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Synthesis of Oligo-enynes Using [Fe(alkene)(CO)$_n$] Scaffolds. *Z*/*E*-Selective Wittig- and Horner-type Olefination Reactions of β-Carbonyl Groups in η^4-Diene and γ-Carbonyl Groups in η^2-Alkene Complexes of Iron

Jutta Böhmer and Rainer Schobert*

Institut für Organische Chemie der Universität Erlangen-Nürnberg, Henkestraße 42,
D-91054 Erlangen, Germany

β-Oxo-dienetricarbonyliron complexes **4** and γ-oxo-alkenecarbene complexes **5** undergo olefinations with a wide range of phosphonates and phosphoranes with high *E*- or *Z*-selectivity and give the free oligo-en(yn)es or carbamates, respectively, upon oxidative demetalation.

Natural products with methylene-separated alkatrien(yn)e cores are of considerable pharmaceutical interest. As their bioactivity seems to be linked to specific configurations of the double bonds, any synthetic approach relies on stereoselective olefination steps, like Wittig and Horner reactions. Performing them on complexed ('scaffolded') instead of free (di)enes is an advantage as trien(yn)es having only a part of their π-system protected are amenable to further functionalization of either the coordinated or the unligated π-moiety. Moreover, coordination prevents the whole of the π-system from being shifted.

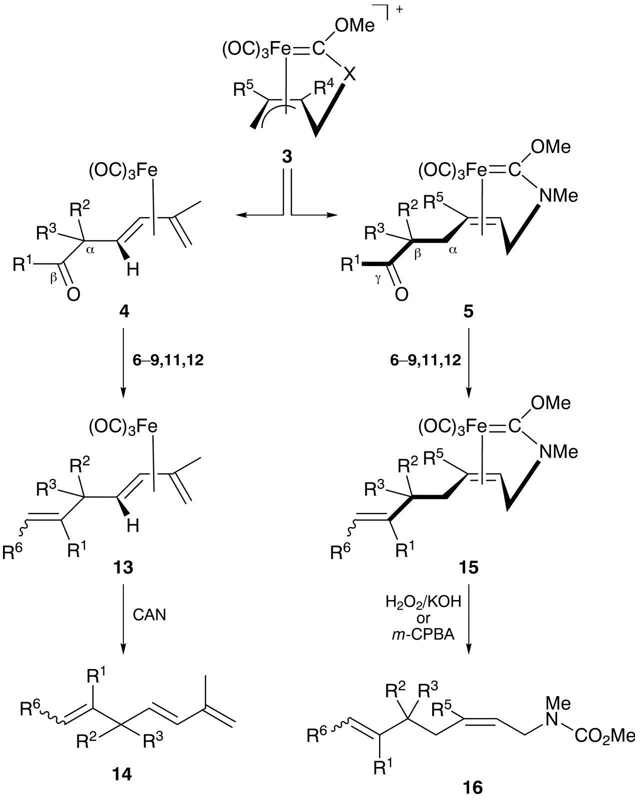
We now report on the ease and selectivity of such olefination reactions between β-oxo-dienetricarbonyliron complexes **4** as well as γ-oxo-alkenecarbene complexes **5**, both available from (η^3-allyl)ironcarbene complexes **3**[11,12] and various phosphonates **6–10** or phosphoranes **11** and **12**. Very little was known in literature about the activating and stereodirective influence of an Fe(CO)$_3$ fragment in combination with two different residues (R^{2,3}) adjacent to the carbonyl carbon. In general, we found no such stereodirective but a small overall deactivating effect. The observed stereoselectivities are high in most cases.

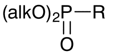
Li- or K-salts of phosphonates **7** and **8** readily react with **4** and **5** to give exclusively the *E*-olefins (**13c**,**d**, **15b**). Olefination with **7** leads directly to unsaturated aldehydes like **13c** which can be olefinated once more to yield **13h** and so forth.

Phosphorane **11** gives exclusively *E*-olefins with complexes **4a** (**13f**) and **5a** (**15d**) in a slow reaction; phosphorane **12** quickly reacts to the *Z*-products **13g** and **15e**. Neither ylide reacts with keto-terminated complexes **4** or **5**!

6/KH reacts with **4a** (R^1 = H) to give a *Z*/*E*-mixture (5:1) of **13a** but with **4b** (R^1 = Me) exclusively the *E*-complex **13b** results. With both pure diastereomers **5d** and **5d′** (R$^{2/3}$ = Ph/Me), the olefins **15a** and **15a′**, respectively, are formed at the same ratio *Z*/*E* = 4:1. In terms of reactivity, there are distinct differences between such diastereomers, though, which is shown by reaction of **11** with a 2:1 diastereomeric mixture of **5c** and **5c′**, to give a 1:1 mixture (55%) of **15d** and **15d′** beside residual and now diastereomerically pure **5c** (28%).

Cyanophosphonate **9** merely gives *Z*/*E*-mixtures (1.5:1) with **4** and **5**. α-Diazophosphonate **10** reacts with **5** to give metallacycles with a terminal acetylene (not shown here). Oxidative demetalation of **13** furnishes the free trien(yn)es **14** and of **15** the carbamates **16** both with unchanged *Z*/*E*- ratios.




$(alkO)_2P(=O){-}R$

	R
6	CH$_2$C≡CTMS
7	HC=CHNH(cyc)
8	CH$_2$COMe
9	CH$_2$CN
10	C(N$_2$)COMe

Ph$_3$P=CHR

	R
6	CO$_2$Me
7	Et

Scheme

Techniques used: ^{1}H and ^{13}C NMR, IR, MS, elemental analysis

References: 28

Tables: 2 (yields, conditions, *Z*/*E* ratios)

Figures: 2

Schemes: 8

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*To receive any correspondence.

Table 1 Iron complexes **13**, **15** by olefination of **4** or **5**

	R^1	R^2	R^3	R^5	R^6	Conditions	Yield (%)	*Z*:*E*
13a	H	Me	Me	–	TMS-CC-	–78 °C/1 h	69	5:1
13b	Me	Me	Me	–	TMS-CC-	–78 °C/1 h	70	only *E*
13c	H	Me	Me	–	CHO	–30 °C/1 h	73	only *E*
13d	H	Me	Me	–	MeCO	25 °C/5 h	61	only *E*
13e	H	Me	Me	–	CN	–78 °C/1 h	55	1.4:1
13f	H	Me	Me	–	CO_2Me	60 °C/11 d	61	only *E*
13f	H	Me	Me	–	CO_2Me	SiO_2/25 °C/30 h	64	only *E*
13g	H	Me	Me	–	Et	–78 °C/10 min	67	only *Z*
13h	H	Me	Me	–	C=CCHO	–30 °C/1 h	63	only *E*
15a	H	Me	Ph	Me	TMS-CC-	–78 °C/1 h	72	4:1
15a′	H	Ph	Me	Me	TMS-CC-	–78 °C/1 h	61	4:1
15b	H	Me	Me	H	CHO	–30 °C/1 h	56	only *E*
15c	H	Me	Me	Me	CN	–78 °C/1 h	68	1.5:1
15d(′)	H	Me /	Ph	H	CO_2Me	SiO_2/25 °C/30 h	55	only *E*
15e	H	Me	Me	H	Et	–78 °C/10 min	54	only *Z*

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