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THE REACTIONS OF FISCHER-TYPE CARBENE COMPLEXES WITH ETHENE

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Summary

The reactions of the anionic carbene complexes $[(CO)_nMCOPh]^-$ (M = Fe, Cr, Mo, W) with ethene are described. The iron and chromium complexes yield predominantly propiophenone, formed by ethene insertion into the M—COPh moiety. For instance, [*cis*-$PPh_3(CO)_4CrCOPh$][$Li \cdot 2Et_2O$] gave 63% yield of propiophenone. At 150°C, a double insertion of ethene, leading to $CH_3CH_2CH(CH_3)COPh$, is observed. At this temperature products incorporating an odd number of carbon atoms, viz.: $CH_3CH_2CH_2COPh$, $CH_3CH(CH_3)COPh$, $CH_3CH_2CH_2CH(CH_3)COPh$ are also formed and have been isolated in up to 15% yield; a metathetic reaction path and ethene insertion are proposed to account for their formation.

Introduction

Since the pioneering work by Fischer and coworkers [1] there has been a prodigious growth in studies of carbene complexes and their reactions. Such complexes have been proposed as mechanistic models for metal-catalyzed organic reactions such as olefin cyclopropanation, Fischer—Tropsch synthesis and olefin metathesis [2,3].

In principle, the transfer of carbene ligands from transition-metal carbene complexes to alkenes with formation of cyclopropanes represents a type of reaction with considerable potential synthetic utility. However, few of the stable, isolable carbene complexes prepared to date show this mode of reactivity [4]. Reactions of carbene complexes leading to linear addition products have also been studied [5—9], knowledge of such reactions could be important for providing a better understanding of metal-catalyzed oligomerization and polymerization of olefins.

During our studies aimed at improving the understanding of oligomerization reactions of ethene, which can proceed by a metal-hydride or metallacyclo-

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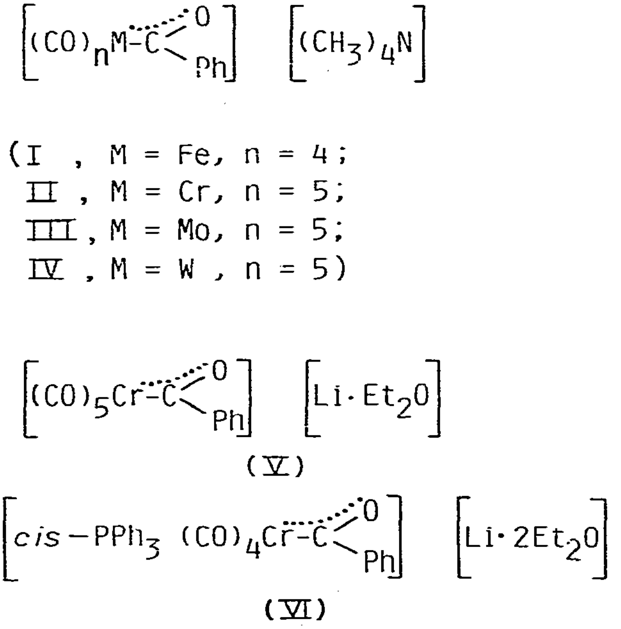
butane mechanism, we became interested in the reaction of carbene complexes with ethene [10].

We report below the results obtained upon treating carbene complexes of Fe, Cr, Mo and W with ethene. These complexes behave as electrophiles at C_α, and differ from the Schrock-type complexes which are nucleophilic [9].

Results and discussion

The complexes listed in Scheme 1 were selected for our investigations and were synthesized by the following route:



(I , M = Fe, n = 4;
II , M = Cr, n = 5;
III , M = Mo, n = 5;
IV , M = W , n = 5)

(V)

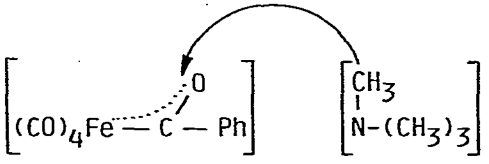
(VI)

SCHEME 1. Carbene complexes used

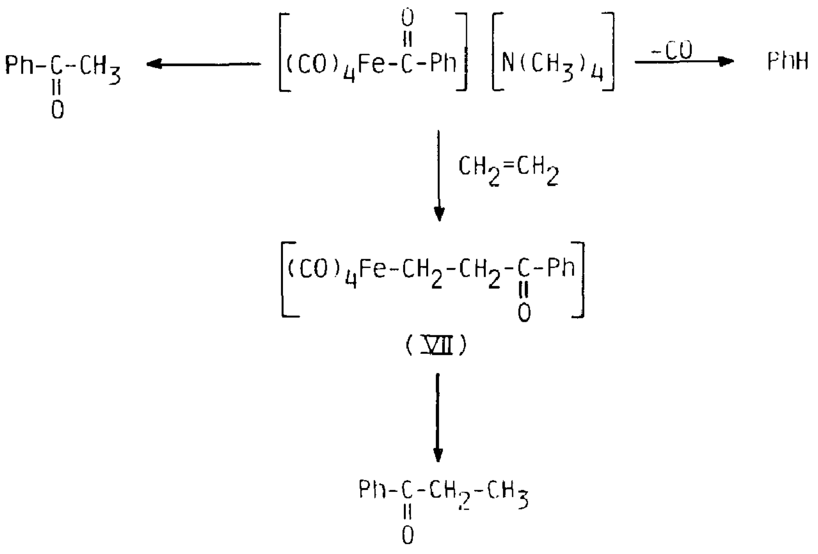
$$LM(CO)_n + RLi \rightarrow [LM(CO)_{n-1}COR]Li$$

When a tetrahydrofuran solution of I is treated with ethene at 30 bar and 125°C, in addition to propiophenone small amounts of benzene and acetophenone are formed (Table 1). All the products can be derived from the Fe—CO—Ph moiety, as depicted in Scheme 2.

Benzene is formed by decarbonylation, while acetophenone is formed by a migration of a methyl group from the cation $[N(CH_3)_4]^+$ of complex I [11,12].



Insertion of ethene into the Fe—C bond leads to propiophenone. A complex such as VII is a likely intermediate. The reaction of II to IV with ethene at



SCHEME 2. Formation of propiophenone.

similar conditions also leads to the formation of propiophenone (Table 1), however, the chromium complex II gives better results than the molybdenum (III) and tungsten (IV) analogues. The latter yield mainly benzophenone in addition to benzene.

Results similar to those outlined for complex II in Table 1 were obtained with complex V. Interestingly, when complex V reacted with ethene at 150°C, along with propiophenone the formation of sizable amounts (yields of up to 15%) of $CH_3CH_2CH_2COPh$, $CH_3CH(CH_3)COPh$, $CH_3CH_2CH(CH_3)COPh$ and $CH_3CH_2CH_2CH(CH_3)COPh$ were observed. The formation of $CH_3CH_2CH(CH_3)$-COPh can be understood in terms of a second ethene insertion, as in Scheme 3.

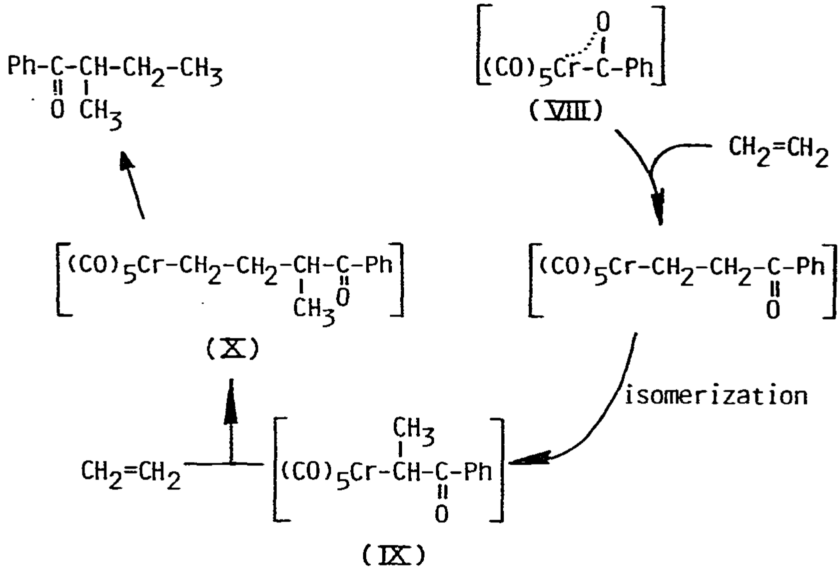
To account for the formation of $CH_3CH_2CH_2COPh$, $CH_3CH(CH_3)COPh$ and for $CH_3CH_2CH_2CH(CH_3)COPh$ a metathetic reaction path involving $(CO)_5Cr=CH_2$ as an intermediate is proposed [13]. Reaction of $(CO)_5Cr=CH_2$ with VIII, IX and X could lead to the observed products in which an odd number carbon atoms has been incorporated.

TABLE 1

REACTION OF CARBENE COMPLEXES WITH ETHENE [a]

	Selectivity (%)			
	I	II	III	IV
Propiophenone	74.2	78.9	1.9	2.1
Acetophenone	1.0	0.1	—	1.8
Benzene	8.3	1.9	45.8	45.5
Benzophenone	—	1.3	10.1	42.1
Conversion %	31.1	45.5	23.5	44.7

[a] Reaction conditions: 2 mmol complex; 20 ml tetrahydrofuran; 30 bar of ethene (cold); 125°C; 16 h.



SCHEME 3

In an attempt to increase the yield of propiophenone complex VI (Scheme 1) was synthesized by a procedure described by Fischer et al. [14]; treatment of VI with 20 bar of ethene increased the yield of propiophenone to 63%, and furthermore the temperature could be lowered to 75°C. All experiments to alter the product distribution by varying the pressure of ethene failed. Best results were always obtained at pressures between 20 and 30 bar of ethene.

All attempts to isolate intermediate complexes were unsuccessful. The reaction can be monitored by the colour change from yellow to red. The solutions seem quite stable.

The formation of propiophenone and of $CH_3CH_2CH_2COPh$, $CH_3CH(CH_3)COPh$, $CH_3CH_2CH(CH_3)COPh$ and $CH_3CH_2CH_2CH(CH_3)COPh$ requires an additional source of hydrogen. It would be plausible to assume that the hydrogen comes from the solvent tetrahydrofuran; because of the costs we have not used deuterated tetrahydrofuran, but in experiments with benzene-d_6 no deuterium was incorporated into the propiophenone. We assume, that the additional hydrogen comes from ethene, as is known to be possible [15], and experiments with C_2D_4 may be carried out.

Experimental

All reactions were carried out under argon with exclusion of air and moisture. ^1H NMR spectra were recorded on a Varian EM-390 instrument using TMS as an internal standard. IR spectra were recorded on a Perkin—Elmer 577 spectrometer with tetrahydrofuran as solvent. Elemental analyses were performed by Mikroanalytisches Laboratorium Dr. F. Pascher and E. Pascher in Bonn (D-5300 Bonn 1). $PPh_3(CO)_5Cr$ was prepared by treating $Cr(CO)_6$ with PPh_3 [16]. The complexes $[(CO)_nMCOPh][N(CH_3)_4]$ (M = Cr, Mo, W, $n = 5$; M = Fe, $n = 4$) and

$[(CO)_5CrCOPh][Li \cdot Et_2O]$ were synthesized as described by Fischer et al. [17].

[*cis*-$PPh_3(CO)_4CrCOPh][Li \cdot 2Et_2O]$ was synthesized as described by Fischer [17]: to 2.3 g (5 mmol) of $PPh_3(CO)_5Cr$ in 200 ml ether cooled to 0°C 2.5 ml of 2 molar solution of phenyllithium in ether/benzene (3/1) was added dropwise. After stirring for 1 h the mixture was filtered. The orange-yellow residue was washed with ether and dried (yield 2.4 g, 70%); m.p. 85—87°C (dec.). (Found: C, 62.88; H, 5.56; P, 4.65; Cr, 7.40. $C_{37}H_{40}O_7PCrLi$ calcd.: C, 64.75; H, 5.83; O, 4.51; Cr, 7.58%). IR-spectra: 2020m; 1930m; 1892vs; 1850s; 1118s cm^{-1}. ^1H-NMR-spectra (acetone-d_6): δ 1.07 t (12 H), 3.35 q (8 H), 7.23 ppm m (20 H).

The reactions with ethene were carried out in a 70 ml stainless steel autoclave built in our institute [18]. The autoclave was evacuated and filled with argon. A solution of the complex (about 2 mmol) in 20 ml of tetrahydrofurane was admitted to the autoclave by conventional inert gas techniques and pressurized with ethene (20—30 bar). The magnetically stirred autoclave was heated to the appropriate temperature. After 16 h of reaction the autoclave was opened and the contents worked up as follows: the tetrahydrofuran was removed in vacuum, and the products were distilled off under high vaccum. The distillate was analysed by GLC (a 50 m WG 11 capillary column was used), the products being identified by comparison of their spectra with those of authentic samples and by GC/MS examination.

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