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Solution and solid state conformation of Fischer carbene complexes vis-à-vis conformation of aryl carboxamides: complexation of the aromatic ring by tricarbonylchromium makes a difference

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Abstract

Crystallography and proton NMR spectroscopy were used to compare the conformations of aryl amino Fischer carbene complexes with structurally analogous aryl carboxamides. The similarity disappears when the aromatic rings were complexed with tricarbonylchromium groups. Details of synthesis, spectral and analytical data for all new compounds are provided. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

A deviation from coplanarity has often been observed for sterically constrained, *ortho*-substituted aryl carboxamides [1]. The amide plane is twisted away from the plane of the aromatic ring, as presented in Chart 1, giving rise to an axial disymmetry. Since the N-substituent of the amide group faces the aromatic ring in such a structure, the relevant set of protons are likely to be shielded by the aromatic ring current anisotropy.

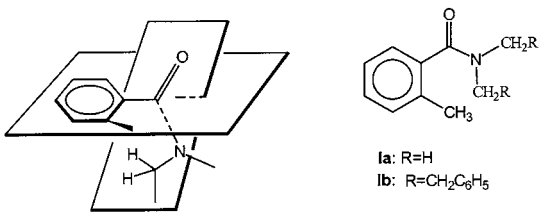

Chart 1.

In our earlier study on the solution conformation of Fischer carbene complexes [2], we have shown that the aromatic ring attached to the carbene carbon is oriented orthogonal to the metal–carbene π-plane, as commonly observed in solid state [3]. The two possible conformers differ in the orientation of the hetero atom substituent which is either *syn* or *anti* with respect to the M $(CO)_5$ group (structures I and II, Chart 2).

In the *anti* orientation (as in I), the substituent is placed in the anisotropic shielding zone of the aromatic ring, so that its protons experience an upfield shift of about 0.9–1.0 ppm compared to the same protons in the *syn* conformer (II). When X is oxygen, the two conformers can be observed at low temperatures (below −40°C). If X is nitrogen, relatively high barrier of rotation about the $C_{carbene}$–N bond allows observation of distinct signals of *syn* and *anti* substituents in the ^{1}H-NMR spectra at ambient temperature. When the aromatic ring attached to the carbene carbon is unsymmetrically substituted, the methylene protons of a benzyl group on X (in the *anti* conformer I) show clear

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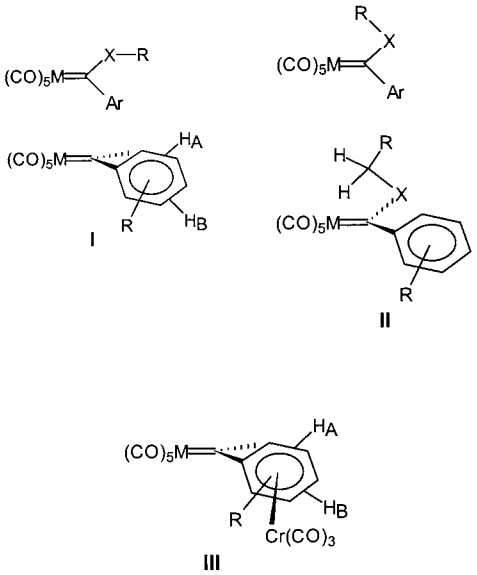


Chart 2.

diastereotopicity, and this feature was indeed used as a corroborative evidence for the conformation assignment. If the conformation of the molecule undergoes no significant change upon complexation of the aromatic ring with a Cr $(CO)_3$ group, one could monitor the relative magnitude of the anisotropic effect of the aromatic ring on hetero atom substituent in presence or in absence of Cr $(CO)_3$ complexation to the aromatic ring (III versus I, Chart 2). Complexation of Cr $(CO)_3$ to an aromatic ring is likely to perturb the ring current [4] which is responsible for its anisotropic shielding effect.

It was of interest, therefore, to compare the structural details of *ortho*-substituted phenyl carboxamides with analogous Fischer carbene complexes (C=O replaced by C=Cr $(CO)_5$ group), and examine the fate of anisotropic shielding of N-substituents when the aromatic ring is coordinated to a tricarbonyl chromium group.

2. Experimental

All reactions were performed under an inert atmosphere of argon. Solvents were dried using standard procedures and distilled under an inert atmosphere prior to use. Methylamine was used as commercially available aqueous solutions as received (40% in water). Infrared spectra were obtained on a Perkin–Elmer 599B spectrometer in chloroform solution. The ^{1}H-NMR spectra were recorded on Bruker AC-200 spectrometer whereas ^{13}C-NMR spectra were recorded on a Bruker AC-200 and Bruker AMX 300 spectrometers at 50.3 and 75.8 MHz, respectively using $CDCl_3$ as the solvent and reported as parts per million downfield of tetramethylsilane. Elemental analyses of compounds were carried out on a Carlo–Erba 1100 automatic analyzer. Melting points in the Celsius scale were determined in open capillary tubes on a Thermonik Campbell melting point apparatus and are uncorrected.

*2.1. General procedure for the preparation of pentacarbonyl (ethoxy aryl)-chromium (0) complexes **1a–f***

All alkoxy carbene complexes were prepared according to Fischer's original procedure [9]. Appropriate aryllithiums (1.5 n mmol) were treated with chromium hexacarbonyl (1 n mmol) in diethyl ether at 0°C. The temperature was raised to 20–25°C in about 30 min. The solvent was evaporated to dryness under reduced pressure and the residue was dissolved in a small amount cold water. A dichloromethane solution of triethyloxonium tetrafluoroborate (1.5 n mmol) was added to the aqueous solution and the complexes were extracted with petroleum ether. Pure product was obtained after filtration through a small plug of flash silica. For **1a**, **1b**, **1c** see ref. [2].

*2.1.1. Preparation of complex **1d***

2-Methylanisole (0.86 ml, 6.81 mmol) was treated with *n*-butyllithium (4.68 ml, (1.6 M solution in hexane), 7.5 mmol) at 10–20°C in diethyl ether (20 ml) and the reaction mixture stirred at room temperature (r.t.) for 20 h. After treatment with Cr $(CO)_6$ (1 g, 4.54 mmol) and triethyl oxoniumtetrafluoroborate (6.8 ml, 6.8 mmol) as described before, the product was obtained (1.1 g, 65%) as a red liquid, IR ν (CO) 2069.2 (m), 1974 (sh), 1930 (s) cm^{-1} ^{1}H-NMR ($CDCl_3$) δ 1.6 (t, $J = 6$ Hz, 3H, ethyl-CH_3), 2.35 (s, 3H, CH_3), 3.75 (s, 3H, OCH_3), 4.45 (bs, 2H, ethyl-CH_2), 6.75–7.3 (m, 3H, Phenyl). ^{13}C-NMR ($CDCl_3$) δ 14.81 (ethyl-CH_3), 16.39 (CH_3), 55.25 (OCH_3), 60.71 (ethyl-CH_2), 110.92, 120.30, 123.74, 128.23, 131.85, 145.25 (each as for phenyl ring), 216.29, 224.66 (CO), 359.2 (=C).

*2.1.2. Preparation of complex **1e***

3,4-Dimethylanisole (0.95 ml, 6.81 mmol) was treated with *n*-Butyllithium (4.68 ml, (1.6 M in hexane), 7.5 mmol) at 10–20°C in diethyl ether (20 ml) and the reaction mixture stirred at r.t. for 20 h. This solution was treated with Cr $(CO)_6$ (1 g, 4.54 mmol) and triethyl oxoniumtetrafluoroborate (6.8 ml, 6.8 mmol) yielded the product (1.20 g, 69%) as a red liquid, IR ν (CO) 2068.2 (m), 1972 (sh), 1942.5 (s) cm^{-1}, ^{1}H-NMR ($CDCl_3$) δ 1.52 (t, $J = 6$ Hz, 3H, ethyl-CH_3), 2.20 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 3.8 (s, 3H, OCH_3), 4.38 (bs, 2H, ethyl-CH_2), 6.55 (s, 1H, phenyl *meta* proton), 6.7 (s, 1H, phenyl *ortho* proton).^{13}C-NMR ($CDCl_3$) δ 15.34 (ethyl-CH_3), 19.34 (CH_3), 20.60 (CH_3), 55.85 (OCH_3), 75.71 (ethyl-CH_2), 112.95, 122.85, 129.04, 130.61, 137.28, 147.27 (each as for phenyl ring), 216.98, 226.12 (CO), 355.12 (=C).

*2.1.3. Preparation of complex **1f***

4-Trimethylsilyl anisole (1.25 g, 6.81 mmol) was treated with *n*-butyllithium (4.68 ml, (1.6 M in hexane), 7.5 mmol) at 10–20°C in diethyl ether (20 ml) and the reaction mixture stirred at r.t. for 20 h. This solution was treated with Cr $(CO)_6$ (1g, 4.54 mmol) and triethyloxoniumtetrafluoroborate (6.8 ml, 6.8 mmol) yielded the product (1.25 g, 63%) as a red liquid, IR *v* (CO) 2070 (m), 1976 (sh), 1935 (s) cm^{-1}, ^{1}H-NMR ($CDCl_3$) δ 0.35 (s, 9H, $SiMe_3$), 1.58 (t, $J = 6$ Hz, 3H, ethyl-CH_3), 3.88 (s, 3H, OCH_3), 4.42 (bs, 2H, ehtyl-CH_2), 6.95 (m, 2H, phenyl *meta* and *para* proton), 7.5 (m, 1H, phenyl *ortho* proton). ^{13}C-NMR ($CDCl_3$) δ −1.25 ($SiMe_3$), 14.69 (ethyl-CH_3), 55.03 (OCH_3), 75.24 (ethyl-CH_2), 110.33, 113.52, 125.96, 131.75, 134.72, 149.18 (each as for phenyl ring), 216.20, 225.32 (CO), 360.23 (=C).

*2.1.4. General procedure for the preparation of amino carbene complexes **3a–f***

All amino carbene complexes were prepared according to the literature procedure [10]. Corresponding pentacarbonyl (ethoxy aryl) chromium (0) complexes (n mmol) in diethyl ether (3 n ml) was treated with methylamine (1.2 n mmol) at room temperature under argon until the color changed from red to yellow. The reaction mixture was diluted with water, extracted with dichloromethane, and the organic extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The pure product was isolated by flash chromatography using dichloromethane (10–20%) in petroleum ether as the eluent.

*2.1.5. Preparation of complex **3a***

Reaction of the complex **1a** (0.90 g, 2.76 mmol) in diethyl ether (8 ml) and methylamine (0.280 ml, 3.31 mmol) afforded the product (0.791 g, 92%) as a yellow solid, m.p. 121°C, IR *v* (CO) 2052.1 (m), 1971.1 (sh), 1926.8 (s) cm^{-1}, ^{1}H-NMR δ ($CDCl_3$) syn:anti = 30:70, *syn*-**3a** 3.75 (d, $J = 6$ Hz, 3H, N–CH_3), 8.76 (bs, 1H, N–H), *anti*-**3a** 2.96 (d, $J = 6$ Hz, 3H, N–CH_3), 9.13 (bs, 1H, N–H) overlap regions 6.65–7.55 (m, 5H, phenyl protons). ^{13}C-NMR δ ($CDCl_3$), *syn*-**3a** 39.78 (N–CH_3), 223.40 (CO), 280.02 (=C), *anti*-**3a** 37.48 (N–CH_3), 223.16 (CO), 282.92 (=C) overlap regions 118.73, 120.77, 126.63, 127.60, 128.26, 128.50, 149.17, 155.27 (each as for phenyl ring), 216.92 (CO). Anal. Calc. for $C_{13}H_9CrO_5N$: C, 50.17; H, 2.91; N, 4.50. Found: C, 50.58; H, 2.68; N, 4.46%.

*2.1.6. Preparation of complex **3b***

Reaction of the complex **1b** (0.85 g, 2.5 mmol) in diethyl ether (7 ml) and methylamine (0.25 ml, 3 mmol) afforded the product (0.75 g, 92.5%) as a yellow solid, m.p. 115°C, IR *v* (CO) 2056 (m), 1980 (sh), 1930 (s) cm^{-1}, ^{1}H-NMR ($CDCl_3$) δ *syn:anti* = 25:75, *anti*-**3b** 2.96 (d, $J = 5$ Hz, 3H, N–CH_3), 9.15 (bs, 1H, N–H), *syn*-**3b** 3.74 (d, $J = 5$ Hz, 3H, N–CH_3), 8.69 (bs, 1H, N–H), overlap regions: 2.38 (s, 3H, CH_3), 6.4-7.45 (m, 4H, phenyl protons). ^{13}C-NMR ($CDCl_3$) δ *syn*-**3b** 37.42 (N–CH_3), 280.0 (=C) *anti*-**3b** 39.02 (N–CH_3), 283.32 (=C) overlap regions 21.31 (CH_3), 115.82, 117.52, 119.18, 122.13, 127.33, 128.38, 138.42, 149.04, 154.54 (each as for phenyl ring), 216.99, 223.92 (CO). Anal. Calc. for $C_{14}H_{11}CrO_5N$: C, 51.70; H, 3.40; N, 4.307. Found C, 51.72; H, 3.35; N, 4.32%.

*2.1.7. Preparation of complex **3c***

Reaction of the complex **1c** (1 g, 2.80 mmol) in diethyl ether (8 ml) and methylamine (0.286 ml, 3.36 mmol) afforded the product (0.87 g, 90%) as yellow solid, m.p. 113°C IR *v* (CO) 2056.5 (m), 1975.3 (sh). 1932.6 (s) cm^{-1}, ^{1}H-NMR ($CDCl_3$) δ syn:anti = 25:75, *syn*-**3c** 3.73 (d, $J = 6$ Hz, 3H, N–CH_3), 3.77 (s, 3H, OCH_3), 8.69 (bs, 1H, N–H), *anti*-**3c** 2.93 (d, $J = 6$ Hz, 3H, N–CH_3), 3.82 (s, 3H, OCH_3), 9.13 (bs, 1H, N–H), overlap regions 6.74 (t, $J = 8$ Hz, 1H,), 6.90–7.06 (m, 2H), 7.22 (t, $J = 8$ Hz, 1H) (each as for 4 phenyl protons). ^{13}C-NMR ($CDCl_3$) δ *anti*-**3c** 37.48 (N–CH_3), 223.85 (CO), 280.50 (=C) *syn*-**3c** 39.30 (N–CH_3), 224.05 (CO), 280.01 (=C) overlap regions 55.45 (OCH_3), 111.24, 120.99,123.45, 128.53, 137.94, 140.25, 149.06, 151.43 (each as for phenyl ring), 217.52 (CO). Anal. Calc. for $C_{14}H_{11}CrO_6N$: C, 49.28; H, 3.25; N, 4.11. Found: C, 49.38; H, 3.06; N, 4.01%.

*2.1.8. Preparation of complex **3d***

Reaction of the complex **1d** (0.95 g, 2.70 mmol) in diethyl ether (8 ml) and methylamine (0.275 ml, 3.24 mmol) afforded the product (0.79 g, 85%) as a yellow liquid IR *v* (CO) 2066.4 (m), 1965.8 (sh). 1933.5 (s) cm^{-1} ^{1}H-NMR ($CDCl_3$) δ *syn:anti* = 40:60, *syn*-**3d** 2.32 (s, 3H, CH_3), 8.87 (bs, 1H, N-H), *anti*-**3d** 2.29 (s, 3H, CH_3), 2.98 (d, $J = 5$ Hz, 3H, N–CH_3), 3.67 (s, 3H, OCH_3), 9.11 (bs, 1H, N–H), overlap regions 3.70–3.80 (m, 6H, N–CH_3 and OCH_3), 6.6–7.1 (m, 3H, phenyl protons).

*2.1.9. Preparation of complex **3e***

Reaction of the complex **1e** (0.90 g, 2.60 mmol) in diethyl ether (7 ml) and methylamine (0.265 ml, 3.13 mmol) afforded the product (0.81 g, 94%) as a yellow solid, m.p. 118°C, IR *v* (CO) 2057 (m), 1980 (sh), 1930 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ syn:anti 45:55 *syn*-**3e**, 8.85 (bs, 1H, N–h), *anti*-**3e** 2.96 (d, $J = 6$ Hz, 3H, N–CH_3), 9.15 (bs, 1H, N–H) overlap regions 2.17 (s, 3H), 2.25 (s, 3H) (each as for CH_3), 3.60–3.85 (m, 6H) (N–CH_3, OCH_3) 6.4–6.7 (m, 2H, phenyl protons). ^{13}C-NMR ($CDCl_3$) δ *syn*-**3e** 39.51 (N–CH_3), 224.08 (CO), 279.93 (=C), *anti*-**3e** 37.08 (N–CH_3), 223.49 (CO), 280.57 (=C), overlap regions 18.47, 18.62, 19.72 (each as for CH_3), 55.02 (OCH_3), 112.08, 121.74, 122.77, 127.73, 128.37, 134.98, 136.29, 140.54, 146.51, 148.07 (each as for phenyl ring), 217.25 (CO). Anal. Calc. for $C_{16}H_{15}CrO_6N$: C, 52.04; H, 4.10; N, 3.79. Found: C, 52.28; H, 4.50; N, 3.68%.

2.1.10. Preparation of complex ***3f***

Reaction of the complex **1f** (0.90 g, 2.32 mmol) in diethyl ether (7 ml) and methylamine (0.24 ml, 2.78 mmol) afforded the product (0.82 g, 95%) as a yellow solid, m.p. 100°C IR ν (CO) 2054 (m), 1973 (sh), 1926 (s) cm^{-1}, ^{1}H-NMR ($CDCl_3$) δ syn:anti = 45:55 *syn*-**3f** 3.00 (d, $J = 6$ Hz, 3H, N–CH_3), 9.2 (bs, 1H, N–H), *anti*-**3f** 3.75 (d, $J = 6$ Hz, 3H, N–CH_3), 8.8 (bs, 1H, N–H), overlap regions 0.30 (s, 9H, $SiMe_3$), 3.80 (s, 3H, OCH_3), 6.9–7.00 (m , 2H), 7.4 d, $J = 6$ Hz, 1H) (for 3 phenyl protons). ^{13}C-NMR ($CDCl_3$) δ *syn*-**3f** 37.19 (N–CH_3), 54.80 (OCH_3), 223.39 (CO), 280.89 (=C), *anti*-**3f** 39.55 (N–CH_3), 54.93 (OCH_3), 223.94 (CO), 280.43 (=C), overlap regions −1.38 ($SiMe_3$), 110.03, 110.22, 125.58, 126.4, 131.04, 131.73, 133.32, 133.46, 142.20, 149.08, 150.68 (each as for phenyl ring), 217.14 (CO). Anal. Calc. for $C_{17}H_{19}CrO_6NSi$: C, 49.39; H, 4.63; N, 3.39. Found: C, 49.50; H, 4.50; N, 3.42%.

2.2. General procedure for the alkylation of amino carbene complexes

The carbene complex (n mmol) and tetrabutylammonium bromide (0.1 n mmol) in benzene (10 n ml) was treated with 50% aqueous NaOH and methyl iodide (5 n mmol) or benzyl bromide (1.5 n mmol). The mixture was stirred at r.t. under argon until the starting material was consumed (TLC, 2 h). The reaction mixture was diluted with water, extracted with dichloromethane, dried, and concentrated under reduced pressure. The pure product was isolated by flash chromatography.

2.2.1. Preparation of complex ***5a***

Complex **3a** (0.50 g, 1.60 mmol), TBAB (51 mg, 0.16 mmol), 50% aq. NaOH (1 ml) and methyl iodide (0.5 ml, 8 mmol) in benzene (15 ml) were stirred for 2 h yielded the product (0.455 g, 87%) as yellow solid, m.p. 82°C, IR ν (CO) 2056 (m), 1971 (sh), 1930 (s) cm^{-1} ^{1}H-NMR ($CDCl_3$) δ 3.04 (s, 3H, N–CH_3), 3.99 (s, 3H, N–CH_3), 6.70 (d, $J = 8$ Hz, 2H), 7.05–7.45 (m, 3H) (each as for 5 phenyl protons). ^{13}C-NMR ($CDCl_3$) δ 45.69 (N–CH_3), 51.10 (N–CH_3), 118.67, 125.62, 128.36,152.62 (each as for phenyl ring), 217.01, 223.79 (CO), 273.94 (=C), Anal. Calc. for $C_{14}H_{11}CrO_5N$: C, 51.72; H, 3.40; N, 4.307. Found: C, 52.02; H, 3.54; N, 4.39%.

2.2.2. Preparation of complex ***5b***

Complex **3b** (0.50 g, 1.54 mmol), TBAB (49 mg, 0.154 mmol), 50% aq. NaOH (1 ml) and methyl iodide (0.48 ml, 7.7 mmol) in benzene (15 ml) were stirred for 2 h yielded the product (0.472 g, 90.5%) as a yellow solid, m.p. 83°C, IR ν (CO) 2054 (m), 1973.0 (sh), 1928.7 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 2.35 (s, 3H, CH_3), 3.05 (s, 3H, N–CH_3), 3.98 (s, 3H, N–CH_3), 6.45–6.55 (m, 2H), 6.97 (d, $J = 6$ Hz, 1H), 7.23 (d, $J = 6$ Hz, 1H) (for 4 phenyl protons). ^{13}C-NMR ($CDCl_3$) δ 21.46 (CH_3), 45.77 (N–CH_3), 51.22 (N–CH_3), 115.95, 119.41, 126.47, 128.42, 138.34, 152. 86 (each as for phenyl ring), 217.28, 223.95 (CO), 274.72 (=C). Anal. Calc. for $C_{15}H_{13}CrO_5N$: C, 53.10; H, 3.86; N, 4.12. Found: C, 53.40; H, 3.78; N, 4.08%.

2.2.3. Preparation of complex ***5c***

Complex **3c** (0.40 g, 1.12 mmol), TBAB (36 mg, 0.112 mmol), 50% aq. NaOH (1 ml) and methyl iodide (0.35 ml, 5.6 mmol) in benzene (11ml) were stirred for 2 h yielded the product (0.381 g, 91.5%) as yellow solid, m.p. 82°C, IR ν (CO) 2051.1 (m), 1971.1 (sh), 1922.9 (s) cm^{-1}, ^{1}H-NMR ($CDCl_3$) 3.06 (s, 3H, N–CH_3), 3.79 (s, 3H, OCH_3), 3.97 (s, 3H, N–CH_3), 6.67 (d, $J = 8$ Hz, 1H), 6.87 (d, $J = 8$ Hz, 1H), 6.99 (t, $J = 8$ Hz, 1H), 7.15 (t, $J = 8$ Hz, 1H) (for 4 phenyl protons). ^{13}C-NMR ($CDCl_3$) δ 45.02 (N–CH_3), 50.67 (N–CH_3), 54.87 (OCH_3), 110.57, 120.47, 127.16, 140.94, 147.92 (each as for phenyl ring), 217.17, 223.83 (CO), 271.72 (=C). Anal. Calc. for: $C_{15}H_{13}CrO_5N$: C, 50.71; H, 3.68; N, 3.94. Found: C, 51.06; H, 3.97; N, 3.94%.

2.2.4. Preparation of complex ***5d***

Complex **3d** (0.45 g, 1.22 mmol), TBAB (39 mg, 0.122 mmol), 50% aq. NaOH (1 ml) and methyl iodide (0.38 ml, 6.08 mmol) in benzene (12 ml) were stirred for 2 h yielded the product (0.32 g, 68.5%) as a yellow liquid. IR ν (CO) 2054.1 (m), 1970.5 (sh), 1928.2 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 2.30 (s, 3H, CH_3), 3.13 (s, 3H, N–CH_3), 3.75 (s, 3H, OCH_3), 4.03 (s, 3H, N–CH_3), 6.65 (m, 1H), 6.85–7.25 (m, 2H) (for 3 phenyl protons).

2.2.5. Preparation of complex ***5e***

Complex **3e** (0.50 g, 1.36 mmol), TBAB (43 mg, 0.136 mmol), 50% aq. NaOH (1 ml) and methyl iodide (0.42 ml, 6.8 mmol) in benzene (13 ml) were stirred for 2 h yielded the product (0.463 g, 89.2%) as a yellow solid, m.p. 96°C. IR ν (CO) 2056 (m), 1976.9 (sh), 1932.5 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 2.17 (s, 3H, CH_3), 2,27 (s, 3H, CH_3), 3.05 (s, 3H, N–CH_3), 3.75 (s, 3H, OCH_3), 3,95 (s, 3H, N–CH_3), 6.43 (s, 1H), 6.65 (s, 1H) (for 2 phenyl protons). ^{13}C-NMR ($CDCl_3$) δ 18.60, 19.60 (CH_3) 44.83, 50.61 (N–CH_3), 54.87 (OCH_3), 111.93, 121.52, 128.08, 135.11, 138.64, 145.82 (each as for phenyl ring) 217.27, 223.87 (CO), 272. 60 (=C). Anal. Calc. for $C_{17}H_{17}CrO_6N$: C, 53.27; H, 4.47; N, 3.65. Found: C, 53.61; H, 4.80; N, 3.80%.

2.2.6. Preparation of complex ***5f***

Complex **3f** (0.45 g, 1.08 mmol), TBAB (35 mg, 0.108 mmol), 50% aq. NaOH (1 ml) and methyl iodide (0.34 ml, 5.4 mmol) in benzene (11 ml) were stirred for 2 h yielded the product (0.432 g, 93%) as a yellow solid, m.p. 87°C IR ν (CO) 2080 (m), 2000 (sh), 1955 (s)

cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.25 (s, 9H, $SiMe_3$), 3.08 (s, 3H, N–CH_3), 3.8 (s, 3H, OCH_3), 4.0 (s, 3H, N–CH_3), 6.8 (s, 1H), 6.9 (d, $J = 7.5$ Hz, 1H), 7.28–7.35 (m, 1H) (for 3 phenyl protons). ^{13}C-NMR ($CDCl_3$) δ −1.37 ($SiMe_3$), 44.95, 50.64 (N–CH_3), 54.76 (OCH_3), 109.99, 125.09, 131.41, 132.419, 140.48, 148.62 (each as for phenyl ring), 217.15, 223.86 (CO), 272.31 (=C). Anal. Calc. for $C_{18}H_{21}CrO_6NSi$: C, 50.58; H, 4.95; N, 3.28. Found: C, 50.53; H, 4.90; N, 3.20%.

2.2.7. Preparation of complex **5g**

Complex **3a** (0.50 g, 1.6 mmol), TBAB (52 mg, 0.16 mmol), 50% aq. NaOH (1 ml) and benzyl bromide (0.274 ml, 2.4 mmol) in benzene (16 ml) were stirred for 2 h yielded the product (0.506 g, 84%) as yellow solid, m.p. 85°C, IR ν (CO) 2066 (m), 1979 (sh), 1934 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ *syn:anti* = 30:70 *syn*-**5g**. 2.78 (s, 3H N–CH_3), 5.51 (s, 2H, N–CH_2–), *anti*-**5g**. 3.77 (s, 3H, N–CH_3), 4.51 (s, 2H, N–CH_2–), overlap regions 6.74 (d, $J = 8$ Hz, 2H), 7.00–7.37 (m, 8H) (for 10 phenyl protons). ^{13}C-NMR ($CDCl_3$) δ 43.25, 48.35 (N–CH_3), 61.65, 67.08 (N–CH_2–), 118.66, 125.78, 127.00, 127.19, 128.49, 128.59, 129.11, 134.01, 152.92 (each as for phenyl rings), 216.83, 223.83 (CO), 276.32 (=C). Anal. Calc. for $C_{20}H_{15}CrO_5N$: C, 59.86; H, 3.76; N, 3.49. Found: C, 59.76; H, 3.80; N, 3.50%.

2.2.8. Preparation of complex **5h**

Complex **3b** (0.5 g, 1.54 mmol), TBAB (49 mg, 0.154 mmol), 50% aq. NaOH (1 ml) and benzyl bromide (0.26 ml, 2.3 mmol) in benzene (15 ml) were stirred for 2 h yielded the product (0.475 g, 79%) as yellow solid, m.p. 93°C. IR ν (CO) 2054.0 (m), 1970.1 (sh), 1928 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ *syn:anti* = 4060, *anti*-**5h** 2.25 (s, 3H CH_3), 3.76 (s, 3H, N–CH_3), 4.52 (d, $J = 5$ Hz, 2H, N–CH_2–), *syn*-**5h** 2.30 (s, 3H, CH_3), 2.79 (s, 3H, N–CH_3), 5.50 (s, 2H, N–CH_2–), overlap regions 6.52–7.37 (m, 9H) (for phenyl ring). ^{13}C-NMR ($CDCl_3$) δ 21.37 (CH_3), 42.87, 48.39 (N–CH_3), 61.40, 66.98 (N–CH_3), 115.64, 115.86, 119.09, 119.40, 126.36, 126.93, 127.12, 128.09, 128.37, 129.02, 133.85, 138.29, 152.82 (each as for phenyl rings), 216.70, 217.08, 223.46 (CO), 277.36 (=C), Anal. Calc. for $C_{21}H_{17}CrO_5N$: C, 60.72; H, 4.13; N, 3.37. Found C, 60.72; H, 4.07; N, 3.30%.

2.3. General procedure for the preparation of pentacarbonyl {ethoxy [(tricarbonylchromium)-η^6-aryl]carbene}chromium (0) complexes **2a–f**

All alkoxy carbene complexes were prepared according to Fischer's original procedure [9]. Arene tricabonyl chromium complex (1.1 n mmol) was dissolved in (3 n ml) THF under argon, the reaction mixture was cooled to −78°C using acetone–dry ice bath. The reaction mixture was treated with butyllithium (1.21 n mmol) and stirred for 2 h at −78°C. Cr $(CO)_6$ (n mmol) was introduced at −78° C to the reaction mixture. 3 n ml of diethyl ether was added after 30 min. The reaction mixture was slowly warmed to 0°C (3 h). To this a dichloromethane solution of triethyloxonium tetrafluoroborate (1.5 n mmol) was added. The reaction mixture was filtered through a small plug of neutral alumina and the solvent was removed under vacuum at low temperature. The residue was purified by flash chromatography (20% dichloromethane in petroleum ether).

2.3.1. Preparation of complex **2a**

Benzene tricarbonylchromium complex (1 g, 4.77 mmol) in THF ~15 ml treated with butyllithium (3.24 ml (1.6M in hexane), 5.19 mmol) at −78°C for 2 h. After reaction with $Cr(CO)_6$ (0.943 g, 4.28 mmol) and triethyloxoniumtetrafluoroborate (6.5 ml, 6.5 mmol) yielded the product (1.51 g, 69%) as a dark red solid, IR ν (CO) 2061.8 (m), 1980 (sh), 1946 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.74 (t, $J = 7$ Hz, 3H, ethyl CH_3), 5.10–5.40 (m, 4H, 2-OCH_2, 2-aromatic protons), 5.71 (t, $J = 6$ Hz, 1H, phenyl H), 6.01 (d, $J = 6$Hz, 2H, phenyl H), ^{13}C-NMR ($CDCl_3$) δ 15.70 (CH_3), 78.39 (CH_2), 89.36, 93.47, 95.83, 113.25 (each as for aromatic carbons), 216.70, 223.61, 231.63 (each as for COs), 335.48 (=C).

2.3.2. Preparation of complex **2b**

3-Trimethyltin toluene tricarbonylchromium complex (1 g, 2.56 mmol) in THF ~8 ml treated with butyllithium (1.76 ml (1.6M in hexane), 2.82 mmol) at −78°C for 2 h. After reaction with Cr $(CO)_6$ (0.512 g, 2.33 mmol) and triethyloxoniumtetrafluoroborate (3.5 ml, 3.5 mmol) yielded the product (0.892 g, 73%) as a dark red solid. IR ν (CO) 2061.8 (m), 1976 (sh), 1948 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.75 (t, $J = 6$ Hz, 3H, ethyl CH_3), 2.26 (s, 3H, CH_3), 5.10–5.40 (m, 3H, 2-OCH_2, 1 aromatic proton), 5.59 (d, $J = 6$ Hz, 1H), 5.77 (s, 1H), 5.83 (d, $J = 6$ Hz, 1H) (each as for aromatic protons) ^{13}C-NMR ($CDCl_3$) δ 15.72 (ethyl CH_3), 21.57 (CH_3), 78.55 (O–CH_2), 90.70, 93.54, 95.39, 95.95, 106.18, 113.91 (each as for aromatic carbons), 216.72, 223.41, 232.41 (each as for COs), 336.75 (=C).

2.3.3. Preparation of complex **2c**

Anisole tricarbonylchromium complex (1 g, 4.1 mmol) in THF ~12 ml treated with butyllithium (1.76 ml (1.6M in hexane), 4.5 mmol) at −78°C for 2 h. After reaction with $Cr(CO)_6$ (0.82 g, 3.72 mmol) and triethyloxonium tetrafluoroborate (6.2 ml, 6.2 mmol) yielded the product (1.431 g, 71%) as a dark red solid. IR ν (CO) 2067.7 (s), 2016 (sh), 1959.5 (s), 1890.5 (s) cm^{-1}, ^{1}H-NMR ($CDCl_3$) δ 1.60 (t, $J = 6$ Hz, 3H, ethyl CH_3), 3.45 (s, 3H, O–CH_3), 4.82 (t, $J = 6$ Hz, 1H, aromatic proton), 5.02 (d, $J = 6$ Hz, 1H, aromatic proton),

5.15–5.35 (m, 3H, 2-OCH_2, 1 aromatic H), 5.65 (t, $J = 6$ Hz, 1H, aromatic H).

2.3.4. Preparation of complex ***2d***

2-Methylanisole tricarbonylchromium complex (1 g, 3.88 mmol) in THF ~12 ml treated with butyllithium (2.66 ml (1.6M in hexane), 4.26 mmol) at −78°C for 2 h. After reaction with Cr $(CO)_6$ (0.776 g, 3.53 mmol) and triethyloxonium-tetrafluoroborate (5.3 ml, 5.3 mmol) yielded the product (1.33 g, 68%) as a dark red solid. IR ν (CO) 2065.7 (s), 2012 (sh), 1950.5 (s), 1885 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.82 (t, $J = 6$ Hz, 3H, ethyl CH_3), 2.24 (s, 3H, CH_3), 3.69 (s, 3H, O–CH_3), 4.80–4.90 (m, 1H, aromatic proton), 5.19–5.35 (m, 4H, 2-OCH_2, 1 aromatic proton).

2.3.5. Preparation of complex ***2e***

3,4-Dimethylanisole tricarbonylchromium complex (1 g, 3.68 mmol) in THF ~12 ml treated with butyllithium (2.52 ml (1.6 M in hexane), 4.04 mmol) at −78°C for 2 h. After reaction with $Cr(CO)_6$ (0.736 g, 3.35 mmol) and triethyloxonium tetrafluoroborate (5 ml, 5 mmol) yielded the product (1.412 g, 74%) as a dark red solid. IR ν (CO) 2063.7 (s), 2010 (sh), 1959.5 (s), 1880.5 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.75 (t, $J = 6$Hz, 3H, ethyl CH_3), 2.08 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 3.75 (s, 3H, OCH_3), 4.97 (s, 1H, aromatic proton), 5.1–5.3 (m, 3H, 2-OCH_2, 1 aromatic proton).

2.3.6. Preparation of complex ***2f***

4-Trimethylsilylanisole tricarbonylchromium complex (1 g, 3.13 mmol) in THF ~10 ml treated with butyllithium (2.15 ml (1.6 M in hexane), 3.44 mmol) at −78°C for 2 h. After reaction with $Cr(CO)_6$ (0.626 g, 2.84 mmol) and triethyloxonium tetrafluoroborate (4.25 ml, 4.25 mmol) yielded the product (1.26 g, 71%) as a dark red solid. IR ν (CO) 2063.7 (m), 2023.2 (sh), 1961.5 (s), 1882.4 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.28 (s, 9H, $SiMe_3$), 1.77 (t, $J = 6$ Hz, 3H, ethyl CH_3), 3.71 (s, 3H,OCH_3), 5.01 (d, $J = 5$Hz, 1H), 5.10 (d, $J = 5$Hz, 1H) (each as for aromatic protons), 5.23 (q, $J = 6$Hz, 2H, OCH_2–), 5.55–5.65 (s, 1H, aromatic proton).

2.4. General procedure for the preparation of amino carbene complexes ***4a–h***

All amino carbene complexes were prepared according to the literature procedure [10]. Pentacarbonyl {ethoxy [(tricarbonylchromium)-η^6-aryl]carbene}chromium complexes (n mmol) in diethyl ether (3 n ml) was treated with methylamine/benzylamine (1.2 n mmol) at room temperature under argon until the color changes from red to yellow. The reaction mixture was diluted with water, extracted with dichloromethane, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The pure product was isolated by flash chromatography using dichloromethane (30–40%) in petroleum ether as the eluent.

2.4.1. Preparation of complex ***4a***

Reaction of the complex **2a** (1 g, 2.16 mmol) in diethyl ether (6 ml) and methylamine (0.221 ml, 2.59 mmol) afforded the product (0.91 g, 94%) as a yellow solid: m.p. 168°C. IR ν (CO) 2080 (m), 2000 (sh), 1950 (s), 1900 (m), 1860 (sh) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 3.82 (d, $J = 5$Hz, 3H, NCH_3), 5.13 (d, $J = 6$ Hz, 2H), 5.25 (t, $J = 6$ Hz, 2H), 5.70 (t, $J = 6$ Hz, 1H) (each as for aromatic protons), 9.44 (bs, 1H, NH). ^{13}C-NMR ($CDCl_3$) δ 40.97 (NCH_3), 88.62, 90.85, 96.48 (each as for aromatic protons), 217.19, 223.02, 232.45 (each as for COs), 270.12 (=C). Anal. Calc. for $C_{16}H_9Cr_2O_8N$: C, 42.97; H, 2.02; N, 3.13. Found: C, 43.30; H, 1.87; N, 3.27%.

2.4.2. Preparation of complex ***4b***

Reaction of the complex **2b** (0.6 g, 1.26 mmol) in diethyl ether (4 ml) and methylamine (0.130 ml, 1.512 mmol) afforded the product (0.513 g, 88.5%) as a yellow solid, m.p. 165°C. IR ν (CO) 2080 (m), 1990 (sh), 1950 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 2.22 (s, 3H, CH_3), 3.82 (d, $J = 6$ Hz, 3H, N–CH_3), 4.91–5.05 (m, 2H), 5.32 (t, $J = 6$ Hz, 1H), 5.54 (d, $J = 6$ Hz, 1H (each as for aromatic protons), 9.48 (bs, 1H, N–H). ^{13}C-NMR ($CDCl_3$) δ 21.51 (CH_3), 40.95 (N–CH_3), 88.59, 91.59, 93.49, 95.03, 96.63, 106.60 (each as for aromatic carbons), 217.30, 223.20, 233.95 (each as for COs), 272.16 (=C), Anal. Calc. for $C_{17}H_{11}Cr_2O_8N$: C, 44.27; H, 2.40; N, 3.04. Found: C, 44.62; H, 2.02; N, 2.96%.

2.4.3. Preparation of complex ***4c***

Reaction of the complex **2c** (1 g, 2.03 mmol) in diethyl ether (6 ml) and methylamine (0.208 ml, 2.44 mmol) afforded the product (0.895 g, 92.5%) as a yellow solid, m.p. 160°C. IR ν (CO) 2057.9 (m), 1971.1 (sh), 1932.5 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 3.69 (s, 3H, O–CH_3), 3.82 (d, $J = 6$ Hz, 3H, N–CH_3), 4.84 (t, $J = 6$ Hz, 1H), 5.08 (d, $J = 6$ Hz, 1H), 5.27 (d, $J = 6$ Hz, 1H), 5.78 (t, $J = 6$ Hz, 1H) (each as for aromatic protons), 9.48 (bs, 1H, N–H). ^{13}C-NMR ($CDCl_3$) δ 40.89 (N–CH_3), 56.34 (O–CH_3), 73.13, 82.57, 92.67, 96.73, 122.01, 138.00 (each as for aromatic carbons), 217.45, 223.65, 232.97 (each as for COs), 270.67 (=C). Anal. Calc. for $C_{17}H_{11}Cr_2O_9N$: C, 42.78; H, 2.32; N, 2.94. Found: C, 42.35; H, 2.35; N, 2.80%.

2.4.4. Preparation of complex ***4d***

Reaction of the complex **2d** (1 g, 1.98 mmol) in diethyl ether (6 ml) and methylamine (0.202 ml, 2.37 mmol) afforded the product (0.88 g, 90.5%) as a yellow solid, m.p. 158°C. IR ν (CO) 2057.9 (m), 1971.1 (sh), 1934.5 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 2.25 (s, 3H, CH_3), 3.75 (s, 3H, O–CH_3), 3.85 (d, $J = 5$Hz, 3H,

N–CH_3), 5.00–5.2 (m, 2H), 5.55–5.65 (m, 1H) (each as for aromatic protons), 9.6 (bs, 1H, N–H). ^{13}C-NMR ($CDCl_3$) δ 17.04 (CH_3), 40.31 (N–CH_3), 63.18 (O–CH_3), 78.02, 86.01, 89.08, 96.88, 102.10, 128.85 (each as for aromatic carbons), 216.69, 224.75, 232.42 (each as for COs), 270.02 (=C) Anal. Calc. for $C_{18}H_{13}Cr_2O_9N$: C, 44.01; H, 2.67; N, 2.85. Found: C, 44.30; H, 2.85; N, 2.95%.

2.4.5. Preparation of complex **4e**

Reaction of the complex **2e** (1 g, 1.93 mmol) in diethyl ether (6 ml) and methylamine (0.198 ml, 2.32 mmol) afforded the product (0.875 g, 90%) as a yellow solid, m.p. 126°C, 2058.0 (m), 1963 (sh), 1932 (s), 1894 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 2.04 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 3.65 (s, 3H, O–CH_3), 3.8 (d, $J = 5$Hz, 3H, N–CH_3), 5.00 (s, 1H), 5.24 (s, 1H) (each as for aromatic protons), 9.47 (bs, 1H, N–H). ^{13}C-NMR ($CDCl_3$) δ 17.66 (CH_3), 19.13 (CH_3), 39.84 (N–CH_3), 55.31 (O–CH_3), 75.28, 94.08, 96.91, 110.24, 119.04, 135.32 (each as for aromatic protons), 216.57, 222.75, 232.79 (each as for COs), 269.30 (=C), Anal. Calc. for $C_{19}H_{15}Cr_2O_9N$: C, 45.16; H, 2.99; N, 2.77. Found: C, 45.30; H, 3.15; N, 2.45%.

2.4.6. Preparation of complex **4f**

Reaction of the complex **2f** (1 g, 1.76 mmol) in diethyl ether (5 ml) and methylamine (0.18 ml, 2.12 mmol) afforded the product (0.92 g, 94.5%) as a yellow solid, m.p. 117°C. IR ν (CO) 2075 (m), 1995 (sh), 1950 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.26 (s 9H, $SiMe_3$), 3.69 (s, 3H, O–CH_3), 3.83 (d, $J = 6$Hz), 3H, N–CH_3), 5.12 (d, $J = 6$Hz, 1H), 5.18 (s, 1H), 5.76 (d, $J = 6$Hz, 1H) (each as for aromatic protons), 9.4 (bs, 1H, N–H). ^{13}C-NMR ($CDCl_3$) δ 1.37 ($SiMe_3$), 40.05 (N–CH_3), 55.43 (O–CH_3), 72.71, 91.25, 96.10, 100.44, 120.59, 137.22 (each as for aromatic carbons), 216.80, 223.04, 232.79 (each as for COs), 270.17 (=C). Anal. Calc. for $C_{20}H_{18}Cr_2O_9NSi$: C, 43.80; H, 3.31; N, 2.55. Found: C, 44.14; H, 3.47; N, 2.41%.

2.4.7. Preparation of complex **4g**

Reaction of the complex **2a** (0.5 g, 1.08 mmol) in diethyl ether (3 ml) and benzylamine (0.141 ml, 1.30 mmol) afforded the product (0.525 g, 92.5%) as a yellow solid, m.p. 120°C. IR ν (CO) 2057.9 (m), 1976 (sh), 1934.5 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 5.12–5.31 (m, 6H, 5Cr(CO)$_3$-aromatic protons, 1 N–CH_2–H), 5.65–5.73 (m, 1H, N–CH_2–H), 7.47 (s, 5H, phenyl protons)), 9.51 (bs, 1H, N–H). ^{13}C-NMR ($CDCl_3$) δ 30.41 (N–CH_2), 58.41, 87.94, 91.48, 96.97, 128.91, 130.01, 130.33, 134.13 (each as for aromatic carbons), 217.24, 223.33, 232.09 (each as for COs), 270.33 (=C). Anal. Calc. for $C_{22}H_{13}Cr_2O_8N$: C, 50.30; H, 2.88; N, 2.67. Found: C, 50.01; H, 2.71; N, 2.47%.

2.4.8. Preparation of complex **4h**

Reaction of the complex **2b** (0.5 g, 1.05 mmol) in diethyl ether (3 ml) and benzylamine (0.137 ml, 1.26 mmol) afforded the product (0.53 g, 94 %) as a yellow solid, m.p. 105°C. IR ν (CO) 2057.9 (m), 1973 (sh), 1934 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 2.21 (s, 3H, CH_3), 5.0–5.10 (m, 2H, N–CH_2), 5.15–5.35 (m, 3H, Cr(CO)$_3$-aromatic protons)), 5.56 (d, $J = 8$Hz, 1H, aromatic protons), 7.47 (s, 5H, phenyl protons), 9.57 (bs, 1H, N–H)). ^{13}C-NMR ($CDCl_3$) δ 21.33 (CH_3), 30.42 (N–CH_2), 58.49, 89.17, 92.10, 97.12, 105.02, 128.99, 130.00, 130.30, 130.52, 134.11 (aromatic carbons), 217.57, 223.37, 232.63 (each as for COs), 270.27 (=C). Anal. Calc. for $C_{23}H_{15}Cr_2O_8N$: C, 51.22; H, 3.12; N, 2.60. Found: C, 51.35; H, 3.07; N, 2.51%.

2.5. General procedure for the alkylation of amino carbene complexes

The carbene complex (n mmol) and tetrabutylammonium bromide (0.1 n mmol) in benzene (10 n ml) was treated with 50% aqueous NaOH and methyl iodide (5 n mmol). The mixture was stirred at r.t. under argon until the starting material was consumed (TLC, 2–3 h). The reaction mixture was diluted with water and extracted with dichloromethane. The organic extract was dried, and concentrated under reduced pressure. The pure product was isolated by flash chromatography (30% dichloromethane in petroleum ether).

2.5.1. Preparation of complex **6a**

Complex **4a** (0.50 g, 1.12 mmol), TBAB (37 mg, 0.112 mmol), 50% aq. NaOH (1 ml) and methyl iodide (0.348 ml, 5.6 mmol) in benzene (11 ml) were stirred for 2.5 h yielded the product (0.451 g, 87.5%) as an orange–yellow solid, m.p. 126°C. IR ν (CO) 2055.0 (m), 1965 (sh), 1926 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 4.03 (s, 3H, N–CH_3), 4.05 (s, 3H, N–CH_3), 5.12 (d, $J = 6$ Hz, 2H), 5.34 (t, $J = 6$ Hz, 2H), 5.70 (t, $J = 6$ Hz, 1H) (each as for aromatic protons). ^{13}C-NMR ($CDCl_3$) δ 44.43 (N–CH_3), 54.39, 88.81, 89.61, 96.34 (each as for aromatic carbons), 217.10, 223.88, 233.34 (each as for COs), 270.21 (=C) Anal. Calc. for $C_{17}H_{11}Cr_2O_8N$: C, 44.27; H, 2.40; N, 3.04. Found: C, 44.16; H, 2.80; N, 2.70%.

2.5.2. Preparation of complex **6b**

Complex **4b** (0.30 g, 0.650 mmol), TBAB (20 mg, 0.065 mmol), 50% aq. NaOH (1 ml) and methyl iodide (0.202 ml, 3.25 mmol) in benzene (7 ml) were stirred for 2 h yielding the product (0.272 g, 88%) as an orange–yellow solid, m.p. 132°C. IR ν (CO) 2080 (m), 2000 (sh), 1940 (s), 1920 (sh), 1860 (sh) cm^{-1}, ^{1}H-NMR ($CDCl_3$) δ 2.24 (s, 3H, CH_3), 4.02 (s, 3H, N–CH_3), 4.04 (s, 3H, N–CH_3), 4.99 (d, $J = 6$ Hz, 1H), 5.07 (s, 1H), 5.37 (t, $J = 6$ Hz, 1H), 5.58 (d, $J = 6$ Hz, 1H) (each as

for aromatic protons). ^{13}C-NMR ($CDCl_3$) δ 21.44 (CH_3), 44.47 (N–CH_3), 54.56 (N–CH_3), 88.09, 89.38, 91.16, 97.13, 105.17, 121.08 (each as for aromatic carbons), 217.20, 223.81, 233.75 (each as for COs), 269.68 (=C). Anal. Calc. for $C_{18}H_{13}Cr_2O_8N$: C, 45.48; H, 2.75; N, 2.94. Found: C, 45.15; H, 2.56; N, 2.82%.

2.5.3. Preparation of complex **6c**

Complex **4c** (0.50 g, 1.05 mmol), TBAB (34n mg, 0.105 mmol), 50% aq. NaOH (1 ml) and methyl iodide (0.325 ml, 5.25 mmol) in benzene (11 ml) were stirred for 2.25 h yielding the product (0.472 g, 92%) as an orange–yellow solid, m.p. 125°C. IR ν (CO) 2054 (m), 1965 (sh), 1924 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 3.79 (s, 3H, O–CH_3), 4.02 (s, 3H, N–CH_3), 4.04 (s, 3H, N–CH_3), 4.98 (t, $J = 6$ Hz, 1H), 5.24 (d, $J = 6$ Hz, 1H), 5.36 (d, $J = 6$ Hz, 1H), 5.73 (t, $J = 6$ Hz, 1H) (each as for aromatic protons). ^{13}C-NMR ($CDCl_3$) δ 44.59 (N–CH_3), 54.27 (N–CH_3), 56.48 (O–CH_3), 74.73, 83.23, 91.01, 96.61, 111.54, 132.93 (each as for aromatic carbons), 217.29, 223.91, 233.94 (each as for COs), 266. 21 (=C). Anal. Calc. for $C_{18}H_{13}Cr_2O_9N$: C, 44.01; H, 2.67; N, 2.85. Found: C, 43.96; H, 2.35; N, 2.69%.

2.5.4. Preparation of complex **6d**

Complex **4d** (0.50 g, 1.02 mmol), TBAB (33 mg, 0.102 mmol), 50% aq. NaOH (1 ml) and methyl iodide (0.320 ml, 5.1 mmol) in benzene (10 ml) were stirred for 2.75 h, yielding the product (0.443 g, 86%) as an orange–yellow solid, m.p. 141°C. IR ν (CO) 2054 (m), 1967 (sh), 1931 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 2.29 (s, 3H, CH_3), 3.76 (s, 3H, O–CH_3), 4.02 (s, 3H, N–CH_3), 4.06 (s, 3H, N–CH_3), 5.06 (t, $J = 6$Hz, 1H), 5.27 (d, $J = 6$Hz, 1H), 5.66 (d, $J = 6$Hz, 1H) (each as for aromatic protons). ^{13}C-NMR ($CDCl_3$) δ 17.33 (CH_3), 45.27 (N–CH_3), 53.80 (N–CH_3), 60.72 (O–CH_3), 79.23, 84.79, 97.54, 100.20, 113.74 (each as for aromatic carbons), 216.57, 22.72, 232.97 (each as for COs), 282.62 (=C). Anal. Calc. for $C_{19}H_{15}Cr_2O_9N$: C, 45.16; H, 2.99; N, 2.77. Found C, 45.60; H, 3.05; N, 2.83%.

2.5.5. Preparation of complex **6e**

Complex **4e** (0.50 g, 0.99 mmol), TBAB (32 mg, 0.099 mmol), 50% aq. NaOH and methyl iodide (0.31 ml, 4.95 mmol) in benzene (10 ml) were stirred for 3 h, yielding the product (0.46 g, 90%) as an orange–yellow solid, m.p. 95°C. IR ν (CO) 2054.0 (m), 1950 (sh), 1903. (s),1880 (s), 1840 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 2.09 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 3.76 (s, 3H, O–CH_3), 3.97 (s, 3H, N–CH_3), 4.02 (s, 3H, N–CH_3), 5.18 (s, 1H), 5.35 (s, 1H) (each as for aromatic protons). ^{13}C-NMR ($CDCl_3$) δ 17.97 (CH_3), 19.07 (CH_3), 44.05 (N–CH_3), 53.44 (N–CH_3), 55.61 (O–CH_3), 78.85, 93.21, 98.06, 109.75, 131.11 (each as for aromatic carbons), 216.76, 223.15, 232.92 (each as for COs), 265.87 (=C). Anal. Calc. for $C_{20}H_{17}Cr_2O_9N$: C, 46.25; H, 3.30; N, 2.68. Found C, 46.44; H, 3.12; N, 2.64%.

2.5.6. Preparation of complex **6f**

Complex **4f** (0.50 g, 0.91 mmol), TBAB (29 mg, 0.091 mmol), 50% aq. NaOH (1 ml) and methyl iodide (0.280 ml, 4.52 mmol) in benzene (9 ml) were stirred for 2 h, yielding the product (0.438 g, 85.4%) as an orange–yellow solid, m.p. 104°C. IR ν (CO) 2054.0 (m), 1967.3 (sh), 1930.6 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.29 (s, 9H, $SiMe_3$), 3.78 (s, 3H, O–CH_3), 4.00 (s, 3H, N–CH_3), 4.03 (s, 3H, N–CH_3), 5.20 (d, $J = 6$ Hz, 1H), 5.30 (s, 1H), 5.67 (d, $J = 6$ Hz, 1H) (each as for aromatic protons). ^{13}C-NMR ($CDCl_3$) δ 1.28 ($SiMe_3$), 29.26 (N–CH_3), 53.48 (N–CH_3), 55.51 (O–CH_3), 74.14, 91.75, 94.72, 99.53, 111.83, 132.80 (each as for aromatic carbons), 216.63, 223.17, 233.61 (each as for COs), 266.27 (=C). Anal. Calc. for $C_{21}H_{20}Cr_2O_9NSi$: C, 44.84; H, 3.58; N, 2.49. Found C, 44.80; H, 3.43; N, 2.34%.

2.5.7. Preparation of complex **6g**

Complex **4g** (0.25 g, 0.47 mmol), TBAB (15 mg, 0.047 mmol), 50% aq. NaOH (1 ml) and methyl iodide (0.145 ml, 2.35 mmol) in benzene (5 ml) were stirred for 2 h, yielding the product (0.215 g, 84%) as an orange–yellow solid, m.p. 110°C,. IR ν (CO) 2056.0 (m), 1971.1 (sh), 1930.6 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 3.80 (s, 3H, N–CH_3), 5.22 (d, $J = 8$ Hz, 2H, aromatic protons), 5.38 (t, $J = 8$ Hz, 2H, aromatic protons), 5.63 (s, 2H, N–CH_2), 5.67–5.79 (m, 1H, aromatic proton), 7.25–7.46 (m, 5H, phenyl protons). ^{13}C-NMR ($CDCl_3$) δ 30.30 (N–CH_3), 42.14 (N–CH_2–), 70.63, 88.63, 89.87, 96.31, 127.96, 129.79, 130.23, 133.93 (each as for aromatic carbons), 216.85, 223.74, 233.19 (each as for COs), 277.26 (=C). Anal. Calc. for $C_{23}H_{15}Cr_2O_8N$: C, 51.41; H, 2.82; N, 2.60. Found: C, 51.35; H, 3.07; N, 2.51%.

2.5.8. Preparation of complex **6h**

Complex **4h** (0.25 g, 0.46 mmol), TBAB (15 mg, 0.046 mmol), 50% aq. NaOH (1 ml) and methyl iodide (0.140 ml, 2.30 mmol) in benzene (5 ml) were stirred for 2 h, yielding the product (0.225 g, 87.5%) as an orange–yellow liquid. IR ν (CO) 2057.0 (m), 1969.1 (sh), 1929.6 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 2.27 (s, 3H, CH_3), 3.79 (s, 3H, N–CH_3), 5.01–5.50 (m, 4H, aromatic protons), 5.64 (s, 2H, N–CH_2) 7.25–7.50 (m, 5H, phenyl protons), ^{13}C-NMR ($CDCl_3$) δ 21.48 (CH_3), 30.42 (N–CH_3), 42.15 (N–CH_2), 70.66, 88.48, 89.35. 91.53, 97.22, 105.05, 127.97, 129.76, 130.21, 134.02 (each as for aromatic carbons), 216.94, 223.81, 233.66 (each as for COs) 271.35 (=C).

2.6. X-ray structure solution of complex **Ib**, **IIb**, **5c** and **6c**

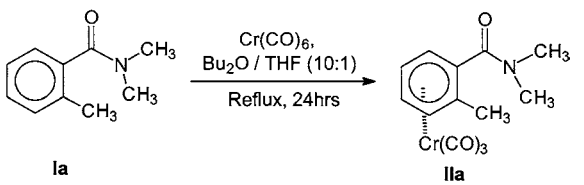
The crystals of the complex **Ib** were grown from a petroleum ether–dichloromethane mixture as colorless prisms. Diffraction data were collected on an Enraf–Nonius CAD-4 single-crystal X-ray diffractometer. Unit cell dimensions were determined using 25 machine centered reflections in the range $13 \leq \theta \leq 21$. The structure was

solved using SHELXS-86. Least-squares refinement of scale factors and positional and anisotropic thermal parameters for non-hydrogen atoms were carried out using SHELXL-93 [16]. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0914\ P)^2 + 0.9733P]$ where $P = (F_o^2 + 2F_c^2)/3$. The refinement converged to $R = 0.0594$ for 2578 observed reflections.

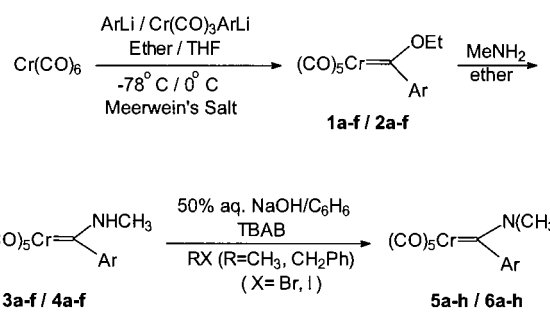
The crystals of the complex **IIa** were grown from petroleum ether–dichloromethane mixture as pale yellow prisms. Diffraction data were collected on a crystal of size $0.2 \times 0.24 \times 0.4\,mm^3$ on an Enraf–Nonius CAD-4 single-crystal X-ray diffractometer, using MoKα radiation. Unit cell dimensions were determined using 25 machine centered reflections in the range $8 \leq \theta \leq 16$. The compound, $C_{13}H_{13}CrNO_4$, $M = 299.4$, crystallizes in the monoclinic space group $P2_1/n$ with 4 molecules per unit cell. $a =$ 10.259 (5), $b = 12.391$ (13), $c = 10.708$ (6) Å, $\beta = 100.04$ (5)°, $V = 1340.3$ (17) Å^3, Z = 4, $D_{calc} = 1.483$ Mg m^{-3}. The structure was solved by direct methods using SHELXS and subsequent difference Fourier synthesis and refined by full-matrix least squares on F^2 using SHELXL-97 [17]. All the atoms were refined anisotropically and the refinement converged with a reliability criteria for the structure of $R_1 = 0.0433$, $R_w = 0.1069$, $w = 1/\sigma^2[(Fo^2) + (0.0731P)^2 + 0.0000P]$ where $P = (Fo^2 + 2Fc^2)/3$ from 2352 unique reflections ($[I > 2\sigma(I)]$), from a total of 2591 collected. The residual density in the difference map for peak and hole is 0.443 and -0.332 e Å^{-3}, respectively.

The crystals of the complex **5c** were grown from petroleum ether–dichloromethane mixture as yellow needles. Diffraction data were collected on a Brucker P4 single-crystal X-ray diffractometer for both crystals. Unit cell dimensions were determined using 25 machine centered reflections in the range $4.81 \leq \theta \leq 56.76$. The structure was solved using SHELXS-93. Least-squares refinement of scale factors and positional and anisotropic thermal parameters for non-hydrogen atoms were carried out using SHELXL-97 [17]. The weighting scheme was $\omega = 1/[\sigma^2(F_0)^2 + (0.920P)^2 + 0.3958P]$ where $P = (F_0^2 + 2Fc^2)/3$. The refinement converged to $R = 0.0553$ for 2139 observed reflections.

The crystals of the complex **6c** were grown from petroleum ether–dichloromethane mixture as orange blocks. Unit cell dimensions were determined using 25 machine centered reflections in the range $2.93 \leq \theta \leq 56.75$. The structure was solved using SHELXS-93. Least-squares refinement of scale factors and positional and anisotropic thermal parameters for non-hydrogen atoms were carried out using SHELXL-97. The weighting scheme was $\omega = 1/[\sigma^2(F_0)^2 + (0.1224P)^2 + 0.5297P]$ where $P = (F_0^2 + 2Fc^2)/3$. The refinement converged to $R = 0.0632$ for 2433 observed reflections.



Scheme 1.



Scheme 2.

3. Synthesis

3.1. Preparation of amides

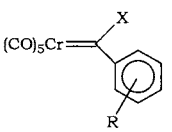
The amides **Ia** [5] and **Ib** [6] were readily synthesized from the corresponding acids. While amide **Ia** is a liquid at ambient temperature, amide **Ib** is a crystalline solid.

Complexation with tricarbonyl chromium was accomplished by thermolysis of amide **Ia** under standard conditions [7] (Scheme 1). The metal complex **IIa** is crystalline solid and provided satisfactory spectral and analytical data [8].

3.2. Preparation of amino carbene complexes

The requisite Fischer carbene complexes were synthesized in three steps: Fischer's original preparation [9] of alkoxy carbene complexes, displacement of alkoxy group by methylamino group, and finally methylation of the methylamino carbene complexes, as depicted in Scheme 2.

The alkoxy carbene complexes bearing *ortho*-OMe substituent on the aromatic ring are relatively unstable, they provided satisfactory NMR data but not accurate elemental analysis. These were immediately converted to the more stable amino carbene complexes [10] (Chart 3



R	X = OC_2H_5	X= $NHCH_3$	Yield of aminolysis %
H	**1a**	**3a**	75
3-CH_3	**1b**	**3b**	73
2-OCH_3	**1c**	**3c**	70
2-OCH_3-3-CH_3	**1d**	**3d**	55
2-OCH_3-4,5-CH_3	**1e**	**3e**	65
2-OCH_3-5-$SiMe_3$	**1f**	**3f**	60

Chart 3.

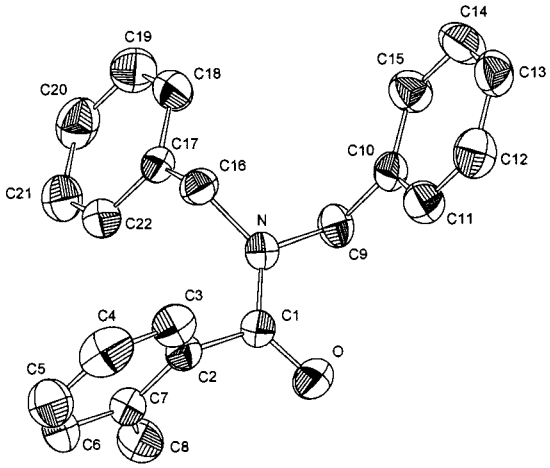
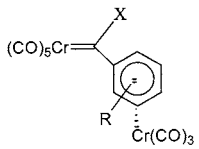


Fig. 1. ORTEP diagram of amide **Ib**.

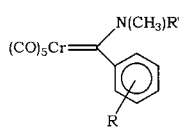
and 4). In Scheme 2, the complex **4a-f** and **6a-h** contain aromatic rings complexed with tricarbonylchromium.



R	X= OC_2H_5	X= NHR'	Yield of aminolysis %
H	**2a**	**4a** (R' = CH_3)	65
3-CH_3	**2b**	**4b** (R' = CH_3)	65
2-OCH_3	**2c**	**4c** (R' = CH_3)	66
2-OCH_3-3-CH_3	**2d**	**4d** (R' = CH_3)	62
2-OCH_3-4,5-CH_3	**2e**	**4e** (R' = CH_3)	67
2-OCH_3-5-$SiMe_3$	**2f**	**4f** (R' = CH_3)	67
H		**4g** (R'=CH_2Ph)	64
3-CH_3		**4g** (R'=CH_2Ph)	69

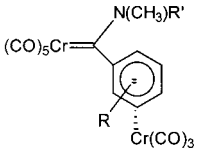
Chart 4.

Based on our earlier experience of C-alkylation [11], alkylation of monoalkylamino complexes was carried out by a biphasic protocol [12] using 50% aq. NaOH as base, benzene as the solvent and tetrabutylammonium bromide as the phase-transfer catalyst (Chart 5 and 6). Barring three, all amino carbene complexes were isolated as crystalline solids, and their structural characterization was validated by spectral and analytical data.



Complex	R	R'	Yield %
5a	H	CH_3	87
5b	3-CH_3	CH_3	90.5
5c	2-OCH_3	CH_3	91.5
5d	2-OCH_3-3-CH_3	CH_3	68.5
5e	2-OCH_3-4,5-CH_3	CH_3	89.2
5f	2-OCH_3-5-$SiMe_3$	CH_3	93
5g	H	CH_2Ph	84
5h	3-CH_3	CH_2Ph	79

Chart 5.



Complex	R	R'	Yield %
6a	H	CH_3	87.5
6b	3-CH_3	CH_3	88
6c	2-OCH_3	CH_3	92
6d	2-OCH_3-3-CH_3	CH_3	86
6e	2-OCH_3-4,5-CH_3	CH_3	90
6f	2-OCH_3-5-$SiMe_3$	CH_3	85.5
6g	H	CH_2Ph	84
6h	3-CH_3	CH_2Ph	87.5

Chart 6.

4. Comparison of structures

The ^{1}H-NMR spectrum of the amide **Ia** reveals that the chemical shifts of the methyl groups on nitrogen differ by 0.3 ppm. The lines are slightly broad at 25°C due to onset of a slow site exchange. For the dibenzylamino group in amide **Ib**, the methylene protons appear as four two line signals indicating extensive chemical shift nonequivalence, the spectra being recorded at -40°C to obtain clearly resolved lines (two protons are shielded relative to their expected position by 0.35 ppm). Since the amide **Ia** was a liquid, crystal structure was determined for amide **Ib** to gain an insight into the molecular conformation. The ORTEP diagram is depicted in Fig. 1, Table 1.

The structure reveals that one N–CH_2– group is located above the aromatic ring plane (C_2–C_1–N–C_{16} = 0.1°) and thus can experience anisotropic shielding effect of the aromatic ring current. The chemical shift difference between two sets of methylene protons is moderate (0.3 ppm). It may be due to the orientation of the aromatic ring is not entirely orthogonal (C_3–C_2–C_1–O = 102.4°, C_3–C_2–C_1–N = -77.1°, C_7–C_2–C_1–O = -72.9°, C_7–C_2–C_1–N = 107.6°).

When the aromatic ring of the amide **Ia** is complexed by Cr $(CO)_3$ moiety, the difference in chemical shift between two methyl signals diminishes from 0.30 ppm ppm to 0.03 ppm. This would reflect depletion of the π-electron density of the aromatic ring. Crystal structure of complex **IIa** confirms this explanation (Fig. 2, Table 2).

The orientation of the amide function with respect to the aromatic ring is maintained in the same way as the amide **Ia**, one methyl group still tilted towards the ring from a near perpendicular direction. The distance parameters remaining just about the same, the absence of anisotropic shielding can be attributed to metal coordination to the ring [4].

The *anti* conformer predominates for all the methylamino carbene complexes (**3a**–**3f**), as was earlier observed for the benzylamino complexes [2]. The methyl doublets corresponding to the two conformers appear between 2.90 (*anti*) and 3.76 (*syn*) ppm for all complexes except **3d**. For **3d**, the –NCH_3 signal appears at 2.30 (*anti*) and 2.98 (*syn*) ppm.

In dimethylamino carbene complexes (**5a**–**5f**) two signals for N– $(CH_3)_2$ (*syn* and *anti*) are observed at 3.05 and 4.00 ppm. This difference in chemical shift is typical, the *anti* Me group is shielded compared to the *syn* Me group. A comparison of N–Me signals in monomethylamino complexes (**3a**–**3f**) with dimethylamino complexes (**5a**–**5f**) is presented in Table 3.

Table 1
Crystal data and structure refinement for **Ib**

Empirical formula	$C_{22}H_{21}NO$
Formula weight	315.40
Temperature (K)	293 (2)
Wavelength (Å)	Mo $-K_\alpha$ radiation, $\lambda = 0.7093$
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	7.339 (2)
b (Å)	12.997 (3)
c (Å)	18.348 (4)
β (°)	94.53 (2)
V (Å^3)	1744.7 (7)
Z	4
D_{calc} (Mg m^{-3})	1.201
Absorption coefficient (mm^{-1})	0.073
F (000)	498
Crystal size (mm)	$0.63 \times 0.45 \times 0.25$
θ max (°)	23.44
Index ranges	$-8 \le h \le 8$, $0 \le k \le 14$, $0 \le l \le 20$
Reflections collected/unique	2578/2331
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.010
Final R indices $R[I > 2\sigma\ (I)]$	$R_1 = 0.0594$, $wR_2 = 0.1537$
Largest difference peak and hole (e Å^{-3})	0.140 and -0.315

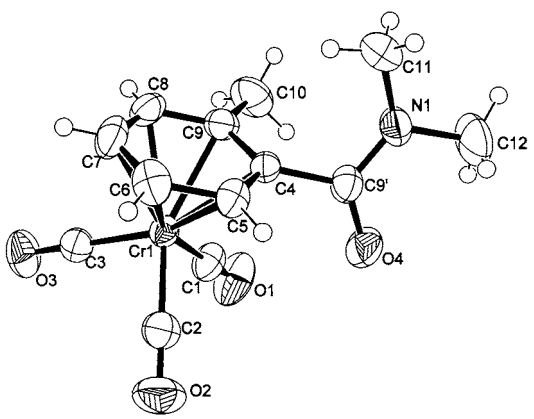


Fig. 2. ORTEP diagram of amide **IIa**.

Table 2
Crystal data and structure refinement for **IIa**

Empirical formula	$C_{13}H_{13}CrNO_4$
Formula weight	299.24
Temperature (K)	293 (2)
Wavelength (Å)	Mo $-K_\alpha$ radiation, $\lambda = 0.7093$
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	10.259 (5)
b (Å)	12.391 (13)
c (Å)	10.708 (6)
β (°)	100.04 (5)
V (Å^3)	1340.3 (17)
Z	4
D_{calc} (Mg m^{-3})	1.483
Absorption coefficient (mm^{-1})	0.862
F (000)	616
Crystal size (mm^3)	$0.2 \times 0.24 \times 0.4$
θ range for data collection (°)	2.53–24.98
Index ranges	$-12 \le h \le 12$, $0 \le k \le 14$, $0 \le l \le 12$
Reflections collected/unique	2591/2352 [$R_{int} = 0.0000$]
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.011
Final R indices $[R[I > 2\sigma\ (I)]$	$R_1 = 0.0433$, $wR_2 = 0.1069$
R indices (all data)	$R_1 = 0.0657$, $wR_2 = 0.1157$
Largest difference peak and hole (e A^{-3})	0.443 and -0.332

Crystal structure determination of a representative complex, **5c** was undertaken, and the ORTEP diagram is displayed in Fig. 3**.** As is evident from the structure, one of the methyl groups attached to the nitrogen, the C-9 carbon, is placed in the expected region above the aromatic ring [defined by C (2) to C (7)] to experience a shielding effect due to aromatic ring current anisotropy. The dihedral angle defined by C (9), N (1), C (1) and C (2) is only 5.3°, while the dihedral angle defined by C (10), N (1), C (1) and C (2) is $-174.7°$. This indicates planarity of the nitrogen substituents-a consequence of extensive delocalization of the non-bonded pair of electrons from nitrogen to the metal. The bond length [C (1)–N (1) 1.307 Å] is thus much shorter than [N (1)–C (10) 1.464 Å] and [N (1)–C (9) 1.456 Å]. The dihedral angle of N (1)–C (1)–C (2)–C (7) 94.4° ascertain that the plane of NMe_2 is perpendicular to the aromatic ring. This establishes the orientation of the shielded methyl group unequivocally. The dihedral angles C (15)–CR (1)–C (1)–N (1)– 34.9° and C (15)–CR (1)–C (1)–C (2)– 143.2° further reveal that the aminocarbene group has a staggered conformation with respect to the Cr– $(CO)_5$ groups, as predicted by theory [13]. The molecular structure of **5c,** therefore, confirms the relative orientation of groups [14] as deduced from NMR data (see Tables 4 and 5).

Table 3

Compound No.	N–CH_3 peak position in ppm			Compound No.	N–CH_3 peak position in ppm		
	syn	*anti*	$\Delta\delta$		*syn*	*anti*	$\Delta\delta$
3a	3.76	2.96	0.80	**5a**	3.99	3.04	0.95
3b	3.75	2.96	0.79	**5b**	3.98	3.05	0.93
3c	3.72	2.94	0.78	**5c**	3.97	3.06	0.91
3d	2.98	2.30	0.68	**5d**	4.00	3.12	0.88
3e	3.73	2.96	0.77	**5e**	3.97	3.05	0.92
3f	3.73	2.94	0.79	**5f**	3.95	3.05	0.90
				5g	3.77	2.78	0.99
				5h	3.76	2.79	0.97

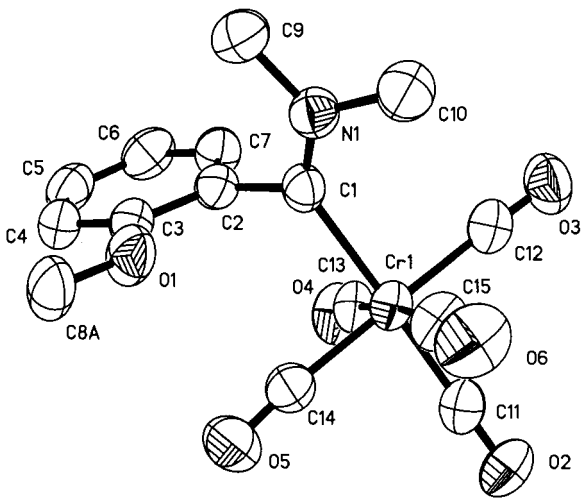


Fig. 3. ORTEP diagram of complex **5c**.

Table 4
Selected Bond lengths [Å] and angles [°] for **5c**

Cr(1)–C(11)	1.856(6)	C(14)–Cr(1)–C(1)	89.3(2)
Cr(1)–C(1)	2.133(5)	C(12)–Cr(1)–C(1)	91.7(2)
N(1)–C(1)	1.307(6)	C(1)–N(1)–C(9)	125.0(5)
N(1)–C(9)	1.456(7)	C(1)–N(1)–C(10)	123.6(4)
N(1)–C(10)	1.464(7)	C(9)–N(1)–C(10)	111.4(5)
C(1)–C(2)	1.499(7)	N(1)–C(1)–C(2)	114.0(4)
C(11)–Cr(1)–C(1)	178.3(2)	N(1)–C(1)–Cr(1)	130.1(3)
C(15)–Cr(1)–C(1)	94.0(2)	C(2)–C(1)–Cr(1)	115.9(3)

In analogous Fischer carbene complexes **6a**–**f**, where the aromatic ring is complexed with tricarbonylchromium, the chemical shift difference between *syn* and *anti* Me groups decrease dramatically; the difference in chemical shift is barely 0.02–0.05 ppm indicating a drastic reduction in anisotropic shielding effect of the aromatic ring [15] (see Table 6).

The complexes **6g** and **6h** illustrate this point vividly. The chemical shift of N–CH_3 (*syn*) signal is 3.80 ppm for **6g** and 3.79 ppm for **6h**, while the methylene signal of N–CH_2–Ph appears at 5.63 and 5.64 ppm. It may be recalled that methyl and methylene signals shielded by aromatic ring anisotropy in **5g** appear at 2.78 and 4.51 ppm respectively. Thus, the data indicate that an anisotropic effect is practically absent in complexes with Ar–Cr $(CO)_3$ group. In this respect, the result is consistent with expectations based on the results of chromium complexed amide **2a** described above. The absence of aromatic ring current could be manifested in the diminished $\Delta\delta$ of *syn*/*anti* Me groups. The crystal structure however revealed a different story.

The crystal structure of a representative complex **6c** was determined by the usual method and has been described in the Section 3. The ORTEP diagram is represented in Fig. 4 (see Tables 7 and 8).

Table 5
Crystal data and structure refinement for **5c**

Empirical formula	$C_{15}H_{13}CrNO_6$
Formula weight	355.26
Temperature (K)	300 (2)
Wavelength (Å)	1.54178
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	9.4463 (5)
b (Å)	11.3796 (12)
c (Å)	15.5903 (17)
V (Å^3)	1675.9 (3)
Z	4
Calculated density (Mg m^{-3})	1.408
Absorption coefficient (mm^{-1})	5.884
F (000)	728
Crystal size (mm^3)	$0.10\times0.30\times0.50$
θ range for data collection (°)	4.81–56.76
Index ranges	$-10\le h\le 10$, $-12\le k\le 12$, $-15\le l\le 16$
Reflections collected/unique	2501/2139 [$R_{int}=0.0334$]
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.068
Final *R* indices [$R[I>2\sigma(I)]$]	$R_1=0.0553$, $wR_2=0.1351$
R indices (all data)	$R_1=0.0580$, $wR_2=0.1376$
Largest difference peak and hole (e Å^{-3})	0.453 and −0.316

Table 6

Compound No.	$N–CH_3$ peak position in ppm		
	Syn	*anti*	$\Delta\delta$
6a	4.05	4.03	0.02
6b	4.04	4.02	0.02
6c	4.04	4.01	0.03
6d	4.06	4.02	0.04
6e	4.02	3.97	0.05
6f	4.03	4.00	0.03
6g	3.80		
6h	3.79		

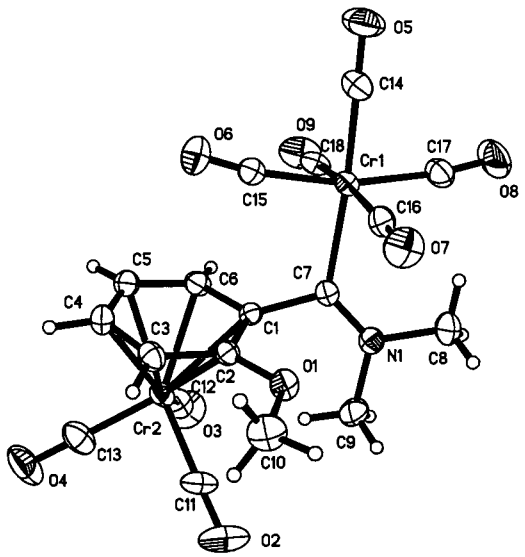


Fig. 4. ORTEP diagram of the complex **6c**.

Table 7
Selected bond lengths (Å) and angles (°) for **6c**

Cr(1)–C(14)	1.861(7)	C(7)–N(1)–C(9)	126.6(5)
Cr(1)–C(7)	2.146(5)	C(8)–N(1)–C(9)	110.6(5)
N(1)–C(7)	1.289(7)	C(2)–C(1)–C(6)	116.8(5)
N(1)–C(8)	1.471(7)	C(2)–C(1)–C(7)	117.8(4)
N(1)–C(9)	1.473(8)	C(6)–C(1)–C(7)	123.3(4)
C(1)–C(7)	1.495(7)	N(1)–C(7)–C(1)	118.6(4)
C(2)–O(1)–C(10)	118.0(5)	N(1)–C(7)–Cr(1)	129.3(4)
C(7)–N(1)–C(8)	122.8(5)	C(1)–C(7)–Cr(1)	112.0(3)

Evidently, the molecular structure of **6c** is considerably different in the terms of orientation of the $–NMe_2$ group with respect to the aromatic ring. The $Cr(CO)_3$ group and one of the N–Me group are actually on the same side, instead of occupying opposite faces of the plane containing the aromatic group! This explains, albeit in a disappointing way, why the chemical shifts of the methyl groups on the nitrogen are similar. The bulk of the $Cr(CO)_3$ group is perhaps too large to be accommodated in the vicinity of the $Cr(CO)_5$ group. The amino group is coplanar (as expected) as seen from the dihedral angles: C (9)–N (1)–C (7)–C (1) $-6.3°$ and C (8)–N (1)–C (7)–C (1) $-172.4°$. One of the N-methyl group (C-9) is twisted (about 80° with respect to the aromatic plane) towards the chromium tricarbonyl moiety.

Table 8
Crystal data and structure refinement for **6c**

Empirical formula	$C_{18}H_{13}Cr_2NO_9$
Formula weight	491.29
Temperature (K)	299 (2)
Wavelength (Å)	1.54178
Crystal system,	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	15.4039 (5)
b (Å)	10.0630 (3)
c (Å)	13.3601 (8)
β (°)	101.607 (4)
V (Å^3)	2028.59 (15)
Z	4
D_{calc} (Mg m^{-3})	1.609
Absorption coefficient (mm^{-1})	9.294
F (000)	992
Crystal size (mm^3)	$0.20 \times 0.26 \times 0.30$
θ range for data collection (°)	2.93–56.75
Index ranges	$-16 \le h \le 16$, $-10 \le k \le 1$, $-1 \le l \le 14$
Reflections collected/unique	3061/2433 [$R_{int} = 0.0594$]
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.042
Final R indices [$R[I > 2\sigma\ (I)]$]	$R_1 = 0.0632$, $wR_2 = 0.1636$
R indices (all data)	$R_1 = 0.0722$, $wR_2 = 0.1731$
Largest difference peak and hole (e Å^{-3})	0.477 and -0.220

5. Conclusions

In summary, we have described synthesis and characterization of new and structurally related sets of aryl amino carbene complexes. The aryl group of one set is complexed with tricarbonylchromium. We compared the conformation of these complexes with amide compounds of similar structure and sought to use chemical shift of $N–CH_3$ groups as a convenient conformational probe. We surmized that absence of anisotropic shielding of these methyl signals is a reflection of electron-density withdrawal from arene ring by $Cr(CO)_3$ group, and hence should represent similarity of conformation between isostructural amides and carbene complexes. The crystal structures of representative compounds revealed that such correlation would have been in great error since the conformation of a carbene complex bearing an arene–$Cr(CO)_3$ group is vastly different from the expected structure.

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[14] This situation is close to the structure suggested in an earlier paper [8] on conformation of $Cr(CO)_3$-complexed aryl dialkylamides (pentacarbonylmetal fragment replaced by C=O group). However, no compelling structural evidence was provided either to support such a suggestion, or to discard a conformation similar to carbene complexes **5a**–**f**.

[15] For the carbene complexes **4a**–**f**, only one doublet signal for the methyl group is seen in their NMR spectra. This is markedly different from the set **3a**–**f**, which showed the presence of both *syn* and *anti* conformers. It is not possible to assign the orientation of methyl groups in complexes **4a**–**f** unambiguously as *syn* or *anti* based on this spectral data alone, though *anti* appears more reasonable on steric grounds.

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