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A stereochemical study of the reaction between tricarbonyl(vinylketene)iron(0) complexes and alkynes

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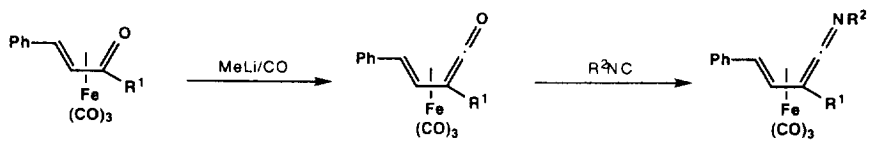
Abstract: The formation of 1:1 adducts between tricarbonyl(vinylketene)iron(0) complexes and alkynes, and their subsequent conversion into tricarbonyl(cyclohexadienone)iron(0) complexes occur with complete retention of planar chirality.

Defining and controlling the stereochemical outcome of chemical reactions is currently of interest to a wide range of researchers. To date attention has focused mainly on reactions of organic compounds, and this has led to a sophisticated level of understanding and control of such processes. In contrast, stereochemical studies of organometallic reactions, particularly those in which both the metal centre and its ligands play a significant role, are still relatively rare.[1]

Our interest in the chemistry of tricarbonyl(vinylketene)iron(0) complexes **1** has led us to probe the stereochemical outcome of the organometallic processes involved both in their synthesis and in their subsequent reactions with fundamental classes of molecules. After devising an effective route to highly enantiomerically enriched samples of tricarbonyl(vinylketene)iron(0) complexes **1**,[2] we have discovered to date that a) the methyllithium/carbon monoxide mediated synthesis of vinylketene complexes **1** from tricarbonyl(vinylketone)iron(0) complexes **2**,[3] and b) the isonitrile promoted conversion of vinylketene complexes **1** to tricarbonyl(vinylketenimine)iron(0) complexes **3**,[4] proceed with complete retention of planar chirality, findings which have provided us with significant mechanistic insight into these reactions.



2 **1** **3**

Tricarbonyl(vinylketene)iron(0) complexes **1** react with electron-deficient alkynes such as dimethyl acetylenedicarboxylate to give 1:1 adducts **4** which are relatively stable to further manipulation. In contrast, reaction of complexes **1** with electron-rich alkynes such as ethyl ethynyl ether gives 1:1 adducts **5** which on thermolysis give phenols **6**.[5] As the formation of adducts **4** and **5** may proceed by a mechanistic pathway quite different to those followed in the synthesis of **1** from **2** and the conversion of **1** to **3**, we were interested to discover whether the formation of these adducts proceeded with inversion, retention or racemisation of planar chirality. The results of our stereochemical study and our subsequent discovery that adducts **5** may be converted into tricarbonyl(cyclohexadienone)iron(0) complexes are described herein.

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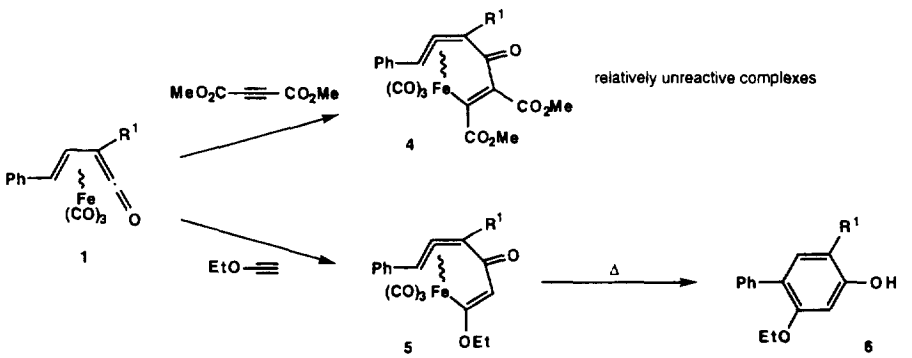
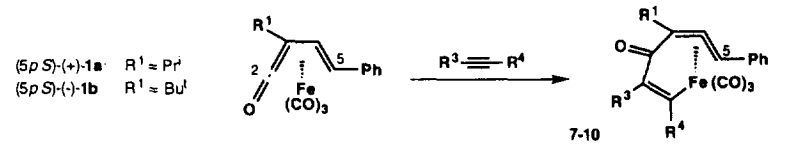
Table 1. Reaction of vinylketene complexes **1** with alkynes to give adducts **7–10**

entry	substrate	R^1	e.e. (%)	*pR/pS*	R^3	R^4	product	yield (%)	e.e. (%)	$[\alpha]_D$[a]	*pR/pS*
1	**1a**	Pr^i	95±1[b]	5*pS*	H	CO_2Me	**7**	70	97±1[b]	+544±20	5*pS*
2	**1a**	Pr^i	98±1[b]	5*pS*	CO_2Me	CO_2Me	**8**	52	99±1[b]	+586±20	5*pS*
3	**1a**	Pr^i	95±1[b]	5*pS*	H	OEt	**9**	57	95±2[c]	+509±15	5*pS*
4	**1b**	Bu^t	95±1[b]	5*pS*	H	OEt	**10**	57	93±2[c]	+405±20	5*pS*

[a] All values measured in CH_2Cl_2 in the temperature range 24-28 °C and in the concentration range 0.5-1.65; [b] Measured by HPLC (Chiralcel OD-H); [c] Measured by ^1H NMR spectroscopy in the presence of (*R*)-(-)-1-(9-anthryl)-2,2,2-trifluoroethanol.



Samples of enantiomerically enriched tricarbonyl(vinylketene)iron(0) complexes (5*pS*)[6]-(+)-**1a** (R^1=Pr^i) and (5*pS*)-(+)-**1b** (R^1=Bu^t) were prepared by reacting racemic **1a** and **1b** with 0.5 equiv. of deprotonated (*S*)-α-methylbenzyl diethylphosphoramidate.[2] In an initial experiment, (5*pS*)-(+)-**1a** of 95±1% e.e. was reacted with 2 equiv. of methyl propiolate at 72°C for 2 h. Work-up gave adduct **7**[5] in 70% yield as a yellow oil, the e.e. of which was found to be 97±1% by HPLC analysis (Table 1, Entry 1). Thus the conversion of the vinylketene complex **1a** to its methyl propiolate adduct **7** had evidently proceeded without loss of stereochemical integrity, indicating that its reaction co-ordinate does not pass through a symmetrical species.



In order to determine whether or not altering the electronic and steric properties of the alkyne affected the mechanism and hence the transfer of stereochemical information in the reaction, (5*pS*)-(+)-**1a** was reacted with dimethyl acetylenedicarboxylate and ethyl ethynyl ether. These reactions each gave yellow crystalline products **8**[5] and **9**[5] of enantiomeric purity essentially equivalent to that of the substrate (Table 1, Entries 2 and 3) indicating that the mechanistic pathway in all the cases examined is probably identical. Finally, in order to test the effect of increasing the steric demands of the vinylketene substituent R^1, the vinylketene complex (5*pS*)-(+)-**1b** was reacted with ethyl ethynyl ether. Once again the e.e. of the product from this reaction was found to be essentially the same as that of the substrate (Table 1, Entry 4). Moreover, X-ray crystallography[7] of the novel adduct **10**[8] revealed that its absolute configuration was (5*pS*). Subsequent comparison of the CD spectra of complexes **7–10** revealed that they all had the same absolute stereochemistry thereby demonstrating that the insertion of alkynes of differing steric and electronic properties into the iron/carbon-2 bond of vinylketene complexes proceeds with overall retention of planar chirality.

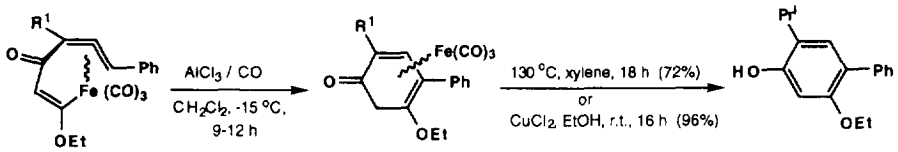
At this point, racemic samples of complexes **7–10** were subjected to a range of new reaction

Table 2. Conversion of alkyne adducts to cyclohexadienone complexes

entry	substrate	R^1	e.e. (%)	*pR/pS*	product	yield (%)	e.e. (%)	$[\alpha]_D^a$	*pR/pS*
1	(+)-**9**	Pr^i	95±2[b]	5*pS*	**11**	68	95±1[c]	-164±10	4*pS*
2	(+)-**10**	Bu^t	93±2[b]	5*pS*	**12**	22	94±1[c]	-94±10	4*pS*

[a] Values measured in CH_2Cl_2 at 25 °C in the concentration range 0.8-1.3; [b] Measured by ^1H NMR spectroscopy in the presence of (*R*)-(-)-1-(9-anthryl)-2,2,2-trifluoroethanol; [c] Measured by HPLC (Chiralcel OD-H).

conditions in order to probe their chemistry further. Whilst complexes **7** and **8** remained obstinately unreactive, complex **9** was found to react relatively cleanly in the presence of aluminium trichloride under an atmosphere of carbon monoxide to give a low melting point yellow solid which was identified by X-ray crystallography[7] as the novel cyclohexadienone complex **11**. Complex **10** also reacted under these conditions to give the analogous novel complex **12**. (The cyclohexadienone complex **11** was subsequently converted to the corresponding phenol **13**[5] both by thermolysis and copper(II) promoted oxidation.)



9 $R^1 = Pr^i$ **11** $R^1 = Pr^i$ 46%
10 $R^1 = Bu^t$ **12** $R^1 = Bu^t$ 61%

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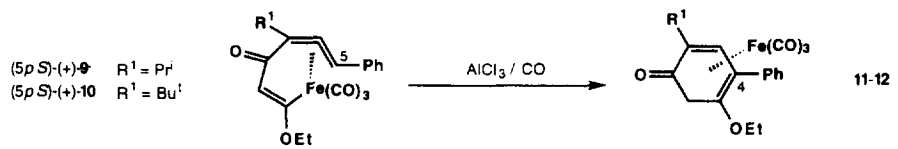
In order to probe the stereochemical outcome of the conversion of the alkyne adducts **9** and **10** to the cyclohexadienone complexes **11** and **12**, an enantiomerically enriched sample of complex **9** was used as the reaction substrate. Reaction of alkyne adduct (5*pS*)-(+)-**9** of 95±2% e.e. with aluminium trichloride under an atmosphere of carbon monoxide gave cyclohexadienone complex **11** which, on HPLC analysis, was found to have an e.e. of 95±1% (Table 2, Entry 1). Similarly a sample of enantiomerically enriched alkyne adduct (5*pS*)-(+)-**10** of 93±2% e.e. gave the product cyclohexadienone complex **12** in 94±1% e.e. (Table 2, Entry 2). Thus the conversion of the alkyne adducts of tricarbonyl(vinylketene)iron(0) complexes to tricarbonyl(cyclohexadienone)iron(0) complexes proceeds without loss of stereochemical integrity.

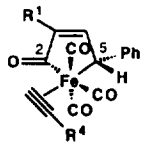


11-12

Attempts to determine the absolute configuration of the tricarbonyl(cyclohexadienone)iron(0) complexes (−)-**11** and (−)-**12** were initially thwarted by difficulties encountered in growing suitable crystals for X-ray crystallography. Their absolute configuration was ultimately defined as 4*pS*, however, by comparison of their CD spectra with those of tricarbonyl(cyclohexadienone)iron(0) complexes of established absolute configuration.[9] Thus the conversion of tricarbonyl(vinylketene)iron(0)–alkyne adducts to tricarbonyl(cyclohexadienone)–iron(0) complexes proceeds with retention of planar chirality.

Our finding that the insertion of alkynes into tricarbonyl(vinylketene)iron(0) complexes occurs with retention of configuration together with the mechanistic insight provided by our previous study of the conversion of tricarbonyl(vinylketene)iron(0) complexes into tricarbonyl(vinylketenimine)iron(0) complexes,[4] leads us to propose that complex **13**, in which stereochemical information is preserved at C-5, is a key intermediate in the alkyne insertion reaction. Subsequent alkyne insertion into the iron/C-2 bond and recoordination of carbons 3 and 4 provide the product adduct. Finally, conversion of the

vinylketene–alkyne adducts to cyclohexadienone complexes with retention of planar chirality reveals that the metal centre remains tightly bound to one face of the organic ligand during the formation of the cyclohexadienone.



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Acknowledgements

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References

1. Of note, in this context, is a recent study in which the insertion of dimethyl acetylenedicarboxylate into the palladium–carbon bond of a partially enantiomerically enriched cyclopalladated 8-ethylisoquinoline derivative was shown to give a product of essentially the same enantiomeric enrichment. This led the authors to the conclusion that the alkyne insertion is concerted, although whether it occurs with inversion or retention of stereochemistry at the palladium-bound carbon of the substrate has yet to be established; J. Spencer and M. Pfeffer, *Tetrahedron: Asymmetry*, 1995, **6**, 419.
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6. Application of the Cahn–Ingold–Prelog convention for π complexes to the iron-bound carbon bearing the phenyl group leads to the *pS* designation; R. S. Cahn, C. Ingold and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 385.
7. Details of this analysis will be published in the full account of this study.
8. The novel complexes **10–12** gave satisfactory spectroscopic (IR, ^{1}H NMR, ^{13}C NMR and low-resolution MS) and microanalytical or high-resolution MS data.
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