Convenient RCM-Mediated Synthesis and Spectroscopic Study of Novel Ferrocenyl-Substituted 2,5,8,9-Tetrahydro-3*H*-imidazo[1,2-*a*][1,3]diazepin-3-ones[‡]

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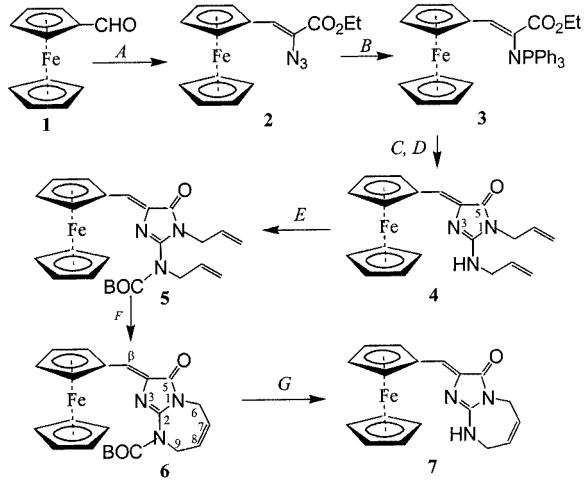
The ferrocene-containing *N*-BOC-protected 1-allyl-2-(allylamino)imidazolones **5** and **13** were transformed into mono- and bis(2,5,8,9-tetrahydro-3*H*-imidazo[1,2-*a*][1,3]diazepin-3-ones) **7** and **15** in a ring-closing metathesis (RCM) reaction using Grubbs' catalyst $[RuCl_2(CHPh)\{P(cyclo\text{-}C_6H_{11})_3\}_2]$. The structures of the novel compounds were identified by IR and multinuclear NMR spectroscopy.

Introduction

In recent years olefin ring closing metathesis (RCM) reactions conducted under homogeneous catalytic conditions have become a widely used and efficient synthetic method for furnishing homo- and heterocycles containing a C=C double bond.[2a][2b] Although the great number of successful experiments[3] suggests that the size of the ring constructed is highly variable, only one example of an RCM-protocol[4] and a ring-opening metathesis[5] have been reported so far for the conversion of metallocene-containing precursors.

In the framework of our program investigating synthetic routes to novel ferrocenyl-substituted heterocycles, by means of the reaction sequence described by Molina et al.[6a–6c] we converted formylferrocene (**1**) and 1,1′-diformylferrocene (**8**)[7] into the corresponding mono- and bis-(imidazolones) **4** and **12** (Schemes 1 and 2, respectively) carrying 1-allyl-2-(allylamino) substituents which may be involved in RCM reactions.



Scheme 1. *A*: $N_3CH_2CO_2Et$/NaOEt, −30 °C, abs. ethanol; *B*: PPh_3, room temp., CH_2Cl_2; *C*: allyl isocyanate, room temp., CH_2Cl_2; *D*: allylamine, room temp., CH_2Cl_2; *E*: $(BOC)_2O$, TEA, DMAP, reflux in CH_2Cl_2; *F*: 10 mol % $[RuCl_2(CHPh)(PCy_3)_2]$, reflux in CH_2Cl_2; *G*: 30% F_3CCO_2 H, reflux in CH_2Cl_2; the numbering in compound **6** refers to the NMR signal assignments

Results and Discussion

The RCM reaction of mono(imidazolone) **5**, the *N*-BOC-protected form of **4**, catalyzed by $[RuCl_2(CHPh)\{P(cyclo\text{-}C_6H_{11})_3\}_2]$ in refluxing CH_2Cl_2 resulted in the expected

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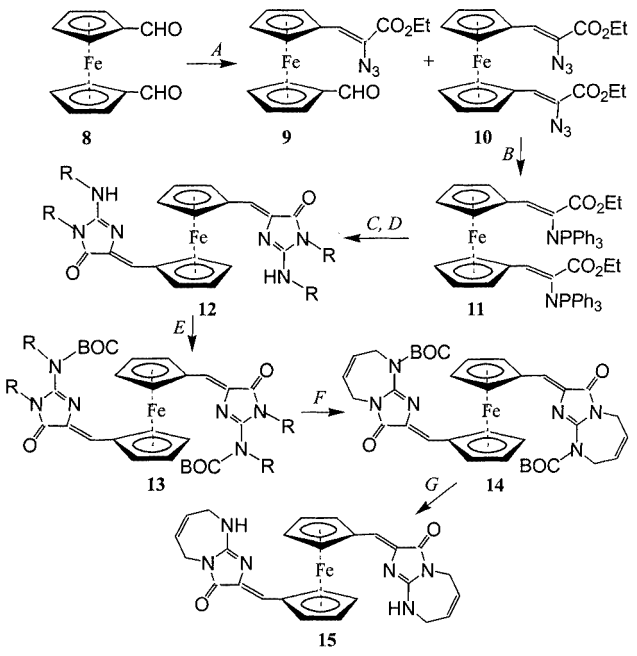
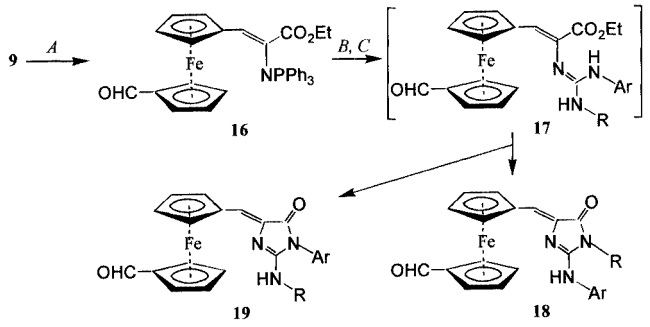


Scheme 2. R = allyl; *A*: $N_3CH_2CO_2Et$/NaOEt, −30 °C, abs. ethanol; *B*: PPh_3, room temp., CH_2Cl_2; *C*: allyl isocyanate, room temp., CH_2Cl_2; *D*: allylamine, room temp., CH_2Cl_2; *E*: $(BOC)_2O$, TEA, DMAP, reflux in CH_2Cl_2; *F*: 10 mol % $[RuCl_2(CHPh)(PCy_3)_2]$, reflux in CH_2Cl_2; *G*: 30% F_3CCO_2H, reflux in CH_2Cl_2



Scheme 3. R = allyl, Ar = *p*-chlorophenyl; *A*: PPh_3, room temp., CH_2Cl_2; *B*: *p*-chlorophenyl isocyanate, room temp., CH_2Cl_2; *C*: allylamine, room temp., CH_2Cl_2

condensed diazepine **6** in excellent yield (86%). With an increased amount of catalyst the yield did not change significantly, although the reaction was complete within a considerably shorter period of time (TLC monitoring; see Exp. Sect.). Treatment of **6** with TFA in dry CH_2Cl_2 gave **7**, a novel imidazo[1,2-*a*][1,3]diazepine derivative (Scheme 1), which is suitable for a series of further coupling reactions at the NH group.

Although RCM reaction of **13**, the *N*-BOC-protected form of **12**, may also connect the two imidazolone units forming a doubly bridged ferrocene, the catalytic ring condensation took place independent of the concentration affording bis(imidazo[1,2-*a*][1,3]diazepine) **14** (Scheme 2), deprotection of which yielded **15**, which contains a ferrocene double core that is useful for further transformations.

It should be noted that Knoevenagel-type condensation of 1,1′-diformylferrocene (**8**) gave a mixture of the expected bis(azidoacrylate) **10** and mono(azidoacrylate) **9** having an unchanged formyl group (Scheme 2). Probably due to steric hindrance the bridge-forming intramolecular aza-Wittig reaction of the iminophosphorane derivative **16** (Scheme 3) could not be effected even on prolonged heating in refluxing toluene.

However, on subsequent treatment with 4-chlorophenyl isocyanate and allylamine, compound **16** gave the expected 1-allyl-2-[(4-chlorophenyl)amino]imidazolone derivative **18** in only moderate yield (18%), while its isomer, 2-(allylamino)-1-[(4-chlorophenyl)amino]imidazolone (**19**), was formed as the major product (78%). On the basis of the observations made by Molina et al.[6a−6c] and our group[1] the formation of the imidazolone ring in the guanidino intermediate **17** should have occurred by attack of the more nucleophilic nitrogen atom in the allylamino moiety on the ethoxycarbonyl group to afford mainly **18**. This unexpected reactivity of the guanidino intermediate **17** can probably be ascribed to the repulsive interaction between the bulky arylamino group and the freely rotating formyl−Cp ring.

Structures

The spectroscopic data (Tables 1, 2, 3, and 4) are self-explanatory and only a few additional remarks are necessary. It is to be noted that the numbering used in the text and tables is given in Scheme 1 and is different from the IUPAC numbering (see Exp. Sect.).

The sandwich nature of ferrocene is mediating rather than isolating the electronic effects of the substituents on the two Cp rings. For example, the mutual $-I$ effects of the CH=C(N_3)COOEt moieties are revealed by an increase of the $\nu(N_3)$ IR frequency by 30 cm^{-1} in **10** relative to **9**. Similarly, the signal of the exocyclic olefinic H in the FcCH= moiety is shifted upfield by 0.3 ppm in compounds **12** and **13** relative to their counterparts **4** and **5**. The electron-withdrawing effect of the substituent on the other Cp ring probably hinders the enone polarization leading to partial positive character − and hence a downfield shift of its signal − of the H in question (H_β in the enone group) as observed for **4** and **5**. In contrast, the two imidazole rings have practically the same electron distribution in **12**−**14** as both Cp rings are identically substituted.

The downfield shift of the H_β singlet (by 0.5 ppm) in **5** and **13** due to the $-I$ effect of the BOC group was detected for the pairs **4/5** and **12/13**, and similar shift differences were also found for the pairs **7/6** and **15/14**. In agreement with this effect, the signal of the olefinic carbon atom of the Fc*C*H= group is also shifted significantly downfield (by more than 10 ppm) in the BOC-protected derivatives **5**, **6**, **13**, and **14** relative to the corresponding unsubstituted NH compounds (**4**, **7**, **12**, **15**), demonstrating a strong delocalization along the chain N(*exo*)−C(2)−N(3)−C(4)−C(β).

Table 1. ^{1}H NMR (500 MHz) spectroscopic data (ppm, δ_{TMS} = 0 ppm, in $CDCl_3$, for **5** and **19** [D_6]DMSO, coupling constants in Hz) of compounds **4**−**7**, **9**−**16**, **18**, and **19**; assignments are supported by HMQC and for **4**, **6**, **13**, **15**, **16**, **18**, and **19** also by 2D-COSY measurements

Compound	CH_3/NH[a]	CH_2	=CH	substituted Cp ring		=CH[b]	*N*(*exo*)-allyl group[c]				*N*(1)-allyl group[c]			
	s/t (3 H)	q (2 H)	s (1 H)	2,5-H (2 H)	3,4-H (2 H)	s (5 H)	CH_2 [d]	=CH−	$=CH_2$ [e]	$=CH_2$ [f]	CH_2 [g]	=CH−	$=CH_2$ [e]	$=CH_2$ [f]
4	≈ 4.7	−	6.65	4.93	4.38	4.13[h]	4.15[h]	6.00	5.21	≈ 5.28[i]	4.22	5.85	≈ 5.28[i]	≈ 5.28[i]
5	1.50	−	7.15	4.97	4.55	4.17	4.29	6.00	5.22	5.31	4.24	5.78	5.17	5.15
6	1.52	−	7.22	4.98	4.57	4.17	4.30	5.70	−	−	4.22	5.78	−	−
7	−	−	6.61	4.81	4.43	4.18	3.62	≈ 6.13[h]	−	−	4.35	≈ 6.13[h]	−	−
9	1.32	4.27	6.53	4.75, 4.68[j]	4.39, 4.49[j]	9.80	−	−	−	−	−	−	−	−
10	1.40	4.33	6.48	4.75	4.39	−	−	−	−	−	−	−	−	−
11[k]	0.93	3.77	6.53[l]	4.81	4.10	−	−	−	−	−	−	−	−	−
12	5.39	−	6.35	4.89	4.30	−	4.08	5.96	5.12	5.22[h]	4.21	5.80	5.17	5.22[h]
13	1.50	−	6.85	4.96	4.49	−	4.30	6.03	5.28	5.33	4.22	5.84	5.18[h]	5.17[h]
14	1.51	−	6.79	4.98	4.51	−	4.38	5.75[h]	−	−	4.16	5.75[h]	−	−
15		−	6.49	4.86	4.58	−	4.15	6.36	−	−	4.50	6.26	−	−
16[k]	0.98	3.83	6.32[l]	4.98, 4.47[j]	4.26, 4.66[j]	9.83	−	−	−	−	−	−	−	−
18[m]	9.20	−	6.34	4.97, 4.66[j]	4.47, 4.53[j]	9.66	−	−	−	−	4.33	5.82	5.07	5.00
19[m]	≈ 4.4	−	6.48	4.99, 4.67[j]	4.42, 4.51[j]	9.81	4.10	5.92	5.16	5.20	−	−	−	−

[a] For **5**, **6**, **13**, and **14** s (9 H), for **9**, **10**, **11**, and **16** t (J = 6.8, 7.1, 7.0 and 7.2, 3 H), NH, broad s (1 H) for **4**, **18**, and **19**, t (J = 5.3) for **12**. [b] Unsubstituted Cp ring (**4**−**7**). Formyl =CH (1 H) for **9**, **16**, **18**, and **19**. [c] CH_2 (pos. 9/6) and CH-8/-7 in azepines **6**, **7**, **14**, and **15**. [d] Multiplicity: ≈ d (J = 6.3) for **5** and **13**, ≈ t (J = 5.2) for **12** and with coalesced lines for **19**, m for **6**, **7**, **14**, and **15**, ≈ s for **18**. [e] *cis*-H of $=CH_2$ group, ≈ d [J = 10.2±0.2, for *N*(1)-allyl group in **5** J = 14.4]. [f] *trans*-H of $=CH_2$ group, ≈ d [J = 17.2, in **5** J = 16.1 and 14.4 for the *N*(*exo*)- and *N*(1)-allyl groups]. [g] Multiplicity: ≈ d for **4**, **5**, **12**, and **13** (J = 5.3, 5.5, 4.7, and 5.9), m for **6**, **7**, **14**, and **15**. [h] Overlapping signals. [i] Overlapping signals. [j] Formyl-substituted ring. [k] Phenyl; 2-,6-H: 7.42 (12 H, **11**), 7.45 (6 H, **16**), ≈ dd (J ≈ 11 and 8) due to ^3J-type P-H and *ortho* H-H couplings, 3-,4-,5-H, m: 7.42 (18 H, **11**), 7.45 (9 H, **16**). [l] d, ^3J(P,H) = 6.6 (**11**), 7.2 (**16**). [m] *p*-Chlorophenyl, 2 × ≈ d (2 × 2 H, J = 8.1 and 8.5), 2-,6-H: 7.89 (**18**), 7.21 (**19**), 3-,5-H: 7.39 (**18**), 7.44 (**19**).

The anisotropic shielding effect of the phenyl rings[8] on the ethyl group can be observed in the ^{1}H NMR spectra of **11** and **16**; the methyl and methylene signals are shifted upfield to δ = 0.93 and 3.77 ppm (**11**) and δ = 0.98 and 3.83 ppm (**16**), respectively, while these shifts are δ = 1.40 and 4.33 and δ = 1.32 and 4.27 ppm in **10** and **9**, respectively, where instead of an N=PPh_3 group an N_3 substituent is attached to C-α (vicinal to the COOEt group).

The chemical equivalence of C-2/2-H and C-5/5-H and, similarly, C-3/3-H and C-4/4-H of the substituted Cp rings proves the free rotation around the C(1,Cp)−C(β) bond. Due to asymmetric structures of the compounds invertigated these pairs of H/C atoms are diastereotop and potentially chemically non-equivalent.

The very strong ν(C=N) (stretching) band of the iminophosphoranes **11** and **16** is remarkable and has diagnostic value for this functional group. The higher IR frequency of the Fe−Cp bond in the iminophosphorane compounds is also noteworthy (cf. Table 3) as a proof, again, of the significant influence of the side-chain attached to the Cp ring of the ferrocenyl moiety.

The ring closure is confirmed by the existence of the N−CH_2−CH=CH−CH_2−N chain in compounds **6**, **7**, **14**, and **15**, which follows from the spectroscopic data, including 2D-COSY and 2D-HMBC measurements. The significantly higher ^{15}N NMR shifts of the N(*exo*) atoms in the diazepine derivatives (δ = 81−98 ppm, as compared to δ = 71−73 ppm in other compounds, c.f. Table 4) are direct proof of the seven-membered heterocycle-containing structures.

The *N*(*exo*)−aryl−*N*(1)−allyl structure of **18** follows directly from the HMBC measurements. A correlation was observed between C-5 and the methylene-H attached to the sp^3-carbon atom of the allylic group on the one hand and between the *ortho*-carbon atoms of the aryl group and the NH hydrogen atom on the other hand. The latter interaction is proof of the preferred tautomeric form containing an *exo*-NH group in **18**.

A direct proof of the reversed *N*(*exo*)−allyl−*N*(1)−aryl substitution in **19** was not found by HMBC. However, comparison of the ^{1}H and ^{13}C NMR chemical shifts of **4** and **19** strongly supports this structure. The mean values of the chemical shift differences for the four H and three C atoms of the allylic groups on comparing **19** and the *N*(*exo*)- or *N*(1)-allyl groups in **4** are $\Delta\delta_H$ = 0.065 [N(*exo*)] and 0.122 ppm [N(1)] and $\Delta\delta_C$ = 0.425 [N(*exo*)] and 1.433 ppm [N(1)], respectively. The ^{15}N NMR chemical shifts in **4** and **19** (c.f. Table 4) prove the *N*(1)−aryl structure directly, while they are the same for N-3 and N(*exo*); a shift difference of 13 ppm was observed for N(1). Similarly, in the case

Table 2. ^{13}C NMR (125 MHz) chemical shifts (ppm, $\delta_{TMS} = 0$ ppm, in $CDCl_3$ solution, $[D_6]$DMSO for **5** and **19**, coupling constants in Hz) of compounds **4**−**7**, **9**−**16**, **18**, and **19**; assignments are supported by DEPT (except for **15**), HMQC and also by HMBC measurements (except for **10** and **12**); further lines: C-1−5 (unsubst. Cp): 69.6 (**4**), 70.4 (**5** and **6**), 70.0 (**7**), phenyl/*p*-chlorophenyl ring [$J_{P,C}$], C-1′: 134.0 d ([103.6], **11**), 138.6 (**18**), 135.6[g] (**19**); C-2′,6′: 132.8 d ([9.6], **11**, **16**), 122.5 (**18**), 129.0 (**19**); C−3′,5′: 128.5 d ([12.5], **11**, [12.0], **16**), 129.5 (**18**), 130.9 (**19**); C-4′: 131.1 (**11**), 131.3 d ([2.4], **16**), 127.6 (**18**), 129.4 (**19**)

Compound	Subst. Cp ring[a]			=CH[b]	Imidazolinone ring			*N*(*exo*)-allyl group			*N*(1)-allyl group			CH_3	C_q or CH_2[e]	C=O BOC[f]
	C-1′	C-2′,5′	C-3′,4′		C-2	C-4[b,c]	C=O(5)[b]	CH_2[d]	=CH[d]	$=CH_2$	CH_2[d]	=CH[d]	$=CH_2$			
4	79.4	71.2	70.8	120.3	155.9	137.4	169.3	44.6	134.5	117.3	41.9	133.0	118.3	−	−	−
5		72.4	72.5	131.7	154.6	135.6	168.9	52.2	133.7	118.9	43.9	133.0	117.9	28.6	83.3	152.9
6	76.9	72.4	72.8	133.2	154.2	136.3	167.7	45.9	128.0	−	38.0	123.0	−	28.6	82.8	153.2
7	79.0	70.7	71.0	118.4	158.6	135.3	167.7	39.1	133.1[g]	−	37.5	128.5[g]	−	−	−	−
9	78.7, 80.6	72.4, 71.2	72.2, 74.9	124.7	−	124.9	163.5	−	−	−	−			14.6	62.5	193.4
10	78.6	72.3	72.0	125.0	−	123.5	163.9	−	−	−	−	−	−	14.6	62.5	−
11	83.2	70.9	70.6	118.0		129.0	168.1	−	−	−	−	−	−	14.5	60.7	−
12	80.8	71.9	71.5	117.8	155.8	137.2	169.0	44.3	134.2	116.8	41.7	133.0	118.1	−	−	−
13	78.5	73.1	73.8	128.6	155.1	136.0	168.5	51.9	133.5	118.3	43.8	132.7	117.5	28.2	82.9	152.4
14	78.6	73.3	73.7	128.9	154.9	136.5	167.5	45.7	128.0	−	38.2	122.2	−	28.2	82.5	152.8
15		72.6	73.5	118.6	155.2		163.1	38.8	132.4	−	37.0	128.4	−			−
16	86.1, 80.1	71.1, 74.9	70.1, 70.7	113.6	−	136.5	167.8	−	−	−	−	−	−	14.4	61.0	193.7
18	81.5, 81.2	72.37, 71.5	72.33, 75.0	117.4	154.0	138.7[g]	168.2	−	−	−	41.6	133.7	116.6	−	−	193.6
19	81.4, 80.6	72.5, 71.3	72.1, 74.9	117.7	154.8	138.4	168.5	44.8	134.0	117.9	−	−	−	−	−	193.6

[a] The data in the second row (**9**, **16**, **18**, and **19**) refer to the formyl-substituted cyclopentadiene ring. [b] d due to P,C couplings, ^2J = 6.4 (**16**); ^3J for the CH and C=O groups: 18.2 and 6.7 (**11**), 21.0 and 6.8 (**16**). [c] C_α to the ester group (**9**−**11** and **16**). [d] CH_2 and =CH groups in diazepine ring α and β to N(*exo*)/N(1). [e] Quaternary C of the *t*Bu (**5**, **6**, **13**, **14**) or OCH_2 of the ester group (**9**−**11**, **16**). [f] Formyl C=O for **9**, **16**, **18**, and **19**. [g] Interchangeable assignments.

Table 3. Characteristic IR frequencies [cm^{-1}] of compounds **4**−**7**, **9**−**16**, **18**, and **19** (KBr discs)

Compound	ν(NH)[a] or $\nu(N_3)$[b]	ν(C=O)	Amide-I	ν(C=N)	ν(C=C)	ν(C−O)	ν_{as}(Cp−Fe−Cp) and tilt of Cp
4	3337	−	1694	1650	1580	−	491
5	−	1718[c]	1718[c]	1641	1558	1240, 1144	490
6	−	1714[c]	1714[c]	1645	1568	1245, 1132	495[d]
7	3250−2600	−	1712[d]	1666	1612	−	489
9	2111	1710	1685[e]	−	1621	1275, 1244, 1194	498
10	2141	1708, 1693	−	−	1616	1279, 1246, 1196, 1080	491
11[f]	−	1685	−	1405[g]	1587	1214, 1105, 1038	528
12	3352	−	1688	1656	1586	−	487
13	−	1715	1705	1646	1552	1242, 1146	489
14	−	1721	1698	1646	1572	1288, 1136	484
15	≈ 3430	−	1696	1675		−	486
16[f]	−	1693	1680[e]	1411[g]	1657	1253, 1216, 1105	527
18	≈ 3330	1718[e]	1656	1603	1564	−	492
19	≈ 3320	1719[e]	1656	1593	1524	−	490

[a] Diffuse (**7**), broad (**15**). [b] For **9** and **10**. [c] Overlapped maxima. [d] Doubled band with the second maximum at 476 (**6**) and 1697 (**7**). [e] ν(C=O) (formyl group). [f] $\gamma(C_{Ar}H)$ and $\gamma(C_{Ar}C_{Ar})$ bands: 740, 717 and 700 (**11**), 741, 713 and 694 (**16**), 826 (**18**) 837 (**19**). [g] ν(P=N) band (very strong).

of **4** and **18** only small differences were found for N(1) and N(3), while for N(*exo*) this difference is significantly larger at 23 ppm.

Experimental Section

General: The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ or $[D_6]$DMSO solution in 5-mm tubes at room temperature, with a Bruker DRX 500 spectrometer at 500.13 (^1H) and 125.76 (^{13}C) MHz, with the deuterium signal of the solvent as the lock and TMS as internal standard. DEPT spectra were run in a standard manner, using only the $\Theta = 135°$ pulse to separate CH/CH_3 and CH_2 lines phased "up" and "down", respectively. The 2D-HMQC and 2D-HMBC spectra were obtained by using the standard Bruker pulse programs INV4GSSW and INV4GSLRNDSW, respectively. The IR spectra were recorded as KBr pellets with a Bruker IFS 55 spectrometer. Starting from formylferrocene (**1**), the

Table 4. ^{15}N NMR (50.7 MHz) chemical shifts (ppm, δ_{NH3} = 0 ppm, in $CDCl_3$, ([D_6]DMSO for **19**) of compounds **4**, **6**, **7**, **14**, **15**, **18**, and **19** (assignments are based on ^{15}N,^{1}H-HMBC measurements)

Compound	N-1	N-3	N(*exo*)
4	142	179	71
6	157	231	97
7	143	162	81
14	156	228	98
15	141	118	92
18	145	185	94
19	155	178	73

azido ester **2** was synthesized as described in the literature.[6a−6c] The bis(azido) ester **10** was obtained by the same procedure applied to diformylferrocene (**8**).[7] In the course of the preparation of **10**, the formyl derivative **9** was also isolated as a slowly eluting component by chromatography on silica (eluent: *n*-hexane/ethyl acetate, 3:1).

1-(2-Azido-2-ethoxycarbonylethenyl)-1′-formylferrocene (9): Yield 35% (350 mg), red powder, m.p. 89−91 °C. $C_{16}H_{15}FeN_3O_3$ (353.1): calcd. C 54.39, H 4.24, N 11.89; found C 54.40, H 4.22, N 11.92.

1,1′-Bis(2-azido-2-ethoxycarbonylethenyl)ferrocene (10): Yield 65% (650 mg), red plates, m.p. 94−96 °C. $C_{20}H_{20}FeN_6O_4$ (464.2): calcd. C 51.72, H 4.31, N 18.10; found C 51.68, H 4.33, N 17.99.

Bis(iminophosphorane) compound **11** and mono(iminophosphorane) compound **16** were obtained from **10** and **9**, respectively, as reported for the transformation **2** → **3**.[6a−6c]

1,1′-Bis{2-ethoxycarbonyl-2-[(triphenylphosphoranylidene)amino]-ethenyl}ferrocene (11): Yield 95% (475 mg), red powder, m.p. 161−163 °C. $C_{56}H_{50}FeN_2O_4P_2$ (932.7): calcd. C 74.67, H 5.36, N 3.00; found C 74.71, H 5.34, N 2.98.

1-{2-Ethoxycarbonyl-2-[(triphenylphosphoranylidene)amino]ethenyl}-1′-formylferrocene (16): Yield 93% (279 mg), red powder, m.p. 88−90 °C. $C_{34}H_{30}FeNO_3P$ (587.4): calcd. C 70.95, H 5.21, N 2.43; found C 70.99, H 5.18, N 2.46.

General Procedure for Preparation of Imidazolones 4, 12, 18, and 19: A reaction mixture containing stoichiometric amounts of iminophosphorane (0.001 mol) and allyl or *p*-chlorophenyl isocyanate in anhydrous dichloromethane (30 mL) was stirred at room temperature for 24 h to form the corresponding carbodiimides. After completion, a stoichiometric amount of allylamine was added to the solution which was then stirred for another 6 h at room temperature. The solvent was then removed under reduced pressure and the crude solid was chromatographed on silica gel (Kieselgel type 9385; eluent: *n*-hexane/ethyl acetate, 1:1). Recrystallization from diisopropyl ether gave the pure products.

1-[{1-Allyl-2-(allylamino)-5-oxo-1,5-dihydro-4*H*-imidazol-4-ylidene}methyl]ferrocene (4): Yield 92% (345 mg), red plates, m.p. 54−56 °C. $C_{20}H_{21}FeN_3O$ (375.2): calcd. C 64.00, H 5.60, N 11.20; found C 63.95, H 5.62, N 11.17.

1,1′-Bis[{1-allyl-2-(allylamino)-5-oxo-1,5-dihydro-4*H*-imidazol-4-ylidene}methyl]ferrocene (12):Yield 63% (355 mg), red powder, m.p. 77−79 °C. $C_{30}H_{32}FeN_6O_2$ (564.4): calcd. C 63.82, H 5.67, N 14.89; found C 63.85, H 5.68, N 14.93.

1-({1-Allyl-2-[(*p*-chlorophenyl)amino]-5-oxo-1,5-dihydro-4*H*-imidazol-4-ylidene}methyl)-1′-formylferrocene (18): Yield 18% (85 mg), red powder, m.p. 140−143 °C. $C_{24}H_{20}ClFeN_3O_2$ (473.7): calcd. C 60.82, H 4.22, N 8.87; found C 60.87, H 4.23, N 8.95.

1-{[1-(*p*-Chlorophenyl)-2-(allylamino)-5-oxo-1,5-dihydro-4*H*-imidazol-4-ylidene]methyl}-1′-formylferrocene (19): Yield 78% (369 mg), red powder, m.p. 149−151 °C. $C_{24}H_{20}ClFeN_3O_2$ (473.7): calcd. C 60.82, H 4.22, N 8.87; found C 60.90, H 4.27, N 8.91.

General Procedure for the Preparation of *tert*-Butoxycarbonyl-Protected (Allylamino)imidazoles 5 and 13: A reaction mixture containing diallyl precursor **4** (0.0005 mol) and $(BOC)_2O$ (0.003 mol), TEA (0.001 mol), and DMAP (0.001 mol); or tetraallyl precursor **12** (0.0005 mol) and $(BOC)_2O$ (0.006 mol), TEA (0.002 mol), and DMAP (0.002 mol) was stirred for 30 min in refluxing anhydrous dichloromethane (30 mL). The solvent was removed under reduced pressure and the crude solid was chromatographed on silica gel (Kieselgel type 9385; eluent: chloroform/ethyl acetate, 3:1). Recrystallization from absolute ethanol gave the pure products.

1-({1-Allyl-2-[(allyl)(*tert*-butoxycarbonyl)amino]-5-oxo-1,5-dihydro-4*H*-imidazol-4-ylidene}methyl)ferrocene (5): Yield 96% (228 mg), red powder, m.p. 83−85 °C. $C_{25}FeH_{29}N_3O_3$ (475.3) calcd. C 63.15, H 6.10, N 8.84; found C 63.19, H 6.13, N 8.82.

1,1′-Bis({1-allyl-2-[(allyl)(*tert*-butoxycarbonyl)amino]-5-oxo-1,5-dihydro-4*H*-imidazol-4-ylidene}methyl)ferrocene (13): Yield 93% (356 mg), red powder, m.p. 105−107 °C. $C_{40}FeH_{49}N_6O_6$ (765.7) calcd. C 62.82, H 6.41, N 10.99; found C 62.80, H 6.39, N 11.01.

General Procedure for RCM Reactions: A reaction mixture containing the corresponding *N*-BOC-protected di- or tetraallyl precursor **5** or **13** (0.0005 mol) and 10 mol % of $[RuCl_2(CHPh)\{P(c\text{-}C_6H_{11})_3\}_2]$ was stirred at room temperature in anhydrous dichloromethane (30 mL) for 8 h. The solvent was removed under reduced pressure and the crude solid was chromatographed on silica gel (Kieselgel type 9385; eluent: chloroform/ethyl acetate, 3:1). Recrystallization from *n*-hexane gave the pure products.

1-({9-(*tert*-Butoxycarbonyl)-3-oxo-8,9-dihydro-3*H*-imidazo[1,2-*a*][1,3]diazepin-2(5*H*)-ylidene}methyl)ferrocene (6): Yield 86% (192 mg), red powder, m.p. 166−168 °C. $C_{23}FeH_{25}N_3O_3$ (447.3) calcd. C 61.74, H 5.59, N 9.39; found C 61.77, H 5.63, N 9.36.

1,1′-Bis({9-(*tert*-butoxycarbonyl)-3-oxo-8,9-dihydro-3*H*-imidazo-[1,2-*a*][1,3]diazepin-2(5*H*)-ylidene}methyl)ferrocene (14): Yield 62% (219 mg), red powder, m.p. 201−203 °C. $C_{36}FeH_{40}N_6O_6$ (708.6) calcd. C 61.01, H 5.64, N 11.86; found C 60.98, H 5.62, N 11.89.

With increasing molar percent of the catalyst from 10 to 40%, we found that the yield did not change significantly, but the reaction could be completed within a shorter period of time (e.g. 10% catalyst: 8 h; 30% catalyst: ca. 4 h; 40% catalyst: less than 2 h).

General Procedure for Deprotection of BOC Derivatives: The corresponding *N*-BOC-protected diazepine **6** or **14** was refluxed in a mixture of F_3CCO_2H and anhydrous dichloromethane (9 mL and 21 mL) for 30 min. The solvent was removed under reduced pressure and the crude solid was chromatographed on silica (Kieselgel type 9385; eluent: ethyl acetate). Recrystallization from abs. ethanol gave the pure products.

1-({3-Oxo-8,9-dihydro-3*H*-imidazo[1,2-*a*][1,3]diazepin-2(5*H*)-ylidene}methyl)ferrocene (7): Yield 96% (96 mg), red powder, m.p.159−161 °C. $C_{18}FeH_{17}N_3O$ (347.2) calcd. C 62.24, H 4.89, N 12.10; found C 62.28, H 4.93, N 12.14.

1,1′-Bis({3-oxo-8,9-dihydro-3*H*-imidazo[1,2-*a*][1,3]diazepin-2(5*H*)-ylidene}methyl)ferrocene (15): Yield 92% (184 mg), red powder, m.p. 197−199 °C. $C_{26}FeH_{24}N_6O_2$ (515.3) calcd. C, 61.41, H 4.72, N 16.53; found C 61.46, H 4.70, N 16.58.

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[1] V. Zsoldos-Mády, A. Csámpai, P. Sohár, *J. Organomet. Chem.*, submitted.
[2] [2a] R. R. Schrock, J. S. Murdzek, G. C. Bazan, J. Robbins, M. DiMare, M. O′Regan, *J. Am. Chem. Soc.* **1990**, *112*, 3875−3886 and references therein.[2b] R. H. Grubbs, S. Chang, *Tetrahedron* **1998**, *54*, 4413−4450 and references therein.
[3] A recent rewiew: A. J. Phillips, A. D. Abell, *Aldrichim. Acta* **1999**, *32*, 75−88.
[4] A. J. Locke, C. Jones, C. J. Richards, *J. Organomet. Chem.* **2001**, *637−639*, 669−676 and references therein.
[5] M. A. Bretea, T. D. Tilley, *Organometallics* **1997**, *16*, 1507.
[6] [6a] P. Molina, A. Pastor, M. J. Vilaplana, M. V. Desamparados, *Organometallics* **1997**, *16*, 5836−5843. [6b] P. Molina, A. Tarraga, D. Curiel, C. R. de Arellano, *Tetrahedron* **1999**, *55*, 1417−1426. [6c] A. Tarraga, P. Molina, D. Curiel, J. L. Lopez, M. V. Desamparados, *Tetrahedron* **1999**, *55*, 14701−14718.
[7] G. G. A. Balavoine, G. Doisneau, T. Fillebeen-Khan, *J. Organomet. Chem.* **1991**, *412*, 381−382.
[8] P. Sohár, *Nuclear Magnetic Resonance Spectroscopy*, CRC Press, Boca Raton, Florida, **1983**, vol. 1, pp. 35−38.

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