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The chemistry of metallacyclic alkenylcarbene complexes Part 9. Synthesis and reactions of chelated η^2-alkene- and η^3-allyl-carbene complexes of cobalt, manganese and chromium☆

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Abstract

Cobaltalactams **7** with alkyl substituents at the nitrogen atom are accessible by UV-irradiation of $CpCo(CO)_2$ **6** in the presence of the appropriate vicinal aminoalkenol **8**. Thus chelated (η^3-allyl)cobaltcarbene complexes with either (*endo*-amino)oxo (**3**), (*exo*-amino)oxo (**11**), or dioxo (**2**) substitution at the carbene carbon atom are now available. A synthetic route to chelated (η^2-alkene)-carbene complexes of chromium with allylically situated hydroxy groups is also presented.

Keywords: Carbene complexes; Metallacycles; Co; Cr; Mn

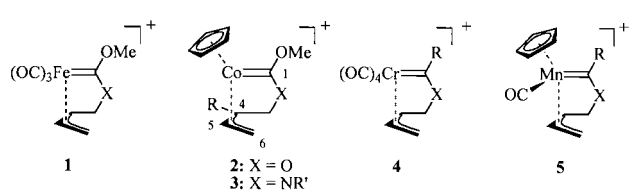
1. Introduction

Over the last years we have reported reactions of different types of chelated (η^3-allyl)-ironcarbene complexes **1** with a variety of nucleophiles. We also examined the influence of the nature of the nucleophile, of the substituents at the carbene carbon atom and at the organic periphery on the course and selectivity of such reactions, especially those proceeding with C–C bond formation [2]. In the current paper we report on new variations regarding the central metal fragment, on a versatile synthesis of cobaltalactams bearing alkyl substituents at the nitrogen atom, and on the effect of donor groups like OH in the vicinity of potential π-ligating C=C bonds tethered to the carbene carbon atom.

2. Results and discussion

Complexes **2** and **3** are isoelectronic to the iron analogues **1** but were expected to show different reactivities. For systematic studies on their chemistry we prepared an array of derivatives of them. Analogous complexes of chromium **4** and manganese **5** are unknown, so far (Fig. 1).

The first notes on the preparation of cobaltalactones and -lactams were published by Aumann et al., although without providing detailed experimental data [3]. Their synthesis of cobaltalactams from vinyl aziridines and (η^5-cyclopentadienyl)dicarbonylcobalt (**6**) seemed to be restricted to derivatives bearing elec-



1 **2:** X = O **3:** X = NR' **4** **5**

Fig. 1. η^3-Allyl carbene complexes.

☆ For Part 8, see Ref. [1].

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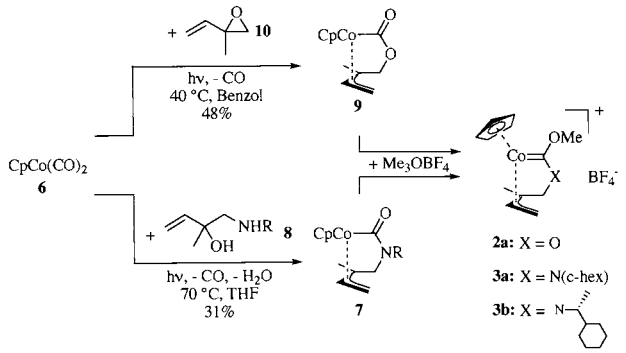


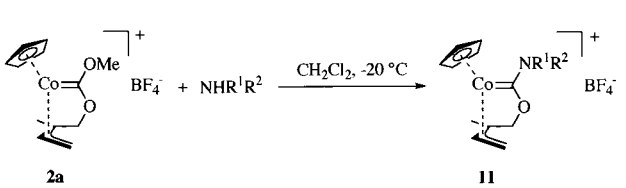
Scheme 1.

tron-withdrawing groups at the nitrogen atom. We have now opened access to cobaltalactams **7** with alkyl substituents on the ring nitrogen atom by UV-irradiation of **6** in the presence of 1-amino-3-buten-2-ols **8**. We also optimised our previous protocol [4a] for the synthesis of cobaltalactone **9** from isoprene oxide **10** and **6** [4b]. The corresponding carbene complexes **2a** and **3a**/**b** are readily available by subsequent alkylation of **7** and **9** with Meerwein salt (Scheme 1).

Whereas the iron complexes **1** mostly react with nucleophiles at their allyl ligand [2], the cobalt analogues **2** and **3** behave more like typical Fischer carbene systems. With primary amines in acetonitrile at room temperature (r.t.) complex **2a**, for instance, undergoes aminolysis to give the (*exo*-amino)oxo-substituted carbene complexes **11** [4a].

α-Amino esters also give rise to the corresponding derivatives of **11** in good yields upon reaction with **2a** at −20°C in dichloromethane (Scheme 2). Secondary amines are either inert (at −20°C) or merely lead to demethylation to give **9** (at r.t.), with the sole exception of dimethylamine which reacts with **2a** to leave the corresponding carbene complex **11i** upon chromatographic workup. Table 1 shows some derivatives of **11** prepared by this carefully optimised aminolysis reaction. As expected, the (*endo*-amino)oxocarbene complexes **3** do not react with any types of amines at all, presumably due to a more effective stereoelectronic shielding of their carbene carbon atoms by the ring nitrogen atom and its substituent.

Similar (η^3-allyl)complexes of chromium **4** and manganese **5** should in principle be accessible via the corresponding η^2-alkene precursors bearing suitable leaving

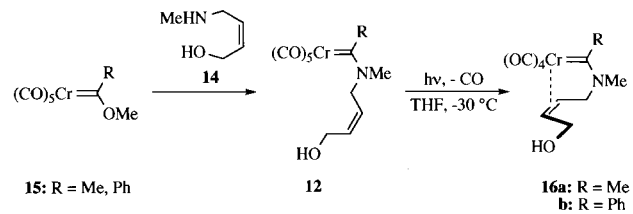


Scheme 2.

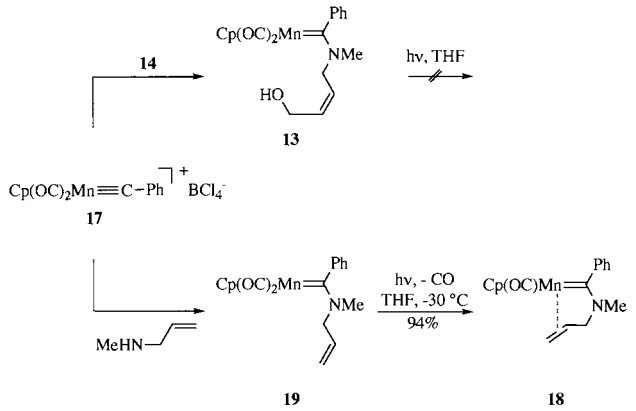
Table 1
Preparation of aminooxocobaltcarbene complexes **11** by aminolysis reaction

Amine	R^1	R^2	Product	Yield (%)
Methylamine	CH_3	H	**11a**	98
Benzylamine	CH_2Ph	H	**11b**	68
Allylamine	CH_2CHCH_2	H	**11c**	64
(−)-Myrthanylamine	$C_{10}H_{17}$	H	**11d**	17
Glycine methylester	CH_2COOCH_3	H	**11e**	87
β-Alanine methylester	$CH_2CH_2COOCH_3$	H	**11f**	79
Aminoacetaldehyde dimethylacetal	$CH_2CH(OCH_3)_2$	H	**11g**	91
Aminoacetonitrile	CH_2CN	H	**11h**	81
Dimethylamine	CH_3	CH_3	**11i**	32

groups in the allylic position. Hitherto, little was known about the effect of such groups on the coordination tendency of the adjacent π-ligand. Neither manganese nor chromium form any stable oxo-substituted (η^2-alkene)carbene complexes (X = O) at all [5]. Aza-substituted (η^2-alkene)carbene complexes (X = NR′) had been synthesised by Hegedus et al. (Cr) [6], Rudler et al. (Cr, W) [7] and Templeton et al. (Mn) [8] but were lacking allylic groups amenable to cleavage. We prepared the aminocarbene complexes **12** and **13** starting from 4-methylamino-2-buten-1-ol **14**, with the intention of removing their hydroxy groups as water by treatment with tetrafluoroboric acid after coordination of the double bond. The chromium complexes **12** are available by a normal aminolysis reaction [9–11] of **14** and the respective methoxycarbene complexes **15**. Whereas π-coordination of unsaturated ligands like olefins and acetylenes, including tethered ones, to chromiumcarbene complexes is quite often achieved by thermically induced substitution [12,13] of other ancillary ligands like carbon monoxide, warming of **12** only leads to its decomposition. However, the alkenechromiumcarbene complexes **16** can be obtained in excellent yields by irradiation of **12** at −30°C. They form yellow–red oils stable at r.t. (Scheme 3)



Scheme 3.



Scheme 4.

The manganese complex **13** is accessible by addition of the amino group of **14** onto the carbyne complex **17** [14,15]. Interestingly, irradiation of **13** even at low temperature leads to decomposition, whereas the corresponding (π-alkene)carbene complex **18** lacking a terminal hydroxy group can be easily prepared in this way from the allylamino substituted carbene complex **19**. It is obviously the OH group itself that prevents ligation of the adjacent olefin moiety from yet unknown reasons. As moderately electron-withdrawing substituents, such as allylically situated alkoxy and ester groups, are known [16] to activate the alkene toward metal coordination due to an enhanced d–π* back-bonding component, electronic reasons are unlikely to be responsible here, even more so as the Cp(CO)Mn-fragment should bear more electron density than the $(OC)_4Cr$-core. Either the respective Mn-analogues of **16** are too sensitive to survive the conditions of their preparation for long enough a time, or the hydroxy group enables formation of Mn–O-chelate complexes which then undergo rapid decomposition to give products of higher oxidation states than the rather uncommon Mn(I) in **13** and **18** (Scheme 4).

Attempts to cleave the OH-group in **16** with tetrafluoroboric acid failed and only led to decomposition. We are currently testing other acids and also different leaving groups like tosylate as well as different combinations of leaving groups/cleavage reagents like halide/silver tetrafluoroborate to complete the synthesis of **4**.

3. Experimental

3.1. General information

All reactions were carried out under an atmosphere of argon. All solvents were dried according to literature procedures and freshly distilled under argon prior to use. The starting complexes **15** [17] and **17** [18] were prepared as published; the α-aminoesters and aminoacetonitriles were freshly prepared from their respective, commercially available hydrochlorides prior to use (see the following procedure). Melting points are uncorrected and boiling points quoted for Kugelrohr distillations refer to the temperature of the air bath. IR: Beckmann Acculab A1, A3 A8; Perkin–Elmer 1420. NMR: Jeol JNM PMX 60, JNM-PS 100 and GNM GX 400 FT; TMS as internal standard. MS: Varian MAT-CH-4B (EFO-4B-source; 70 eV). MA: Heraeus Mikromat C-H-N. hν: Hanau TQ 150 mercury vapour lamp.

3.2. (η^5-Cyclopentadienyl)-[(4-6-η^3)-4-methyl-2-oxa-1-oxo-4-hexen-1,6-diyl]-cobalt(III) (**9**) [3,4]

An irradiation apparatus was set up consisting of a mercury pressure lamp, a double-jacketed reaction vessel (suitable for water-cooling the reaction mixture both at the wall separating it from the centrally mounted mercury vapour lamp and at the outer wall) equipped with a nitrogen inlet and a water-cooled reflux condenser topped by a mercury valve or a septa/balloon combination. The reaction vessel was flushed with dry nitrogen and then charged with $CpCo(CO)_2$ **6** (12.01 g of 85% material, 56.70 mmol), isoprene oxide **10** (5.61 g, 66.71 mmol) and benzene (100 ml). The mixture was irradiated for 3 h maintaining a temperature of ca. 40°C within the solution by a slight stream of cooling water in the vessel jackets. The reflux condenser was operated at its maximum performance to prevent any loss of the volatile oxirane **10**. The progress of the reaction was monitored by TLC (silica gel, diethyl ether). Once the reaction had come to a halt, another 1.00 ml (0.86 g, 10.26 mmol) of isoprene oxide **10** was added and irradiation continued for a further hour. The lamp was finally switched off, the entire set-up was dismantled and all volatile components were removed in vacuo. The residue thus obtained was then purified by column chromatography. Eluting first with diethyl ether removed any impurities and residual starting materials. The pure product **9** could be washed off the column with 1:1 acetonitrile–dichloromethane. After concentration of the eluate on a rotary evaporator and drying on an oil pump 6.20 g (48%) of **9** was obtained as orange crystals of m.p. 137°C (dec.); R_f (Et_2O) = 0.17, R_f (1:1 CH_3CN–CH_2Cl_2) = 0.50. ^{1}H-NMR ($CDCl_3$): $\delta = 1.44$ [dd, ^2J(6-H^{exo}/6-H^{endo}) = 2.50 Hz, ^3J(5-H/6-H^{endo}) = 11.96 Hz, 1H, 6-H^{endo}], 1.86 [s, 3H, 4-CH_3], 3.10 [d, ^2J(3-H^{exo}/3-H^{endo}) = 10.99 Hz, 1H, 3-H^{endo}], 3.57 [d, ^2J(3-H^{endo}/3-H^{exo}) = 10.99 Hz, 1H, 3-H^{exo}], 3.66 [dd, ^2J(6-H^{endo}/6-H^{exo}) = 2.50 Hz, ^3J(5-H/6-H^{exo}) = 4.10 Hz, 1H, 6-H^{exo}], 5.02 [s, 5H, Cp],

5.05 [mc, 1H, 5-H]. ^{13}C-NMR ($CDCl_3$): $\delta = 27.91$ (4-Me), 42.40 (6-C), 67.74 (3-C), 79.60 (5-C), 87.77 (Cp-C), 88.48 (4-C), 203.61 (1-C). IR (KBr): $\nu = 3090$ cm^{-1}, 2960, 2920, 2870, 1630, 1420, 1410, 1370, 1240, 1050, 980, 950, 830, 810, 610. MS (70 eV): m/z (%) = 236 (70) [M^+], 208 (68) [$M^+ - CO$, $M^+ - C_2H_4$], 192 (37) [$M^+ - C_2H_4O$], 180 (80), 178 (90), 124 (100) [$CoCp^+$], 98 (75), 59 (100), 39 (50), 28 (72) [CO^+, $C_2H_4^+$].

3.3. (η^5-Cyclopentadienyl)-[(4-6-η^3)-1-methoxy-4-methyl-2-oxa-4-hexen-6-yl-1-ylidene] cobalt(III) tetrafluoroborate (**2a**)

Under an atmosphere of dry nitrogen complex **9** (4.00 g, 16.94 mmol) was dissolved in dry dichloromethane (50 ml). Trimethyloxonium tetrafluoroborate (2.50 g, 16.94 mmol) was added at once and the resulting mixture was stirred for ca. 3 h. Once the reaction was completed (as to TLC-monitoring on silica gel with 1:1 acetonitrile–dichloromethane, all volatile components were removed in vacuo and the remaining residue was finally purified by column chromatography. Any by-products and residual starting materials were first washed off with neat diethyl ether, the product complex **2a** could then be eluted with 1:1 acetonitrile–dichloromethane and was obtained as a yellow–olive solid upon drying on an oil pump. Yield: 4.34 g (76%), m.p. 114°C (dec.); R_f (1:1 CH_3CN–CH_2Cl_2) = 0.45. ^{1}H-NMR (CD_3CN): $\delta = 1.78$ [dd, ^2J(6-H^{exo}/6-H^{endo}) = 2.75 Hz, ^3J(5-H/6-H^{endo}) = 12.10 Hz, 1H, 6-H^{endo}], 1.93 [s, 3H, 4-CH_3], 3.95 [d, ^2J(3-H^{exo}/3-H^{endo}) = 12.09 Hz, 1H, 3-H^{endo}], 4.04 [s, 3H, OCH_3], 4.18 [dd, ^2J(6-H^{endo}/6-H^{exo}) = 2.75 Hz, ^3J(5-H/6-H^{exo}) = 7.70 Hz, 1H, 6-H^{exo}], 4.40 [d, ^2J(3-H^{endo}/3-H^{exo}) = 12.09 Hz, 1H, 3-H^{exo}], 5.36 [s, 5H, Cp], 5.52 [dd, ^3J(6-H^{endo}/5-H) = 12.10 Hz, ^3J(6-H^{exo}/5-H) = 7.70 Hz, 1H, 5-H]. ^{13}C-NMR (CD_3CN): $\delta = 27.38$ (4-Me), 47.03 (6-C), 61.32 (OCH_3), 79.05 (3-C), 85.20 (5-C), 90.24 (Cp-C), 93.14 (4-C), 245.86 (1-C). IR (KBr): $\nu = 3095$ cm^{-1}, 2960, 2920, 2870, 1640, 1425, 1415, 1375, 1290, 1245, 1160–1020, 980, 950, 830, 810, 610. MS (70 eV): m/z (%) = 250 (100) [cation-H], 190 (39) [cation-$C_2H_4O_2$], 124 (72) [$CoCp^+$], 95 (52), 67 (34), 59 (20) [Co^+], 49 (24), 41 (31), 31 (26) [CH_3O^+], 28 (12) [CO^+]. Anal. Calc. for $C_{12}H_{16}BCoF_4O_2$ (338.0): C, 42.64; H, 4.77. Found: C, 42.53; H, 4.68%.

3.4. Synthesis of aminoalkenols (**8**) [19]—general procedure

To a mixture of the respective amine (300 mmol), 1.05 g (58.00 mmol) H_2O and 0.50 g (5.80 mmol) conc. HCl, isoprene oxide **10** (10.00 ml, 102.00 mmol) was added dropwise over a period of 3 h. The temperature of the solution rose to ca. 50°C. After 12 h of refluxing of the mixture, all volatile components were removed in vacuo. The residue thus obtained was purified by column chromatography with ethyl acetate on silica gel.

3.4.1. 1-Cyclohexylamino-2-methyl-3-buten-2-ol (**8a**)

Yield: 16.89 g (90%) from 30 g of cyclohexylamine as a colourless, strongly refractive liquid. ^{1}H-NMR ($CDCl_3$): $\delta = 1.16$ [mc, 6H, H^{cyc}], 1.21 [s, 3H, CH_3], 1.71 [mc, 5H, H^{cyc}, N–H], 2.38 [mc, 1H, N–CHCC], 2.47 [d, ^2J(1-H^a/1-H^b) = 11.47 Hz, 1H, 1-H^a], 2.69 [d, ^2J(1-H^a/1-H^b) = 11.47 Hz, 1H, 1-H^b], 5.05 [dd, ^2J(4-H^{cis}/4-H^{trans}) = 1.77 Hz, ^3J(3-H/4-H^{cis}) = 10.74 Hz, 1H, 4-H^{cis}], 5.28 [dd, ^2J(4-H^{cis}/4-H^{trans}) = 1.77 Hz, ^3J(3-H/4-H^{trans}) = 17.09 Hz, 1H, 4-H^{trans}], 5.80 [dd, ^3J(3-H/4-H^{cis}) = 10.74 Hz, ^3J(3-H/4-H^{trans}) = 17.09 Hz, 1H, 3-H]. ^{13}C-NMR ($CDCl_3$): $\delta = 25.05$ (C^{cyc}), 25.87 (5-C), 26.16 (C^{cyc}), 33.87 (C^{cyc}), 55.92 (1-C), 56.82 (NCH), 71.29 (2-C), 112.76 (4-C), 144.06 (3-C). IR (NaCl): $\nu = 3470$ cm^{-1}, 3100, 2980, 2940, 2865, 1460, 1450, 1370, 1260, 1115, 1015, 920, 890, 795, 785, 745, 680, 670, 650.

3.4.2. 1-[(R)-Cyclohexylethylamino]-2-methyl-3-buten-2-ol (**8b**)

Compound **8b** is a mixture of two diastereomers (ratio 1:0.68), which are indicated as **8b^1** and **8b^2**. Yield: 20.73 g (96%) from 38.17 g of (*R*)-(−)-cyclohexylethylamine as a colourless, strongly refractive liquid. ^{1}H-NMR ($CDCl_3$): $\delta = 0.98$ [mc, 5H, NCCH_3, H^{cyc}], 1.23 [s, 3H, 2-CH_3], 1.42 [mc, 8H, H^{cyc}], 2.57 [mc, 5H, 1-H, CH_3–C*H*, H^{cyc}, N–H], 5.08 [mc, 1H, 4-H^{cis}], 5.30 [mc, 1H, 4-H^{trans}], 5.80 [mc, 1H, 3-H]. ^{13}C-NMR ($CDCl_3$): $\delta = 17.01$ (NC*Me*^{1}), 17.38 (NC*Me*^{2}), 25.82 (5-Me^2), 25.85 (5-Me^1), 26.46 (C^{cyc1}), 26.58 (C^{cyc2}), 26.64 (C^{cyc2}), 26.71 (C^{cyc1}), 27.88 (C^{cyc1}), 28.52 (C^{cyc2}), 29.71 (C^{cyc2}), 29.86 (C^{cyc1}), 42.81 (C^{cyc1}), 43.12 (C^{cyc2}), 56.11 (1-C^1), 56.27 (1-C^2), 58.06 (NC^1), 58.30 (NC^2), 71.29 (2-Me^1), 71.40 (2-Me^2), 112.94 (4-C^2), 113.02 (4-C^1), 143.86 (3-C). IR (NaCl): $\nu = 3430$ cm^{-1}, 3380, 3100, 2980, 2930, 2860, 1655, 1640, 1560, 1445, 1370, 1260, 1110, 1010, 985, 920, 880, 830, 780, 750, 670.

3.4.3. 1-Methylamino-2-methyl-3-buten-2-ol (**8c**)

(The solution was cooled to −20°C prior to addition of methylamine). Yield: 7.40 g (63%) from 13.31 ml of methylamine as a colourless, strongly refractive liquid. ^{1}H-NMR ($CDCl_3$): $\delta = 1.24$ [s, 3H, 2-CH_3], 2.42 [s, 3H, NCH_3], 2.49 [d, ^2J(1-H$_a$/1-H$_b$) = 11.48 Hz, 1H, 1-H$_a$], 2.63 [d, ^2J(1-H$_a$/1-H$_b$) = 11.48 Hz, 1H, 1-H$_b$], 5.07 [dd, ^2J(4-H^{cis}/4-H^{trans}) = 1.72 Hz, ^3J(3-H/4-H^{cis}) = 10.74 Hz, 1H, 4-H^{cis}], 5.28 [dd, ^2J(4-H^{cis}/4-H^{trans}) = 1.72 Hz, ^3J(3-H/4-H^{trans}) = 17.34 Hz, 1H, 4-H^{trans}], 5.85 [dd, ^3J(3-H/4-H^{cis}) = 10.74 Hz, ^3J(3-H/4-H^{trans}) = 17.34 Hz, 1H, 3-H]. ^{13}C-NMR ($CDCl_3$): $\delta = 26.27$ (NMe), 37.09 (2-

Me), 61.75 (1-C), 72.26 (2-C), 113.11 (4-C), 144.20 (3-C).

3.5. Photochemical synthesis of cobaltalactams **7** from **6** and **8**—general procedure

The irradiation apparatus described in the protocol for the preparation of complex **9** was flushed with dry nitrogen and then charged with $CpCo(CO)_2$ **6** (2.60 g, 14.44 mmol), amino alcohol **8** (10.00 mmol) and THF (100 ml). The mercury lamp was switched on and the entire mixture irradiated at 70°C (gentle reflux) for 3 h. Then, all volatile components were removed in vacuo and the remaining crude product was finally purified by column chromatography (silica gel, neat diethyl ether).

3.5.1. (η^5-Cyclopentadienyl)-[(4-6-η^3)-2-aza-2-cyclohexyl-4-methyl-1-oxo-4-hexen-1,6-diyl]-cobalt(III) (**7a**)

Yield: 980 mg (3.1 mmol, 31%) as an orange solid from 1.85 g (10.09 mmol) **8a**; R_f (Et_2O) = 0.43, R_f (1:1 CH_3CN–CH_2Cl_2) = 0.56. ^{1}H-NMR ($CDCl_3$): δ = 0.98 [dd, ^2J(6-H^{exo}/6-H^{endo}) = 1.80 Hz, ^3J(5-H/6-H^{endo}) = 11.23 Hz, 1H, 6-H^{endo}], 1.42 [mc, 10H, H^{cyc}], 1.79 [s, 3H, 4-CH_3], 2.39 [d, ^2J(3-H^{exo}/3-H^{endo}) = 11.24 Hz, 1H, 3-H^{endo}], 2.91 [d, ^2J(3-H^{endo}/3-H^{exo}) = 11.24 Hz, 1H, 3-H^{exo}], 3.55 [dd, ^2J(6-H^{endo}/6-H^{exo}) = 1.80 Hz, ^3J(5-H/6-H^{exo}) = 6.83 Hz, 1H, 6-H^{exo}], 3.87 [mc, 1H, NCH^{cyc}], 4.87 [mc, 1H, 5-H], 4.88 [s, 5H, Cp]. ^{13}C-NMR ($CDCl_3$): δ = 25.69 (2 C^{cyc}), 25.91 (C^{cyc}), 30.07 and 30.53 (C^{cyc}), 30.15 (4-Me), 42.68 (3-C), 48.05 (6-C), 51.17 (NC^{cyc}), 77.88 (4-C), 79.55(5-C), 87.73 (Cp-C), 198.14 (1-C). IR (KBr): ν = 3070 cm^{-1}, 2920, 2840, 1550, 1390, 1235, 1175, 1130, 930, 900, 810. MS (70 eV): m/z (%) = 317 (100) [M$^+$], 247 (20) [M$^+$ − C_5H_{10}], 192 (37) [CoCp$C_5H_8^+$], 124 (59) [CoCp$^+$], 112 (57) [$CoC_4H_5^+$], 44 (34), 30 (42) [H_2CO^+, $C_2H_6^+$]. Anal. Calc. for $C_{17}H_{24}CoNO$ (317.3): C, 64.35; H, 7.62; N, 4.41. Found: C, 64.12; H, 7.73; N, 4.52%.

3.5.2. (η^5-Cyclopentadienyl)-{(4-6-η^3)-2-aza-2-[(R)-1′-cyclohexylethyl]-4-methyl-1-oxo-4-hexen-1,6-diyl}-cobalt(III) (**7b**)

Yield: 955 mg (2.77 mmol, 30%) as an orange oil from 2.05 g (9.70 mmol) **8b**; mixture of diastereomers indicated as **7b^1** [R_f (Et_2O) = 0.76, R_f (1:1 CH_3CN–CH_2Cl_2) = 0.51] and **7b^2** [R_f (Et_2O) = 0.64, R_f (1:1 CH_3CN–CH_2Cl_2) = 0.49], which was separated by CC (silica gel, neat diethyl ether). IR (NaCl/mixture): ν = 3100 cm^{-1}, 2990, 2940, 2870, 1580, 1570, 1480, 1455, 1410, 1380, 1265, 1200, 1180, 1150, 930, 860, 825, 740, 650. MS (70 eV): m/z (%) = 345 (100) [M$^+$], 275 (20) [M$^+$ − C_5H_{10}], 235 (21) [M$^+$ − C_8H_{14}], 192 (37) [CoCp$C_5H_8^+$], 140 (57) [CoCpO$^+$], 124 (54) [CoCp$^+$], 111 (19) [$CoC_4H_4^+$], 69 (49), 55 (33) [$C_3H_5N^+$], 41 (26) [$C_3H_5^+$], 30 (37) [H_2CO^+, $C_2H_6^+$]. $C_{19}H_{28}CoNO$ (345.4): C 66.08, H 8.17, N 4.06; Found: C 66.15, H 8.26, N 4.12.

*3.5.2.1. Compound **7b^1** (pure).* ^{1}H-NMR ($CDCl_3$): δ = 0.97 [d, ^3J(NCH/NCCH_3) = 6.59 Hz, 3H, NCCH_3], 1.30 [mc, 11H, H^{cyc}], 1.40 [dd, 1H, ^2J(6-H^{endo}/6-H^{exo}) = 2.19 Hz, ^3J(5-H/6-H^{endo}) = 12.65 Hz, 1H, 6-H^{endo}], 1.81 [s, 3H, 4-CH_3], 2.32 [d, ^2J(3-H^{endo}/3-H^{exo}) = 11.72 Hz, 1H, 3-H^{endo}], 2.93 [d, ^2J(3-H^{endo}/3-H^{exo}) = 11.72 Hz, 1H, 3-H^{exo}], 3.53 [dd, ^2J(6-H^{endo}/6-H^{exo}) = 2.19 Hz, ^3J(5-H/6-H^{exo}) = 7.84 Hz, 1H, 6-H^{exo}], 3.77 [q, ^3J(NCH/NCCH_3) = 6.59 Hz, 1H, NCH], 4.84 [mc, 1H, 5-H], 4.86 [s, 5H, Cp]. ^{1}H-NMR (CD_3CN): δ = 0.89 [dd, ^2J(6-H^{endo}/6-H^{exo}) = 1.10 Hz, ^3J(5-H/6-H^{endo}) = 11.55 Hz, 1H, 6-H^{endo}], 1.29 [mc, 11H, H^{cyc}], 1.75 [d, ^3J(NCH/NCCH_3) = 6.50 Hz, 3H, NCCH_3], 1.97 [s, 3H, 4-CH_3], 2.33 [d, ^2J(3-H^{endo}/3-H^{exo}) = 11.00 Hz, 1H, 3-H^{endo}], 2.87 [d, ^2J(3-H^{endo}/3-H^{exo}) = 11.00 Hz, 1H, 3-H^{exo}], 3.49 [dd, ^2J(6-H^{endo}/6-H^{exo}) = 1.10 Hz, ^3J(5-H/6-H^{exo}) = 7.70 Hz, 1H, 6-H^{exo}], 3.70 [q, ^3J(NCH/NCCH_3) = 6.50 Hz, 1H, NCH], 4.82 [s, 5H, Cp], 4.94 [dd, ^3J(5-H/6-H^{endo}) = 11.55 Hz, ^3J(5-H/6-H^{exo}) = 7.70 Hz, 1H, 5-H]. ^{13}C-NMR ($CDCl_3$): δ = 15.71 (NC*C*), 25.82 (2 C^{cyc}), 23.73 (2 C^{cyc}), 30.09 (C^{cyc}), 30.26 (4-Me), 41.07 (NC*C^{cyc}*), 41.86 (3-C), 48.38 (6-C), 51.83 (NCH), 78.58 (4-C), 79.53 (5-C), 87.64 (Cp-C), 199.00 (1-C).

*3.5.2.2. Compound **7b^2** (pure).* ^{1}H-NMR ($CDCl_3$): δ = 0.71 [d, ^3J(NCH/NCCH_3) = 6.59 Hz, 3H, NCCH_3], 1.25 [mc, 11 H, H^{cyc}], 1.30 [dd, 1H, ^2J(6-H^{endo}/6-H^{exo}) = 2.20 Hz, ^3J(5-H/6-H^{endo}) = 12.65 Hz, 1H, 6-H^{endo}], 1.79 [s, 3H, 4-CH_3], 2.33 [d, ^2J(3-H^{endo}/3-H^{exo}) = 11.48 Hz, 1H, 3-H^{endo}], 2.72 [d, ^2J(3-H^{endo}/3-H^{exo}) = 11.48 Hz, 1H, 3-H^{exo}], 3.55 [dd, ^2J(6-H^{endo}/6-H^{exo}) = 2.20 Hz, ^3J(5-H/6-H^{exo}) = 8.06 Hz, 1H, 6-H^{exo}], 3.83 [q, ^3J(NCH/NCCH_3) = 6.59 Hz, 1H, NCH], 4.85 [mc, 1H, 5-H], 4.87 [s, 5H, Cp]. ^{13}C-NMR ($CDCl_3$): δ = 15.80 (NC*Me*), 25.91 (2 C^{cyc}), 26.20 (2 C^{cyc}), 30.04 (C^{cyc}), 30.37 (4-Me), 39.70 (NC*C^{cyc}*), 42.30 (3-C), 46.97 (6-C), 51.10 (NCH), 78.57 (4-C), 79.46 (5-C), 87.55 (Cp-C), 198.21 (1-C).

3.6. Synthesis of cobaltcarbene complexes **3a** and **3b**—general procedure

Under an atmosphere of dry nitrogen complex **7** was dissolved in dry dichloromethane (50–100 ml). Trimethyloxonium tetrafluoroborate (1.2 to 1.5 equivalents) was added at once and the resulting mixture was stirred for ca. 5 h. Once the reaction was completed (as to TLC monitoring on silica gel with 1:1 acetonitrile–dichloromethane), all volatile components were re-

moved in vacuo and the remaining residue was finally purified by column chromatography. Any by-products and residual starting materials were first washed off with neat diethyl ether, the product complex **3** could then be eluted with 1:1 acetonitrile–dichloromethane and was obtained as orange solid upon drying on an oil pump.

*3.6.1. (η^5-Cyclopentadienyl)-[(4-6-η^3)-2-aza-2-cyclohexyl-1-methoxy-4-methyl-4-hexen-6-yl-1-ylidene]-cobalt(III) tetrafluoroborate (**3a**)*

Yield: 50 mg (82%) from 60 mg (0.19 mmol) **7a** and 42 mg (0.28 mmol) Me_3OBF_4; R_f (Et_2O) = 0.00, R_f (1:1 CH_3CN–CH_2Cl_2) = 0.68. ^{1}H-NMR (CD_3CN): δ = 1.24 [dd, ^2J(6-H^{exo}/6-H^{endo}) = 2.08 Hz, ^3J(5-H/6-H^{endo}) = 12.33 Hz, 1H, 6-H^{endo}], 1.49 [mc, 10H, H^{cyc}], 1.87 [s, 3H, 4-CH_3], 3.06 [d, ^2J(3-H^{exo}/3-H^{endo}) = 14.65 Hz, 1H, 3-H^{endo}], 3.54 [d, ^2J(3-H^{endo}/3-H^{exo}) = 14.65 Hz, 1H, 3-H^{exo}], 3.91 [mc, 1H, NCH], 4.27 [dd, ^2J(6-H^{endo}/6-H^{exo}) = 2.08 Hz, ^3J(5-H/6-H^{exo}) = 8.42 Hz, 1H, 6-H^{exo}], 4.32 [s, 3H, OCH_3], 5.09 [dd, ^3J(5-H/6-H^{endo}) = 12.33 Hz, ^3J(5-H/6-H^{exo}) = 8.42 Hz, 1H, 5-H], 5.28 [s, 5H, Cp]. ^{13}C-NMR (CD_3CN): δ = 25.80 (C^{cyc}), 26.07 (C^{cyc}), 29.82 (4-Me), 30.44 (C^{cyc}), 48.97 (6-C), 53.48 (3-C), 57.94 (NC^{cyc}), 65.17 (OCH_3), 83.72 (5-C), 84.12 (4-C), 88.56 (Cp-C), 224.43 (1-C). IR (KBr): ν = 3060 cm^{-1}, 2940, 2870, 1525, 1450, 1420, 1380, 1310, 1250, 1175, 1100–1000, 835, 800, 675. MS (70 eV): m/z (%) = 332 (5) [cation], 304 (19) [cation-C_2H_4], 221 (22) [$CoC_{11}H_{16}N^+$], 192 (49) [$CoCpC_5H_8^+$], 124 (67) [$CoCp^+$], 112 (54) [$CoC_4H_5^+$], 86 (66) [$C_5H_{12}N^+$], 70 (100) [$C_4H_8N^+$, $C_5H_{10}^+$], 41 (32) [$C_3H_5^+$], 30 (23) [H_2CO^+, $C_2H_6^+$]. Anal. Calc. for $C_{18}H_{27}BCoF_4NO$ (419.2): C, 51.58; H, 6.49; N, 3.34. Found: C, 51.46; H, 6.47; N, 3.29%.

*3.6.2. (η^5-Cyclopentadienyl)-{(4-6-η^3)-2-aza-2-[(R)-1′-cyclohexylethyl]-1-methoxy-4-methyl-4-hexen-6-yl-1-ylidene}-cobalt(III) tetrafluoroborate (**3b**)*

Yield: 75 mg (76%) from 76 mg (0.22 mmol) of **7b** and 42 mg (0.28 mmol) Me_3OBF_4; inseparable mixture of diastereomers **3b^1** and **3b^2** [R_f (1:1 CH_3CN–CH_2Cl_2) = 0.80 for both]. IR (KBr): ν = 3080 cm^{-1}, 2990, 2940, 2870, 1530, 1470, 1455, 1415, 1380, 1310, 1255, 1200, 1180, 1150, 1100–1000, 825, 790, 675. MS (70 eV): m/z (%) = 360 (12) [$M^+ - BF_4$], 345 (19) [$M^+ - CH_3OBF_4$], 332 (19) [$M^+ - C_2H_4$], 290 (42) [$M^+ - C_5H_{10}BF_4$], 250 (67) [$M^+ - C_8H_{14}BF_4$], 192 (73) [$CoCpC_5H_8^+$], 124 (100) [$CoCp^+$], 112 (48) [$CoC_4H_5^+$], 70 (77) [$C_4H_8N^+$, $C_5H_{10}^+$], 41 (41) [$C_3H_5^+$], 30 (42) [H_2CO^+, $C_2H_6^+$]. Anal. Calc. for $C_{20}H_{31}BCoF_4NO$ (447.2): C, 53.72; H, 6.99; N, 3.13. Found: C, 53.66; H, 6.86; N, 3.08%.

Pure samples of both **3b^1** and **3b^2** were prepared from the respective diastereomerically pure starting compounds **7b^1** or **7b^2** which could be readily obtained by chromatographic separation of the mixture **7b**.

*3.6.2.1. Compound **3b^1**.* ^{1}H-NMR (CD_3CN): δ = 1.04 [d, ^3J(NCH/NCCH_3) = 6.60 Hz, 3H, NCCH_3], 1.23 [mc, 6H, H^{cyc}], 1.40 [dd, ^2J(6-H^{endo}/6-H^{exo}) = 2.19 Hz, ^3J(5-H/6-H^{endo}) = 12.65 Hz, 1H, 6-H^{endo}], 1.63 [mc, 5H, H^{cyc}], 1.87 [s, 3H, 4-CH_3], 2.99 [d, ^2J(3-H^{endo}/3-H^{exo}) = 14.85 Hz, 1H, 3-H^{endo}], 3.54 [d, ^2J(3-H^{endo}/3-H^{exo}) = 14.85 Hz, 1H, 3-H^{exo}], 3.75 [mc, 1H, NCH], 4.27 [dd, ^2J(6-H^{endo}/6-H^{exo}) = 2.19 Hz, ^3J(5-H/6-H^{exo}) = 8.25 Hz, 1H, 6-H^{exo}], 4.29 [s, 3H, OCH_3], 5.06 [dd, ^3J(5-H/6-H^{endo}) = 12.65 Hz, ^3J(5-H/6-H^{exo}) = 8.25 Hz, 1H, 5-H], 5.27 [s, 5H, Cp]. ^{13}C-NMR (CD_3CN): δ = 16.15 (NCCH_3), 26.26 (C^{cyc}), 26.44 and 26.67 (C^{cyc}), 29.94 (4-Me), 30.48 and 30.66 (C^{cyc}), 41.18 (NCC^{cyc}), 47.92 (6-C), 54.23 (3-C), 59.51 (NCH), 65.02 (OCH_3), 83.81 (5-C), 84.68 (4-C), 88.58 (Cp-C), 225.31 (1-C).

*3.6.2.2. Compound **3b^2**.* ^{1}H-NMR (CD_3CN): δ = 0.80 [d, ^3J(NCH/NCCH_3) = 7.15 Hz, 3H, NCCH_3], 1.12 [mc, 6H, H^{cyc}], 1.28 [dd, ^2J(6-H^{endo}/6-H^{exo}) = 2.20 Hz, ^3J(5-H/6-H^{endo}) = 12.65 Hz, 1H, 6-H^{endo}], 1.65 [mc, 5H, H^{cyc}], 1.87 [s, 3H, 4-CH_3], 3.01 [d, ^2J(3-H^{endo}/3-H^{exo}) = 14.84 Hz, 1H, 3-H^{endo}], 3.36 [d, ^2J(3-H^{endo}/3-H^{exo}) = 14.84 Hz, 1H, 3-H^{exo}], 3.89 [mc, 1H, NCH], 4.26 [dd, ^2J(6-H^{endo}/6-H^{exo}) = 2.20 Hz, ^3J(5-H/6-H^{exo}) = 8.25 Hz, 1H, 6-H^{exo}], 4.27 [s, 3H, OCH_3], 5.10 [dd, ^3J(5-H/6-H^{endo}) = 12.65 Hz, ^3J(5-H/6-H^{exo}) = 8.25 Hz, 1H, 5-H], 5.28 [s, 5H, Cp]. ^{13}C-NMR (CD_3CN): δ = 16.63 (NCCH_3), 26.47 (C^{cyc}), 26.59 and 26.88 (C^{cyc}), 29.92 (4-Me), 30.48 and 30.66 (C^{cyc}), 39.78 (NCC^{cyc}), 48.77 (6-C), 52.42 (3-C), 58.31 (NCH), 65.17 (OCH_3), 83.83 (5-C), 84.09 (4-C), 88.52 (Cp-C), 225.23 (1-C).

*3.7. Aminolysis of **2a** to give **11**—general procedure*

Carbene complex **2a** was dissolved in dichloromethane (50 ml mmol^{-1}) which was then chilled to −18°C. The respective amine was added at once and the resulting mixture was allowed to stir for a certain period of time (as indicated for each of the following examples). The reaction mixture was finally warmed up to ambient temperature, all volatile components were evaporated on an oil pump and the remaining residue was purified by column chromatography. First, traces of the by-product **9** were washed off with neat diethyl ether, then pure product complex **11** could be obtained by eluting with 1:1 acetonitrile–dichloromethane, concentrating of the eluate and drying on an oil pump. Residual starting complex **2a** could be regained in some cases by continued elution of the column with the same solvent mixture.

*3.7.1. (η^5-Cyclopentadienyl)-[(4-6-η^3)-1-methylamino-4-methyl-2-oxa-4-hexen-6-yl-1-ylidene]-cobalt(III) tetrafluoroborate (**11a**)*

Yield: 253 mg (98%) as a yellow–orange solid from 0.77 mmol of **2a** and 1.00 ml (2.50 mmol) methylamine; reaction time 1 h; R_f (1:1 CH_3CN–CH_2Cl_2) = 0.75. ^{1}H-NMR (CD_3CN): $\delta = 1.50$ [d, ^3J(5-H/6-H^{endo}) = 12.20 Hz, 1H, 6-H^{endo}], 1.86 [s, 3H, 4-CH_3], 2.79 [d, ^3J(N–H/N–CH_3) = 4.88 Hz, 3H, N–CH_3], 3.73 [d, ^2J(3-H^{exo}/3-H^{endo}) = 11.96 Hz, 1H, 3-H^{endo}], 4.11 [d, ^3J(5-H/6-H^{exo}) = 9.04 Hz, 1H, 6-H^{exo}], 4.14 [d, ^2J(3-H^{endo}/3-H^{exo}) = 11.96 Hz, 1H, 3-H^{exo}], 5.25 [s, 5H, Cp], 5.27 [mc, 1H, 5-H], 8.61 [s, 1H, N–H]. ^{13}C-NMR (CD_3CN): $\delta = 27.46$ (4-Me), 31.20 (N–Me), 47.99 (6C), 77.94 (3-C), 84.09 (5-C), 89.13 (Cp-C), 92.32 (4-C), 225.36 (1-C). IR (KBr): $\nu = 3360$ cm^{-1}, 3090, 3030, 2960, 2920, 2900, 2820, 1720, 1570, 1460–1400, 1385, 1260, 1130–980, 835. MS (70 eV): m/z (%) = 249 (79) [cation-H], 183 (29) [cation-CpH_2], 127 (60), 124 (33) [$CoCp^+$], 108 (32), 70 (63), 58 (100), 55 (54), 49 (34), 41 (64), 28 (16) [CO^+]. Anal. Calc. for $C_{12}H_{17}BCoF_4NO$ (337.0): C, 42.77; H, 5.05; N, 4.16. Found: C, 42.54; H, 4.78; N, 4.12%.

*3.7.2. (η^5-Cyclopentadienyl)-[(4-6-η^3)-1-benzylamino-4-methyl-2-oxa-4-hexen-6-yl-1-ylidene] cobalt(III) tetrafluoroborate (**11b**)*

Yield: 227 mg (68%) as an orange oil from 269 mg (0.80 mmol) of **2a** and 128 mg (1.19 mmol) of benzylamine; reaction time 3 h; R_f (1:1 CH_3CN–CH_2Cl_2) = 0.64. ^{1}H-NMR (CD_3CN): $\delta = 1.40$ [dd, ^2J(6-H^{exo}/6-H^{endo}) = 2.18 Hz, ^3J(5-H/6-H^{endo}) = 12.10 Hz, 1H, 6-H^{endo}], 1.87 [s, 3H, 4-CH_3], 3.75 [d, ^2J(3-H^{exo}/3-H^{endo}) = 12.11 Hz, 1H, 3-H^{endo}], 4.15 [mc, 2H, 3-H^{exo}, 6-H^{exo}], 4.42 [mc, 2H, PhCH_2], 5.26 [s, 5H, Cp], 5.27 [mc, 1H, 5-H], 7.37 [mc, 5H, Ph], 9.02 [s, 1H, NH]. ^{13}C-NMR (CD_3CN): $\delta = 27.37$ (4-Me), 48.39 (6-C), 68.39 (PhCH_2), 78.10 (3-C), 84.04 (5-C), 89.23 (Cp-C), 92.30 (4-C), 128.71(*m*-C^{ar}), 128.72 (*p*-C^{ar}), 129.52 (*o*-C^{ar}), 137.61 (*ipso*-C^{ar}), 226.51 (1-C). IR (NaCl): $\nu = 3360$ cm^{-1}, 3050, 2980, 1720, 1555, 1495, 1470–1415, 1380, 1340, 1260, 1130–1010, 895, 845. MS (70 eV): m/z (%) = 325 (38) [cation-H], 260 (19) [cation-CpH], 203 (39), 91 (100) [Bn^+], 69 (42), 41 (30). Anal. Calc. for $C_{18}H_{21}BCoF_4NO$ (413.1): C, 52.55; H, 5.12; N, 3.39. Found: C, 52.32; H, 4.98; N, 3.43%.

*3.7.3. (η^5-Cyclopentadienyl)-[(4-6-η^3)-1-allylamino-4-methyl-2-oxa-4-hexen-6-yl-1-ylidene]-cobalt(III) tetrafluoroborate (**11c**)*

Yield: 487 mg (64%) as a brown oil from 680 mg (2.09 mmol) of **2a** and 0.24 ml (3.14 mmol) allylamine; reaction time 3 h; R_f (1:1 CH_3CN–CH_2Cl_2) = 0.74. ^{1}H-NMR (CD_3CN): $\delta = 1.48$ [dd, ^2J(6-H^{exo}/6-H^{endo}) = 1.95 Hz, ^3J(5-H/6-H^{endo}) = 12.20 Hz, 1H, 6-H^{endo}], 1.87 [s, 3H, 4-CH_3], 3.76 [d, ^2J(3-H^{exo}/3-H^{endo}) = 11.96 Hz, 1H, 3-H^{endo}], 3.85 [mc, 2H, NCH_2], 4.17 [mc, 2H, 3-H^{exo}, 6-H^{exo}], 5.16 [mc, 3H, 5-H, =CH_2], 5.27 [s, 5H, Cp], 5.78 [mc, 1H, NCCH], 8.72 [s, 1H, NH]. ^{13}C-NMR (CD_3CN): $\delta = 27.41$ (4-Me), 47.16 (NCH_2), 48.38 (6-C), 78.11 (3-C), 84.06 (5-C), 89.22 (Cp-C), 92.34 (4-C), 117.73 (=CH_2), 133.46 (NC*C*), 224.96 (1-C). IR (NaCl): $\nu = 3360$ cm^{-1}, 3050, 2980, 1725, 1565, 1475–1410, 1380, 1340, 1260, 1130–1010, 905, 865. MS (70 eV): m/z (%) = 275 (36) [cation-H], 151 (29) [$CoCpCNH^+$], 124 (35) [$CoCp^+$], 81 (30), 67 (25), 41 (100). Anal. Calc. for $C_{14}H_{19}BCoF_4NO$ (363.05): C, 49.65; H, 5.00; N, 3.86. Found: C, 49.76; H, 4.94; N, 3.92%.

*3.7.4. (η^5-Cyclopentadienyl)-[(4-6-η^3)-4-methyl-1-(cis)-myrtanylamino-2-oxa-4-hexen-6-yl-1-ylidene]-cobalt(III) tetrafluoroborate (**11d**)*

Yield: 92 mg (17%) as an orange oil from 410 mg (1.21 mmol) of **2a** and 0.50 ml (3.00 mmol) (*cis*)-(−)-myrtanylamine; reaction time 3 h; R_f (1:1 CH_3CN–CH_2Cl_2) = 0.89. **11d** was obtained as a mixture of two diastereomers **11d^1** and **11d^2** (1:0.88), assignment of the NMR signals to these isomers was possible by integration in some cases. ^{1}H-NMR (CD_3CN): δ = 0.95 [s, 3H, Me^1], 0.97 [s, 3H, Me^2], 1.14 [s, 3H, Me^1], 1.20 [s, 3H, Me^2], 1.47 [mc, 16 H, 6-H^{endo}, CH^{cyc}, CH_2^{cyc}], 1.87 [s, 3H, 4-Me^1], 1.96 [s, 3H, 4-Me^2], 3.20 [mc, 8H, NCH_2, CH^{cyc}], 3.74 [mc, 2H, 3-H^{endo}], 4.14 [mc, 4H, 3-H^{exo}, 6-H^{exo}], 5.25 [s, 5H, Cp^1], 5.26 [s, 5H, Cp^2], 5.25 [mc, 2H, 5-H], 8.63 [s, 1H, NH]. ^{13}C-NMR (CD_3CN): $\delta = 19.85$ (Me^1), 19.89 (Me^2), 23.18 (Me^1), 23.23 (Me^2), 26.60 (H_2C^2), 27.40 (H_2C^1), 28.22 (4-Me^1), 28.30 (4-Me^2), 33.66 (H_2C^{cyc1}), 33.78 (H_2C^{cyc2}), 39.32 (*quart*-C^1), 39.36 (*quart*-C^2), 41.39 (HC^{cyc1}), 42.23 (HC^{cyc2}), 44.18 (HC^{cyc1}), 44.24 (HC^{cyc2}), 48.16 (6-C^2), 48.34 (6-C^1), 50.33 (NCH_2^2), 50.45 (NCH_2^1), 77.75 (3-C^1), 77.81 (3-C^2), 83.95 (5-C^1), 84.00 (5-C^2), 89.15 (Cp^2), 89.19 (Cp^1), 92.19 (4-C^1), 92.23 (4-C^2), 225.14 (1-C). IR (NaCl): $\nu = 3350$ cm^{-1}, 3100, 3040, 2900, 1700, 1555, 1460–1410, 1370, 1340, 1255, 1100–1000, 895, 840. MS (70 eV): m/z (%) = 371 (100) [cation-H], 249 (42) [cation-C_9H_{14}], 180 (27) [$CoCpC_2H_5NO^+$], 136 (33) [$C_8H_{10}NO^+$, $CoCpC^+$], 124 (73) [$CoCp^+$], 114 (44), 93 (36), 81 (43), 69 (84) [$C_4H_5O^+$, $C_5H_9^+$], 67 (53) [$C_5H_7^+$], 55 (56), 49 (32), 41 (100), 30 (97) [$C_2H_6^+$, H_2CO^+]. Anal. Calc. for $C_{21}H_{31}BCoF_4NO$ (459.2): C, 54.92; H, 6.80; N, 3.05. Found: C, 54.76; H, 6.74; N, 2.97%.

*3.7.5. (η^5-Cyclopentadienyl)-[(4-6-η^3)-1-(methoxycarbonylmethyl)amino-4-methyl-2-oxa-4-hexen-6-yl-1-ylidene]-cobalt(III) tetrafluoroborate (**11e**)*

Yield: 234 mg (87%) as an orange solid from 230 mg (0.70 mmol) of **2a** and 0.50 ml (3.00 mmol) glycine

methylester; reaction time 3 h; R_f (1:1 CH_3CN–CH_2Cl_2) = 0.67. ^{1}H-NMR (CD_3CN): δ = 1.64 [dd, ^2J(6-H^{exo}/6-H^{endo}) = 2.20 Hz, ^3J(5-H/6-H^{endo}) = 12.10 Hz, 1H, 6-H^{endo}], 1.85 [s, 3H, 4-CH_3], 3.66 [s, 3H, OCH_3], 3.75 [s, ^2J(3-H^{exo}/3-H^{endo}) = 12.09 Hz, 1H, 3-H^{endo}], 3.97 [mc, 2H, NCH_2], 4.15 [d, ^2J(3-H^{exo}/3-H^{endo}) = 12.09 Hz, 1H, 3-H^{exo}], 4.19 [dd, ^2J(6-H^{exo}/6-H^{endo}) = 2.20 Hz, ^3J(5-H/6-H^{exo}) = 8.25 Hz, 1H, 6-H^{exo}], 5.28 [mc, 1H, 5-H], 5.29 [s, 5H, Cp]. ^{13}C-NMR (CD_3CN): δ = 27.33 (4-Me), 45.33 (NCH_2), 48.57 (6-C), 53.17 (OMe), 78.46 (3-C), 84.25 (5-C), 89.25 (Cp-C), 92.22 (4-C), 169.10 (C=O), 229.56 (1-C). IR (KBr): ν = 3520 cm^{-1}, 3380, 3100, 2940, 1745, 1735, 1550, 1465, 1430, 1400, 1375, 1330, 1200, 1100–1000, 845. MS (70 eV): m/z (%) = 308 (13) [cation], 307 (72) [cation-H], 185 (100) [cation-CoC_5H_4], 149 (23), 124 (73) [$CoCp^+$], 96 (55) [$C_6H_8O^+$], 88 (76) [$C_3H_6NO_2^+$], 70 (84) [$C_4H_5O^+$, $C_5H_9^+$], 55 (58), 41 (85) [$C_3H_5^+$], 30 (52) [$C_2H_6^+$, H_2CO^+]. Anal. Calc. for $C_{14}H_{19}BCoF_4NO_3$ (395.05): C, 41.11; H, 4.68; N, 3.42. Found: C, 40.96; H, 4.74; N, 3.37%.

3.7.6. (η^5-Cyclopentadienyl)-[(4-6-η^3)-1-(2′-methoxycarbonylethyl)amino-4-methyl-2-oxa-4-hexen-6-yl-1-ylidene]-cobalt(III) tetrafluoroborate ***(11f)***

Yield: 191 mg (79%) as an orange solid from 200 mg (0.59 mmol) of **2a** and 100 mg (0.97 mmol) β-alanine methylester; reaction time 3 h; R_f (1:1 CH_3CN–CH_2Cl_2) = 0.67. ^{1}H-NMR (CD_3CN): δ = 1.50 [dd, ^2J(6-H^{exo}/6-H^{endo}) = 2.20 Hz, ^3J(5-H/6-H^{endo}) = 12.10 Hz, 1H, 6-H^{endo}], 1.89 [s, 3H, 4-CH_3], 2.53 [t, ^3J(NCH_2/$NCCH_2$) = 7.15 Hz, 2H, $NCCH_2$], 3.45 [t, ^3J(NCH_2/$NCCH_2$) = 7.15 Hz, 2H, NCH_2], 3.65 [s, 3H, OCH_3], 3.75 [d, ^2J(3-H^{exo}/3-H^{endo}) = 12.09 Hz, 1H, 3-H^{endo}], 4.15 [mc, 2H, 3-H^{exo}, 6-H^{exo}], 5.24 [s, 5H, Cp], 5.25 [mc, 1H, 5-H], 8.63 [s, 1H, NH]. ^{13}C-NMR (CD_3CN): δ = 27.41 (4-Me), 33.82 (NC*C*), 40.67 (NC), 48.59 (6-C), 52.41 (OCH_3), 78.12 (3-C), 84.12 (5-C), 89.20 (Cp-C), 92.30 (4-C), 172.47 (C=O), 226.66 (1-C). IR (KBr): ν = 3350 cm^{-1}, 3080, 2920, 1735, 1535, 1450, 1415, 1390, 1370, 1320, 1200, 1100–1000, 835, 720, 690. MS (70 eV): m/z (%) = 321 (13) [cation-H], 284 (88), 241 (92) [cation-C_6H_{10}], 205 (52), 185 (33) [$CoC_8H_{14}O^+$], 156 (100) [$CoC_5H_7NO^+$, $CoC_6H_9O^+$], 128 (99) [Cp_2^+], 108 (57), 100 (98) [$CoC_3H_5^+$], 86 (96) [$C_4H_6O_2^+$, $C_3H_4NO_2^+$], 57 (100) [$C_3H_5O^+$], 41 (92) [$C_3H_5^+$], 28 (65) [CO^+]. Anal. Calc. for $C_{15}H_{21}BCoF_4NO_3$ (409.1): C, 44.04; H, 5.17; N, 3.40. Found: C, 43.87; H, 5.02; N, 3.27%.

3.7.7. (η^5-Cyclopentadienyl)-[(4-6-η^3)-1-(2′-dimethoxymethyl)amino-2-oxa-4-hexen-6-yl-1-ylidene]-cobalt(III) tetrafluoroborate ***(11g)***

Yield: 290 mg (91%) as an orange–brown oil from 262 mg (0.78 mmol) of **2a** and 263 mg (2.50 mmol) aminoethanal dimethylacetal; reaction time 2 h; R_f (1:1 CH_3CN–CH_2Cl_2) = 0.65. ^{1}H-NMR (CD_3CN): δ = 1.48 [dd, ^2J(6-H^{exo}/6-H^{endo}) = 2.20 Hz, ^3J(5-H/6-H^{endo}) = 12.09 Hz, 1H, 6-H^{endo}], 1.85 [s, 3H, 4-CH_3], 3.28 and 3.29 [s each, 6H, OCH_3, OCH_3'], 3.30 [mc, 2H, NCH_2], 3.74 [d, ^2J(3-H^{exo}/3-H^{endo}) = 12.09 Hz, 1H, 3-H^{endo}], 4.14 [mc, 2H, 3-H^{exo}, 6-H^{exo}], 4.42 [t, ^3J(NCH_2/$CH(OMe)_2$) = 5.50 Hz, 1H, C*H*($OMe)_2$], 5.24 [mc, 1H, 5-H], 5.25 [s, 5H, Cp], 8.59 [s, 1H, NH]. ^{13}C-NMR (CD_3CN): δ = 27.36 (4-Me), 46.17 (NCH_2), 48.47 (6-C), 54.77 and 54.80 (OMe, OMe′), 78.05 (3-C), 84.90 (5-C), 89.24 (Cp-C), 92.20 (4-C), 102.45 (*C*$(OMe)_2$), 227.42 (1-C). IR (NaCl): ν = 3350 cm^{-1}, 3030, 2950, 2810, 1700, 1555, 1410, 1370, 1250, 1100–1000, 885, 840. MS (70 eV): m/z (%) = 323 (20) [cation-H], 291 (100) [cation-CH_5O], 279 (20) [cation-C_2H_5O], 250 (22) [cation-$C_3H_6O_2$], 230 (68), 191 (27), 180 (27) [$CoCpC_2H_5NO^+$], 169 (100), 150 (100), 136 (88) [$C_8H_{10}NO^+$, $CoCpC^+$], 124 (100) [$CoCp^+$], 108 (64), 100 (89) [$CoC_3H_5^+$], 95 (83) [$C_6H_8O^+$], 75 (100) [CoO^+], 57 (99) [$C_3H_5O^+$], 41 (98), 29 (63) [$C_2H_5^+$, HCO^+]. Anal. Calc. for $C_{15}H_{23}BCoF_4NO_3$ (411.1): C, 43.83; H, 5.64; N, 3.40. Found: C, 43.66; H, 5.52; N, 3.32%.

3.7.8. (η^5-Cyclopentadienyl)-[(4-6-η^3)-1-cyanomethylamino-4-methyl-2-oxa-4-hexen-6-yl-1-ylidene]-cobalt-(III) tetrafluoroborate ***(11h)***

Yield: 218 mg (81%) as a brown oil from 250 mg (0.74 mmol) of **2a** and 140 mg (2.50 mmol) aminoacetonitrile; reaction time 3 h; R_f (1:1 CH_3CN–CH_2Cl_2) = 0.74. ^{1}H-NMR (CD_3CN): δ = 1.52 [dd, ^2J(6-H^{exo}/6-H^{endo}) = 2.20 Hz, ^3J(5-H/6-H^{endo}) = 12.21 Hz, 1H, 6-H^{endo}], 1.88 [s, 3H, 4-CH_3], 3.88 [d, ^2J(3-H^{exo}/3-H^{endo}) = 12.21 Hz, 1H, 3-H^{endo}], 4.15 [s, 2H, NCH_2], 4.19 [dd, ^2J(6-H^{exo}/6-H^{endo}) = 2.20 Hz, ^3J(5-H/6-H^{exo}) = 8.06 Hz, 1H, 6-H^{exo}], 4.28 [d, ^2J(3-H^{exo}/3-H^{endo}) = 12.21 Hz, 1H, 3-H^{exo}], 5.30 [s, 5H, Cp], 5.34 [dd, ^3J(5-H/6-H^{exo}) = 8.06 Hz, ^3J(5-H/6-H^{endo}) = 12.21 Hz, 1H, 5-H], 8.95 [s, 1H, NH]. ^{13}C-NMR (CD_3CN): δ = 27.34 (4-Me), 31.50 (NCH_2), 48.58 (6-C), 79.19 (3-C), 84.56 (5-C), 89.51 (Cp-C), 92.80 (4-C), 115.76 (CN), 228.45 (1-C). IR (NaCl): ν = 3360 cm^{-1}, 3110, 2960, 2070, 1660, 1540, 1470, 1430, 1410, 1380, 1330, 1250, 1190, 1160, 1110–970, 900, 850. MS (70 eV): m/z (%) = 274 (21) [cation-H], 180 (41) [$CoCpC_2H_5NO^+$], 152 (36) [$CoCpCO^+$], 124 (100) [$CoCp^+$], 95 (43), 69 (70) [$C_4H_5O^+$, $C_5H_9^+$], 67 (43) [$C_5H_7^+$], 59 (35) [Co^+], 41 (100), 28 (22) [$C_2H_4^+$, CO^+], 27 (24) [$C_2H_3^+$, CHN^+]. Anal. Calc. for $C_{13}H_{16}BCoF_4N_2O$ (362.0): C, 43.13; H, 4.46; N, 7.74. Found: C, 42.96; H, 4.32; N, 7.57%.

3.7.9. (η^5-Cyclopentadienyl)-[(4-6-η^3)-1-dimethylamino-4-methyl-2-oxa-4-hexen-6-yl-1-ylidene]-cobalt(III) tetrafluoroborate ***(11i)***

Yield: 141 mg (32%) as an orange solid from 410 mg (1.21 mmol) of **2a** and 0.50 ml (3.00 mmol) dimethyl-

amine; reaction time 5 h; R_f (1:1 CH_3CN–CH_2Cl_2) = 0.67. ^{1}H-NMR (CD_3CN): $\delta = 1.47$ [dd, ^2J(6-H^{exo}/6-H^{endo}) = 2.44 Hz, ^3J(5-H/6-H^{endo}) = 12.45 Hz, 1H, 6-H^{endo}], 1.87 [s, 3H, 4-CH_3], 2.96 and 3.57 [s each, 6H, NCH_3, NCH_3'], 3.62 [d, ^2J(3-H^{exo}/3-H^{endo}) = 12.70 Hz, 1H, 3-H^{endo}], 4.14 [d, ^2J(3-H^{exo}/3-H^{endo}) = 12.70 Hz, 1H, 3-H^{exo}], 4.32 [dd, ^2J(6-H^{exo}/6-H^{endo}) = 2.44 Hz, ^3J(5-H/6-H^{exo}) = 8.30 Hz, 1H, 6-H^{exo}], 5.14 [dd, ^3J(5-H/6-H^{exo}) = 8.30 Hz, ^3J(5-H/6-H^{endo}) = 12.45 Hz, 1H, 5-H], 5.28 [s, 5H, Cp]. ^{13}C-NMR (CD_3CN): $\delta = 27.63$ (4-Me), 39.87 and 46.41 (NMe, NMe′), 48.25 (6-C), 76.17 (3-C), 84.30 (5-C), 88.92 (Cp-C), 92.01 (4-C), 228.87 (1-C). IR (KBr): $\nu = 3100$ cm^{-1}, 3040, 2900, 1700, 1555, 1460–1410, 1370, 1340, 1255, 1100–1000, 895, 840. MS (70 eV): m/z (%) = 263 (35) [cation-H], 197 (21) [cation-CpH_2], 127 (75), 124 (56) [$CoCp^+$], 108 (22), 70 (54), 59 (100) [Co^+], 41 (82), 28 (26) [CO^+]. Anal. Calc. for $C_{13}H_{19}BCoF_4NO$ (351.0): C, 44.48; H, 5.45; N, 3.99. Found: C, 44.66; H, 5.42; N, 3.89%.

3.8. Synthesis of aminooxochromiumcarbene complexes **12** [6,12] from **14** and **15**—general procedure

Carbene complex **15** was dissolved in THF (10 ml mmol^{-1}) and then the amine **14** (1.2–2 equivalents) was added at once. The colour of the mixture changed from red to yellow within the following 5 min. This mixture was allowed to stir for a further 3 h. All volatile components were removed in vacuo and finally the remaining crude product was purified by column chromatography (silica gel, neat diethyl ether; first fraction contains some residual starting material **15**, second fraction contains the product **12**).

3.8.1. Pentacarbonyl-[(5Z)-3-aza-3-methyl-7-hydroxy-5-hepten-2-ylidene]-chromium(0) (**12a**)

Yield: 2.11 g (47%) [beside 492 mg (12%) of chelated complex **16a**] from 3.52 g (14.07 mmol) pentacarbonyl-(1-methoxy-1-ethylidene)-chromium(0) **15a** (R/Me) and 2.74 g (27.06 mmol) of 4-methylamino-2-buten-1-ol **14**; air-sensitive red oil; R_f (Et_2O) = 0.57, R_f (CH_2Cl_2) = 0.10. ^{1}H-NMR (acetone-d_6): $\delta = 2.74$ [s, 3H, 1-H], 3.31 [s, 3H, NCH_3], 4.31 [mc, 4H, 4-H, 7-H], 5.82 [mc, 2H, 5-H, 6-H]. ^{13}C-NMR (acetone-d_6): $\delta = 40.42$ (1-C), 40.80 (N–Me), 58.65 (4-C), 63.54 (7-C), 125.19 (5-C), 136.22 (6-C), 218.58 (*cis*-CO), 224.39 (*trans*-CO), 273.77 (2-C). IR (NaCl): $\nu = 3385$ cm^{-1}, 2960, 2855, 2055, 1970, 1940, 1930, 1530, 1400, 1260, 1025, 800. MS (70 eV): m/z (%) = 319 (17) [M^+], 291 (9) [M^+ − CO], 263 (11) [M^+ − 2 CO], 235 (23) [M^+ − 3 CO], 207 (19) [M^+ − 4 CO], 179 (14) [M^+ − 5 CO], 163 (54), 100 (83), 71 (100), 28 (68) [CO^+]. Anal. Calc. for $C_{12}H_{13}CrNO_6$ (319.2): C, 45.15; H, 4.11; N, 4.39. Found: C, 45.22; H, 4.21; N, 4.29%.

3.8.2. Pentacarbonyl-[(4Z)-2-aza-6-hydroxy-2-methyl--1-phenyl-4-hexen-1-ylidene]-chromium(0) (**12b**)

Yield: 432 mg (42%) [beside 152 mg (16%) of chelated complex **16b**] from 840 mg (2.70 mmol) pentacarbonyl-(1-methoxy-1-phenyl-methylidene)-chromium(0) (**15b**) and 816 mg (8.07 mmol) of 4-methylamino-2-buten-1-ol (**14**); air-sensitive red oil; R_f (Et_2O) = 0.61, R_f (CH_2Cl_2) = 0.12. ^{1}H-NMR (acetone-d_6): $\delta = 3.97$ [s, 3H, N–CH_3], 4.18 [mc, 4H, 3-H, 6-H], 5.59 [mc, 2H, 4-H, 5-H], 7.17 [mc, 5H, Ph]. ^{13}C-NMR (acetone-d_6): $\delta = 49.05$ (NMe), 56.19 (3-C), 58.23 (6-C), 120.02 (*m*-C^{ar}), 124.49 (4-C), 126.40 (*p*-C^{ar}), 129.11 (*o*-C^{ar}), 136.11 (5-C), 153.33 (*ipso*-C^{ar}), 218.06 (*cis*-CO), 224.83 (*trans*-CO), 272.31 (1-C). IR (NaCl): $\nu = 3380$ cm^{-1}, 2965, 2860, 2065, 1970, 1935, 1920, 1400, 1260, 1020, 820, 660. MS (70 eV): m/z (%) = 381 (21) [M^+], 353 (12) [M^+ − CO], 325 (29) [M^+ − 2 CO], 297 (15) [M^+ − 3 CO], 269 (24) [M^+ − 4 CO], 241 (13) [M^+ − 5 CO], 176 (85), 145 (37), 112 (100), 77 (63) [Ph^+], 52 (45) [Cr^+], 28 (68) [CO^+]. Anal. Calc. for $C_{17}H_{15}CrNO_6$ (381.3): C, 53.55; H, 3.97; N, 3.67. Found: C, 53.59; H, 4.00; N, 3.63%.

3.9. Photochemical synthesis of chelated (η^2-alkene)aminochromiumcarbene complexes **16** from **12**—general procedure

The irradiation apparatus described in the protocol for the preparation of complex **9** was flushed with dry nitrogen and then charged with a solution of the respective complex **12** in THF. The reaction mixture was chilled to − 30°C and then irradiated for 3 h at this temperature. Then all volatile components were removed in vacuo and the remaining crude product metallacycle was finally purified by column chromatography (silica gel, neat diethyl ether).

3.9.1. Tetracarbonyl-[(4Z)-(4-5-η^2)-2-aza-6-hydroxy-1,2-dimethyl-4-hexen-1-ylidene]-chromium(0) **16a**

Yield: 481 mg (77%) as an air-sensitive yellow oil from 683 mg (2.14 mmol) of **12a**; R_f (Et_2O) = 0.22, R_f (CH_2Cl_2) = 0.00. ^{1}H-NMR (acetone-d_6): $\delta = 2.38$ [s, 3H, 1-CH_3], 3.24 [s, 3H, NCH_3], 3.53 [t, ^3J(6-H/OH) = 10.84 Hz, 1H, O–H], 4.33 [mc, 6H, 3-H, 4-H, 5-H, 6-H]. ^{13}C-NMR (acetone-d_6): $\delta = 33.46$ (1-Me), 38.52 (NMe), 61.64 (3-C), 62.02 (6-C), 76.49 (4-C), 87.65 (5-C), 224.92 and 225.92 (*cis*/*eq*-CO), 226.98 and 233.88 (*trans*-CO, *cis*/*ap*-CO), 275.50 (1-C). IR (NaCl): $\nu = 3380$ cm^{-1}, 2960, 2855, 2020, 1940, 1930, 1840, 1445, 1225, 1130, 1020, 800, 740, 675. MS (70 eV): m/z (%) = 291 (23) [M^+], 263 (14) [M^+ − CO], 235 (36) [M^+ − 2CO], 207 (17) [M^+ − 3 CO], 179 (25) [M^+ − 4 CO], 163 (76), 100 (74), 71 (100), 28 (54) [CO^+]. Anal. Calc. for $C_{11}H_{13}CrNO_5$ (291.3): C, 45.15; H, 4.11; N, 4.39. Found: C, 45.22; H, 4.21; N, 4.31%.

3.9.2. Tetracarbonyl-[(4E)-(4-5-η²)-2-aza-6-hydroxy-2-methyl-1-phenyl-4-hexen-1-ylidene]-chromium(0) ***16b***

Yield: 287 mg (72%) as an air-sensitive yellow oil from 432 mg (1.13 mmol) of **12b**; R_f (Et_2O) = 0.27, R_f (CH_2Cl_2) = 0.00. ^{1}H-NMR (acetone-d_6): δ = 3.06 [s, 3H, NCH_3], 4.38 [mc, 7H, 3-H, 4-H, 5-H, 6-H, O–H], 6.84 [mc, 2H, *m*-H^{ar}], 7.19 [mc, 1H, *p*-H^{ar}], 7.39 [mc, 2H, *o*-H^{ar}]. ^{13}C-NMR (acetone-d_6): δ = 41.44 (NMe), 60.70 (3-C), 61.99 (6-C), 77.60 (4-C), 89.35 (5-C), 120.60 (*m*-C^{ar}), 127.06 (*p*-C^{ar}), 129.13 (*o*-C^{ar}), 149.64 (*ipso*-C^{ar}), 224.81 (*cis*/*eq*-CO), 224.87 (*cis*/*eq*-CO), 228.18 and 231.66 (*trans*-CO, *cis*/*ap*-CO), 276.23 (1-C). IR (NaCl): ν = 3370 cm^{-1}, 3060, 3020, 2965, 2930, 2055, 2000, 1875, 1860, 1690, 1600, 1555, 1540, 1440, 1405, 1260, 1210, 1100, 1020, 870, 810, 745, 655. MS (70 eV): *m*/*z* (%) = 353 (32) [M$^+$], 325 (21) [M$^+$ − CO], 297 (19) [M$^+$ − 2 CO], 269 (28) [M$^+$ − 3 CO], 241 (17) [M$^+$ − 4 CO], 176 (71), 145 (48), 112 (100), 77 (82) [Ph$^+$], 52 (61) [Cr$^+$], 28 (57) [CO$^+$]. Anal. Calc. for $C_{16}H_{15}CrNO_5$ (353.3): C, 54.40; H, 4.28; N, 3.97. Found: C, 54.46; H, 4.35; N, 4.01%.

3.10. (Z)-4-Methylamino-2-buten-1-ol ***(14)*** *[20]*

3.10.1. (Z)-4-Chloro-2-buten-1-ol

(*Z*)-2-Butene-1,4-diol (50.00 g, 568 mmol) and pyridine (37.50 ml, 478 mmol) were dissolved in diethyl ether (100 ml). The resulting solution was then chilled to − 5°C and treated with thionyl chloride (41 ml) during which operation the temperature was not allowed to exceed + 5°C. After completion of the addition, stirring of the mixture was continued for another 2 h. Then water (150 ml) was added, the phases were separated, and after repeated extraction of the aqueous one with diethyl ether (2 × 30 ml) and dichloromethane (2 × 30 ml), the combined organic layers were dried over $MgSO_4$ and filtered. All volatile components were removed on a rotary evaporator and the remaining residue was purified by distillation in a Kugelrohr apparatus. Yield: 28.19 g (47%) as a colourless liquid of a burning odour, b.p. = 76°C, 13 Torr. ^{1}H-NMR (DMSO-d_6): δ = 4.16 [mc, 4H, 1-H, 4-H], 4.45 [s, 1H, O–H], 5.55 [mc, 2H, 2-H, 3-H]. ^{13}C-NMR (DMSO-d_6): δ = 40.10 (4-C), 57.00 (1-C), 125.64 (3-C), 135.34 (2-C).

3.10.2. (Z)-4-Methylamino-2-buten-1-ol ***(14)***

To a solution of (*Z*)-4-chloro-2-buten-1-ol (10.36 g, 97.20 mmol) in dichloromethane (150 ml) was added methylamine (10 ml). The resulting mixture was stirred overnight and then filtered to remove any precipitated methylammonium chloride, which was washed thoroughly with dichloromethane. The combined clear filtrate and washings were concentrated on a rotary evaporator and the crude product thus obtained was finally purified by distillation in a Kugelrohr apparatus. Yield: 4.16 g (42%), colourless liquid with a typical 'amine smell', b.p. = 112°C, 0.02 Torr. ^{1}H-NMR (DMSO-d_6): δ = 2.24 [s, 3H, NCH_3], 3.09 [d, ^3J(3-H/4-H) = 6.59 Hz, 2H, 4-H], 4.01 [d, ^3J(1-H/2-H) = 5.61 Hz, 2H, 1-H], 5.43 [dt, ^3J(2-H/3-H) = 11.72 Hz, ^3J(3-H/4-H) = 6.59 Hz, 1H, 3-H], 5.60 [dt, ^3J(2-H/3-H) = 11.72 Hz, ^3J(1-H/2-H) = 5.61 Hz, 1H, 2-H]. ^{13}C-NMR (DMSO-d_6): δ = 35.48 (N–Me), 47.83 (4-C), 57.11 (1-C), 128.54 (3-C), 132.11 (2-C).

3.11. Synthesis of functionalized amines from their hydrochlorides—general procedure

An 18% solution of ammonia in dichloromethane (1 l) was freshly prepared by saturation of the solvent with NH_3 gas at − 18°C (it can be stored at − 20°C for some time). Two to three equivalents of this solution were added to a suspension of the respective hydrochloride in chloroform (1.00 ml mmol^{-1}), whereupon a white precipitate of ammonium chloride was instantly formed. After stirring of the mixture for a further hour, it was filtered, the residue was thoroughly washed with dichloromethane and then the combined organic phases were concentrated on a rotary evaporator (temperature was kept below 35°C). The residue thus obtained, was dried in vacuo to give a colourless, viscous oil, clean enough to be used as such without further purification. Storage of these amines is possible under an atmosphere of argon at − 20°C for a couple of days. Yields: aminoacetonitrile 91%, methylaminoacetonitrile 74%, glycine methylester 89%, sarcosine methylester 65%, β-alanine methylester 99%.

3.12. Synthesis of allylaminomanganesecarbene complexes ***13*** *and* ***19*** *from* ***17****—general procedure*

Under an atmosphere of dry nitrogen (η^5-cyclopentadienyl)-benzylidyne-dicarbonyl-manganese(III) tetrachloroborate (**17**) was dissolved in dry dichloromethane (30 ml mmol^{-1}) and the resulting solution chilled to − 78°C. One equivalent of the respective allylamine (together with an excess of pyridine or TEA as a base) was added at once, whereupon an instantaneous change of the colour from yellow to red occurred and a white precipitate of ammonium tetrachloroborate was formed. The solution was allowed to warm up to ambient temperature with continued stirring and was finally concentrated on an oil pump to a volume of ca. 5 ml. By column chromatography of this solution on silica gel with neat diethyl ether and evaporation of the eluate pure complexes **13** and **19** were obtained. Dicarbonyl-(η^5-cyclopentadienyl)-(2-aza-2-methyl-1-phenyl-4-penten-1-ylidene)-manganese(I) (**19**)

Yield: 284 mg (55%) as an air-sensitive red oil from 680 mg (1.63 mmol) **17**, 1.00 ml (12.50 mmol) pyridine, and 1.00 ml (14.62 mmol) of allylmethylamine; R_f (Et_2O) = 0.95, R_f (benzene) = 0.65. Mixture (1:0.52) of

E/Z isomers as to the configuration about the 1C–2N bond. Assignment of the NMR-signals by their integration where possible, isomers indicated as **19¹** (E isomer) and **19²** (Z isomer): ^{1}H-NMR (benzene-d_6): $\delta = 2.09$ [s, 2H, 3-H], 3.08 [s, 3H, NCH_3^2], 3.24 [s, 3H, NCH_3^1], 3.88 [s, 5H, Cp], 4.61 [mc, 3H, 4-H, 5-H], 6.76 [mc, 5H, Ph]. ^{13}C-NMR (acetone-d_6): $\delta = 42.22$ (NMe^2), 46.46 (NMe^1), 59.75 (3-C^1), 64.09 (3-C^2), 84.37 (Cp^2), 85.09 (Cp^1), 117.69 (5-C^1), 118.89 (5-C^2), 120.49 (m-C^{ar2}), 120.80 (m-C^{ar1}), 124.98 (p-C^{ar2}), 125.02 (p-C^{ar1}), 127.77 (o-C^{ar1}), 128.25 (o-C^{ar2}), 132.40 (4-C^2), 133.29 (4-C^1), 154.23 (*ipso*-C^{ar1}), 154.62 (*ipso*-C^{ar2}), 234.12 (CO^2), 234.95 (CO^1), 283.70 (1-C^1), 285.05 (1-C^2). IR (NaCl, THF): $\nu = 2975$ cm^{-1}, 2680, 1965, 1920, 1855, 1460, 1365, 655. MS (70 eV): m/z (%) = 335 (23) [M^+], 307 (4) [$M^+ - CO$], 279 (100) [$M^+ - 2$ CO], 223 (40) [$C_{12}H_{10}MnN^+$], 158 (23) [$C_7H_5MnN^+$], 120 (49) [$C_5H_5Mn^+$], 55 (39) [Mn^+]. Anal. Calc. for $C_{18}H_{18}MnNO_2$ (353.3): C, 64.48; H, 5.41; N, 4.18. Found: C, 64.53; H, 5.46; N, 4.13%.

3.12.1. Dicarbonyl-(η⁵-cyclopentadienyl)-[(4Z)-2-aza-6-hydroxy-2-methyl-1-phenyl-4-hexen-1-ylidene]-manganese(I) (13)

Yield: 440 mg (49%) as an air-sensitive red oil from 1.04 mg (2.49 mmol) **17**, 1 ml triethylamine, and 2.00 g (19.77 mmol) of aminobutenol **14**; R_f (Et_2O) = 0.65, R_f (benzene) = 0.00. Mixture (1:0.7) of E/Z isomers as to the configuration about the 1C–2N bond. Assignment of the NMR-signals by their integration where possible; isomers indicated as **13¹** (E isomer) and **13²** (Z isomer): ^{1}H-NMR (benzene-d_6): $\delta = 2.42$ [s, 2H, 3-H], 3.54 [s, 3H, NCH_3], 4.14 [s, 5H, Cp], 4.91 [mc, 2H, 6-H], 5.57 [mc, 2H, 4-H, 5-H], 6.86 [mc, 5H, Ph]. ^{13}C-NMR (benzene-d_6): $\delta = 42.29$ (NMe^2), 46.42 (NMe^1), 54.72 (3-C^1), 58.17 (3-C^2), 58.81 (6-C^1), 68.93 (6-C^2), 84.51 (Cp^2), 84.93 (Cp^1), 120.46 (m-C^{ar2}), 121.00 (m-C^{ar1}), 124.99 (p-C^{ar2}), 125.08 (p-C^{ar1}), 127.35 (o-C^{ar2}), 127.39 (o-C^{ar1}), 128.54 (4-C^1), 131.29 (4-C^2), 133.20 (5-C^1), 134.02 (5-C^2), 154.20 (*ipso*-C^{ar2}), 154.48 (*ipso*-C^{ar2}), 234.36 (CO^2), 234.80 (CO^1), 282.88 (1-C^2), 283.12 (1-C^1). IR (NaCl): $\nu = 3375$ cm^{-1}, 2960, 1905, 1840, 1595, 1505, 1435, 1395, 1360, 1260, 1185, 1025, 805, 705, 655. MS (70 eV): m/z (%) = 365 (43) [M^+], 309 (100) [$M^+ - 2$ CO], 243 (47) [$M^+ - C_7H_6O_2$], 223 (27) [$C_{12}H_{10}MnN^+$], 120 (100) [$C_5H_5Mn^+$], 77 (38), [$C_6H_5^+$], 66 (23) [$C_5H_6^+$], 55 (70) [Mn^+]. Anal. Calc. for $C_{19}H_{20}MnNO_3$ (365.3): C, 62.47; H, 5.52; N, 3.83. Found: C, 62.37; H, 5.46; N, 3.79%.

3.13. (η⁵-Cyclopentadienyl)-carbonyl-[(4-5-η²)-2-aza-2-methyl-1-phenyl-4-penten-1-ylidene]-manganese(I) (18)

The irradiation apparatus described in the protocol for the preparation of complex **9** was flushed with dry nitrogen and then charged with **19** (304 mg, 0.90 mmol) and THF (100 ml). The solution was chilled to −30°C and then irradiated for 3 h. All volatile components were removed in vacuo and the remaining crude product was finally purified by column chromatography (silica gel, neat diethyl ether). 260 mg (94%) as an air-sensitive red oil; R_f (Et_2O) = 0.91, R_f (benzene) = 0.96. ^{1}H-NMR (benzene-d_6): $\delta = 1.57$ [mc, 3H, 4-H, 5-H], 1.98 [s, 3H, NCH_3], 2.27 [mc, 2H, 3-H], 3.75 [s, 5H, Cp], 6.77 [mc, 5H, Ph]. ^{13}C-NMR (benzene-d_6): $\delta = 33.38$ (5-C), 38.04 (NMe), 41.56 (3-C), 51.95 (4-C), 86.14 (Cp-C), 120.33 (m-C^{ar}), 124.58 (m-C^{ar}), 126.33 (p-C^{ar}), 127.55 (o-C^{ar}), 128.43 (o-C^{ar}), 151.66 (*ipso*-C^{ar}), 241.61 (CO), 281.87 (1-C). IR (NaCl, THF): $\nu = 3410$ cm^{-1}, 2955, 2280, 1965, 1925, 1850, 1460, 755, 705, 655. MS (70 eV): m/z (%) = 307 (22) [M^+], 279 (77) [$M^+ - CO$], 223 (37) [$C_{12}H_{10}MnN^+$], 158 (32) [$C_7H_5MnN^+$], 120 (49) [$C_5H_5Mn^+$], 118 (51) [$C_5H_3Mn^+$], 105 (86) [$C_4H_2Mn^+$], 77 (35) [$C_6H_5^+$], 55 (42) [Mn^+], 42 (100) [$C_3H_6^+$]. Anal. Calc. for $C_{17}H_{18}MnNO$ (307.3): C, 66.45; H, 5.91; N, 4.56. Found: C, 66.51; H, 5.86; N, 4.59%.

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