The Chemistry of Metallacyclic Alkenylcarbene Complexes, 8[◇]

Chelated Allyl–Ironcarbene Complexes with a Centrally Tethered π-Ligand – Synthesis and Reactions with Nucleophiles

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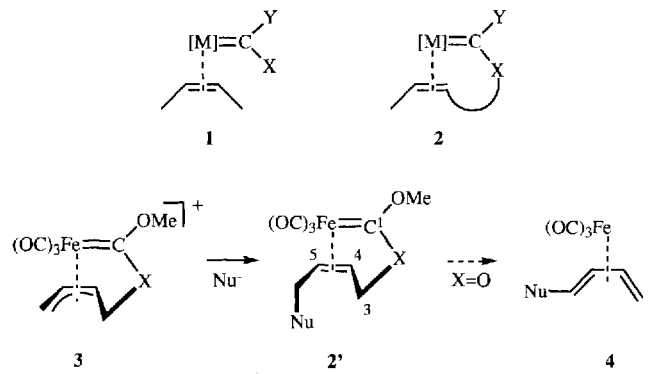
The title complexes **8** and **9** are easily prepared in two or three steps from iron carbonyls and isobutene diol **5** by Meerwein alkylation of the intermediate acyl complexes **6** and **7**. With carbon and heteroatom nucleophiles like enolates and triphenylphosphane they form either stable 4-substituted alkene–carbene complexes **10** and **11**, or substituted trimethylenemethane tricarbonyliron complexes like **12**. Oxidation with H_2O_2/NaOH both of the alkene–carbene complexes **11** and of the less stable β-oxo-substituted trimethylene–methane complexes **13**, as obtained from reaction of **8** with lithium enolates, yields the corresponding substituted allyl carbamates **15** or the allyl alcohols **14**, which are formally bis- and monosubstituted derivatives, respectively, of the starting isobutene diol.

Alkene–carbene complexes **1** are pivotal intermediates in important olefin reactions like cyclopropanation[1], metathesis[2], and Ziegler-Natta-type polymerizations[3]. By tethering the η^2-alkene ligand to the carbene carbon atom with a spacer of suitable length as in **2**, stabilizing or activating geometry and entropy constraints can be imposed on such reactions, which has been exploited in the elucidation of their mechanisms[4] and in tuning the reactivity of complexes **2** by altering their ring size "on the fly"[5]. In contrast to **1**, complexes **2** are also inherently chiral and can give rise to diastereoselective formation of new stereocentres[6] in the course of respective C–C bond formation processes. Finally, chelating allows concerted cascade or rearrangement reactions of alkene and carbene moieties to take place with the inclusion and participation of an aptly chosen spacer[6,7]. We prepared various alkene–ironcarbene complexes of type **2** on different routes[7,8] to find the reaction of allyl–carbene complexes **3**[8,9] with certain carbon and heteroatom nucleophiles most effective. Lithium enolates, potassium enoxyborates, cuprates, phosphanes, and primary amines attack on the allyl terminus of **3** to give 5-substituted alkene–carbene complexes **2'** which either are sufficiently stable to be isolated (for X = NR), or else undergo a consecutive Claisen-type rearrangement reaction to the diene complexes **4** (for X = O)[10]. Complexes **3** can be readily prepared in two steps from iron carbonyls and vinyloxiranes or 1,4-butenediols (for X = O), or the aza analogues thereof (for X = NR) via Meerwein alkylation of the intermediate ferralactones or -lactams[11,12], respectively.

Scheme 1



With the aim of opening access to 4-substituted alkene–carbene complexes by a similar route, we now prepared the hitherto unknown[13] carbene complexes **8** and **9** and investigated their reactivity towards different nucleophiles. Ley et al. described the synthesis of suitable starting lactone[14] and lactam[12,15] complexes **6** and **7** with a centrally tethered allyl ligand from iron carbonyls and either isobutene diol **5** or unsaturated carbamates. **6** and **7** were now found to yield the corresponding carbene complexes upon treatment with Meerwein salts. In most cases, the required ferralactam complexes **7** are best prepared by aminolysis of the respective ferralacton **6**. Complexes **8** and **9** are normally fairly air-stable, yellow crystalline compounds which can be made in 10-g batches and stored under nitrogen in a freezer for several months. They are formed as isomeric mixtures (90:10 in the case of **8**; ranging from 85:10 to 57:43, de-

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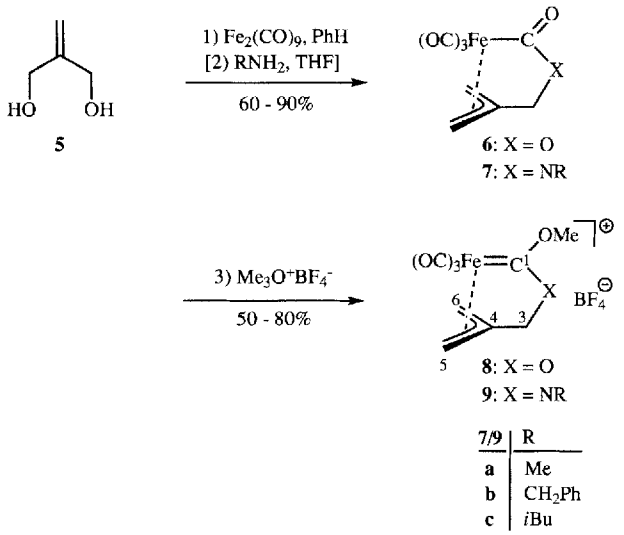
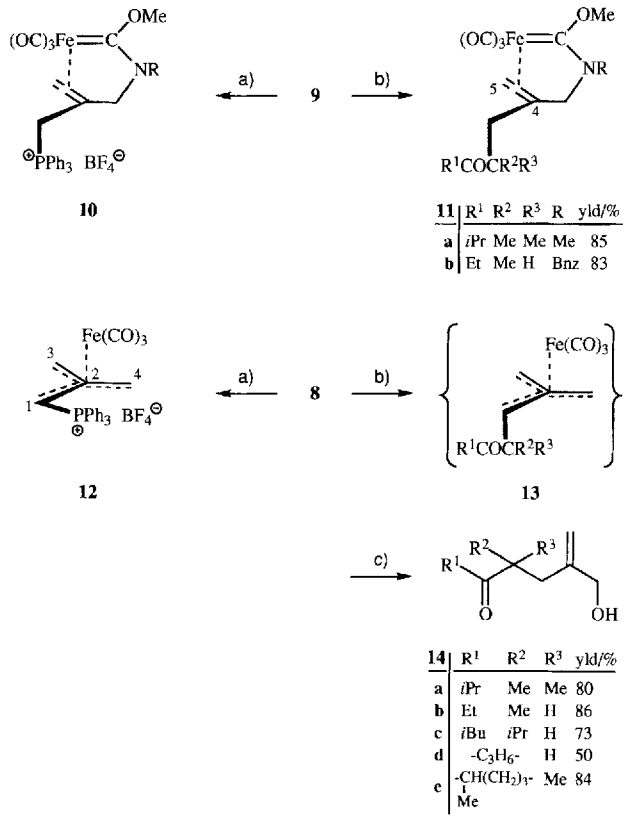
pending on R, in the case of **9**). This isomerism must arise from (*Z*) and (*E*) configurations of the C1–OMe bond as these complexes lack chirality. The occurrence of isomers is somewhat surprising and was never observed for the analogous allyl–carbene complexes **3** which form exclusively either the (*E*) isomer (X = O) or the (*Z*) isomer (X = NR). When solutions of **8** or **9** are heated, the isomeric ratio gradually shifts towards an equilibrium value of 1:1, a behaviour which has not been observed for the linearly tethered complexes **3**, either. This shift is reversible, though. Upon standing at room temperature for a spell, the NMR solutions show the initial ratios of isomers, again.

Scheme 2



Resembling the chemistry of **3**, both types of allyl–carbene complexes **8** and **9** readily react with carbon nucleophiles like lithium enolates (at −78°C in THF) or heteroatom nucleophiles like phosphanes (at room temperature in acetonitrile). In the case of the aminooxocarbene complexes **9**, isolable 4-substituted alkene–carbene complexes **10** and **11** result, according to plan, as products of a nucleophilic attack on a terminal allylic carbon atom (C-5/6). They are exclusively formed with one configuration of the C1–OMe bond – even for residues R as little as methyl (**11a**) – which we think is the (*Z*) one in each case, according to a comparison of their NMR data with those of the 5-substituted analogues **2′** (X = NR), for which X-ray analytical data were obtained earlier[6]. Complex **11b** is formed as a nearly 1:1 isomeric mixture due not to (*E*/*Z*) isomerism of the C–O bond but to a newly generated stereocentre (C2′) next to the keto function. This can be clearly seen from the fact, that the shift differences of the ^{1}H- and ^{13}C-NMR signals of given atoms in both isomers are markedly dependent on these atoms' distances from the new asymmetric carbon atom. For the remote methyl group in the methoxy residue these differences are merely marginal (^{13}C NMR of **11b**: δ = 62.25/62.49), and quite so for the carbene carbon atom C1 itself (δ = 242.53/243.07). The opposite was to be anticipated for (*E*/*Z*) isomers. For comparison, the ^{13}C-NMR shift differences for the OCH_3 groups and the carbene carbon atoms of the (*E*/*Z*) isomers of the starting allyl–carbene complex **9b** are much larger (δ = 63.83/65.04 for the OCH_3 groups and δ = 221.03/227.26 for the atoms C1). The ^{31}C-NMR spectrum of **11b** is depicted in Figure 1. Complex **10a** (R = CH_3) offers an additional means of unambiguously assigning the ^{1}H- and ^{13}C-NMR signals of the skeleton atoms in 4-substituted alkene–carbene complexes of the general types **10** and **11**, as the P/C and P/H coupling constants drastically differ for the three CH_2 groups present in this compound.

Scheme 3. a) 1 equiv. PPh_3, CH_3CN, room temp., 16 h; b) $R^1COCHR^2R^3$/LICA, −78°C, 2 h; c) 6 equiv. H_2O_2/NaOH, CH_3OH, 0°C, 2 h



The dioxocarbene complex **8** on the other hand, reacts with triphenylphosphane – just like its linearly tethered analogue **3** (X = O) – with concomitant loss of carbon monoxide and methanol to give the substituted trimethylenemethane complex **12**. Examples of well-defined monosubstituted tricarbonyliron trimethylenemethane complexes are still rather scarce in literature both in terms of structural investigations[16] and of synthetical applications[17]. Figure 2 shows the molecular structure of the cation of complex **12** which demonstrates the influence of a bulky, formally positively charged residue like triphenylphosphane on the geometry of the trimethylenemethane triangle.

In comparison to the structure of the phenylsubstituted analogue described by Churchill et al.[16] – there are somewhat greater differences in the three bond lengths (C1–C2 1.440, C2–C3 1.446, C2–C4 1.390 Å) and angles

Figure 1. ^{13}C-NMR spectrum of **11b** (100.5 MHz, C_6D_6, TMS_{int})

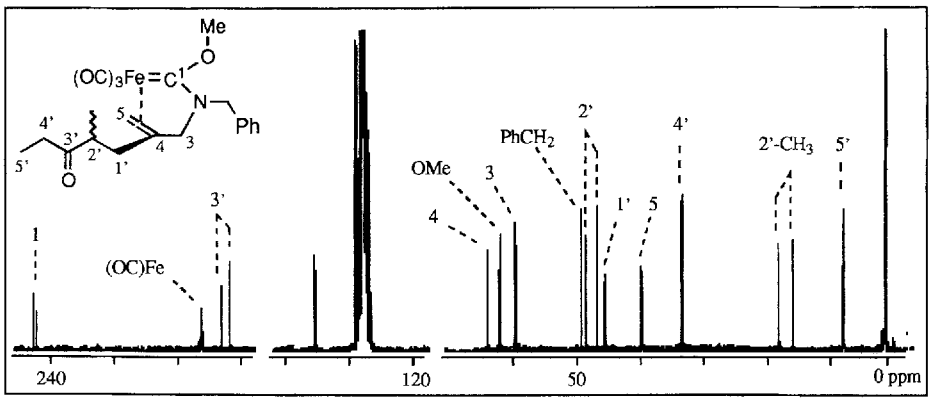
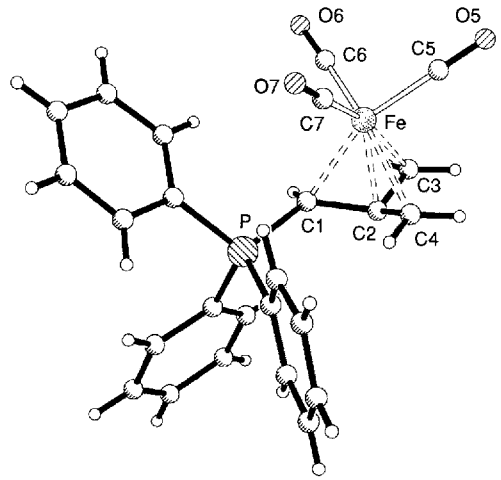


Figure 2. Molecular structure of the cation of **12**[a]

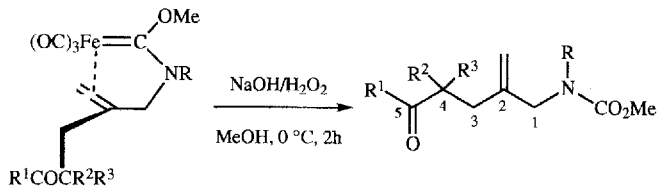


[a] Selected bond lengths [Å] and angles [°]: Fe–C1 2.095(11), Fe–C2 1.937(11), Fe–C3 2.135(11), Fe–C4 2.134(13), C1–C2 1.440(14), C2–C3 1.446(13), C2–C4 1.39(2), C1–P 1.793(11); C1–C2–C3 111.4(11), C1–C2–C4 118.3(10), C3–C2–C4 114.6(11), C1–Fe–C4 70.1(5), C1–Fe–C3 68.6(4), C3–Fe–C4 67.9(4).

(C1–C2–C3 111.4, C1–C2–C4 118.3, C3–C2–C4 114.6°), whereas the "out-of-plane" bending of the central carbon atom C2 away from the iron centre is quite similar in both complexes (ca. 0.30 Å). The structural data for **12** should not be overrated, though, as the standard deviations are rather high. So the assumption that C4, which lies *cisoid* or *syn* to the PPh_3 group is pushed away by the latter towards C3, making C4 less effectively bound to the central metal, is only a speculative one. Whether the bond between C2 and C4 is indeed the shortest, most "olefinic" one within the trimethylenemethane triangle must be shown by independent experiments.

With carbon nucleophiles like lithium enolates, complex **8** reacts to give rather unstable intermediates which we have not been able to isolate and characterize so far and only tentatively ascribe the structure **13**. When immediately treated with H_2O_2/NaOH, these intermediates are oxidized to leave the corresponding allylic alcohols **14** in good yields. As the starting complex **8** itself derives from isobutene diol **5**, this sequence makes for a convenient 3-step procedure for the monosubstitution of one hydroxy group of **5** by a β-oxoalkyl residue. By a similar protocol, the alkene–aminooxocarbene complexes **11** can be oxidatively demetalated to give the corresponding allylic carbamates **15** in good to excellent yields. So in four steps both hydroxy groups of the starting isobutene diol can be substituted, the first one by a heteronucleophilic amine, the second one by a C-nucleophilic lithium enolate to give carbamates with the possibility of introducing various residues at virtually each position of the β-methylene-ε-oxo-substituted carbamate skeleton. It is worthy of note, although not depicted in Scheme 4, that the analogous alkene–aminooxocarbene complexes of type **2'**, featuring a 5-substituted olefin ligand and stemming from the linear 2-butene-1,4-diol undergo quite the same reaction to give the corresponding "linear" allyl carbamates.

Scheme 4



15	R^1	R^2	R^3	R	yld/%
a	*i*Pr	Me	Me	Me	75
b	Et	Me	H	Bnz	92

In summary, a versatile synthesis of chelated allyl–iron-carbene complexes featuring a centrally tethered allyl ligand starting from isobutene diol has been found. The complexes react with heteronucleophiles like phosphanes and carbon nucleophiles like lithium enolates to give either stable alkene–carbene complexes (for X = NR) bearing an additional substituent at the olefinic carbon atom which is already bound to the tether, or in the case of the dioxocarbene complex **8** give the monosubstituted trimethylenemethane tricarbonyliron derivatives. By oxidative demetalation of the chelated alkene–carbene or of the less stable trimethylenemethane complexes, respectively, with NaOH/H_2O_2, highly substituted allyl alcohols **14** or allyl carbam-

ates **15**, which are formally mono- and disubstituted derivatives of the starting diol **5**, are accessible in good yields. Further investigations into the chemistry of differently substituted alkene–carbene complexes are currently underway.

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Experimental Section

All operations were carried out under Ar by using Schlenk equipment. The starting complex **6**[14] was prepared as published. – Melting points are not corrected. – NMR: Jeol JNMX GX-400. – IR: Bruker IFS 48, Beckmann Acculab A1, A3. – MS: Varian MAT CH-4B (EFO-4B-source), Varian MAT 311A (EI/FD source). – MA: Heraeus Mikromat C–H–N. – Isomeric ratios are determined from the relative intensities of the pertaining ^{1}H-NMR signals.

1. *[(4–6-η^3)-1-Methoxy-2-oxa-5-isohexen-6-yl-1-ylidene]tricarbonyliron(II) Tetrafluoroborate* (**8**): Trimethyloxonium tetrafluoroborate (1.63 g; 11.0 mmol) was added to a solution of **6** (2.38 g; 10.0 mmol) in dichloromethane (30 ml) at room temperature. After stirring the mixture for 16 h, any volatile components were evaporated in vacuo. The residue thus obtained was subsequently purified by CC (silica gel; CH_3CN/CH_2Cl_2, 1:1; R_f = 0.54); yield 2.72 g (8.0 mmol; 80%) as a 89:11 mixture of isomers; yellow crystalls, m.p. 129°C (decomp.). – IR (KBr): $\tilde{\nu}$ = 2970 cm^{-1}, 2120, 2050, 2040 (CO), 1430, 1350, 1320, 1265, 1090, 810. – Major isomer (89%): ^{1}H NMR (CD_3CN, 400 MHz): δ = 3.12 (s, 2H, 5-H^{en}, 6-H^{en}), 3.97 (s, 3H, OCH_3), 4.42 (s, 2H, 5-H^{ex}, 6-H^{ex}), 4.99 (s, 2H, 3-H). – ^{13}C NMR (CD_3CN, 100.5 MHz): δ = 59.16 (C-5, C-6), 62.76 (OCH_3), 77.90 (C-3), 121.76 (C-4), 200.69 and 205.07 [Fe(CO)], 245.31 (C-1). – Minor isomer (11%): ^{1}H NMR (CD_3CN, 400 MHz): δ = 2.80 (s, 2H, 5-H^{en}, 6-H^{en}), 3.73 (s, 3H, OCH_3), 4.76 (s, 2H, 5-H^{ex}, 6-H^{ex}), 4.78 (s, 2H, 3-H). – ^{13}C NMR (CD_3CN, 100.5 MHz): δ = 54.43 (C-5, C-6), 61.53 (OCH_3), 79.36 (C-3), 121.76 (C-4), 205.07 and 209.53 [Fe(CO)], 251.67 (C-1). – MS (70 eV); *m/z* (%): 253 (1) [M$^+$, cation], 225 (5) [M$^+$ – CO], 197 (2) [M$^+$ – 2 CO], 194 (5) [(225) – OCH_3], 169 (45) [M$^+$ – 3 CO], 84 (19) [Fe(CO)$^+$], 56 (38) [Fe$^+$], 28 (100) [CO$^+$]. – $C_9H_9BF_4FeO_5$ (339.8): calcd. C 31.81, H 2.66; found C 31.69, H 2.71.

2. *Synthesis of* **9**. – *General Procedure (A)*: The respective primary amine (11.0 mmol) was added to a solution of **6** (2.38 g; 10.0 mmol) in THF (40 ml) at ambient temperature. The resulting mixture was stirred until the starting materials were completely consumed (monitored by tlc; typically 2–5 h). The solvent was then evaporated and the residue purified by CC (silica gel; diethyl ether/petroleum ether, 1:1). The complexes **7** thus obtained were redissolved in dichloromethane (50 ml) at room temperature and treated with trimethyloxonium tetrafluoroborate (1.48 g; 10.0 mmol). After stirring this mixture for 16 h, any volatile components were evaporated in vacuo and the residue then purified by CC (silica gel; CH_3CN/CH_2Cl_2, 1:1).

[(4–6-η^3)-1-Methoxy-2-methyl-2-aza-4-isohexen-6-yl-1-ylidene]tricarbonyliron(II) Tetrafluoroborate (**9a**): 2.12 g (6.0 mmol; 75%) from crude **7a** (2.00 g; 8.0 mmol) as a 85:15 mixture of isomers; yellow crystals of m.p. 121°C (decomp.). – IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}, 2940, 2070, 2000, 1940 (CO), 1480, 1450, 1250, 1080, 1040. – Major isomer (85%): ^{1}H NMR (CD_3CN, 400 MHz): δ = 2.82 (s, 3H, NCH_3), 3.02 (s, 2H, 5-H^{en}, 6-H^{en}), 4.01 (s, 2H, 3-H), 4.17 (s, 3H, OCH_3), 4.32 (s, 2H, 5-H^{ex}, 6-H^{ex}). – ^{13}C NMR (CD_3CN, 100.5 MHz): δ = 35.97 (NCH_3), 56.87 (C-3), 59.12 (C-5, C-6), 64.61 (OCH_3), 117.28 (C-4), 202.62 and 207.55 [Fe(CO)], 218.96 (C-1). – Minor isomer (15%): ^{1}H NMR (CD_3CN, 400 MHz): δ = 2.60 (s, 3H, NCH_3), 2.67 (s, 2H, 5-H^{en}, 6-H^{en}), 3.86 (s, 2H, 3-H), 4.13 (s, 3H, OCH_3), 4.67 (s, 2H, 5-H^{ex}, 6-H^{ex}). – ^{13}C NMR (CD_3CN, 100.5 MHz): δ = 35.00 (NCH_3), 63.50 (C-3), 65.34 (C-5, C-6), 67.23 (OCH_3), 118.52 (C-4), 210.07 and 213.27 [Fe(CO)], 225.39 (C-1). – MS (70 eV); *m/z* (%): 265 (14) [M$^+$, cation], 237 (12) [M$^+$ – CO], 209 (22) [M$^+$ – 2 CO], 181 (45) [M$^+$ – 3 CO], 128 (27), 79 (26), 28 (100) [CO$^+$]. – $C_{10}H_{12}BF_4FeNO_4$ (352.8): calcd. C 34.04, H 3.43, N 3.97; found C 33.86, H 3.51, N 4.01.

[(4–6-η^3)-2-Benzyl-1-methoxy-2-aza-4-isohexen-6-yl-1-ylidene]tricarbonyliron(II) Tetrafluoroborate (**9b**): 2.83 g (6.6 mmol; 72%) from crude **7b** (3.00 g; 9.1 mmol) as a 57:43 mixture of isomers; ropy yellow oil. – IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1}, 3010, 2945, 2090, 2020, 1980 (CO), 1470, 1445, 1250, 1050. – Major isomer (57%): ^{1}H NMR (CD_3CN, 400 MHz): δ = 3.03 (s, 2H, 5-H^{en}, 6-H^{en}), 3.97 (s, 2H, 3-H), 4.25 (s, 3H, OCH_3), 4.27 (s, 2H, CH_2Ph), 4.49 (s, 2H, 5-H^{ex}, 6-H^{ex}), 7.17–7.41 (m, 5H, H^{ar}). – ^{13}C NMR (CD_3CN, 100.5 MHz): δ = 53.00 (*C*H_2Ph), 55.14 (C-3), 59.18 (C-5, C-6), 65.04 (OCH_3), 116.77 (C-4), 129.35 and 130.02 (CH^{ar}), 134.68 (C^{ipso}), 202.71 and 207.28 [Fe(CO)], 221.03 (C-1). – Minor isomer (43%): ^{1}H NMR (CD_3CN, 400 MHz): δ = 2.69 (s, 2H, 5-H^{en}, 6-H^{en}), 3.84 (s, 2H, 3-H), 4.19 (s, 3H, OCH_3), 4.26 (s, 2H, CH_2Ph), 4.63 (s, 2H, 5-H^{ex}, 6-H^{ex}), 7.03–7.41 (m, 5H, H^{ar}). – ^{13}C NMR (CD_3CN, 100.5 MHz): δ = 53.21 (*C*H_2Ph), 57.34 (C-3), 63.83 (OCH_3), 65.42 (C-5, C-6), 117.45 (C-4), 129.02 and 134.68 (CH^{ar}), 135.35 (C^{ipso}), 207.28 and 212.96 [Fe(CO)], 227.26 (C-1). – MS (70 eV); *m/z* (%): 342 (6) [M$^+$, cation], 314 (24) [M$^+$ – CO], 286 (58) [M$^+$ – 3 CO], 91 (100) [$C_6H_5^+$], 28 (87) [CO$^+$]. – $C_{16}H_{16}BF_4FeNO_4$ (429.0): calcd. C 44.80, H 3.76, N 3.27; found C 44.86, H 3.83, N 3.32.

[(4–6-η^3)-2-Isobutyl-1-methoxy-2-aza-4-isohexen-6-yl-1-ylidene]tricarbonyliron(II) Tetrafluoroborate (**9c**): 1.56 g (4.0 mmol; 50%) from crude **7b** (2.30 g; 7.9 mmol) as a 57:43 mixture of isomers; bright yellow crystals of m.p. 126°C. – IR (KBr): $\tilde{\nu}$ = 3030 cm^{-1}, 2975, 2080, 2010, 1970 (CO), 1460, 1445, 1200, 1090. – Major isomer (57%): ^{1}H NMR (CD_3CN, 400 MHz): δ = 0.81 [d, ^3J (CH_3/CH) = 6.70 Hz, 6H, C-CH_3], 1.94 [d sept, ^3J (CH/CH_3) = 6.7, ^3J (Me_2CH/CH_2) = 7.93 Hz, 1H, Me_2CH], 3.05 (s, 2H, 5/6-H^{en}), 3.14 [d, ^3J (CH_2/CH) = 7.93 Hz, 2H, CH_2CMe], 4.06 (s, 2H, 3-H), 4.18 (s, 3H, OCH_3), 4.33 (s, 2H, 5/6-H^{ex}). – ^{13}C NMR (CD_3CN, 100.5 MHz): δ = 20.06 (CH_3), 27.01 (*C*Me_2), 55.93 (C-3), 56.61 (C-5/6), 64.67 (OCH_3), 116.86 (C-4), 202.38 and 207.42 (C=O), 220.27 (C-1). – Minor isomer (43%): ^{1}H NMR (CD_3CN, 400 MHz): δ = 0.72 [d, ^3J (CH_3/CH) = 6.70 Hz, 6H, C-CH_3], 1.80 [d sept, ^3J (CH/CH_3) = 6.7, ^3J (Me_2CH/CH_2) = 7.93 Hz, 1H, Me_2CH], 2.69 (s, 2H, 5/6-H^{en}), 2.91 [d, ^3J (CH_2/CH) = 7.93 Hz, 2H, CH_2CMe$_2$], 3.91 (s, 2H, 3-H), 4.14 (s, 3H, OCH_3), 4.68 (s, 2H, 5/6-H^{ex}). – ^{13}C NMR (CD_3CN, 100.5 MHz): δ = 19.89 (CH_3), 26.92 (*C*Me_2), 55.87 (C-3), 58.04 (C-5/6), 63.43 (OCH_3), 117.54 (C-4), 207.42 and 213.12 (C=O), 231.27 (C-1). – MS (70 eV); *m/z* (%): 308 (2) [M$^+$, cation], 280 (3) [M$^+$ – CO], 252 (5) [M$^+$ – 3 CO], 28 (100) [CO$^+$]. – $C_{13}H_{18}BF_4FeNO_4$ (395.0): calcd. C 39.53, H 4.59, N 3.54; found C 39.42, H 5.00, N 3.45.

3. *[(4–5-η^2)-1-Methoxy-2-methyl-4-triphenylphosphoniomethylene-2-aza-4-penten-1-ylidene]tricarbonyliron(0) Tetrafluoroborate* (**10a**): A solution of carbene complex **9a** (3.52 g; 10.0 mmol) in CH_3CN (50 ml) was treated with triphenylphosphane (2.62 g; 10.0 mmol) at room temperature and then stirred for 16 h. All volatile components were removed in vacuo and the residue thus obtained was purified by CC over silica gel. Pure **10a** could be eluted with CH_3CN/CH_2Cl_2 (1:1, R_f = 0.88), giving bright yellow needles

upon evaporation of the eluate; m.p. 146°C (decomp.); yield 5.41 g (8.8 mmol; 88%). – IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2940, 2000, 1930, 1910 (CO), 1425, 1390, 1270, 1180, 1050. – ^1H NMR (CD_3CN, 400 MHz): δ = 1.61 and 1.78 (s each, 2H, 5-H), 2.58 (s, 3H, NCH_3), 3.11 [d, ^2J (3-H/3-H′) = 12.64 Hz, 1H, 3-H], 3.49 [dd, ^2J (1′-H/1′-H′) = 14.50, ^4J (P/1′-H) = 14.29 Hz, 1H, 1′-H], 3.62 [d, ^2J (3-H/3-H′) = 12.64 Hz, 1H, 3-H′], 4.09 (s, 3H, OCH_3), 4.67 [dd, ^2J (1′-H/1′-H′) = 14.50, ^3J (P/1′-H′) = 8.24 Hz, 1H, 1′-H′], 7.71–7.91 (m, 15H, H^{ar}). – ^{13}C NMR (CD_3CN, 100.5 MHz): δ = 33.87 (NCH_3), 38.27 [^1J (P/C-1′) = 30.05 Hz, C-1′], 39.48 (C-5), 52.95 [^2J (P/C-4) = 10.7 Hz, C-4], 63.19 (C-3), 63.79 (OCH_3), 119.58 [^1J = (P/C^{ipso}) = 82.4 Hz, C^{ipso}], 131.25 [^2J (P/C^{ortho}) = 12.2 Hz, C^{ortho}], 135.05 [^3J (P/C^{meta}) = 9.2 Hz, C^{meta}], 136.16 [^4J (P/C^{para}) = 3 Hz, C^{para}], 214.70 [Fe(CO)], 238.67 (C-1). – ^{31}P NMR [CD_3CN, 162 MHz, H_3PO_4 (external)]: δ = 18.68. – MS (70 eV); *m/z* (%): 445 (9), 262 (100) [PPh_3^+], 181 (98), 126 (38), 108 (67), 28 (94). – $C_{28}H_{27}BF_4FeNO_4P$ (615.2): calcd. C 54.67, H 4.42; found C 54.89, H 4.67.

4. *Synthesis of Alkene–Carbene Complexes* **11**. – *General Procedure* (B): First, solutions of the required lithium enolates in THF were prepared by treating a solution of isopropylcyclohexylamine (LICA; 164 µl; 1.1 mmol) in THF (5 ml) with a 2.5 M solution of *n*BuLi in hexane (0.44 ml; 1.1 mmol) at 0°C. The mixture was stirred for 30 min, then chilled to −78°C and subsequently treated with the carbonyl compound (1.1 mmol). After stirring at −78°C for 60 min, the resulting enolate solution was transferred via a cannula into a slurry of the respective carbene complex **9** (1.0 mmol) in THF (5 ml) kept at −78°C as well. The entire mixture was stirred for a further 2 h at −78°C, then allowed to warm up to room temperature and all volatile components were finally removed in vacuo. The resulting residue was repeatedly extracted with diethyl ether (3 × 10 ml), the combined extracts were concentrated on an oil pump and then purified by CC (silica gel; diethyl ether/petrol ether 1:2).

Tricarbonyl[4–5-η²)-1-methoxy-2-methyl-4-(2′,2′,4′-trimethyl-3′-oxopentyl)-2-aza-pent-4-en-1-ylidene]iron(0) (**11a**): 292 mg (0.85 mmol; 85%) from 352 mg of **9a** and 125 mg of diisopropyl ketone; yellow oil, R_f = 0.60 (diethyl ether/petroleum ether, 1:2). – IR (KBr): $\tilde{\nu}$ = 3040, 2960, 2920, 2860 (C–H), 2000, 1940, 1910, 1690 (CO), 1545, 1460, 1230. – ^1H NMR (C_6D_6, 400 MHz): δ = 0.95 [d, ^3J (CH_3/4′-H) = 6.60 Hz, 3H, 5′-H], 0.96 (s, 3H, 2′-CH_3), 0.99 [d, ^3J(CH_3/4′-H) = 6.60 Hz, 3H, 4′-CH_3], 1.12 (s, 3H, 2′-CH_3), 1.74 (s, 1H, 5-H), 1.83 [d, ^2J(1′-H/1′-H′) = 14.30 Hz, 1H, 1′-H], 1.96 (s, 3H, NCH_3), 2.19 [s, 1H, 5-H′], 2.75 [qq, ^3J(4′-H/CH_3) = 6.60 Hz, 1H, 4′-H], 3.15 [d, ^2J(1′-H/1′-H′) = 14.30 Hz, 1H, 1′-H′], 3.21 [d, ^2J(3-H/3-H′) = 12.65 Hz, 1H, 3-H], 3.41 [d, ^2J(3-H/3-H′) = 12.65 Hz, 1H, 3-H′], 3.71 (s, 3H, OCH_3). – ^{13}C NMR (C_6D_6, 100.5 MHz): δ = 20.62 and 20.66 (C-5′, 4′-C), 23.74 and 26.78 (2′-C), 32.63 (NCH_3), 34.49 (C-4′), 42.44 (C-1′), 50.28 (C-2′), 52.63 (C-5), 62.39 (OCH_3), 62.85 (C-3), 63.31 (C-4), 216.84 [Fe(CO)], 218.26 (C-3′), 241.14 (C-1). – MS (70 eV); *m/z* (%): 351 (8) [M^+ – CO], 323 (22) [M^+ – 2 CO], 295 (90) [M^+ – 3 CO], 183 (100), 95 (68). – $C_{17}H_{25}FeNO_5$ (379.2): calcd. C 53.84, H 6.65, N 3.39; found C 54.01, H 6.73, N 3.55.

Tricarbonyl[(4–5-η²)-2-benzyl-1-methoxy-4-(2′-methyl-3′-oxopentyl)-2-azapent-4-en-1-ylidene]iron(0) (**11b**): 352 mg (0.83 mmol; 83%) as a 52:48 diastereoisomeric mixture from 283 mg of **9b** and 95 mg of diethyl ketone; yellow oil, R_f = 0.67/0.76 (diethyl ether/petroleum ether, 1:2). – IR (KBr): $\tilde{\nu}$ = 3060, 3030, 2990, 2860 (C–H), 1990, 1950, 1900, 1690 (CO), 1530, 1460, 1240. – ^1H NMR (C_6D_6, 400 MHz): δ = 0.82–1.00 (m, 6H, 5′-H, 2′-CH_3), 1.67/1.76 (s, 1H, 5-H), 1.93–2.13 (m, 3H, 4′-H, 1′-H), 2.02/2.09 (s, 1H, 5-H′), 2.45–2.58/2.81–2.87 (m, 1H, 2′-H), 3.25–3.52 (m, 2H, 1′-H′, 3-H), 3.38 [d, ^2J (3-H/3-H′) = 12.65 Hz, 1H, 3-H′], 3.65 [d, ^2J (PhCH/PhCH′) = 14.85 Hz, 1H, PhC*H* of one diastereoisomer], 3.75 and 3.78 (s each, 3H, OCH_3), 3.90 [dd, ^2J PhCH′/PhCH) = 14.85, ^2J (PhCH/PhCH′) = 14.85, 2H, PhC*H* of one and PhC*H*′ of the other diastereoisomer], 4.05 [d, ^2J (PhCH′/PhCH) = 14.85 Hz, 1H, PhC*H*′ of one diastereoisomer], 6.98–7.14 [m, 5H, H^{ar}]. – ^{13}C NMR (C_6D_6, 100.5 MHz): δ = 7.91/7.98 (C-5′), 16.49/18.34 (2′-C), 33.67/33.72 (C-4′), 40.05/40.29 (C-5), 45.98/46.24 (C-1′), 47.11/48.83 (C-2′), 49.60/49.62 (PhCH_2), 59.88/60.00 (C-3), 62.25/62.49 (OCH_3), 63.99 (C-4), 127.25/127.42 and 129.02/129.09 (C^{ar}), 135.57/135.64 (C^{ipso}), 211.58/212.07 (C-3′), 216.52 [Fe(CO)], 242.53/243.07 (C-1). – MS (70 eV); *m/z* (%): 399 (4) [M^+ – CO], 371 (8) [M^+ – 2 CO], 343 (52) [M^+ – 3 CO], 178 (100), 91 (100), 57 (78). – $C_{21}H_{25}FeNO_5$ (427.3): calcd. C 59.03, H 5.90, N 3.43; found C 58.61, H 6.13, N 3.57.

5. *Tricarbonyl[η⁴-(triphenylphosphonio)trimethylenemethane]-iron(0) Tetrafluoroborate* (**12**): A solution of carbene complex **8** (3.40 g; 10.0 mmol) in CH_3CN (50 ml) was treated with triphenylphosphane (2.62 g; 10.0 mmol) at room temperature and then stirred for 12 h. All volatile components were removed in vacuo and the residue thus obtained was purified by CC on silica gel. Pure **12** could be eluted with CH_3CN/CH_2Cl_2 (1:1), giving yellow crystals upon evaporation of the eluate; m.p. 178°C (decomp.); yield 4.44 g (8.2 mmol; 82%). – IR (KBR): $\tilde{\nu}$ = 3075 cm^{-1}, 2970, 2060, 1990, 1975 (CO), 1430, 1045. – ^1H NMR (CD_3CN, 400 MHz): δ = 1.83 [dd, ^4J (3-H^b/4-H^a) = 4.3, ^2J (4-H^a/4-H^b) = 1.22 Hz, 1H, 4-H^a], 2.31 [dd, ^2J (4-H^a/4-H^b) = 1.22, ^4J (1-H/4-H^b) = 2.44 Hz, 1H, 4-H^b], 2.59 [d, ^4J (3-H^a/P) = 10.7 Hz, 1H, 3-H^a], 2.87 [d, ^4J (3-H^b/4-H^a) = 4.3 Hz, 1H, 3-H^b], 3.21 [dd, ^2J (1-H/P) = 5.8, ^4J (1-H/4-H^b) = 2.44 Hz, 1H, 1-H], 7.72–7.88 (m, 15H, H^{ar}). – ^{13}C NMR (CD_3CN, 100.5 MHz): δ = 47.60 [d, ^1J (P/C-1) = 74.80 Hz, C-1], 57.22 (C-4), 60.24 [d, ^3J (P/C-3) = 18.30 Hz, C-3], 110.68 (C-2), 121.40 [d, ^1J (P/C^{ipso}) = 88.50 Hz, C^{ipso}], 131.20 [d, ^2J (P/C^{ortho}) = 12.20 Hz, C^{ortho}], 135.00 [d, ^3J (P/C^{meta}) = 10.7 Hz, C^{meta}], 136.20 [d, ^4J (P/C^{para}) = 3.0 Hz, C^{para}], 208.55 and 208.75 and 209.9 (CO). – ^{31}P NMR (CD_3CN, 162 MHz, H_3PO_4 external): δ = 22.2. – MS (70 eV); *m/z* (%): 317 (63) [M^+ – $Fe(CO)_3$], 262 (100) [Ph_3P^+], 181 (78), 124 (58), 44 (69), 28 (36). – $C_{25}H_{20}BF_4FeO_5P$ (542.1): calcd. C 55.39, H 3.72; found C 55.81, H 3.90.

Crystal Structure of **12**[18,19]: Clear, bright yellow single crystals were obtained by slowly cooling a solution of **12** in dichloromethane/diethyl ether, 1:1, to 0°C: formula $C_{25}H_{20}BClF_4FeO_3P$, molar mass 584.00 g mol^{-1} (including CH_2Cl_2), crystal size 0.30 × 0.20 × 0.10 mm, *a* = 32.78(1), *b* = 7.928(2), *c* = 20. 434(6) Å, β = 92.08(2)°, *V* = 5307(3) Å^3, *T* = 293(2) K; $d_{calcd.}$ = 1.462 g cm^{-3}, μ = 7.83 cm^{-1}, *Z* = 8, monoclinic, space group *C2/c*, Nonius MACH3 diffractometer, λ = 0.71073 Å, Θ range 2.31–22.76°; ω/Θ scans, index ranges $0 \le h \le 35$, $0 \le k \le 8$, $-22 \le l \le 22$, 3579 collected reflections, 1154 reflections [$I > 2\sigma(I)$], 330 refined parameters, absorption correction with scans. Structure solution: direct methods (SHELXS86); structure refinement: full-matrix least squares on F^2 (SHELXL93), H atoms calculated and not included into least-squares refinement, *R*1 = 0.0730, *wR*2 = 0.2310 (all data), largest diff. peak and hole 0.476 and −0.383 eÅ^{-3} with $R1 = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR2 = \Sigma w(F_o^2 - F_c^2)^2|/\Sigma w(F_o^2)^2)^{0.5}$.

6. *Synthesis of 2-(γ-Oxoalkyl)prop-1-en-3-ols* **14**. – *General Procedure (C):* According to the general procedure (B), solutions of the required lithium enolates in THF were prepared from 1.1 mmol of the carbonyl compound and then added via a cannula into a slurry of the carbene complex **8** (340 mg; 1.0 mmol) in THF (5 ml)

kept at −78°C. The entire mixture was stirred for 2 h at −78°C, then allowed to warm to room temperature and all volatile components were finally removed in vacuo. The resulting residue was quickly extracted with diethyl ether, the extracts were concentrated on an oil pump and then swiftly chromatographed on a short plug of silica gel (diethyl ether/petroleum ether, 1:2). The crude products **13** thus obtained were weighed and immediately redissolved in methanol (20 ml) and chilled with ice. H_2O_2 (6 ml of a 30% aqueous solution; 6.0 mmol) was added, whereupon the solutions turned brownish. Then solid sodium hydroxide (240 mg; 6.0 mmol) was added within 2 h and stirring was continued for another 2 h. Finally, the mixtures were extracted thrice with diethyl ether (100 ml) and the combined extracts were washed with saturated aqueous NH_4Cl solution and dried with $MgSO_4$. After removal of the solvent in a rotary evaporator, the crude products were purified by CC (silica gel; diethyl ether/petroleum ether, 1:2).

6-Methylene-3-oxo-2,4,4-trimethylheptan-7-ol (**14a**): 145 mg (0.78 mmol; 78%) from 125 mg of diisopropyl ketone; yellow oil. − IR (film): $\tilde{\nu}$ = 3400 cm^{-1} (OH), 3060 (=CH), 2940, 2910, 2850 (CH), 1690 (CO), 1460, 1370, 1250, 1080. − ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.06 [d, ^3J (2-H/CH_3) = 6.60 Hz, 6H, 1-H, 2-Me], 1.18 (s, 6H, 4-CH_3), 2.35 (s, 2H, 5-H), 2.79 (s, 1H, OH), 3.13 [sep, ^3J (2-H/CH_3) = 6.60 Hz, 1H, 2-H], 3.98 (s, 2H, 7-H), 4.81 and 5.09 (s each, 2H, $=CH_2$). − ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 20.15 (C-1 and 2-CH_3), 24.88 (4-CH_3), 34.55 (C-2), 41.22 (C-5), 47.92 (C-4), 66.14 (C-7), 114.06 ($=CH_2$), 145.85 (C-6), 219.13 (C-3). − MS (70 eV); *m/z* (%): 184 (3) [M^+], 141 (12) [M^+ − *i*Pr], 111 (22), 95 (94), 71 (62), 43 (100) [*i*Pr^+]. − $C_{12}H_{20}O_2$ (184.3): calcd. C 71.70, H 10.94; found C 71.63, H 10.87.

4-Methyl-6-methylene-3-oxoheptan-7-ol (**14b**): 135 mg (0.86 mmol; 86%) from 95 mg of diethyl ketone; yellowish oil. − IR (film): $\tilde{\nu}$ = 3450 cm^{-1} (OH), 3080 (=CH), 2970, 2935, 2880 (CH), 1710 (CO), 1460, 1370, 1100. − ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.04 [t, ^3J (2-H/1-H) = 7.70 Hz, 3H, 1-H], 1.11 [d, ^3J (4-H/4-CH_3) = 7.15 Hz, 3H, 4-CH_3], 2.06 [dd, ^3J (4-H/5-H) = 6.60, ^2J (5-H/5-H′) = 14.30 Hz, 2H, 5-H, 5-H′], 2.09 (s, 1H, OH), 2.46 [q, ^3J (1H/2-H) = 7.70 Hz, 3H, 2-H], 2.81 [dq, ^3J (4-H/4-Me) = 7.15, ^3J (4-H/5-H) = 6.60 Hz, 1H, 4-H], 4.05 (s, 2H, 7-H), 4.84 and 5.06 (s each, 2H, $=CH_2$). − ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 7.65 (C-1), 16.83 (4-CH_3), 34.33 (C-2), 35.91 (C-5), 44.47 (C-4), 65.77 (C-7), 111.62 ($=CH_2$), 146.51 (C-6), 214.96 (C-3). − MS (70 eV); *m/z* (%): 156 (4) [M^+], 139 (4) [M^+ − OH], 127 (11), 82 (81), 67 (98), 57 (100). − $C_9H_{16}O_2$ (156.2): calcd. C 69.19, H 10.32; found C 69.22, H 10.31.

5-Isopropyl-2-methyl-7-methylene-4-oxooctan-8-ol (**14c**): 155 mg (0.73 mmol; 73%) from 156 mg of diisobutyl ketone; colourless, slowly solidifying oil. − IR (film): $\tilde{\nu}$ = 3390 cm^{-1} (OH), 3050 (=CH), 2940, 2900, 2870 (CH), 1690 (CO), 1480, 1450, 1080. − ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.88 [d, ^3J (2-H/CH_3) = 6.59 Hz, 6H, 1-H, 2-Me], 0.96 [d, ^3J (1′-H/1′-CH_3^a) = 6.59 Hz, 3H, 1′-CH_3^a], 1.21 [d, ^3J (1′-H/1′-CH_3^b) = 6.35 Hz, 3H, 1′-CH_3^b], 1.94 [qq, ^3J (1′-H/1′-CH_3^a) = 6.59, ^3J (1′-H/1′-CH_3^b) = 6.35 Hz, 1H, 1′-H], 2.10−2.17 (m, 2H, 6-H), 2.30−2.57 (m, 3H, 3-H, 5-H), 2.85 (m, 1H, OH), 3.47 [dd, ^3J (5-H/6-H) = 7.08, ^3J (5-H/1′-H) = 6.35 Hz, 1H, 5-H], 4.04 (s, 2H, 8-H), 4.82/5.02 (s, 2H, $=CH_2$). − ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 19.10, 21.05, 22.54, 22.68 (CH_3), 23.65 and 29.94 (*C*HMe_2), 30.16 (C-6), 52.59 (C-3), 57.36 (C-5), 66.02 (C-8), 111.26 ($=CH_2$), 147.28 (C-7), 213.89 (C-4). − MS (70 eV); *m/z* (%): 212 (16) [M^+], 197 (12) [M^+ − CH_3], 169 (49) [M^+ − *i*Pr], 109 (68), 85 (100), 43 (98), 29 (58). − $C_{13}H_{24}O_2$ (212.3): calcd. C 73.54, H 11.39; found C 73.46, H 11.47.

2-(3′-Hydroxy-2′-methylene)propylcyclopentanone (**14d**): 76 mg (0.50 mmol; 50%) from 92 mg of cyclopentanone; yellowish oil. − IR (film): $\tilde{\nu}$ = 3420 cm^{-1} (OH), 3070 (=CH), 2960, 2930, 2870 (CH), 1740 (CO), 1450, 1400, 1250, 1030. − ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.25−2.79 (m, 8H, OH, CH_2^{cyc}), 2.35 [d, ^3J (2-H/1′-H) = 8.05 Hz, 2H, 1′-H], 4.06 (s, 2H, 3′-H), 4.89/5.08 (s, 2H, $=CH_2$). − ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 20.54, 29.73, 33.18 (C^{cyc}), 37.98 (C-1′), 47.96 (C-2), 65.66 (C-3′), 111.45 ($=CH_2$), 146.73 (C-2′), 207.56 (C-1). − MS (70 eV); *m/z* (%): 154 (3) [M^+], 84 (100) [$C_5H_8O^+$], 79 (73), 41 (61). − $C_9H_{14}O_2$ (154.2): calcd. C 70.10, H 9.15; found C 70.18, H 9.19.

2-(3′-Hydroxy-2′-methylenepropyl)-2,6-dimethylcyclohexanone (**14e**): 164 mg (0.83 mmol; 83%) from 140 mg of 2,6-dimethylcyclohexanone; mixture of diastereoisomers; colourless oil, slowly solidifying. − IR (film): $\tilde{\nu}$ = 3380 cm^{-1} (OH), 3060 (=CH), 2940, 2900, 2840 (CH), 1690 (CO), 1470, 1370, 1245, 1080. − ^1H NMR {[D_6]-DMSO, 400 MHz}: δ = 0.87 [d, ^3J (6-H/6-Me) = 6.34 Hz, 3H, 6-CH_3 *cis* or *trans*], 0.89 [d, ^3J (6-H/6-Me) = 5.38 Hz, 3H, 6-CH_3 *trans* or *cis*], 1.17 and 1.19 (s each, 6H, 2-CH_3 *cis* and *trans*], 1.36−2.18 (m, 6H, H^{cyc}), 2.50 and 2.51 (s, 2H, 1′-H, *cis* and *trans*), 2.80−2.93 (m, 2H, 6-H *cis* or *trans*, and OH), 2.85 (m, 1H, OH), 3.47 [ddq, ^3J (6-H/5-H) = 7.08, ^3J (6-H/6-CH_3) = 6.34, ^3J (6-H/5-H′) = 6.59 Hz, 1H, 6-H], 3.35 and 3.70 (s each, 2H, 3′-H *cis* and *trans*), 4.68−5.19 (m, 2H, $=CH_2$). − ^{13}C NMR {[D_6]DMSO, 100.5 MHz}: δ = 14.90 (6-CH_3), 20.50/22.61 (C-4), 22.44/22.66 (2-CH_3), 29.94 (C-2), 32.70/35.51 (C-6), 36.60/36.76 (C-5), 40.08 (C-1′), 41.88 (C-3), 63.93/69.44 (C-3′), 111.70/115.85 ($=CH_2$), 140.09/146.28 (C-2′), 215.93/216.04 (C-1). − MS (70 eV); *m/z* (%): 196 (15) [M^+], 181 (11) [M^+ − CH_3], 126 (75), 95 (72), 55 (100), 41 (92). − $C_{12}H_{20}O_2$ (196.3): calcd. C 73.43, H 10.27; found C 73.39, H 10.30.

7. *Synthesis of Allyl Carbamates* **15**: According to the general procedure (C), solutions of the carbene complexes **9** (1.1 mmol) in methanol (20 ml) were chilled to 0°C and treated with H_2O_2 (6 ml of a 30% aqueous solution; 6.0 mmol). Then solid sodium hydroxide (240 mg; 6 mmol) was added within 2 h and stirring was continued for another 2 h. Finally, the mixtures were extracted thrice with diethyl ether (100 ml) and the combined extracts were washed with saturated aqueous NH_4Cl solution and dried with $MgSO_4$. After removal of the solvent in a rotary evaporator, the crude products were purified by CC (silica gel; diethyl ether/petroleum ether, 1:2).

Methyl N-Methyl-N-(4,4,6-Trimethyl-2-methylene-5-oxoheptyl)-carbamate (**15a**): 192 mg (0.75 mmol; 75%) from 380 mg of **11a**; faintly yellow oil; R_f = 0.91 (diethyl ether/petroleum ether, 1:2). − IR (film): $\tilde{\nu}$ = 2960 cm^{-1}, 2930 (CH), 1705 (CO), 1470, 1390, 1260, 1090. − ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.05 [d, ^3J (6-H/CH_3) = 6.84 Hz, 6H, 6-CH_3, 7-H], 1.20 (s, 6H, 4-CH_3), 2.23 (s, 2H, 3-H), 2.82 and 2.87 (s, 3H, NCH_3), 3.11 [sept, ^3J (6-H/CH_3) = 6.84 Hz, 1H, 6-H], 3.68 (s, 2H, 1-H), 3.71 (s, 3H, OCH_3), 4.81 and 4.89 (m, 2H, $=CH_2$). − ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 20.19 (C-7, 6-CH_3), 24.48 (4-CH_3), 33.65 (NCH_3), 34.37 (C-6), 41.40/41.71 (C-3), 48.07 (C-4), 52.67 (OCH_3), 54.72/55.19 (C-1), 113.64/114.24 ($=CH_2$), 141.08 (C-2), 157.14 (NCO), 219.64/219.77 (C-5). − MS (70 eV); *m/z* (%): 255 (10) [M^+], 184 (18) [M^+ − *i*PrCO], 142 (100), 110 (20), 95 (98), 43 (85) [*i*Pr^+]. − $C_{14}H_{25}NO_3$ (255.3): calcd. C 65.85, H 9.87, N 5.48; found C 65.83, H 9.90, N 5.40.

Methyl N-Benzyl-N-(4-methyl-2-methylene-5-oxoheptyl)carbamate (**15b**): 280 mg (0.92 mmol; 92%) from 430 mg of **11b**; faintly yellow oil; R_f = 0.55 (diethyl ether/petroleum ether, 1:2). − IR (film): $\tilde{\nu}$ = 3050 cm^{-1} (=CH), 2950 (CH), 1700 (CO), 1450, 1400, 1250, 1100. − ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.05 [d, ^3J (CH_3/4-H) = 7.08 Hz, 3H, 4-CH_3], 1.04 [t, ^3J (7-H/6-H) = 7.32 Hz, 3H, 7-H], 1.93 [ddq, ^3J (4-H/CH_3) = 7.08, ^3J (3-H/4-H) = 7.08, ^3J (3-

H'/4-H) = 7.52 Hz, 1H, 4-H], 2.36–2.85 (m, 4H, 6-H, 3-H, 3-H'), 3.75 (s, 3H, OCH_3), 3.75 and 3.89 (m, 2H, 1-H), 4.34 [d, ^2J (NCH/NCH') = 15.38 Hz, 1H, NCH or NCH'], 4.44 [d, ^2J (NCH'/NCH) = 15.38 Hz, 1H, NCH' or NCH], 4.87 (m, 2H, $=CH_2$), 7.26–7.33 (m, 5H, H^{ar}). – ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 7.69 (C-7), 16.59 (4-CH_3), 34.48 (C-3), 36.61 (C-6), 48.61/49.39 (NCH_2Ph), 49.91/50.10 (C-1), 52.89 (OCH_3), 113.02/114.23 ($=CH_2$), 128.57/128.66/128.88 (C^{ar}), 140.90/142.10 (C-2), 157.16 (NCO), 214.49/214.60 (C-5). – MS (70 eV); *m/z* (%): 303 (8) [M^+], 218 (15), 164 (16), 129 (22), 91 (100), 57 (28). – $C_{18}H_{25}NO_3$ (303.4): calcd. C 71.26, H 8.31, N 4.62; found C 70.98, H 8.24, N 4.71.

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[18] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +44 (0) 1223/336-033, E-mail: deposit@chemcrys.cam.ac.uk).

[19] The moderate *R* value is due to the fact, that **12** is a poorly reflecting compound. Only 30% of all reflections were strong, despite measuring with a rotating anode. Yet in the sphere 2Θ = 41–46°, 80% of the measured reflections were merely weak. Thermal parameters for the anion and the solvent were relatively large.

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