Journal of Organometallic Chemistry, 338 (1988) 217–221
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

(Diene)Fe(CO)$_2$PR$_3$ and [(dienyl)Fe(CO)$_2$PR$_3$]X complexes: altered reactivity towards electrophiles and nucleophiles

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(Received June 17th, 1987)

Abstract

Substitution of carbonyl by PPh$_3$ in (diene)Fe(CO)$_3$ complexes changes the regiospecificity of electrophilic attack and provides easier access to [(allyl)FeL$_4$]X salts. Similar PPh$_3$ substitution in [(dienyl)Fe(CO)$_3$]X complexes results in decreased reactivity towards nucleophiles; the diastereoselectivity of nucleophilic attack using metal-complexed chiral ligands as opposed to chiral nucleophiles has been examined.

The application of cyclic and acyclic (η^4-diene)Fe(CO)$_3$ and [(η^5-dienyl)Fe(CO)$_3$]X complexes as intermediates in organic synthesis continues to be an area of interest [1a–1c]. Improved preparations of the related Fe(CO)$_2$PR$_3$ derivatives also make these complexes attractive candidates, whose advantages (relative to the tricarbonyl) may be summarized as (a) an enhanced reactivity of the (diene)Fe(CO)$_2$PR$_3$ complex towards electrophiles [2], (b) a greater regiospecificity in reactions of [(dienyl)Fe(CO)$_2$PR$_3$]X salts with nucleophiles [3], and (c) an application in asymmetric synthesis involving the use of chiral phosphine ligands [4a–4c]. Differences in reactivity may be expected arising from the increased electron-donating character of the Fe(CO)$_2$PR$_3$ moiety and the possible directing effect of the PR$_3$ ligand which may adopt either an axial or basal position within the square pyramidal geometry, depending on the substitution pattern of the diene or dienyl ligand [5]. We report here results which demonstrate differences in regiospecificity and in kinetic and thermodynamic reactivity which may be of relevance for the synthetic application of these complexes.

(a) Protonation of (diene)Fe(CO)$_2$L complexes

It is well established that protonation of (butadiene)Fe(CO)$_3$ (**1a**) (Scheme 1) in non-coordinating acids yields cation **2a**, which undergoes reaction with CO to

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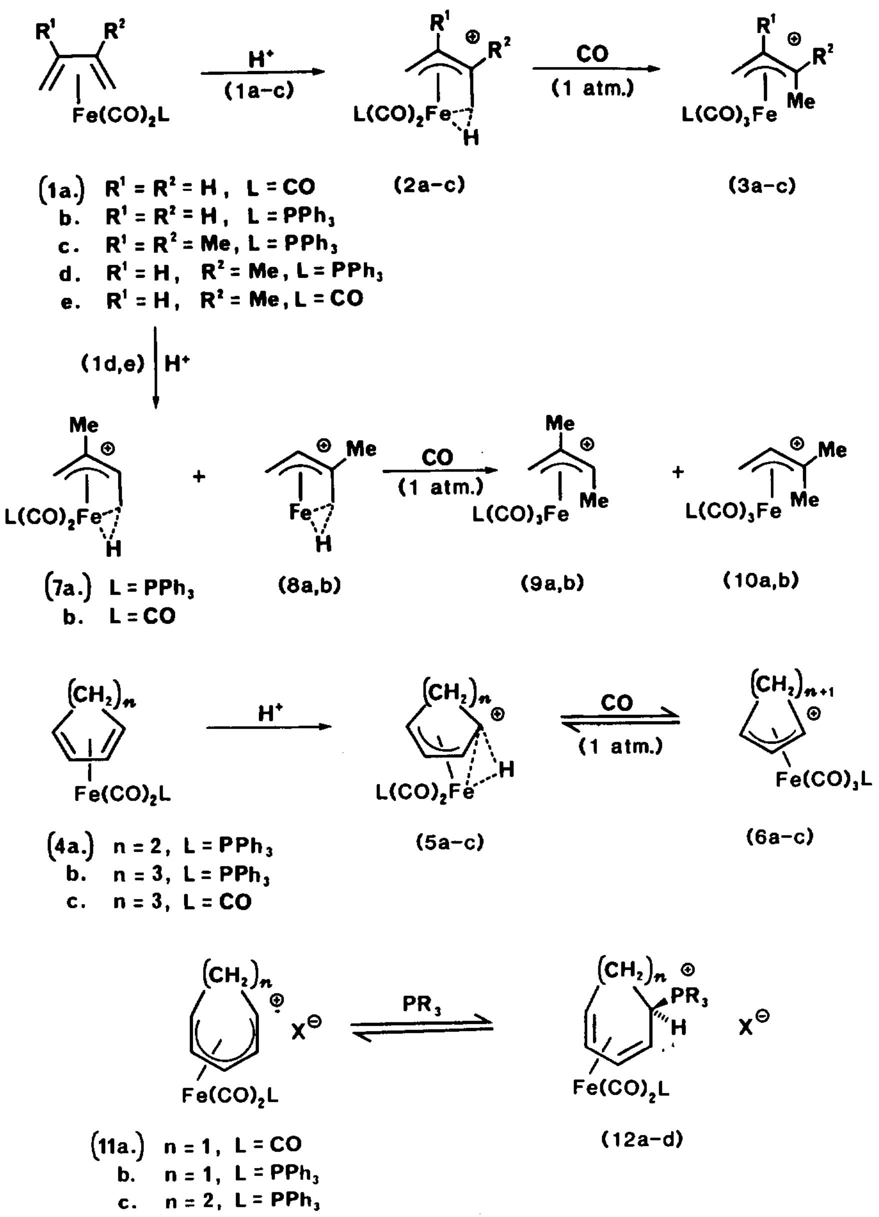

Scheme 1

produce isolable salts of cation **3a** [6]. Regiospecific nucleophilic attack at C(1), usually accompanied by loss of metal, provides substituted alkenes [7]. However, the reaction fails with cyclic dienes and is difficult with internally disubstituted derivatives such as (2,3-dimethylbutadiene)Fe$(CO)_3$ owing to lack of reaction of the initially formed cation with CO. We find that the phosphine substituted derivatives **1b**, **1c** dissolve cleanly in anhydrous HBF_4 to yield in situ the cations **2b**, **2c**, and that both cations undergo complete conversion within minutes under 1 atm of CO into the allyl cations **3b**, **3c**. Tetrafluoroborate salts may be isolated in ca. 70% yield from preparative scale reactions [8*]. Both (cyclohexadiene)- and (cycloheptadiene)-$Fe(CO)_2PPh_3$ (**4a**, **4b**) also dissolve in anhydrous HBF_4 to give in situ the analogous cations **5a**, **5b**. Slow uptake of CO by **5a** eventually yields an equilibrium mixture of **5a** and **6a** (**6a**/**5a** 0.71), but, in contrast, uptake of CO by the seven-membered ring cation proceeds essentially to completion. After the same length of time the protonated tricarbonyl cation **5c** shows only a small conversion into the allyl cation **6c**. The increased kinetic and thermodynamic reactivity may perhaps be ascribed to weakening of the agostic M...H...C interaction on substitution of CO by PPh_3 [9*]. A similar equilibrium has been found for the neutral (cyclohexenyl)$Mn(CO)_x$ case ($x = 3, 4$) with $K = 0.43$ [10]. For the cyclic complexes, the equilibria may be reversed by degassing with N_2, while solid **3c** undergoes loss of CO at room temperature under high vacuum. Addition of basic ligands such as PPh_3 to CH_2Cl_2 solutions of complex **2c** thus formed results in deprotonation to give **1c** rather than addition to give the $[(allyl)Fe(CO)_2(PPh_3)_2]BF_4$ salt. Addition of PPh_3 to **3c** yields $Fe(CO)_3(PPh_3)_2$ and $[Me_2C{=}C(Me)CH_2PPh_3]BF_4$.

The isoprene complexes **1d**, **1e** show differences in both kinetic and thermodynamic regioselectivity. In situ protonation of **1d** in HSO_3F/SO_2 at −60 °C yields a kinetically controlled 3.5/1 mixture of **8a** and **7a**, and this on warming to −20 °C undergoes irreversible isomerization to a thermodynamically controlled 1.5/1 equilibrium mixture, essentially identical to that obtained by protonation using anhydrous HBF_4 at 0 °C. Rapid uptake of CO yields an isolable, non-interconverting mixture of **10a**/**9a** whose ratio (1.5/1) mirrors that of the **8a**/**7a** equilibrium. In contrast, protonation of **1e**, both at −60 °C in HSO_3F/SO_2 and at 0 °C in anhydrous HBF_4, yields in situ an equilibrium **8b**/**7b** mixture in which the regioselectivity is reversed (**8b**/**7b** 0.7); uptake of CO generates in situ a **10b**/**9b** mixture in the same ratio [11*].

(b) Phosphine addition to $[(dienyl)Fe(CO)_2L]X$ salts

It is well established that phosphine addition to $[(cyclohexadienyl)Fe(CO)_3]X$ salts (**11a**) results in ring addition to yield isolable adducts **12a** of some synthetic utility [14a, b]. In keeping with the increased electron donating character of the $Fe(CO)_2PR_3$ moeity, we find that addition of PPh_3 to **11b**, **11c** in CH_2Cl_2 at 25 °C yields instead a thermodynamic equilibrium (eq. 1). The value of K increases with

$$\mathbf{11b},\ \mathbf{11c} + PPh_3 \overset{K}{\rightleftharpoons} \mathbf{12b},\ \mathbf{12c} \qquad (1)$$

$(X^- = PF_6^-)$

decreasing temperature and increases with decreasing ring size (**12b**/**11b**, 6300 M^{-1}, **12c**/**11c**, 145 M^{-1}), thus mirroring the observed kinetic reactivity [14a]. More interestingly from the point of view of asymmetric synthesis, this has allowed an examination of the comparative thermodynamic efficiency of asymmetric induction

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* This and other references marked with asterisks indicate notes occurring in the list of references.

using either metal-bound chiral ligands or chiral nucleophiles using the reactions 2–4.

$$\mathbf{11b} + \mathrm{PPh_2R^{\star}} \rightleftharpoons \mathbf{12b} \tag{2}$$

$\mathrm{X} = \mathrm{PF_6}^-$, $\mathrm{R^{\star}}$ = (+)-neomenthyl)

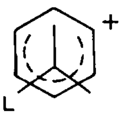
$$\mathbf{11d} + \mathrm{PPh_3} \rightleftharpoons \mathbf{12d} \tag{3}$$

$(\mathrm{X} = \mathrm{BF_4}^-)$

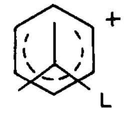
$$\mathbf{11d} + \mathrm{PPh_2R^{\star}} \rightleftharpoons \mathbf{12d} \tag{4}$$

($\mathrm{X} = \mathrm{BF_4}^-$, $\mathrm{R^{\star}}$ = (+)-neomenthyl)

The phosphonium adducts **12b**, **12d** exist as diastereoisomeric pairs, whose population may be determined by integration of the C–P part of the ^{31}P spectrum (Fig. 1). It may be seen that the greatest diastereoisomeric excess is obtained from attack of chiral phosphine on **11b**; indeed, incorporation of metal-bound chiral phosphine in **11d** reduces, rather than enhances the diastereoselectivity. Complexes **11b** and **11d** exist in solution solely as the interconverting basal pair **B**/**B′** which is



(B)



(B′)

enantiomeric where L = $\mathrm{PPh_3}$, and diastereoisomeric but equally populated where L = $\mathrm{PPh_2R^{\star}}$ [15]. The results thus imply a greater thermodynamic discrimination of a chiral nucleophile between the enantiomeric pair of **11b** than of an achiral nucleophile between the diastereoisomeric pair of **11d**. Recent results indicate that this may also be true of kinetically controlled irreversible nucleophilic addition;

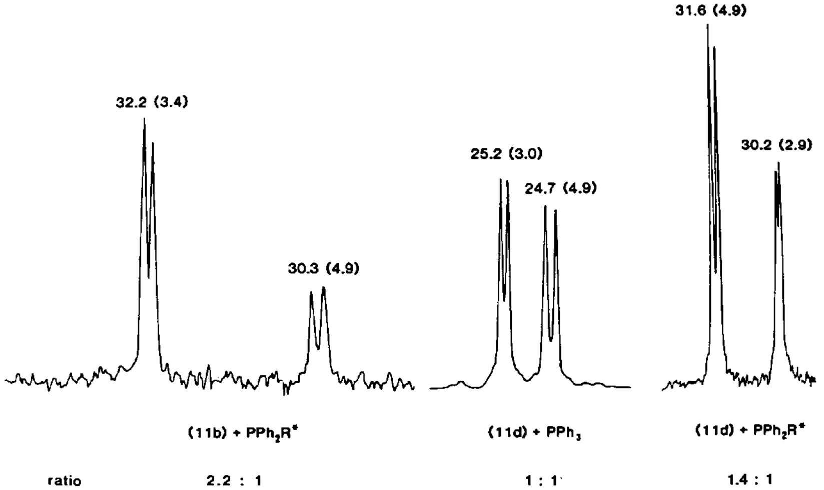


Fig. 1. Chemical shifts in ppm relative to 85% H_3PO_4; values in parentheses represent P–P coupling to metal-bound phosphine.

thus, the reaction of **11d** with CN^- [4b] provides a much lower diastereoisomeric excess than the reaction of [(cycloheptadienyl)$Fe(CO)_2P(OPh)_3]PF_6$ with enolates derived from chiral sulphoximines [16].

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