å^{-3}.

☆ Dedicated to Professor *Hanns-Peter Boehm* on the occasion of his 70th birthday.

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[2] X-ray structural analysis.

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[14] Crystallographic data (excluding structure factors) of the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100512. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB 2 1EZ, UK [fax: int. Code +44(0)1223/336-033, e-mail: deposit@chemcrys.cam.ac.uk].

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