Coordinated 1-Aza-1,3-butadienes: Stable Intermediates in the Formation of Pyridines from [(β-Aminoethenyl)carbene]chromium Complexes

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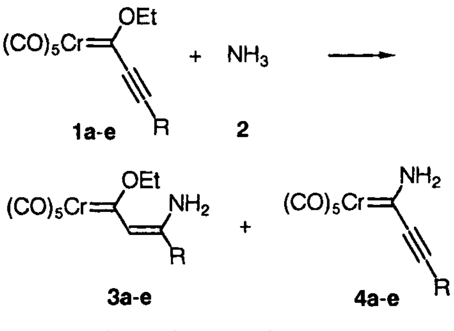
[(β-Aminoethenyl)carbene]chromium complexes **3a–c** rearrange to coordinated 1-aza-1,3-butadienes **6a–c**, which undergo cycloadditions with alkynes **7a, c** to pyridines **9a**, **10a–c**.

Among the Fischer carbene complexes, α,β-unsaturated (alkoxycarbene)chromium complexes have gained the widest interest of all[1]. These complexes cycloadd alkynes with insertion of a carbonyl ligand to form six-membered rings (the so-called Dötz reaction), if alkyl groups or hydrogen are attached to the terminal vinylic carbon. With an amino substituent in this pivotal position, however, a totally different behavior is observed. {[2-(Dialkylamino)ethenyl]carbene}-chromium complexes are converted into cyclopentadienes[2,3] or cyclopenta[*b*]pyrans[4] by reaction with alkynes. [2-(Alkylamino)ethenyl]carbene complexes form 4(1*H*)-pyridinylidene complexes with retention of the pentacarbonylchromium unit[5].

The 1,4-addition of amines to alkynylcarbene complexes[6] is an excellent route from easily available starting materials to (β-aminoethenyl)carbene complexes with a large variety of substituents in very good yields[7]. The addition of ammonia itself leads to [(*Z*)-2-aminoethenyl]carbene complexes **3** along with (1-aminoethynyl)carbene complexes **4** (see Scheme 1, Table 1).

Scheme 1. Addition of ammonia to (alkynylcarbene)chromium complexes **1a–e** (conditions and yields see Table 1)



	a	b	c	d	e
R	*n*Pr	*c*Pr	Ph	*t*Bu	TMS

Table 1. Michael addition of ammonia to (alkynylcarbene)chromium complexes **1a–e**

Entry	Starting material	R	Solvent	Temp. [°C]	Time [s]	Product	Yield (%)	Product	Yield (%)
1	**1a**[8]	*n*Pr	Et_2O	20	10	**3a**	63	**4a**	31
2	**1a**[8]	*n*Pr	THF	65	15	**3a**	87	**4a**	5
3	**1b**[7]	*c*Pr	Et_2O	20	10	**3b**	70	**4b**	28
4	**1b**[7]	*c*Pr	THF	65	15	**3b**	93	**4b**	2
5	**1c**[6]	Ph	Et_2O	20	10	**3c**	13	**4c**	86
6	**1c**[6]	Ph	THF	65	15	**3c**	39	**4c**	29
7	**1d**[9]	*t*Bu	Et_2O	20	15	**3d**	35	**4d**	60
8	**1d**[9]	*t*Bu	THF	65	45	**3d**	90	**4d**	6
9	**1e**[9]	TMS	Et_2O	20	15	**3e**	0	**4e**	27
10	**1e**[9]	TMS	THF	65	45	**3e**	5	**4e**	78

The formation of addition products **3** is favored at elevated temperatures (e.g. 93% **3b** from **1b** at 65 °C). This is in accord with earlier results of Fischer for the addition of dimethylamine[6]. Surprisingly, even the reaction of **1d** gave substitution product **4d** along with **3d**, although previously complexes with bulky groups attached to C-3 had only been observed to yield 3-aminoallenylidene complexes when treated with secondary and primary amines[7,10]. This trend was corroborated by the reaction of **1d** with methylamine. Whereas the reaction of **1d** with dimethylamine gave only the addition together with the addition-elimination product pentacarbonyl[3-(dimethylamino)-4,4-dimethyl-1,2-pentadienylidene]chromium[7] and with ammonia only **3d** and **4d**, the reaction of **1d** with methylamine gave addition (14%), substitution (63%), and addition-elimination products (19%).

When complexes **3a–d** were heated to 50 °C in THF, two products were isolated as light yellow oils in each case except for **3d**, which gave only insoluble material. According to

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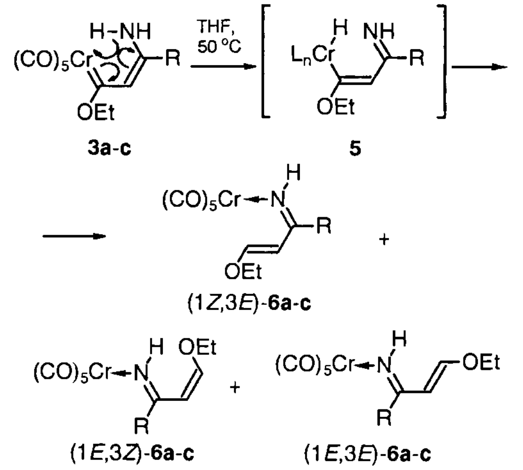
[+] Crystal structure analysis.

Scheme 2. Formation of coordinated 1-aza-1,3-butadienes **6a–c** (in all cases the designation of the configuration of the C=N double bond refers to the pentacarbonylchromium and the ethenyl group independent of the nature of R)



their mass spectra all products were isomers of their respective starting materials **3a–c** and were identified as the coordinated 1-aza-1,3-butadienes **6a–c** on the basis of their ^{1}H- and ^{13}C-NMR spectra. The coupling constant ^3J between the two olefinic protons of the minor isomer of **6b** was found to be 7.1 Hz, i.e. consistent with a 3*Z* configuration. In addition, the structure of this isomer was determined by X-ray crystal structure analysis (see Figure 1).

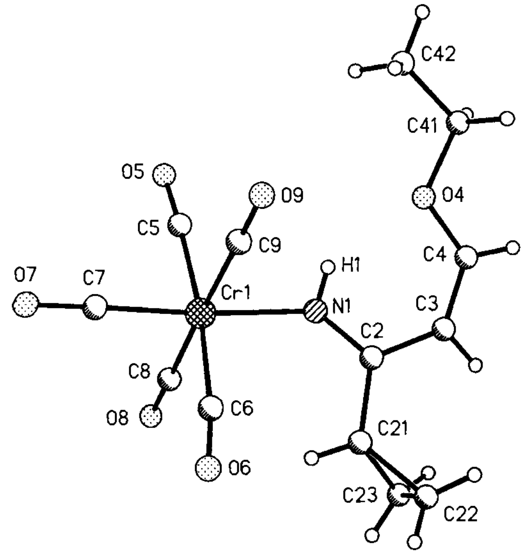


Figure 1. Structure of (1*E*,3*Z*)-**6b** in the crystal. Key interatomic distances [pm] and angles [°]: Cr(1)–N(1) 211.0(1), N(1)–C(2) 129.1(2), C(2)–C(3) 145.9(2), C(3)–C(4) 132.5(3), C(4)–O(4) 134.6(2); Cr(1)–N(1)–C(2) 140.4(1), N(1)–C(2)–C(3) 122.3(2), C(2)–C(3)–C(4) 126.7(2)

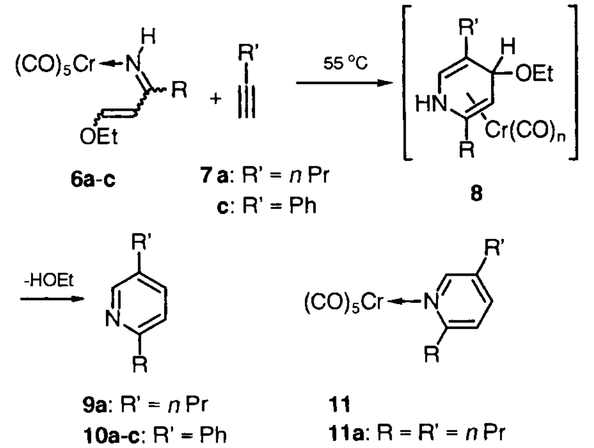
For all other isomers of **6a–c** values of ^3J were between 12.3 and 13.0 Hz, indicating a 3*E* configuration of the ethoxyethenyl groups. Thus, the minor isomers were probably (1*Z*,3*E*)-**6a–c**, (1*E*,3*Z*)-**6b**, while the major ones were (1*E*,3*E*)-**6a–c** (Scheme 2 and Table 2). The mechanism of this rearrangement can only be speculated about: An initial 1,5-hydride shift and subsequent reductive elimination[11] with concomitant shift of the (CO)$_5$Cr fragment from carbon to nitrogen would account for the observed coordinated 1-aza-1,3-butadienes; but it is not even known at this stage whether the reaction is intra- or intermolecular.

Table 2. Formation of coordinated 1-aza-1,3-butadienes **6a–c** from pentacarbonyl[(aminoethenyl)carbene]chromium complexes **3a–c** in THF and their cycloaddition reaction with alkynes **7a, c** yielding pyridines **9a** and **10a–c**

Entry	Starting material	R	Product	Yield (%)	Conversion (%)[a]	Alkyne	R'	Solvent	Product	Yield (%)
1	**3a**	*n*Pr	**6a**[b]	69	72	**7a**	*n*Pr	hexane	**9a**	42[c]
2	**3a**	*n*Pr	**6a**[b]			**7c**	Ph	THF	**10a**	49
3	**3a**	*n*Pr	**6a**[b]			**7c**	Ph	hexane	**10a**	78[d]
4	**3b**	*c*Pr	**6b**[e]	52	77	**7c**	Ph	THF	**10b**	60
5	**3b**	*c*Pr	**6b**[e]			**7c**	Ph	THF	**10b**	28[f]
6	**3c**	Ph	**6c**[g]	57	75	**7c**	Ph	THF	**10c**	72
7	**3d**	*t*Bu	**6d**	0	100					

[a] The reactions were interrupted before total conversion, as the products are slightly unstable. — [b] (1*E*,3*E*)/(1*Z*,3*E*) = 3.4:1. — [c] Including 21% from the oxidation of the tricarbonyl(pyridine)-chromium complex of type **11**. The yield of **9a** increased to 77%, if the 1-aza-1,3-butadiene **6a** was not isolated. — [d] Including 20% from the oxidation of the tricarbonyl(pyridine)chromium complex of type **11**. — [e] (3*E*)/(3*Z*) = 3.7:1. — [f] Direct reaction of **3b** with **7c**. — [g] (1*E*,3*E*)/(1*Z*,3*E*) = 3.0:1.

Scheme 3. [4 + 2] Cycloadditions of pentacarbonylchromium-1-aza-1,3-butadienes **6a–c** to alkynes to form pyridines **9a** and **10a–c**



Uncoordinated 1-aza-1,3-dienes have previously been observed upon decomposition of secondary (β-aminoethenyl)-carbene complexes[5].

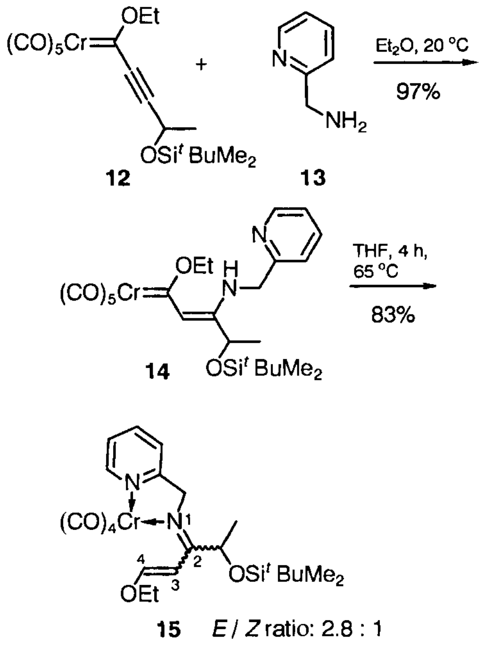
When treated with alkynes in THF solution at 55 °C, coordinated 4-ethoxy-1-aza-1,3-butadienes **6a–c** as well as the [(β-aminoethenyl)carbene]chromium complex **3b** (entry 5 in Table 2) were converted into pyridines **9a**, **10a–c** and the corresponding complexes **11** within two days. The products were separated by column chromatography; the air-sensitive yellow complexes, the coordinated pyridines **11**, were not isolated except for the case of **11a** ($R = R' = n$Pr). Upon stirring of these complexes **11** in air, the corresponding pyridines were liberated.

Recently, the reaction of **3c** with 1-hexyne was reported to yield a pyridine of type **9**. The authors assumed that the transformation proceeds via a 4(1*H*)-pyridinylidene complex, as had been demonstrated for reactions of [β-(alkylamino)ethenyl]carbene complexes of the same type[5]. Our results, however, undoubtedly demonstrate that coordinated 1-aza-1,3-butadienes **6a–c** are intermediates in the formation of pyridines, when the precursors **3** contain a primary amino group.

An even more stable coordinated 1-aza-1,3-butadiene was obtained by heating ethenylcarbene complex **14**, prepared by the addition of 2-(aminomethyl)pyridine (**13**) to alkynylcarbene complex **12**, in THF solution. After only 4 h at 65°C, the air stable chelated tetracarbonylchromium complex **15** was isolated as a mixture of 1*E* and 1*Z* isomers in a ratio of 2.8:1 in 83% yield. This is in line with earlier observations about the facile intramolecular chelation by a pyridinyl group with simultaneous dissociation of one carbonyl ligand[7,11,12]. External pyridine added to a solution of **3a** in THF in catalytic amounts (10 mol-%) did not accelerate the reaction nor increase the product yield. The C,C double bound in **14** is *Z* configurated, as corroborated by the chemical shift of the proton attached to nitrogen of $\delta = 8.62$, caused by a hydrogen bond to the oxygen of the ethoxy group. The ^3J coupling constants between the vinylic protons of the 1*E* as well as the 1*Z* isomer of **15** were found to be 13.2 and 13.3 Hz, respectively, indicating a 3*E* configuration.

1-Aza-1,3-dienes are frequently unstable[13], but have nevertheless been used in Diels-Alder reactions[14], although [2 + 2] cycloadditions usually intervene. Sometimes, they are prepared in situ and directly subjected to reaction with a dienophile[15]. As the chromium-stabilized 1-aza-1,3-butadienes **6a–c** are very easily accessible in three steps from an alkyne, hexacarbonylchromium, and ammonia or primary amines, they may be considered for synthetic applications other than the reported pyridine formation.

Scheme 4. Formation of the chelated complexes (1*E*,3*E*)- and (1*E*,3*Z*)-**15**



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Experimental

All operations were performed under nitrogen. Solvents were dried by distillation from sodium or potassium/benzophenone. – ^{1}H NMR: Bruker AM 250 (250 MHz). – ^{13}C NMR: Bruker AM 250 (62.89 MHz), multiplicities were determined by DEPT. Chemical shifts refer to $\delta_{TMS} = 0.00$ according to the chemical shifts of residual solvent signals. – IR: Bruker IFS 66, Perkin-Elmer 298. – MS: Varian MAT CH 7, MAT 731. – HRMS: Varian MAT 311 A. – Melting points: Büchi 510, uncorrected. – Elemental analysis: Mikroanalytisches Laboratorium der Universität Göttingen.

Molecular composition and bulk purity were determined by microanalyses for representative examples of new compounds, all others molecular masses were confirmed by high resolution mass spectrometry with preselected ion peak matching at $R \approx 10000$ to be within ± 2 ppm of the exact masses.

General Procedure for the Preparation of [(2-Aminoethenyl)carbene]chromium Complexes: Ammonia was added to a solution of 5 mmol of **1** in 50 ml of the solvent until the color changed from blackish red to yellow. The solvents were removed under reduced pressure, and the residue was purified by chromatography over 100 g of silica gel (40 × 3 cm) to afford the pure complex.

(1-Amino-2-hexynylidene)pentacarbonylchromium (**4a**) *and [(2Z)-3-Amino-1-ethoxy-2-hexenylidene]pentacarbonylchromium* (**3a**)

Variant A: To a solution of 1.54 g (4.87 mmol) of pentacarbonyl(1-ethoxy-2-hexynylidene)chromium (**1a**)[8] in 50 ml of diethyl ether was added ammonia at 20°C until a change of color was observed. Purification (130 g of silica gel, 50 × 3 cm) yielded fraction I: 430 mg (31%) of **4a**, $R_f = 0.38$ (pentane/diethyl ether, 3:1), yellow oil. – IR (film): $\tilde{\nu} = 3450$ cm^{-1} (NH), 3340 (NH), 3250 (NH), 2985, 2890, 2190 (C≡C), 2060 (C=O), 1910 (C=O), 1650, 1385, 1225, 655. – ^{1}H NMR (250 MHz, C_6D_6): $\delta = 0.78$ (t, $^3J = 7.0$ Hz, 3H, $CH_2CH_2C\mathit{H}_3$), 1.30 (tq, $^3J = 7.0$, $^3J = 7.0$ Hz, 2H, $CH_2C\mathit{H}_2CH_3$), 2.07 (t, $^3J = 7.0$ Hz, 2H, $C\mathit{H}_2CH_2CH_3$), 6.10 (br. s, 1H, NH), 7.05 (br. s, 1H, NH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): $\delta = 13.45$ (+, C-6), 21.76 (–, C-5), 22.44 (–, C-4), 86.70 (C_{quat}, C-2), 127.07 (C_{quat}, C-3), 217.42, 223.88 (C_{quat}, C=O), 267.75 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 287 (7) [M$^+$], 231 (11) [M$^+$ – 2 CO], 203 (10) [M$^+$ – 3 CO], 175 (16) [M$^+$ – 4 CO], 147 (100) [M$^+$ – 5 CO], 52 (36) [Cr$^+$].

II: 1.02 g (63%) of **3a**, $R_f = 0.13$, yellow crystals, m.p. 61–63°C. – IR (KBr): $\tilde{\nu} = 3480$ cm^{-1} (NH), 3260 (NH), 2960, 2060 (C=O), 1880 (C=O), 1610, 1235, 1110, 910, 880, 815. – ^{1}H NMR (250 MHz, C_6D_6): $\delta = 0.56$ (t, $^3J = 7.2$ Hz, 3H, $CH_2CH_2C\mathit{H}_3$), 0.88 (t, $^3J = 7.0$ Hz, 3H, $OCH_2C\mathit{H}_3$), 1.01 (tq, $^3J = 7.2$, $^3J = 7.2$ Hz, 2H, $CH_2C\mathit{H}_2CH_3$), 1.22 (t, $^3J = 7.2$ Hz, 2H, $C\mathit{H}_2CH_2CH_3$), 3.91 (br. s, 1H, NH), 4.50 (q, $^3J = 7.0$ Hz, 2H, OCH_2), 6.29 (s, 1H, 2-H), 7.35 (br. s, 1H, NH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 13.34, 15.41 (+, C-6, OCH_2CH_3), 21.66 (–, C-5), 38.72 (–, C-4), 74.18 (–, OCH_2), 118.08 (+, C-2), 156.66 (C_{quat}, C-3), 219.41, 224.66 (C_{quat}, C=O), 293.12 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 333 (14) [M^+], 305 (7) [M^+ – CO], 277 (9) [M^+ – 2 CO], 249 (8) [M^+ – 3 CO], 221 (21) [M^+ – 4 CO], 193 (100) [M^+ – 5 CO], 164 (31) [M^+ – 5 CO – C_2H_5], 136 (53), 52 (58) [Cr^+].

Variant B: To a solution of 2.35 g (7.44 mmol) of pentacarbonyl(1-ethoxy-2-hexynylidene)chromium (**1a**)[8] in 75 ml of tetrahydrofuran was added ammonia at 65 °C until a change of color was observed. Purification (200 g of silica gel, 30 × 4.5 cm) yielded fraction I: 105 mg (5%) of **4a**. – II: 2.15 g (87%) of **3a**.

(1-Amino-3-cyclopropylpropynylidene)pentacarbonylchromium (**4b**) *and [(2Z)-3-Amino-3-cyclopropyl-1-ethoxypropenylidene]pentacarbonylchromium* (**3b**): To a solution of 1.09 g (3.47 mmol) of pentacarbonyl(1-ethoxy-3-cyclopropylpropynylidene)chromium (**1b**)[7] in 40 ml of tetrahydrofuran was added ammonia at 65 °C until a change of color was observed. Purification (100 g of silica gel, 40 × 3 cm) yielded fraction I: 40 mg (2%) of **4b**[7], $R_f = 0.34$ (pentane/diethyl ether, 1:1). – II: 1.07 g (93%) of **3b**[7], $R_f = 0.11$.

(1-Amino-3-phenylpropynylidene)pentacarbonylchromium (**4c**) *and [(2Z)-3-Amino-1-ethoxy-3-phenylpropenylidene]pentacarbonylchromium* (**3c**)

Variant A: To a solution of 710 mg (2.03 mmol) of pentacarbonyl-(1-ethoxy-3-phenylpropynylidene)chromium (**1c**)[6] in 20 ml of diethyl ether was added ammonia at 20 °C until a change of color was observed. Purification (90 g of silica gel, 35 × 3 cm) yielded fraction I: 570 mg (86%) of **4c**, $R_f = 0.21$ (pentane/diethyl ether, 3:1), orange crystals, m.p. 89 °C. – IR (KBr): $\tilde{\nu}$ = 3430 cm^{-1} (NH), 3320 (NH), 3240 (NH), 2165 (C≡C), 2055 (C=O), 1905 (C=O), 1635, 1380, 1270, 1190, 950, 765, 695, 655. – ^{1}H NMR (250 MHz, C_6D_6): δ = 6.58 (br. s, 2H, NH_2), 6.91–6.98 (m, 3H, Ph), 7.38–7.45 (m, 2H, Ph). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 92.48 (C_{quat}, C-2), 121.69, 124.00 (C_{quat}, C-3, C-Ph), 128.92, 130.73, 132.30 (+, C-Ph), 217.36, 223.77 (C_{quat}, C=O), 265.87 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 321 (9) [M^+], 265 (20) [M^+ – 2 CO], 237 (24) [M^+ – 3 CO], 209 (31) [M^+ – 4 CO], 181 (100) [M^+ – 5 CO], 102 (35), 52 (44) [Cr^+]. – $C_{14}H_7CrNO_5$ (321.2): calcd. C 52.35, H 2.20, N 4.36; found C 52.46, H 2.36, N 4.30.

II: 100 mg (13%) of **3c**, $R_f = 0.10$, yellow crystals, m.p. 93 °C. – IR (KBr): $\tilde{\nu}$ = 3480 cm^{-1} (NH), 3365 (NH), 2980, 2050 (C=O), 1880 (C=O), 1605, 1475, 1320, 1235, 1105, 990, 930, 735, 665. – ^{1}H NMR (250 MHz, C_6D_6): δ = 1.08 (t, $^3J = 7.0$ Hz, 3H, OCH_2CH_3), 4.59 (q, $^3J = 7.0$ Hz, 3H, OCH_2, NH), 6.80 (s, 1H, 2-H), 6.92–7.25 (m, 5H, Ph), 7.56 (br. s, 1H, NH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 15.39 (+, OCH_2CH_3), 74.53 (–, OCH_2), 117.49 (+, C-2), 127.13, 129.28, 131.44 (+, C-Ph), 136.84 (C_{quat}, C-Ph), 150.67 (C_{quat}, C-3), 219.22, 224.63 (C_{quat}, C=O), 298.43 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 367 (4) [M^+], 339 (4) [M^+ – CO], 311 (8), [M^+ – 2 CO], 283 (8) [M^+ – 3 CO], 255 (27) [M^+ – 4 CO], 227 (98) [M^+ – 5 CO], 198 (41) [M^+ – 5 CO – C_2H_5], 170 (100), 130 (43), 80 (40), 52 (99) [Cr^+].

Variant B: To a solution of 1.55 g (4.40 mmol) of pentacarbonyl(1-ethoxy-3-phenylpropynylidene)chromium (**1c**)[6] in 50 ml of tetrahydrofuran was added ammonia at 65 °C until a change of color was observed. Purification (130 g of silica gel, 40 × 3 cm) yielded fraction I: 416 mg (29%) of **4c**. – II: 626 mg (39%) of **3c**.

(1-Amino-4,4-dimethyl-2-pentynylidene)pentacarbonylchromium (**4d**) *and [(2Z)-3-Amino-1-ethoxy-4,4-dimethyl-2-pentenylidene)pentacarbonylchromium* (**3d**)

Variant A: To a solution of 270 mg (0.82 mmol) of pentacarbonyl-(1-ethoxy-4,4-dimethyl-2-pentynylidene)chromium (**1d**)[9] in 20 ml of diethyl ether was added ammonia at 20 °C until a change of color was oberved. Purification (30 g of silica gel, 24 × 1.5 cm) yielded fraction I: 149 mg (60%) of **4d**, $R_f = 0.30$ (pentane/diethyl ether, 3:1), orange crystals, m.p. 64 °C. – IR (KBr): $\tilde{\nu}$ = 3440 cm^{-1} (NH), 3340 (NH), 3255 (NH), 2960, 2185 (C≡C), 2055 (C=O), 1920 (C=O), 1875 (C=O), 1390, 1255, 1210, 825, 725, 660. – ^{1}H NMR (250 MHz, C_6D_6): δ = 1.12 [s, 9H, $C(CH_3)_3$], 6.66 (br. s, 1H, NH), 7.00 (br. s, 1H, NH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 29.31 [C_{quat}, $C(CH_3)_3$], 29.93 [+, $C(CH_3)_3$], 85.16 (C_{quat}, C-2), 135.83 (C_{quat}, C-3), 217.49, 223.83 (C_{quat}, C=O), 268.18 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 301 (9) [M^+], 273 (1) [M^+ – CO], 245 (13) [M^+ – 2 CO], 217 (11) [M^+ – 3 CO], 189 (20) [M^+ – 4 CO], 161 (100) [M^+ – 5 CO], 52 (33) [Cr^+]. – $C_{12}H_{11}CrNO_5$ (301.2): calcd. C 47.85, H 3.68, N 4.65; found C 48.20, H 3.94, N 4.75.

II: 99 mg (35%) of **3d**, $R_f = 0.06$, yellow crystals, m.p. 98 °C. – IR (KBr): $\tilde{\nu}$ = 3485 cm^{-1} (NH), 3350 (NH), 2970, 2050 (C=O), 1890 (C=O), 1615, 1485, 1255, 1105, 860, 820, 760, 660. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.70 [s, 9H, $C(CH_3)_3$], 0.92 (t, $^3J = 7.0$ Hz, 3H, OCH_2CH_3), 4.38 (br. s, 1H, NH), 4.51 (q, $^3J = 7.0$ Hz, 2H, OCH_2), 6.52 (s, 1H, 2-H), 7.71 (br. s, 1H, NH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = 15.42 (+, OCH_2CH_3), 28.25 [+, $C(CH_3)_3$], 36.63 [C_{quat}, $C(CH_3)_3$], 74.07 (–, OCH_2), 115.47 (+, C-2), 163.59 (C_{quat}, C-3), 219.53, 224.55 (C_{quat}, C=O), 292.48 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 347 (8) [M^+], 319 (8) [M^+ – CO], 291 (11) [M^+ – 2 CO], 263 (14) [M^+ – 3 CO], 235 (20) [M^+ – 4 CO], 207 (100) [M^+ – 5 CO], 178 (48) [M^+ – 5 CO – C_2H_5], 163 (67), 98 (66), 70 (41), 52 (26) [Cr^+]. – $C_{14}H_{17}CrNO_6$ (347.3): calcd. C 48.42, H 4.93, N 4.03; found C 48.20, H 4.98, N 4.13.

Variant B: To a solution of 180 mg (0.55 mmol) of pentacarbonyl-(1-ethoxy-4,4-dimethyl-2-pentynylidene)chromium (**1d**)[9] in 20 ml of tetrahydrofuran was added ammonia at 65 °C until a change of color was observed. Purification (30 g of silica gel, 24 × 1.5 cm) yielded fraction I: 10 mg (6%) of **4d**, $R_f = 0.30$. – II: 172 mg (90%) of **3d**, $R_f = 0.06$.

[1-Amino-3-(trimethylsilyl)propynylidene]pentacarbonylchromium (**4e**) *and [(Z)-3-Amino-1-ethoxy-3-(trimethylsilyl)propenylidene]pentacarbonylchromium* (**3e**): To a solution of 756 mg (2.18 mmol) of pentacarbonyl[1-ethoxy-3-(trimethylsiyl)propynylidene]-chromium (**1e**)[9] in 40 ml of tetrahydrofuran was added ammonia at 65 °C until a change of color was observed. Purification (100 g of silica gel, 40 × 3 cm) yielded fraction I: 564 mg (78%) of **4e**, $R_f = 0.82$ (pentane/diethyl ether, 3:1), orange oil. – IR (film): $\tilde{\nu}$ = 3453 cm^{-1} (NH), 3347 (NH), 2964, 2125 (C≡C), 2060 (C=O), 1930 (C=O), 1637, 1382, 1253, 1212, 974, 848, 652. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.20 [s, 9H, $Si(CH_3)_3$], 6.60 (br. s, 1H, NH), 7.12 (br. s, 1H, NH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = −0.91 [+, $Si(CH_3)_3$], 106.07 (C_{quat}, C-2), 131.71 (C_{quat}, C-3), 217.17, 223.87 (C_{quat}, C=O), 268.42 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 317 (3) [M^+], 233 (3) [M^+ – 3 CO], 205 (16) [M^+ – 4 CO], 177 (100) [M^+ – 5 CO], 52 (33) [Cr^+].

II: 42 mg (5%) of **3e**, $R_f = 0.21$, yellow crystals, m.p. 57 °C. – IR (KBr): $\tilde{\nu}$ = 3470 cm^{-1} (NH), 2921, 2851, 2361 (C=O), 2336 (C=O), 1917 (C=O), 1717, 1616, 1539, 1489, 1394, 1046, 680, 591. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.02 [s, 9H, $Si(CH_3)_3$], 1.57 (t, $^3J = 7.0$ Hz, 3H, OCH_2CH_3), 4.85 (q, $^3J = 7.0$ Hz, 2H, OCH_2CH_3), 5.53 (br. s, 1H, NH), 6.44 (br. s, 1H, 2-H), 8.29 (br. s, 1H, NH). – ^{13}C NMR (62.89 MHz, C_6D_6, plus DEPT): δ = −2.67 [+, $Si(CH_3)_3$], 14.06 (+, OCH_2CH_3), 74.45 (–, OCH_2CH_3), 123.03 (+, C-2), 158.54 (C_{quat}, C-3), 218.48, 224.12 (C_{quat}, C=O), 292.76 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 363 (5) [M^+], 307 (1) [M^+], 307 (1) [M^+ – 2 CO], 251

(8) [M$^+$ − 4 CO], 223 (40) [M$^+$ − 5 CO], 209 (55), 97 (60), 69 (100), 52 (95) [Cr$^+$].

Pentacarbonyl[(1E,3E)- and [(1Z,3E)-4-ethoxy-2-propyl-1-aza-1,3-butadiene-N]chromium [(1*E*,3*E*)-, (1*Z*,3*E*)-**6a**]: A solution of 430 mg (1.29 mmol) of **3a** in 30 ml of tetrahydrofuran was stirred at 48–50°C for 16 h. The solvent was removed under reduced pressure. Flash chromatography (50 g of flash silica gel, 20 × 3 cm) of the crude product yielded fraction I: 297 mg (69%) of a mixture of both isomers [ratio (1*E*,3*E*)/1*Z*,3*E*) = 3.4:1] of **6a**, R_f = 0.32 (pentane/diethyl ether, 15:1), yellow oil. – IR (film): $\tilde{\nu}$ = 3315 cm^{-1} (NH), 2966, 2065 (C=O), 1980 (C=O), 1917 (C=O), 1624 (C=N), 1215, 1188, 1137, 1110, 655. – ^{1}H NMR (250 MHz, CDCl$_3$): (1*E*,3*E*)-**6a**: δ = 0.95 (t, ^3J = 7.0 Hz, 3H, $\mathrm{CH_2CH_2C}H_3$), 1.42 (^3J = 7.0 Hz, 3H, $\mathrm{OCH_2C}H_3$), 1.49–1.65 (m, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 2.40 (t, ^3J = 7.0 Hz, 2H, $CH_2\mathrm{CH_2CH_3}$), 4.06 (q, ^3J = 7.0 Hz, 2H, OCH$_2$), 5.98 (d, ^3J = 12.5 Hz, 1H, 3-H), 7.23 (d, ^3J = 12.5 Hz, 1H, 4-H), 7.76 (br. s, 1H, NH). – (1*Z*,3*E*)-**6a**: δ = 1.07 (t, ^3J = 7.0 Hz, 3H, $\mathrm{CH_2CH_2C}H_3$), 1.33 (t, ^3J = 7.0 Hz, 3H, $\mathrm{OCH_2C}H_3$), 1.49–1.65 (m, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 2.50 (t, ^3J = 7.0 Hz, 2H, $CH_2\mathrm{CH_2CH_3}$), 3.91 (q, ^3J = 7.0 Hz, 2H, OCH$_2$), 5.40 (d, ^3J = 13.0 Hz, 1H, 3-H), 6.97 (d, ^3J = 13.0 Hz, 1H, 4-H), 7.98 (br. s, 1H, NH). – ^{13}C NMR (62.89 MHz, C$_6$D$_6$, plus DEPT): (1*E*,3*E*)-**6a**: δ = 13.15 (+, CH$_2$CH$_2$CH$_3$), 14.06 (+, OCH$_2$CH$_3$), 20.47 (–, $\mathrm{CH_2}CH_2\mathrm{CH_3}$), 39.39 (–, $CH_2\mathrm{CH_2CH_3}$), 65.76 (–, OCH$_2$), 104.23 (+, C-3), 159.43 (+, C-4), 183.52 ($\mathrm{C_{quat}}$, C-2), 215.68, 221.35 ($\mathrm{C_{quat}}$, C=O). – (1*Z*,3*E*)-**6a**: δ = 13.85 (+, $\mathrm{CH_2CH_2}CH_3$), 14.41 (+, $\mathrm{OCH_2}CH_3$), 22.38 (–, $\mathrm{CH_2}CH_2\mathrm{CH_3}$), 35.96 (–, $CH_2\mathrm{CH_2CH_3}$), 66.46 (–, OCH$_2$), 106.78 (+, C-3), 155.71 (+, C-4), 184.81 ($\mathrm{C_{quat}}$, C-2), 215.38, 221.35 ($\mathrm{C_{quat}}$, C=O). – MS (70 eV), *m/z* (%): 333 (14) [M$^+$], 305 (1) [M$^+$ – CO], 277 (5) [M$^+$ – 2 CO], 249 (3) [M$^+$ – 3 CO], 221 (19) [M$^+$ – 4 CO], 193 (82) [M$^+$ – 5 CO], 164 (100) [M$^+$ – 5 CO – C$_2$H$_5$], 149 (81), 113 (64), 98 (78), 70 (74), 52 (64) [Cr$^+$].

II: 123 mg (28%) of **3a**.

Pentacarbonyl[(1E,3E)-2-cyclopropyl-4-ethoxy-1-aza-1,3-butadiene-N]chromium [(1*E*,3*E*)-**6b**] *and Pentacarbonyl[(1E,3Z)-2-cyclopropyl-4-ethoxy-1-aza-1,3-butadiene-N]chromium* [(1*E*,3*Z*)-**6b**]: A solution of 908 mg (2.74 mmol) of **3b** in 60 ml of tetrahydrofuran was stirred at 48–50°C for 19 h. The solvent was removed under reduced pressure. Flash chromatography (100 g of flash silica gel, 40 × 3 cm) of the crude product yielded fraction I: 370 mg (41%) of (1*E*,3*E*)-**6b**, R_f = 0.24 (pentane/diethyl ether 15:1), yellow oil. – IR (film): $\tilde{\nu}$ = 3315 cm^{-1} (NH), 2985, 2065 (C=O), 1880 (C=O), 1620 (C=N), 1440, 1335, 1225, 1200, 1365, 1020, 920, 820, 655. – ^{1}H NMR (250 MHz, C$_6$D$_6$): δ = –0.19 to –0.11 (m, 2H, *c*Pr-H), –0.03–0.10 (m, 2H, *c*Pr-H), 0.75–0.91 (m, 1H, *c*Pr-H), 1.00 (t, ^3J = 7.0 Hz, 3H, $\mathrm{OCH_2C}H_3$), 3.70 (q, ^3J = 7.0 Hz, 2H, OCH$_2$), 6.12 (d, ^3J = 12.9 Hz, 1H, 3-H), 7.12 (d, ^3J = 12.9 Hz, 1H, 4-H), 7.29 (br. s, 1H, NH). – ^{13}C NMR (62.89 MHz, C$_6$D$_6$, plus DEPT): δ = 5.61 (–, C-*c*Pr), 14.10 (+, OCH$_2$CH$_3$), 17.61 (+, C-*c*Pr), 65.89 (–, OCH$_2$), 104.96 (+, C-3), 160.38 (+, C-4), 182.53 ($\mathrm{C_{quat}}$, C-2), 215,59, 221.38 ($\mathrm{C_{quat}}$, C=O). – MS (70 eV), *m/z* (%): 331 (4) [M$^+$], 303 (1) [M$^+$ – CO], 275 (7) [M$^+$ – 2 CO], 247 (3) [M$^+$ – 3 CO], 219 (15) [M$^+$ – 4 CO], 191 (56) [M$^+$ – 5 CO], 162 (51) [M$^+$ – 5 CO – C$_2$H$_5$], 158 (100), 147 (49), 94 (38), 52 (29) [Cr$^+$].

II: 100 mg (11%) of (1*E*,3*Z*)-**6b**, R_f = 0.10, yellow crystals, m.p. 70–73°C. – IR (KBr): $\tilde{\nu}$ = 3325 cm^{-1} (NH), 2980, 2060 (C=O), 1925 (C=O), 1880 (C=O), 1635 (C=N), 1560, 1275, 1140, 1105, 1030, 995, 675, 655. – ^{1}H NMR (250 MHz, C$_6$D$_6$): δ = 0.28–0.41 (m, 2H, *c*Pr-H), 0.45–0.60 (m, 2H, *c*Pr-H), 0.71 (t, ^3J = 7.0 Hz, 3H, $\mathrm{OCH_2C}H_3$), 1.94 (m$_c$, 1H, *c*Pr-H), 2.93 (q, ^3J = 7.0 Hz, 2H, OCH$_2$), 3.53 (d, ^3J = 7.1 Hz, 1H, 3-H), 5.39 (d, ^3J = 7.1 Hz, 1H, 4-H), 9.51 (br. s, 1H, NH). – ^{13}C NMR (62.89 MHz, C$_6$D$_6$, plus DEPT): δ = 7.58 (–, C-*c*Pr), 14.64 (+, OCH$_2$CH$_3$), 19.39 (+, C-*c*Pr), 70.96 (–, OCH$_2$), 96.25 (+, C-3), 155.24 (+, C-4), 182.20 ($\mathrm{C_{quat}}$, C-2), 215.81, 221.86 ($\mathrm{C_{quat}}$, C=O). – MS (70 eV), *m/z* (%): 331 (17) [M$^+$], 303 (5) [M$^+$ – CO], 275 (1) [M$^+$ – 2 CO], 247 (2) [M$^+$ – 3 CO], 223 (44), 219 (31) [M$^+$ – 4 CO], 191 (100) [M$^+$ – 5 CO], 186 (66), 162 (61) [M$^+$ – 5 CO – C$_2$H$_5$], 69 (50).

Pentacarbonyl[(1E,3E)-4-ethoxy-2-phenyl-1-aza-1,3-butadiene-N]chromium [(1*E*,3*E*)-**6c**] *and Pentacarbonyl[(1Z,3E)-4-ethoxy-2-phenyl-1-aza-1,3-butadiene-N]chromium* [(1*Z*,3*E*)-**6c**]: A solution of 600 mg (1.63 mmol) of **3c** in 40 ml of tetrahydrofuran was stirred at 48–50°C for 18 h. The solvent was removed under reduced pressure. Flash chromatography (60 g of flash silica gel, 25 × 3 cm) of the crude product yielded fraction I: 258 mg (43%) of (1*E*,3*E*)-**6c**, R_f = 0.36 (pentane/diethyl ether 10:1), yellow oil. – IR (film): $\tilde{\nu}$ = 3005 cm^{-1} (NH), 2980, 2280, 2060 (C=O), 1880 (C=O), 1610 (C=N), 1425, 1335, 1210, 1090, 1015, 705, 655. – ^{1}H NMR (250 MHz, C$_6$D$_6$): δ = 1.30 (t, ^3J = 7.0 Hz, 3H, $\mathrm{OCH_2C}H_3$), 4.00 (q, ^3J = 7.0 Hz, 2H, OCH$_2$), 6.18 (d, ^3J = 12.8 Hz, 1H, 3-H), 6.80 (d, ^3J = 12.8 Hz, 1H, 4-H), 7.13–7.22 (m, 2H, Ph), 7.29–7.45 (m, 3H, Ph), 7.72 (br. s, 1H, NH). – ^{13}C NMR (62.89 MHz, C$_6$D$_6$, plus DEPT): δ = 14.03 (+, OCH$_2$CH$_3$), 66.38 (–, OCH$_2$), 105.51 (+, C-3), 127.33, 128.78, 130.11 (+, C-Ph), 139.30 ($\mathrm{C_{quat}}$, C-Ph), 164.02 (+, C-4), 183.51 ($\mathrm{C_{quat}}$, C-2), 215.57, 221.34 ($\mathrm{C_{quat}}$, C=O). – MS (70 eV), *m/z* (%): 367 (4) [M$^+$], 339 (1) [M$^+$ – CO], 311 (8) [M$^+$ – 2 CO], 283 (2) [M$^+$ – 3 CO], 255 (20) [M$^+$ – 4 CO], 227 (50) [M$^+$ – 5 CO], 198 (77) [M$^+$ – 5 CO – C$_2$H$_5$], 183 (59), 160 (57), 146 (82), 130 (100), 104 (80), 77 (62), 52 (58) [Cr$^+$].

II: 86 mg (14%) of (1*Z*,3*E*)-**6c**, R_f = 0.24, yellow oil. – IR (film): $\tilde{\nu}$ = 3290 cm^{-1} (NH), 2980, 2280, 2060 (C=O), 1905 (C=O), 1615 (C=N), 1430, 1335, 1210, 1100, 1015, 810, 705, 655. – ^{1}H NMR (250 MHz, C$_6$D$_6$): δ = 0.25 (t, ^3J = 7.0 Hz, 3H, $\mathrm{OCH_2C}H_3$), 2.98 (q, ^3J = 7.0 Hz, 2H, OCH$_2$), 4.80 (d, ^3J = 12.2 Hz, 1H, 3-H), 5.92 (d, ^3J = 12.2 Hz, 1H, 4-H), 6.81–7.92 (m, 2H, Ph), 6.98–7.13 (m, 3H, Ph), 7.59 (br. s, 1H, NH). – ^{13}C NMR (62.89 MHz, C$_6$D$_6$, plus DEPT): δ = 14.31 (+, OCH$_2$CH$_3$), 67.19 (–, OCH$_2$), 110.03 (+, C-3), 128.47, 128.83, 129.93 (+, C-Ph), 136.48 ($\mathrm{C_{quat}}$, C-Ph), 160.26 (+, C-4), 184.06 ($\mathrm{C_{quat}}$, C-2), 215.03, 221.30 ($\mathrm{C_{quat}}$, C=O).

III: 150 mg (25%) of **3c**.

Pentacarbonyl(2,5-dipropylpyridine)chromium (**11a**) *and 2,5-Dipropylpyridine* (**9a**): A solution of 110 mg (0.39 mmol) of (1*E*,3*E*)- and (1*Z*,3*E*)-**6a** and 140 mg (2.03 mmol) of 1-pentyne (**7a**) in 15 ml of hexane was stirred at 50°C for 3 d. Flash chromatography (25 g of flash silica gel, 18 × 1.5 cm) of the crude product yielded fraction I: 26 mg (24%) of (1*E*,3*E*)-, (1*Z*,3*E*)-**6a**.

II: 21 mg (21%) of **11a**, R_f = 0.19 (pentane/diethyl ether 3:1), yellow oil. – IR (film): $\tilde{\nu}$ = 2964 cm^{-1}, 2935, 2875, 2050 (C=O), 1884 (C=O), 1609, 1569, 1489, 1196, 1092, 1066, 677, 660. – ^{1}H NMR (250 MHz, C$_6$D$_6$): δ = 1.04 (t, ^3J = 7.3 Hz, 6H, $\mathrm{CH_2CH_2C}H_3$), 1.61 (tq, ^3J = 7.3, ^3J = 7.3 Hz, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 1.80 (tq, ^3J = 7.3, ^3J = 7.3 Hz, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 2.78 (t, ^3J = 7.3 Hz, 2H, $CH_2\mathrm{CH_2CH_3}$), 2.94 (t, ^3J = 7.3 Hz, 2H, $CH_2\mathrm{CH_2CH_3}$), 6.82 (dd, ^4J = 2.2, ^3J = 7.8 Hz, 1H, 4-H), 7.31 (d, ^3J = 7.8 Hz, 1H, 3-H), 10.95 (br. s, 1H, 6-H). – ^{13}C NMR (62.89 MHz, C$_6$D$_6$, plus DEPT): δ = 13.00, 13.93 (+, $\mathrm{CH_2CH_2}CH_3$), 21.42, 25.25 (–, $\mathrm{CH_2}CH_2\mathrm{CH_3}$), 34.75, 40.72 (–, $CH_2\mathrm{CH_2CH_3}$), 117.24, 128.39, 134.41 (+, C-3, -4, -6), 150.97 ($\mathrm{C_{quat}}$, C-5), 153.15 ($\mathrm{C_{quat}}$, C-2), 219.26, 223.54 ($\mathrm{C_{quat}}$, C=O). – MS (70 eV), *m/z* (%): 355 (1) [M$^+$], 327 (2) [M$^+$ – CO], 299 (2) [M$^+$ – 2 CO], 271 (1) [M$^+$ – 3 CO], 243 (8) [M$^+$ – 4 CO], 215 (84) [M$^+$ – 5 CO], 148 (42), 135 (100), 106 (64), 52 (9) [Cr$^+$].

III: 13 mg (24%) of **9a**, R_f = 0.16, colorless oil. – IR (film): $\tilde{\nu}$ = 2963 cm^{-1}, 2927, 2855, 1733, 1465, 1262, 1101, 865, 799. – ^{1}H

NMR (250 MHz, $CDCl_3$): δ = 0.92 (t, ^3J = 7.0 Hz, 3H, $CH_2CH_2CH_3$), 0.96 (t, ^3J = 7.0 Hz, 3H, $CH_2CH_2CH_3$), 1.62 (tq, ^3J = 7.0, ^3J = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 1.73 (tq, ^3J = 7.0, ^3J = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 2.53 (t, ^3J = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 2.71 (t, ^3J = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 7.02 (d, ^3J = 7.5 Hz, 1H, 3-H), 7.49 (dd, ^3J = 7.5, ^4J = 2.5 Hz, 1H, 4-H), 8.32 (d, ^4J = 2.5 Hz, 1H, 6-H). – ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 13.66, 13.85 ($CH_2CH_2CH_3$), 23.16, 24.30 ($CH_2CH_2CH_3$), 34.66, 39.79 ($CH_2CH_2CH_3$), 122.32 (C-3), 133.11 (C-5), 134.79 (C-4), 136.37 (C-6), 149.03 (C-2). – MS (70 eV), *m/z* (%): 163 (23) [M^+], 148 (31) [$M^+ - CH_3$], 135 (100) [$M^+ - C_2H_4$], 106 (49).

Fraction II was stirred at 20°C for 35 h at air atmosphere. The solvent was removed under reduced pressure. Chromatography (8 g of silica gel, 9 × 1 cm) of the crude product yielded additional 10 mg (18%) of **9a**.

5-Phenyl-2-propylpyridine (**10a**)

Variant A: A solution of 130 mg (0.39 mmol) of (1*E*,3*E*)- and (1*Z*,3*E*)-**6a** and 200 mg (1.96 mmol) of phenylethyne (**7c**) in 10 ml of tetrahydrofuran was stirred at 50°C for 4 d. The solvent was removed under reduced pressure. Chromatography (20 g of silica gel, 16 × 1.5 cm) of the crude product yielded 38 mg (49%) of **10a**, R_f = 0.33 (pentane/diethyl ether 3:1), colorless oil. – The spectroscopic data of **10a** corresponded with those reported in ref.[16].

Variant B: A solution of 231 mg (0.69 mmol) of (1*E*,3*E*)- and (1*Z*,3*E*)-**6a** and 270 mg (2.65 mmol) of phenylethyne (**7c**) in 20 ml of hexane was stirred at 50°C for 4 d. The solvent was removed under reduced pressure. Chromatography (20 g of silica gel, 16 × 1.5 cm) of the crude product yielded fraction I: 85 mg (62%) of **10a**, R_f = 0.33 (pentane/diethyl ether, 3:1).

II: 45 mg, yellow oil, R_f = 0.23. This fraction was stirred at 20°C for 14 h at air atmosphere. The solvents were removed under reduced pressure. Chromatography (8 g of silica gel, 9 × 1 cm) of the crude product yielded additional 22 mg (16%) of **10a**, R_f = 0.33 (pentane/diethyl ether, 3:1).

2-Cyclopropyl-5-phenylpyridine (**10b**)

Variant A: A solution of 97 mg (0.29 mmol) of (1*E*,3*E*)-**6b** and 200 mg (1.96 mmol) of phenylethyne (**7c**) was stirred at 50°C for 2 d. The solvent was removed under reduced pressure. Chromatography (20 g of silica gel, 16 × 1.5 cm) of the crude product yielded 34 mg (60%) of **10b**, R_f = 0.28 (pentane/diethyl ether, 4:1), colorless oil. – IR (film): ṽ = 3008 cm^{-1}, 1601, 1477, 1213, 1024, 904, 771, 751, 697. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.00–1.11 (m, 4H, *c*Pr-H), 2.08 (m_c, 1H, *c*Pr-H), 7.16 (dd, ^3J = 8.1, ^5J = 0.7 Hz, 1H, 3-H), 7.31–7.56 (m, 5H, Ph), 7.73 (dd, ^3J = 8.1, ^4J = 2.4 Hz, 1H, 4-H), 8.66 (d, ^4J = 2.4 Hz, 1H, 6-H). – ^{13}C NMR (62.89 MHz, $CDCl_3$, plus DEPT): δ = 9.90 (–, C-*c*Pr), 14.93 (+,C-*c*Pr), 121.09 (+, C-3), 126.87, 127.63, 129.00 (+, C-Ph), 133.41 (C_{quat}, C-Ph), 134.23 (+, C-4), 138.11 (C_{quat}, C-5), 147.66 (+, C-6), 161.50 (C_{quat}, C-2). – MS (70 eV), *m/z* (%): 195 (69) [M^+], 194 (100) [$M^+ - H$], 192 (28) [$M^+ - 3H$], 169 (10), 154 (5),127 (6), 115 (7), 102 (5), 77 (9), 69 (6), 51 (6).

Variant B: A solution of 330 mg (0.29 mmol) of **3b** and 459 mg (4.50 mmol) of phenylethyne (**7c**) in 20 ml of tetrahydrofuran was stirred at 50°C for 3 d. The solvent was removed under reduced pressure. Chromatography (30 g of silica gel, 27 × 1.5 cm) of the crude product yielded 55 mg (28%) of **10b**, R_f = 0.28 (pentane/diethyl ether, 4:1).

2,5-Diphenylpyridine (**10c**): A solution of 43 mg (0.12 mmol) of (1*E*,3*E*)- and (1*Z*,3*E*)-**6c** and 40 mg (0.39 mmol) of phenylethyne (**7c**) in 2 ml of tetrahydrofuran was stirred at 50°C for 4 d. The solvent was removed under reduced pressure. Chromatography (9 g of silica gel, 9 × 1 cm) of the crude product yielded 20 mg (72%) of **10c**, R_f = 0.17 (pentane/diethyl ether, 3:1), colourless oil. – The spectroscopic data of **10c** corresponded with those reported in ref.[17].

[4-(tert-Butyldimethylsilyloxy)-1-ethoxy-2-pentynylidene]pentacarbonylchromium (**12**) was prepared according to a previously published method[7] from 3.7 g (20 mmol) of 3-(*tert*-butyldimethylsilyloxy)-1-butyne and 4.4 g (20 mmol) of hexacarbonylchromium, yield 5.2 g (63%) of **12**, R_f = 0.49 (pentane), reddish black oil. – IR (film): ṽ = 2950 cm^{-1}, 2922, 2850, 2060 (C=O), 2050 (C=O), 1892 (C=O), 1622, 1539, 1460, 1361, 1249, 1200, 1192, 1105, 1075, 833, 772, 659. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.11 [s, 6H, $Si(CH_3)_2$], 0.89 [s, 9H, $SiC(CH_3)_3$], 1.51 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 1.58 (d, ^3J = 6.8 Hz, 3H, 5-H), 4.66 (q, ^3J = 7.0 Hz, 2H, OCH_2), 5.07 (q, ^3J = 6.8 Hz, 1H, 4-H). – ^{13}C NMR (62.89 MHz, $CDCl_3$, plus DEPT): δ = –5.14 (+, $SiCH_3$), –4.92 (+, $SiCH_3$), 14.93 (+, OCH_2CH_3), 18.14 [C_{quat}, $SiC(CH_3)_3$], 24.40 (+, C-5), 25.60 [+, $SiC(CH_3)_3$], 59.86 (+, C-4), 76.12 (–, OCH_2), 86.39 (C_{quat}, C-2), 138.47 (C_{quat}, C-3), 216.06, 225.43 (C_{quat}, C=O), 316.75 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 432 (6) [M^+], 376 (5) [$M^+ - 2\,CO$], 320 (8) [$M^+ - 4\,CO$], 292 (18) [$M^+ - 5\,CO$], 199 (42), 171 (24), 155 (73), 147 (58), 111 (51), 103 (50), 75 (100), 52 (17) [Cr^+].

{(2Z)-4-(tert-Butyldimethylsilyloxy)-1-ethoxy-3-[(2-pyridinylmethyl)amino]-2-pentenylidene}pentacarbonylchromium [(*Z*)-**14**]: To a solution of 800 mg (1.92 mmol) of **12** in 50 ml of diethyl ether was added 207 mg (1.92 mmol) of 2-(aminomethyl)pyridine (**13**). The solvent was removed under reduced pressure. Chromatography (100 g of silica gel, 40 × 3 cm) of the crude product yielded 1.00 g (97%) of (*Z*)-**14**, R_f = 0.24 (pentane/diethyl ether, 5:1), yellow oil, m.p. 110°C. – IR (KBr): ṽ = 3262 cm^{-1} (NH), 2960, 2937, 2860, 2024 (C=O), 1965 (C=O), 1910 (C=O), 1550, 1442, 1275, 1248, 1208, 1105, 1010, 920, 819, 756, 676. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.10 (s, 3H, $SiCH_3$), 0.20 (s, 3H, $SiCH_3$), 0.94 [s, 9H, $SiC(CH_3)_3$], 1.36 (d, ^3J = 6.8 Hz, 3H, 5-H), 1.55 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 4.51 (d, ^3J = 5.4 Hz, 2H, NCH_2), 4.70 (q, ^3J = 7.0 Hz, 2H, OCH_2), 5.29 (q, ^3J = 6.8 Hz, 1H, 4-H), 6.27 (s, 1H, 2-H), 7.22–7.35 (m, 2H, Pyr-H), 7.71–7.77 (m, 1H, Pyr-H) 8.52–8.59 (m, 1H, Pyr-H). 8.62 (br. s, 1H, NH). – ^{13}C NMR (62.89 MHz, $CDCl_3$), plus DEPT): δ = –5.23 (+, $SiCH_3$), –4.76 (+, $SiCH_3$), 15.49 (+, OCH_2CH_3), 18.04 [C_{quat}, $SiC(CH_3)_3$], 24.90 (+, C-5), 25.60 [+, $SiC(CH_3)_3$], 46.61 (–, NCH_2), 69.02 (+, C-4), 73.51 (–, OCH_2), 112.73 (+, C-2), 121.88, 122.88, 136.96, 148.81 (+, C-Pyr), 153.19, 158.88 (C_{quat}, C-Pyr, C-3), 219.27, 224.22 (C_{quat}, C=O), 289.59 (C_{quat}, C-1). – MS (70 eV), *m/z* (%): 540 (3) [M^+], 456 (3) [$M^+ - 3\,CO$], 428 (4) [$M^+ - 4\,CO$], 400 (31) [$M^+ - 5\,CO$], 356 (2), 268 (32), 189 (19), 97 (24), 75 (100).

{(1Z,3E)- and (1E,3E)-2-[1-(tert-Butyldimethylsilyloxy)ethyl]-4-ethoxy-1-[(2-pyridinylmethyl)amino]-1-aza-1,3-butadiene-N,N′}-tetracarbonylchromium [(1*Z*,3*E*)-, [(1*E*,3*E*)-**15**]: A solution of 970 mg (1.8 mmol) of (*Z*)-**14** in 40 ml of tetrahydrofuran was stirred at 65°C for 4 h. The solvent was removed under reduced pressure. Flash chromatrography (80 g of flash silica gel, 31 × 3 cm) of the crude yielded fraction I: 202 mg (22%) of (1*Z*,3*E*)-**15**, R_f = 0.19 (pentane/diethyl ether, 5:1), yellow oil. – IR (film): ṽ = 2950 cm^{-1}, 2924, 2853, 2004 (C=O), 1951 (C=O), 1830 (C=O), 1620, 1525, 1484, 1316, 1199, 1125, 1093, 960, 836, 792, 703, 642. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.01 (s, 3H, $SiCH_3$), 0.10 (s, 3H, $SiCH_3$), 0.91 [s, 9H, $SiC(CH_3)_3$], 1.40 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 1.44 [d, ^3J = 6.8 Hz, 3H, $CH(OTBDMS)CH_3$], 4.12 (m, 2H, OCH_2), 4.92 [q, ^3J = 6.8 Hz, 1H, $CH(OTBDMS)$], 5.05 (d, ^2J = 17.1 Hz, 1H, NCH), 5.16 (d, ^2J = 17.1 Hz, 1H, NCH), 6.53 (d, ^3J = 13.3 Hz, 1H, 3-H), 7.11–7.22 (m, 2H, Pyr-H), 7.56 (d, ^3J = 13.3 Hz, 1H, 4-H), 7.62–7.70 (m, 1H,

Pyr-H), 8.95 (d, $^3J = 4.8$ Hz, 1 H, Pyr-6-H). – ^{13}C NMR (62.89 MHz, $CDCl_3$, plus DEPT): $\delta = -5.18$ (+, $SiCH_3$), -5.10 (+, $SiCH_3$), 14.37 (+, $OCH_2\mathit{C}H_3$), 18.08 [C_{quat}, $Si\mathit{C}(CH_3)_3$], 22.48 [+, $CH(OTBDMS)\mathit{C}H_3$], 25.69 [+, $SiC(\mathit{C}H_3)_3$], 60.76 (–, NCH_2), 65.06 (–, OCH_2), 67.56 [+, $\mathit{C}H(OTBDMS)$], 109.54 (+, C-3), 120.17, 122.72, 136.69, 152.54, 157.74 (+, C-Pyr, C-4), 160.25 (C_{quat}, C-Pyr), 177.12 (C_{quat}, C-2), 215.69, 216.00, 227.84, 229.24 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 512 (4) [M^+], 428 (2)]$M^+ - 3$ CO], 400 (3) [$M^+ - 4$ CO], 291 (6), 224 (9), 189 (100), 145 (7), 92 (24), 75 (46), 57 (11). – $C_{23}H_{32}CrN_2O_6Si$ (512.6): calcd. C 53.89, H 6.29, N 5.47; found C 54.10, H 6.34, N 5.57.

II: 565 mg (61%) of (1*E*,3*E*)-**15**, $R_f = 0.09$ (pentane/diethyl ether, 5:1), yellow oil. – IR (film): $\tilde{\nu} = 2955$ cm^{-1}, 2930, 2886, 2005 (C=O), 1856 (C=O), 1799 (C=O), 1630, 1447, 1309, 1202, 1124, 1032, 963, 838, 779, 650, 566, 446. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.08$ (s, 3 H, $SiCH_3$), 0.21 (s, 3 H, $SiCH_3$), 0.90 [s, 9 H, $SiC(CH_3)_3$], 1.39 (t, $^3J = 7.0$ Hz, 3 H, $OCH_2C\mathit{H}_3$), 1.57 [d, $^3J = 6.8$ Hz, 3 H, $CH(OTBDMS)C\mathit{H}_3$], 4.01 (q, $^3J = 7.0$ Hz, 2 H, OCH_2), 4.66 (d, $^2J = 17.2$ Hz, 1 H, NCH), 4.90 (d, $^2J = 17.1$ Hz, 1 H, NCH), 5.40 [q, $^3J = 6.8$ Hz, 1 H, $C\mathit{H}(OTBDMS)$], 5.70 (d, $^3J = 13.2$ Hz, 1 H, 3-H), 7.12–7.22 (m, 2 H, Pyr-H), 7.61–7.72 (m, 1 H, Pyr-H), 8.00 (d, $^3J = 13.2$ Hz, 1 H, 4-H), 8.98 (d, $^3J = 4.8$ Hz, 1 H, Pyr-6-H). – ^{13}C NMR (62.89 MHz, $CDCl_3$, plus DEPT): $\delta = -5.00$ [+, $Si(CH_3)_2$], 14.75 (+, $OCH_2\mathit{C}H_3$), 17.73 [C_{quat}, $Si\mathit{C}(CH_3)_3$], 24.29 [+, $CH(OTBDMS)\mathit{C}H_3$], 25.62 [+, $SiC(\mathit{C}H_3)_3$], 61.16 (–, NCH_2), 67.62 (–, OCH_2), 77.64 [+, $\mathit{C}H(OTBDMS)$], 97.79 (+, C-3), 120.28, 122.68, 136.84, 152.00, 159.47, (+, C-Pyr, C-4), 160.98 (C_{quat}, C-Pyr), 178.95 (C_{quat}, C-2), 215.01, 215.39, 225.89, 229.27 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 456 (1) [$M^+ - 2$ CO], 400 (1) [$M^+ - 4$ CO], 291 (10), 224 (11), 189 (100), 145 (7), 92 (58), 75 (79).

Crystallographic Details of (1*E*,3*Z*)-**6b**[18]: Formula $C_{13}H_{13}CrNO_6$, molecular mass 331.24, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 848.4(1)$, $b = 984.4(1)$, $c = 1064.8(2)$ pm, $\alpha = 117.50(1)$, $\beta = 101.25(1)$, $\gamma = 94.03(1)^\circ$, $V = 0.7604(2)$ nm^3, $\varrho_{calcd.} = 1.447$ Mg m^{-3}, $\mu(Mo\text{-}K_\alpha) = 0.776$ mm^{-1}, crystal dimensions 0.4 × 0.5 × 0.5 mm, 2944 reflections (2653 unique) were measured with a Stoe-Siemens four-circle diffractometer with graphite-monochromated Mo-K_α-radiation ($\lambda = 71.073$ pm) at $-120\,^\circ$C, 2Θ-range: $8-50^\circ$. The structure was solved by direct methods (SHELXS-90[19]) and refined on F^2 by full-matrix least-squares techniques (SHELXL-92[20]). All non-hydrogen atoms were refined anisotropically, the hydrogen atoms were included in calculated positions and refined by using a riding model, except for hydrogen atom H1 whose coordinates were refined freely. *R* values: $R1 = \Sigma|F_o\text{-}F_c|/\Sigma F_o$, $wR2 = [\Sigma w(F_o^2 - F_o^2)^2/\Sigma w(F_o^2)^2]^{0.5}$. $R1 = 0.0243$ [for $F > 4\sigma(F)$], $wR2 = 0.0628$ (for all data) with 206 parameters and 2 restraints, $w = 1/[\sigma^2(F_o^2) + (0.0268P)^2 + 0.3934P]$, $P = (F_o^2 + 2\,F_c^2)/3$. Largest difference peak 0.240 e$^-$ nm^{-3} · 10^3, largest difference hole -0.224 e$^-$ nm^{-3} · 10^3.

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[18] Further details of the crystal structure analysis may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, by quoting the depository number CSD-57666, the names of the authors, and the publication.

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