

Preliminary communication

DISUBSTITUTED VINYLIDENE COMPLEXES OF IRON AND RUTHENIUM: NUCLEOPHILIC PROPERTIES OF η^1 -ACETYLIDE LIGANDS

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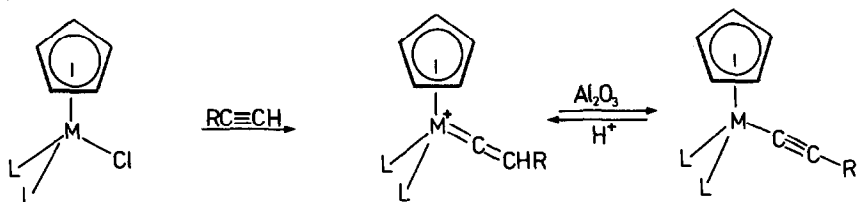
Summary

The η^1 -acetylide complexes $(C_5H_5)ML_2(C\equiv CR)$ ($M = Fe, Ru$; $L = PPh_3$, $L_2 = Ph_2PCH_2CH_2PPh_2$) are nucleophilic at the β -carbon and react with a variety of mild electrophiles to yield the corresponding disubstituted vinylidene complexes $[(C_5H_5)ML_2(=C=CRR')]PF_6$.

Recently several methods have been described for the synthesis of transition metal acetylides and the corresponding monosubstituted vinylidene complexes [1,2,3]. The conversion of terminal acetylenes into such complexes by interaction with chloro-transition metal complexes under mild conditions is particularly attractive with respect to developing useful methods and reagents for organic synthesis. We describe here the nucleophilic properties of some acetylide ligands bonded to iron and ruthenium and demonstrate the formation of a variety of disubstituted vinylidene complexes under mild conditions.

We have previously reported that treatment of $(C_5H_5)Ru(Ph_2PCH_2CH_2PPh_2)Cl$ (1) with terminal acetylenes in methanol containing ammonium hexafluorophosphate efficiently generates the monosubstituted vinylidene complexes 2 [1]. Deprotonation of these monosubstituted vinylidene complexes 2 by filtration through basic alumina yields the η^1 -acetylide complexes 3. This reactivity appears to be general, providing an efficient route to ruthenium and iron monosubstituted vinylidene and acetylide complexes (Scheme 1). Bruce et al. have reported some similar reactivities of ruthenium complexes [2].

Monosubstituted vinylidene complexes are thus readily obtainable either directly from the acetylenes or by reprotonation of the acetylides. Treatment of $(C_5H_5)Fe(Ph_2PCH_2CH_2PPh_2)Cl$ in methanol in the presence of ammonium hexafluorophosphate with acetylene or trimethylsilylacetylene generates the parent vinylidene complex 10 (81% and 69%, respectively). Under similar conditions 4



1, $L_2 = Ph_2PCH_2CH_2PPh_2$, $M = Ru$;

4, $L = Ph_3P$, $M = Ru$;

7, $L_2 = Ph_2PCH_2CH_2PPh_2$, $M = Fe$

2, $R = nBu$, Ph ;

5, $R = Me$, Et , nBu , Ph ;

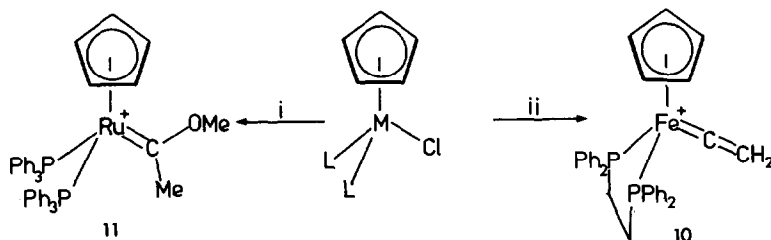
8, $R = Ph$

3

6

9

SCHEME 1. Preparation of monosubstituted vinylidene and acetylide complexes.



SCHEME 2. (i) $M = Ru$, $L = Ph_3P$; $HC\equiv CH$ or $HC\equiv CSiMe_3$ (73%); (ii) $M = Fe$, $L_2 = Ph_2PCH_2CH_2PPh_2$; $HC\equiv CH$ or $HC\equiv CSiMe_3$ (69–81%).

gave the methoxycarbene complex 11 presumably via addition of methanol to the intermediate vinylidene 5 ($R = H$) (Scheme 2).

TABLE 1
PREPARATION OF DISUBSTITUTED VINYLIDENE COMPLEXES

M	R	R'X	$M^+=C=CRR'$	Yield ^a
$(C_5H_5)_2Ru(Ph_2PCH_2CH_2PPh_2)$	nBu	MeI	$M^+=C=C(Me)Bu^n$	83
	Ph	MeI	$M^+=C=C(Ph)Me$	85
	Ph	EtI	$M^+=C=C(Ph)Et$	70
	Ph	$PhCH_2Br$	$M^+=C=C(Ph)(CH_2Ph)$	76
$(C_5H_5)_2Ru(PPh_3)_2$	Me	MeI	$M^+=C=CMe_2$	85
	Me	EtI	$M^+=C=C(Me)Et$	62
	Me	$PhCH_2Br$	$M^+=C=C(Me)CH_2Ph$	87
	Et	MeI	$M^+=C=C(Me)Et$	76
	Et	EtI	$M^+=C=CEt_2$	84
	Et	$PhCH_2Br$	$M^+=C=C(Et)CH_2Ph$	92
	nBu	MeI	$M^+=C=C(Me)Bu^h$	91
	nBu	EtI	$M^+=C=C(Et)Bu^n$	67
	nBu	$PhCH_2Br$	$M^+=C=C(Bu^n)CH_2Ph$	75
	Ph	MeI	$M^+=C=C(Me)Ph$	87
	Ph	EtI	$M^+=C=C(Et)Ph$	72
	Ph	$PhCH_2Br$	$M^+=C=C(Ph)CH_2Ph$	67
$(C_5H_5)_2Fe(Ph_2PCH_2CH_2PPh_2)$	Ph	MeI	$M^+=C=C(Me)Ph$	62
	Ph	EtI	$M^+=C=C(Et)Ph$	70
	Ph	$PhCH_2Br$	$M^+=C=C(Ph)CH_2Ph$	87

^a Yields given are for the hexafluorophosphate salts formed by anion exchange and refer to analytically pure material.

Intramolecular alkylation may also be achieved to give cyclic vinylidene complexes. Treatment of the chlororuthenium complexes **1** or **4** with 6-chlorohex-1-yne yields the protiovinylidene complex **13**. After deprotonation **13** produces the acetylide **14** which slowly cyclises to vinylidene **15** (Scheme 3).

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References

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