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EFFECTS OF LIGAND ENVIRONMENT ON NUCLEOPHILE ADDITION TO CYCLOHEXADIENYLIRON CATIONS.[1]

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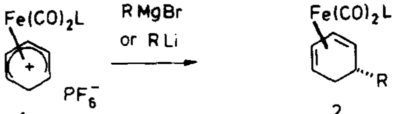
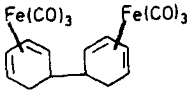
Abstract: Cyclohexadienyl-$Fe(CO)_2PPh_3$ complexes show considerably better control than the $Fe(CO)_3$ analogs during reaction with carbon nucleophiles; a broader range of stereocontrolled double nucleophile addition is accessible using the phosphine complex.

Cyclohexadienyliron complexes are promising intermediates for organic synthesis,[2] but the usual $Fe(CO)_3$ complexes such as 1a show some limitations as to the type of nucleophiles which may be employed for carbon-carbon bond formation. In this communication we illustrate some of the major problems associated with the $Fe(CO)_3$ derivatives and how these may be overcome by the simple expedient of altering the ligand environment of the metal.



1
(a) L = CO
(b) L = PPh_3

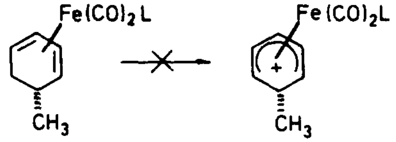
2
(a) L = CO, R = $CH=CH_2$
(b) L = PPh_3, R = $CH=CH_2$
(c) L = PPh_3, R = Me
(d) L = CO, R = Me



3

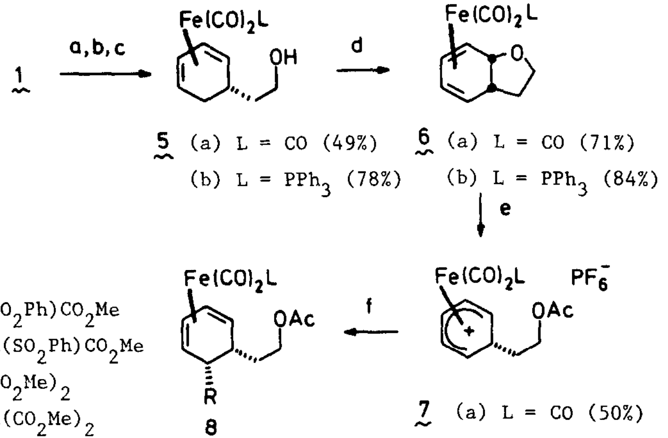
Direct alkylation of 1a using Grignard reagents has proven troublesome. This has been partly overcome by using organo-zinc and cadmium reagents[3], organocuprates[4] and alkyllithium reagents in dichloromethane,[5] but vinyl addition is particularly difficult.[3] In our hands, reaction of vinylmagnesium bromide with 1a (CH_2Cl_2, -78°C) gave the dimer 3 as the major product, only traces of the desired complex 2a being observed.[6] Thus, the major pathway is electron transfer. The triphenylphosphine complex 1b is readily prepared[7], and treatment with vinylmagnesium bromide (CH_2Cl_2, -78°C) gave the adduct 2b as the *sole product* in 98% yield. Similarly, reaction of 1b with methyllithium (CH_2Cl_2, -78°C) gave much higher yield (2c: 98%) than the corresponding methylation of 1a (2d: 45-50% in our hands).

Reconversion of substituted cyclohexadiene complexes to dienyl salts, followed by a second nucleophile addition, is potentially useful for stereocontrolled attachment of vicinal substituents to the cyclohexane ring. We were unable to convert complex 2c or 2d to dienyl complexes 4 by direct hydride abstraction,[8] so in order to establish the effect of ligand environment on double functionalization we prepared the dienyl complexes 7a and 7b as shown in the Scheme.[9] In this sequence it is noteworthy that higher yields were obtained for the phosphine complexes than for $Fe(CO)_3$ derivatives in most of the steps. The result of carbon nucleophile addition to complexes 7a and 7b are shown in the Table, and in all cases the phosphine complex is superior. In several instances no characterizable product or starting material could be isolated from the reactions of the $Fe(CO)_3$ complex, but this was ameliorated by use of the $Fe(CO)_2PPh_3$ derivative. The value of this method for preparing stereodefined cyclohexadienes is illustrated by the conversion of complex 8g to the diene 9 on treatment with copper (II) chloride in ethanol.[10]



2 c,d

4



1

5 (a) L = CO (49%)
(b) L = PPh_3 (78%)

6 (a) L = CO (71%)
(b) L = PPh_3 (84%)

7 (a) L = CO (50%)
(b) L = PPh_3 (85%)

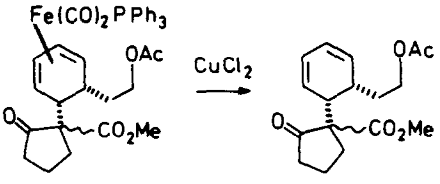
8
(a) L = CO, R = $CH(SO_2Ph)CO_2Me$
(b) L = PPh_3, R = $CH(SO_2Ph)CO_2Me$
(c) L = CO, R = $CH(CO_2Me)_2$
(d) L = PPh_3, R = $CH(CO_2Me)_2$
(e) L = CO, R = CN
(f) L = PPh_3, R = CN
(g) L = PPh_3, R = $-\overline{\mathrm{C(CO_2Me)COCH_2CH_2C}}\mathrm{H_2}$

SCHEME. Reagents: (a) $NaCH(SO_2Ph)CO_2Me$, THF, 0°C; (b) Na-Hg, Na_2HPO_4, MeOH, 0°C; (c) Diisobutylaluminum hydride, THF, -78°C, 1h, 23°C, 15h; (d) MnO_2, benzene, reflux (TLC monitor for completion); (e) HPF_6, Ac_2O, CH_2Cl_2, 0°C; (f) Nucleophile - see Table.

TABLE Results of Nucleophile addition to Complexes **7a** and **7b**.

Complex	Nucleophile	Product	Yield(%)
7a	$NaCH(SO_2Ph)CO_2Me$	**8a**	0
7b	$NaCH(SO_2Ph)CO_2Me$	**8b**	88
7a	$NaCH(CO_2Me)_2$	**8c**	18
7b	$NaCH(CO_2Me)_2$	**8d**	89
7a	NaCN	8e	0
7b	NaCN	**8f**	42
7b	$CH_2{=}CHCH_2MgBr$	**6b**[a]	93
7b	$NaC(CO_2Me)COCH_2CH_2CH_2$	**8g**	81

[a] produced via preferential attack of Grignard reagent on acetate followed by cyclization of resulting magnesium alcoholate.



8g 9

It is noteworthy that 8g is produced by the addition of a relatively hindered enolate to 7b, indicating that there may be considerable scope to this double activation routine provided attention is given to the ancillary ligands on the dienyl-Fe complex.

In conclusion, replacement of CO by PPh_3 in the cyclohexadienyl-$Fe(CO)_2L$ system has a pronounced effect on reactivity. This is undoubtedly due to the increased electron density at the metal when $L = PPh_3$ owing to the poorer π-acceptor capacity of triphenylphosphine which results in: (a) decreased reactivity of the CO ligands toward nucleophile;[11] (b) reduced capacity to accept electrons (and therefore undergo reductive dimerization).[12]

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References and Notes.

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6. All new compounds were characterized by ^{1}H NMR and infrared spectroscopy and molecular composition was established by mass spectrometry and/or combustion analysis. Details will be given in a full paper also describing other aspects of this work.
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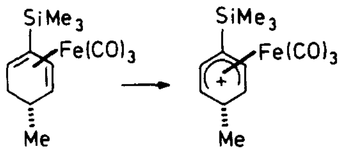
8. Prolonged treatment with Ph_3CPF_6 in boiling dichloromethane gave no dienyl salts. This is due to steric hindrance to the approach of the trityl cation, afforded by the methyl substituent, and is in contrast to the successful conversion of complex A to B reported by Paquette, indicating a profound effect of a trimethylsilyl group:



A B

see: L. A. Paquette, R. G. Daniels and R. Gleiter, Organometallics, 1984, 3, 560.

9. (a) A. J. Pearson and C. W. Ong, J. Org. Chem., 1982, 47, 3780. (b) A. J. Pearson and M. Chandler, J. Chem. Soc. Perkin Trans. 1, 1982, 2641. (c) A. J. Pearson and C. W. Ong, ibid., 1981, 884.
10. D. J. Thompson, J. Organomet. Chem., 1976, 108, 381.
11. We have previously observed addition of malonate carbanion to a CO ligand in related dienyl-$Fe(CO)_3$ complexes, see ref. 9 (c). In the present case no stable products of this type could be isolated from reactions of complex 7a, extensive decomposition of the complex being noted in each case.
12. Related modification of reactivity of cycloheptadienyl-$Fe(CO)_2L$ cations has also been recorded. See reference 1 and literature cited therein.

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