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REACTIONS OF DICARBONYL(η^5-CYCLOPENTADIENYL)(η'-ALLYL)IRON COMPLEXES WITH ELECTRON DEFICIENT OLEFINS AND ACETYLENES

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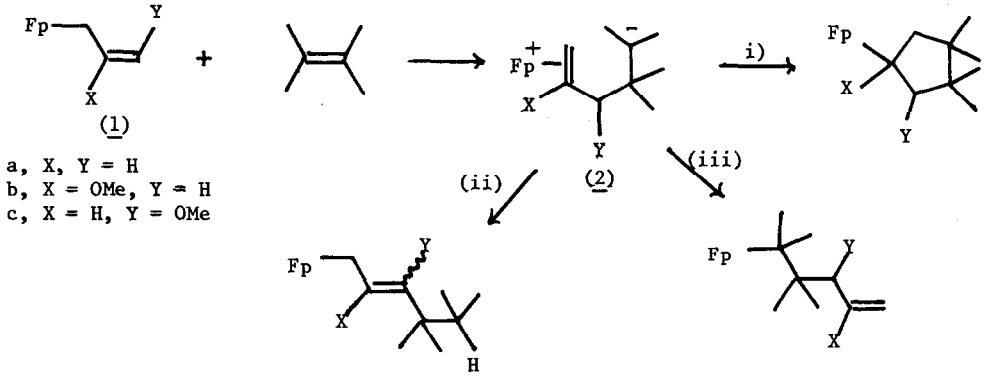
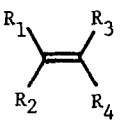
The metal assisted reaction of dicarbonyl(η^5-cyclopentadienyl)(η'-allyl)iron complexes (1) (hereafter denoted as (η'-allyl)Fp complexes) with electron deficient olefins is thought to proceed via the dipolar intermediate (2)[1-3]. Further reaction of this intermediate may follow several routes, i) intramolecular cyclisation[4], ii) H-transfer[4], and iii) insertion. The latter two processes give linear products (Scheme 1).



SCHEME 1

Our investigations of these processes led us to prepare the electron rich (η'-2-methoxyallyl)Fp complex (1b)[6,7]. The expectation was that such a system would enter into reaction with moderately electron deficient olefins such as (3) and also acetylenes (e.g. dimethyl acetylenedicarboxylate or methyl propiolate). These results together with those obtained for the simple (η'-allyl)Fp complex (1a)[8] and (η'-3-methoxyallyl)Fp complex (1c)[9] are the subject of this communication.

In a typical reaction the appropriate (η'-allyl)Fp complex was generated from the corresponding (η^2-olefin)Fp tetrafluoroborate salt on treatment with base and then reacted with an excess of the olefin or acetylene; all operations were performed in an inert atmosphere. The choice of solvent is critical since this governs the rate of reaction and in some instances product composition. In general, if no reaction was observed in dimethylformamide then no other solvent would promote reaction. Products were isolated by removal of solvent under reduced pressure followed by column chromatography using neutral alumina (Act III). The results are summarised in Table 1.



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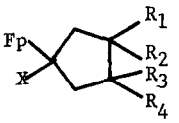

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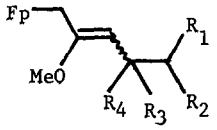

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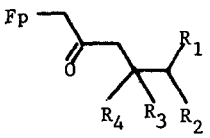


(6)

	R_1	R_2	R_3	R_4
a,	CO_2Me	CO_2Me	H	H
b,	CO_2Et	CO_2Et	H	H
c,	CO_2Me	CO_2Me	CO_2Me	H
d,	CO_2Me	CO_2Me	CO_2Me	CO_2Me
e,	CN	CN	CO_2Et	H

TABLE 1

(η'-allyl)Fp Complex	Olefin	Solvent	Reaction time (hr)	Yield† (%)	Products (%) (4)	(5)	(6)
1a	3b	DMF	24	63	100	-	-
		CH_2Cl_2	22	70	100	-	-
		THF	20	28	100	-	-
	3c	DMF	70	80	100	-	-
	3e	CH_2Cl_2	1	67	100*	-	-
1b	3a or 3b	DMF or Benzene	2	-	-	Polymer	-
	3c	DMF	2	49§	22	47	31
		CH_2Cl_2	8	56§	41	50	9
		THF	8	53§	6	79	15
		Benzene	8	61	13	82	5
	3d	DMF	48	39#	-	-	100
		THF	92	14#	-	-	100
	3e	i) DMF ii) CH_2Cl_2	i) 3 ii) 20	58φ	100*	-	-
1c	3b	DMF	92	5	100	-	-
	3c	DMF	66	4	100	-	-
	3e	CH_2Cl_2	1	85	100*	-	-

DMF = Dimethylformamide THF = Tetrahydrofuran

†Isolated yields from reactions performed at room temperature.

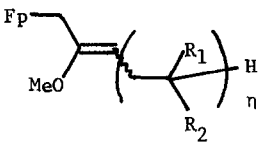
§Yields averaged over three reactions.

#Crude product treated with aqueous THF plus p-toluene sulphonic acid before chromatography.

φProduct decomposed during chromatography (unstable on Al_2O_3, SiO_2 and Florisil) NMR of crude product indicated quantitative conversion to 4e.

*Mixture of stereoisomers produced.

The H-transfer products (5) are susceptible to hydrolysis and indeed this occurs to a large extent during chromatography of the crude reaction mixture thereby giving substantial quantities of the ketones (6). Hydrolysis can be further induced by treatment with p-toluene sulphonic acid in aqueous tetrahydrofuran. The reaction of (1b) with (3a, b) gave the polymeric species (7) which could by hydrolysed to (8). Similar base catalysed polymerisation of these olefins have been reported[10].



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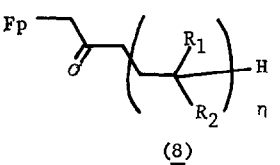


(8)

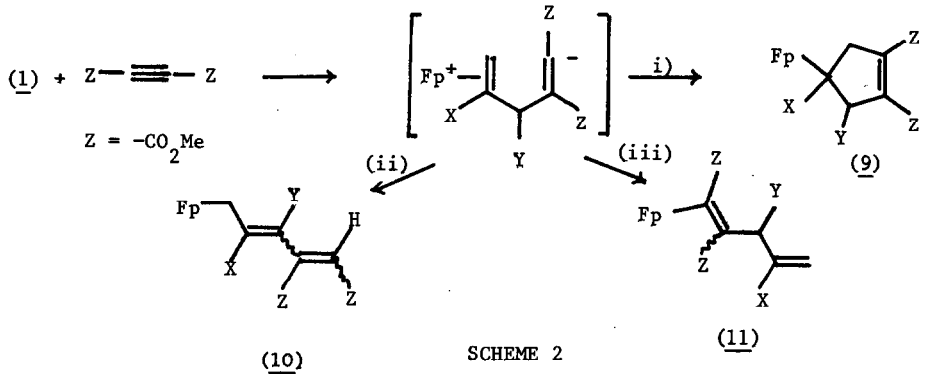
η = 1,2 etc..

From the results obtained it is apparent that the (η'-2-methoxyallyl)Fp complex (1b) is considerably more reactive than both (1a) and (η'-3-methoxyallyl)Fp (1c), i.e. the latter two complexes fail to react with (3d). Furthermore, whereas the C-2 methoxyl group tends to promote reaction, C-3 substitution retards reaction and generally gives lower yields than the unsubstituted allyl. It is also clear that the C-2 methoxyl group leads to the formation of considerable quantities of linear products. This may be explained by the increased stability of intermediate (2) for which processes other than ring closure may then become important. Ring closure is additionally disfavoured on steric grounds since this results in metal-quaternary carbon bond formation. It is interesting that for complex (1c) the C-3 methoxyl substitution entirely eliminates the H-transfer process so giving greater specificity for reactions of this compound. This is further highlighted by the reaction of dimethyl acetylenedicarboxylate (DMAD) with these complexes. Possible reaction pathways are outlined in Scheme 2 and the results are summarised in Table 2.

TABLE 2

(η'-allyl)Fp Complex	Molar Equiv. of DMAD	Solvent	Reaction time (hr)	Yield (%)*	Product (%) (9)	(10)	(11)
1a	2	DMF	91	54	78	5	17
1b	2	DMF	3	70	-	100	-
	1	CH_2Cl_2	24	55	-	100	-
	1	THF	24	24	-	100	-
1c	5	DMF	67	77	100	-	-
	10	CH_2Cl_2	92	51	100	-	-

*Isolated Yields



SCHEME 2

For complex (1b) the H-transfer route (II) is preferred and good yields of the linear adduct were isolated reproducibly. The unsubstituted allyl (1a) gives all possible products. Yields are low, however, since the reaction, which is slow even in DMF, is accompanied by a large degree of decomposition. In contrast, the 3-methoxyl substituted complex (1c) gives exclusively the cyclic product in excellent yield as H-transfer is entirely eliminated by this substitution pattern.

The reaction of methyl propiolate with these complexes (1a - c) gave mixtures of products which, so far, have not been separated since all attempts at isolation resulted in decomposition.

Since the Fp moiety of the cycloaddition products (4) can be easily replaced by a methoxyl or ester group,[2,6] these reactions provide a valuable synthetic method to substituted cyclopentanoid derivatives.

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