

(Diene)Fe(CO)₂PR₃ and [(dienyl)Fe(CO)₂PR₃]X complexes: altered reactivity towards electrophiles and nucleophiles

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Abstract

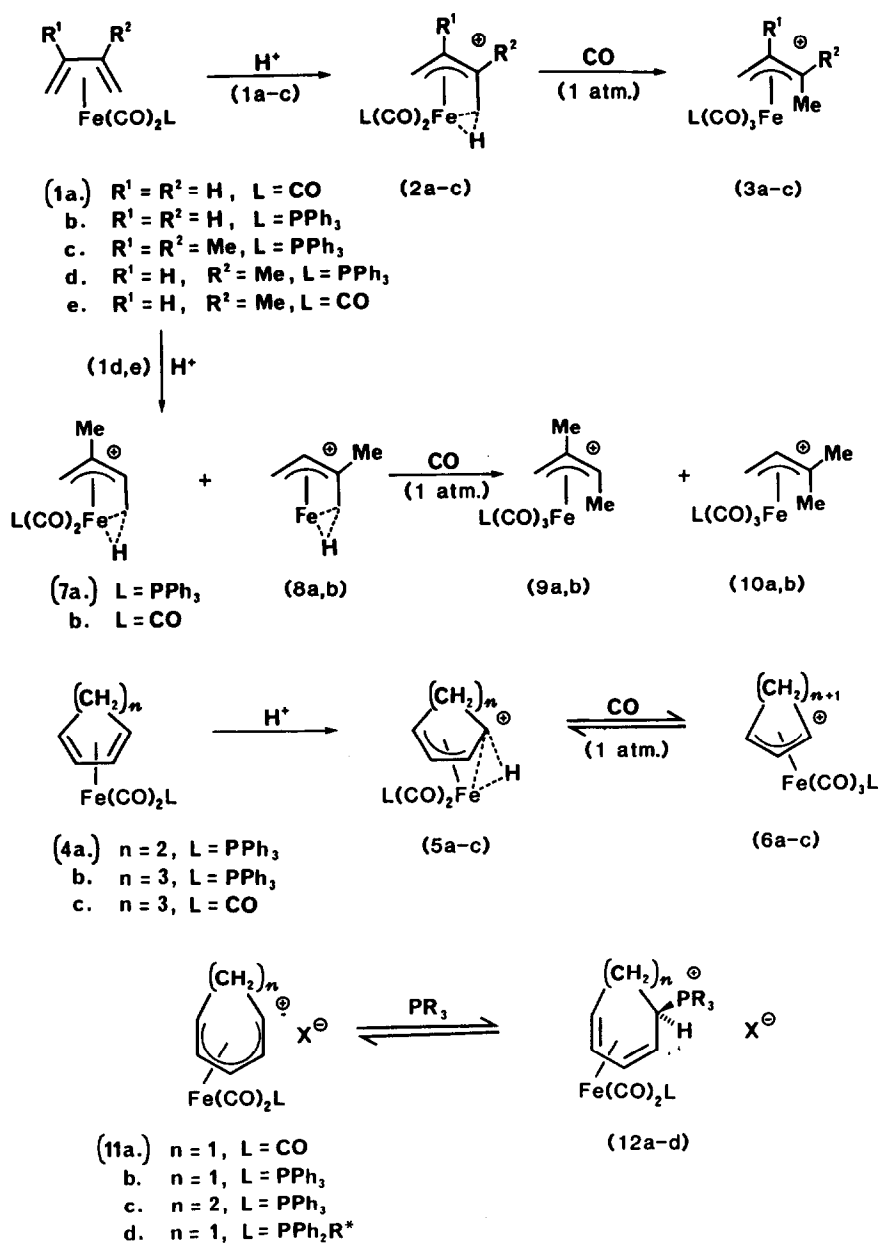
Substitution of carbonyl by PPh₃ in (diene)Fe(CO)₃ complexes changes the regiospecificity of electrophilic attack and provides easier access to [(allyl)FeL₄]X salts. Similar PPh₃ substitution in [(dienyl)Fe(CO)₃]X complexes results in decreased reactivity towards nucleophiles; the diastereoselectivity 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)₂PR₃ 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)₂PR₃ complex towards electrophiles [2], (b) a greater regiospecificity in reactions of [(dienyl)Fe(CO)₂PR₃]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)₂PR₃ moiety and the possible directing effect of the PR₃ 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)₂L 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

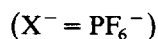
produce isolable salts of cation **3a** [6]. Regiospecific nucleophilic attack at C(1), usually accompanied by loss of metal, provides substituted alkenes [7]. However, the reaction fails with cyclic dienes and is difficult with internally disubstituted derivatives such as (2,3-dimethylbutadiene)Fe(CO)₃ 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 HBF₄ 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)₂PPh₃ (**4a**, **4b**) also dissolve in anhydrous HBF₄ 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 PPh₃ [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 N₂, while solid **3c** undergoes loss of CO at room temperature under high vacuum. Addition of basic ligands such as PPh₃ to CH₂Cl₂ solutions of complex **2c** thus formed results in deprotonation to give **1c** rather than addition to give the [(allyl)Fe(CO)₂(PPh₃)₂]BF₄ salt. Addition of PPh₃ to **3c** yields Fe(CO)₃(PPh₃)₂ and [Me₂C=C(Me)CH₂PPh₃]BF₄.

The isoprene complexes **1d**, **1e** show differences in both kinetic and thermodynamic regioselectivity. In situ protonation of **1d** in HSO₃F/SO₂ 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 HBF₄ 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 HSO₃F/SO₂ and at 0°C in anhydrous HBF₄, 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)₂PR₃ moiety, we find that addition of PPh₃ to **11b**, **11c** in CH₂Cl₂ at 25°C yields instead a thermodynamic equilibrium (eq. 1). The value of K increases with



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

* 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.



$\text{X} = \text{PF}_6^-$, $\text{R}^* = (+)\text{-neomenthyl}$



$(\text{X} = \text{BF}_4^-)$



$(\text{X} = \text{BF}_4^-, \text{R}^* = (+)\text{-neomenthyl})$

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



enantiomeric where $\text{L} = \text{PPh}_3$, and diastereoisomeric but equally populated where $\text{L} = \text{PPh}_2\text{R}^*$ [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;

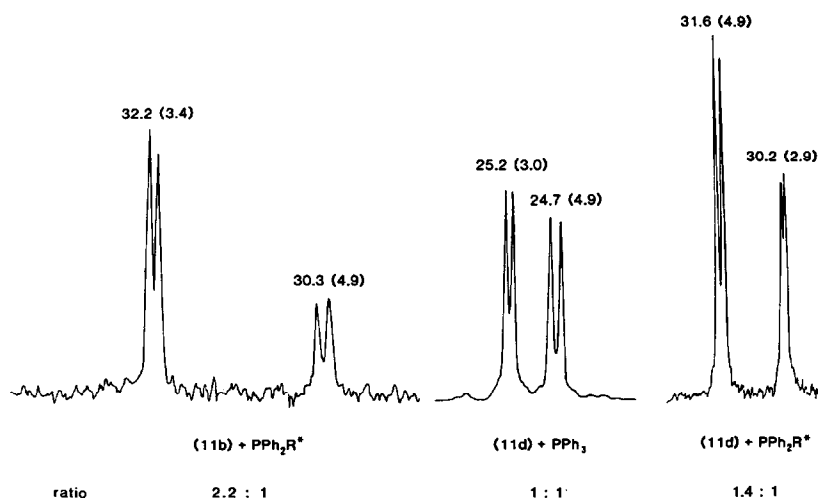


Fig. 1. Chemical shifts in ppm relative to 85% H_3PO_4 ; values in parentheses represent P–P coupling to metal-bound phosphine.

thus, the reaction of **11d** with CN^- [4b] provides a much lower diastereoisomeric excess than the reaction of $[(\text{cycloheptadienyl})\text{Fe}(\text{CO})_2\text{P}(\text{OPh})_3]\text{PF}_6$ with enolates derived from chiral sulfoximines [16].

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