11: ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ = 7.70–7.48 (Ph-H'), 7.45–7.00 (Ph-H', Ph-H), 1.92 (C≡C-CH_3). IR (KBr): $\tilde{\nu}$/cm^{-1}: 3049, 2914, 2850, 2231, 1599, 1511, 1484, 1445, 1396, 1156, 1075, 1023, 980, 900, 814, 764, 698

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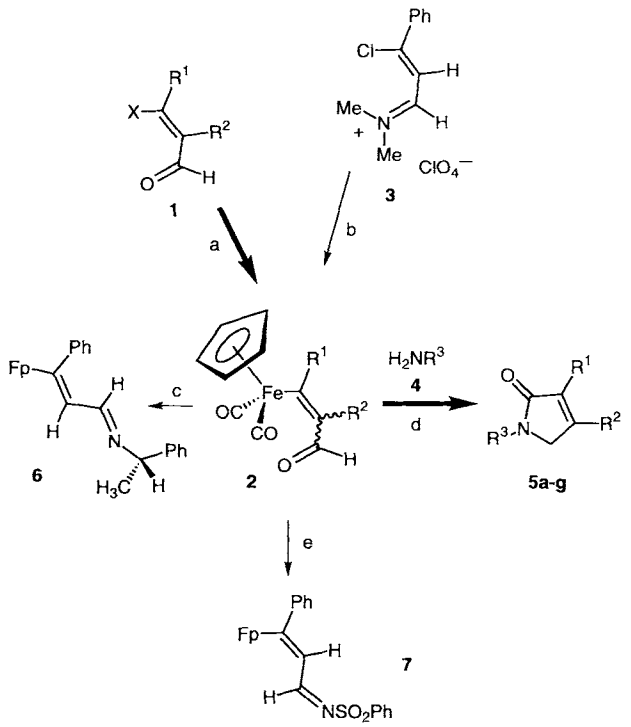
α,β-Unsaturated γ-Lactams from $TiCl_4$-Mediated Transformations of Vinylogous Iron Formyl Complexes**

Karola Rück-Braun*

Domino processes and other reactions that proceed by C–C bond formation in the coordination sphere of a transition metal are of particular interest in organic synthesis.[1] This also holds true for reactions in which carbonyl ligands are inserted from the metal fragment furnishing organic compounds.[2, 3] Very significant is that the electronic surrounding of the metal, in addition to steric factors, directs the reactivity of the attached functional groups, thereby opening various possibilities for specifically influencing the reaction pathways.

Vinylogous iron acyl complexes have been scarcely applied in organic synthesis.[4] Due to the spatial proximity of the aldehyde moiety and the metal fragment in *cis*-configurated iron formyl complexes **2**, chelation interactions are facilitated,[3c, 5] and a specific reactivity pattern is expected. In this paper, the synthesis of **2** from β-bromo or β-chloro vinyl aldehydes **1** (Scheme 1, pathway a) and the reactions of *cis*-configurated **2** with donor-substituted primary amines **4** (H_2NR^3) to yield 2,5-dihydro-1*H*-pyrrol-2-ones **5** (α,β-unsaturated γ-lactams; Scheme 1, pathway d) are described.

The iron formyl compounds **2** were formed by the reaction of ferrates $[Cp(CO)_2FeM]$ (FpM; M = Na, K)[6] with β-bromo or β-chloro vinyl aldehydes of type **1** or with the iminium salt **3** (Scheme 1). These aldehydes and iminium salts are available



Scheme 1. Fp = $Cp(CO)_2Fe$; X = Br, Cl. a) FpNa, −78 °C, THF, 1 h; b) FpK, −78 °C, THF, 1 h, 59% [(*Z*)-**2a**:(*E*)-**2a** = 10:90]; c) solution of (*E*)-**2a** in CH_2Cl_2, addition of **4a** (1 equiv) and NEt_3 (2.33 equiv) at 0 °C, addition of $TiCl_4$ (0.6 equiv, 1 M in CH_2Cl_2) after 30 min, room temperature (IR monitoring). 57% **6**; d) amine **4** (1.05 equiv), Et_3N (2.3 equiv), 0 °C, 30 min, afterwards addition of $TiCl_4$ (1 equiv, 1 M in CH_2Cl_2), room temperature until IR spectrum reveals complete turnover (18–24 h), aqueous workup and subsequent chromatography; e) reaction conditions: analogous to c), (*Z*)-**2a** was allowed to react with H_2NSO_2Ph (1 equiv), 94% **7**.

from α-methylene ketones and Vilsmeier–Haack reagents, according to the procedure of Arnold and Zemlicka.[7] Aldehyde (*Z*)-**1a** (X = Cl, R^1 = Ph, R^2 = H) and FpNa react under kinetic control to form the *cis*-configurated complex (*Z*)-**2a** [81%, (*Z*)-**2a**:(*E*)-**2a** = 83:17 (R^1 = Ph, R^2 = H); Scheme 1], whereas **3**[8] and FpK preferentially deliver the *trans*-configurated complex (*E*)-**2a** (59%, (*Z*)-**2a**:(*E*)-**2a** = 10:90; Scheme 1, pathway b) by a thermodynamically controlled addition–elimination process. The crude product first obtained as an iminium salt is hydrolyzed with 15% NaOH in $CHCl_3/H_2O$. The isomers can be separated by chromatography on silica gel, and the configuration determined by NOE measurements.

Analogous to the procedure by Weingarten et al.[9] for the synthesis of imines, (*E*)-**2a** reacts with (*S*)-phenylethylamine **4a** in the presence of NEt_3 and $TiCl_4$ to give the aldimine **6** in 57% yield after aqueous workup (Scheme 1, pathway c). However, treatment of a solution of (*Z*)-**2a** (1.0 mmol), (*S*)-phenylethylamine (**4a**, 1.05 mmol), and NEt_3 (2.3 mmol) in CH_2Cl_2 at

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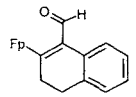
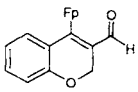
0 °C with $TiCl_4$ (1.0 mmol, 1 M solution in CH_2Cl_2), followed by stirring at room temperature under an argon atmosphere yields pyrrolinone **5a** (Scheme 1, Table 1).[10] Apparently, this product is formed in the coordination sphere of the iron center by attack of the primary amine **4** on the formyl functionality, carbonylation as well as intra- or intermolecular hydrogen transfer, and ring closure. IR spectroscopic monitoring of the reaction shows complete turnover within 18–24 hours, as indicated by the increase in intensity of the C=O band for **5a** at 1680 cm^{-1} as well as the decrease in intensity and disappearance of the C≡O bands for (*Z*)-**2a** and the corresponding aldimine intermediate at about 2028 and 1978 cm^{-1}, respectively. The subsequent aqueous workup, therefore, has no influence on the course of the cascade. ^1H NMR spectra of the crude product only display signals for **5a**. Moreover, no formation of **5a** is observed in the absence of $TiCl_4$ (IR monitoring). Preliminary studies on the reaction of (*Z*)-**2a** with **4a** in the presence of one equivalent of $TiCl_4$ revealed that no **5a** is afforded, even in the absence of a tertiary amine such as NEt_3 or *N*-methylmorpholine. Likewise, lactam formation does not occur if a multifold excess of a primary amine is used instead of a tertiary amine. In conclusion, both the Lewis acid and the tertiary amine determine the course of the reaction cascade.[10]

A variety of primary amines **4** react with (*Z*)-**2a** under standard conditions in the presence of $TiCl_4$ and NEt_3 to deliver exclusively 2,5-dihydro-2*H*-pyrrol-2-ones **5** (Table 1, entries 1–4). Product **5d** was obtained in 44% yield from an amino acid hydrochloride after addition of 3.3 equivalents of NEt_3 (Table 1, entry 4). In the case of acceptor-substituted amines of weaker basicity, such as benzylamine, aniline, or even benzenesulfonamide, solely the formation of the corresponding imines, but no lactams, was observed by IR spectroscopy and thin layer chromatography. Compound **7** was isolated in 94% yield after aqueous workup (Scheme 1, pathway e).

Table 1. Synthesis of vinylogous iron formyl complexes **2** and $TiCl_4$-mediated transformation to 2,5-dihydro-2*H*-pyrrol-2-ones **5** according to Scheme 1.

Entry	2	R^1	R^2	Yield [%] [a, f]	5	R^3	Yield [%] [d, f]
1	(*Z*)-**a**	Ph	H	81 [b, c]	**a**	(*S*)-CH(CH$_3$)Ph	61
2	(*Z*)-**a**	Ph	H		**b**	*t*Bu	80
3	(*Z*)-**a**	Ph	H		**c**	C_6H_{11}	56
4	(*Z*)-**a**	Ph	H		**d**	(*R*)-CH[CH(CH$_3$)$_2$]CO$_2$Me	44 [e]
5	**b**			41	**e**	(S)-CH(CH$_3$)Ph	31 [e]
6	**c**			81	**f**	(*S*)-CH(CH$_3$)Ph	63
7	**d**	$-(CH_2)_4-$		52 [b]	**g**	(*S*)-CH(CH$_3$)Ph	55

[a] According to Scheme 1, pathway a, the vinylogous iron formyl complexes were obtained from the corresponding β-bromo vinyl aldehyde or [b] the β-chloro vinyl aldehyde and FpNa. [c] (*Z*)-**2a**:(*E*)-**2a** = 83:17, separation of isomers by flash chromatography. [d] Yield of isolated product after flash chromatography on florisil or [e] silica gel. [f] Yields are not optimized.

To define the scope of the outlined reaction protocol, conversions of the cyclic formyl derivatives **2b–2d** with **4a** were examined (Table 1, entries 5–7). Compounds **2b–2d** are accessible from cyclic β-halogen vinyl aldehydes and FpNa at −78 °C (Scheme 1, pathway a; Table 1) and are isolated as yellow-brown amorphous powders or crystals after chromatography on silica gel (41–81%).[11] Under standard conditions employing $TiCl_4$ and NEt_3, the reactions proceed smoothly to yield the dihydropyrrolones **5e–5g**[11].

In the case of *cis*-configurated **2**, reaction with donor-substituted primary amines **4** in the presence of $TiCl_4$ and NEt_3 should also proceed first via a hemiaminal or aldimine intermediate.[9] As reactive species that activate the carbonyl group, a complex consisting of the primary amine, the tertiary amine, and $TiCl_4$ can be considered.[9c] Apparently, chelating interactions between the titanium species formed, the metal fragment, and the nitrogen functionality of the imine or hemiaminal intermediate dominate the subsequent course of reaction. However, the exact sequence of the individual steps is as yet unknown.

In the case of 18 electron metal carbonyl complexes, carbonylation reactions[3] can be induced by single electron oxidation,[12] and the reaction rate dramatically increases upon addition of Lewis acids.[13] Complexes of metal carbonyl with Lewis acids have been isolated, and the structure elucidated by X-ray analysis.[13a] Due to the electron deficiency at the metal centers, these compounds and intermediates display increased reactivity towards nucleophiles.[2]

In the current case, CO insertion into the alkenyl–metal bond could be catalyzed by titanium. In a subsequent reaction step, intramolecular nucleophilic attack by the donor-substituted nitrogen residue on the iron acyl moiety should facilitate ring closure to form the lactam. On the other hand, titanium-mediated nucleophilic attack by the amine or imine nitrogen on one of the carbonyl ligands is also likely. This would lead to a carbamoyl complex as the reactive intermediate.[2, 14] Both carbonylation pathways should certainly be favored by donor substituents at the nitrogen atom.

The most surprising aspect of the reaction sequence is the formal reduction of the imine moiety. As the reaction cascade proceeds rapidly, no information about possible inter- or intramolecular hydrogen transfer or hydride intermediates could be obtained so far. The hydrogen atom could stem from the condensation reaction or the tertiary amine[15] and is possibly transferred by an iron hydride species[16] to the aldimine carbon.

Elucidation of the reaction mechanism and application of this novel reaction in natural product synthesis are the aims of further investigations. In light of the results presented, *cis*-configurated vinylogous iron acyl complexes may be useful tools for the synthesis of various γ-lactams, including biologically active 5-substituted 2,5-dihydro-2*H*-pyrrol-2-ones such as microcolin A.[17]

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[10] Compound (*Z*)-**2a** does react with **4a** in the presence of $MgSO_4$ in diethyl ether to yield the aldimine. IR spectroscopic monitoring of the reaction reveals that **5a** forms, but nonreproducibly as a by-product in low yield (0–15%). The addition of $TiCl_4$ and Et_3N to crude aldimine in CH_2Cl_2 gives **5a**, but turnover and yield proved to be low (0–30%) and nonreproduciable relative to the one-pot procedure described here.
[11] Satisfactory spectroscopic data and mass spectra or elemental analyses were obtained for all new compounds. Selected spectroscopic data are given for **2c** and **5f**. **2c**: IR (CH_2Cl_2): $\tilde{\nu}$ = 2028 (C≡O), 1977 (C≡O), 1634 cm^{-1} (CHO); ^1H NMR (200 MHz, [D$_6$]DMSO): δ = 9.92 (s, 1H, CHO), 5.42 (s, 5H, C_5H_5), 4.78 (br. s, 1H, OCH_2), 4.27 (br. s, 1H, OCH_2); ^{13}C NMR (50.3 MHz, [D$_6$]DMSO): δ = 215.1, 194.0, 177.0, 152.8, 144.1, 135.5, 135.4, 130.3, 121.2, 115.4, 87.5, 64.4. **5f**: IR (CH_2Cl_2): $\tilde{\nu}$ = 1684 cm^{-1} (C=O); ^1H NMR (200 MHz, $CDCl_3$): δ = 5.65–5.60 (q, *J* = 7.0 Hz, 1H, $CH(CH_3)$), 5.04 (s, 2H, OCH_2), 3.93–3.83 (d, *J* = 19.9 Hz, 1H, NCH_2), 3.59–3.49 (d, *J* = 19.9 Hz, 1H, NCH_2), 1.64–1.60 (d, *J* = 7.0 Hz, 3H, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 167.6, 152.5, 141.9, 140.8, 129.7, 128.6, 127.5, 126.9, 126.2, 123.9, 121.7, 117.2, 115.6, 65.0 (OCH_2), 49.0 ($CH(CH_3)$), 45.6 (NCH_2), 17.5.
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Supramolecular Assemblies Containing Nucleic Bases and Magnesium(II) Hexahydrate Ions**

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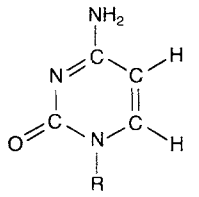
The interaction of metal ions with nucleic acids has been a subject of study for many years.[1] Much effort has been devoted, in particular, to the determination of the coordinating site of the nucleic acids and the explanation of the stabilization (Ca^{II}, Mg^{II}, Mn^{II}) or destabilization (Cu^{II}, Cd^{II}, Pt^{II}, Hg^{II}) induced on DNA by metal ions.[1] The large number of studies on metal–nucleobase complexes in solution[2] contrasts with the lack of studies of these complexes in the solid-state. With regard to cytosine (cyt) and its derivatives such as 1-methylcytosine (1-Mecyt), only nine solid-state structures of compounds with transition metals of the first row, such as Cu^{II}[3], Co^{II}[4], Ni^{II},[5] and Mn^{II}[6], are known to date. Among these, the Ni^{II} and Mn^{II} compounds are particularly interesting, because they are the only ones in which the base is coordinated to the metal ion only through its oxygen atom. Conversely, copper and cobalt are coordinated to the nitrogen atom N(3); the bond to the O(2) atom is only weak.



R = H (cyt), CH_3 (1-Mecyt)

As part of a systematic study of the unusual coordination modes of cytosine and its derivatives towards transition metal and main-group metal ions,[7] we have prepared compounds **1**–**3**.

$[Mg(H_2O)_6(1\text{-Mecyt})_6](ClO_4)_2\cdot(H_2O)$ **1**

$[Mg(1\text{-Mecyt})_2(H_2O)_4](ClO_4)_2\cdot 2(1\text{-Mecyt})$ **2**

$[Mg(cyt)_2(H_2O)_4](ClO_4)_2\cdot 2(cyt)\cdot 2(H_2O)$ **3**

We characterized **1**–**3** by elemental and X-ray structure analyses. As far as we are aware, they are the first isolated cytosine-containing magnesium(II) complexes.

Compound **1** constists of $[Mg(H_2O)_6]^{2+}$ ions, uncoordinated ClO_4^- ions, 1-Mecyt molecules, and water molecules of crystallization. Each magnesium atom in $[Mg(H_2O)_6]^{2+}$ is coordinated to six water molecules in an octahedral environment (Figure 1). The Mg–O distances are in the range 2.027–2.086(4) Å, and are shorter than those found in another previously reported hexaaquamagnesium(II) species.[8] Every $[Mg(H_2O)_6]^{2+}$ ion is linked through ten hydrogen bonds to six 1-Mecyt molecules to form the supramolecular assembly $[Mg(H_2O)_6(1\text{-Mecyt})_6]^{2+}$.[9] Four 1-Mecyt molecules form bridges between the water molecules of the best equatorial plane of the octahedron, through O(3), O(5), O(3a), and O(5a). The last two 1-Mecyt molecules, instead, are linked to the two axial water molecules through single hydrogen bonds, in which only the N(3) nitrogen atom is

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