



Synthesis of Cationic 1-Substituted-Dicarbonyl(η^5 -4-Methoxycyclohexadienyl)- (Triphenylphosphine)Iron Complexes

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ABSTRACT : Cationic 1-substituted-dicarbonyl(η^5 -4-methoxycyclohexadienyl)-(triphenylphosphine)iron complexes **10** form a new class of highly functionalised iron complexes which have never been described. They were obtained from neutral 1-substituted (η^4 -4-methoxy-1,3-cyclohexadiene)Fe(CO)₂PPh₃ iron complexes **9**, prepared by ligand exchange reaction under improved experimental conditions. A quaternary carbon was formed in quantitatively yield by regioselective nucleophilic nitrile attack on cation **10e**. Copyright © 1996 Published by Elsevier Science Ltd

Cationic tricarbonyl(η^5 -cyclohexadienyl) iron complexes are useful synthons in organic synthesis¹ as they undergo regio and stereoselective nucleophilic addition reactions.² Their reactivity depends upon the substituent attached to the dienyl system, and the ligand attached to iron. In particular, replacement of a carbonyl ligand by triphenylphosphine as in **1** modifies the reactivity of the dienyl cation (Figure 1).³ For instance, reaction with Grignard reagents becomes possible.

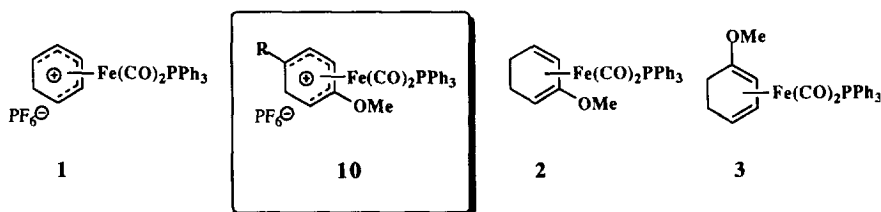
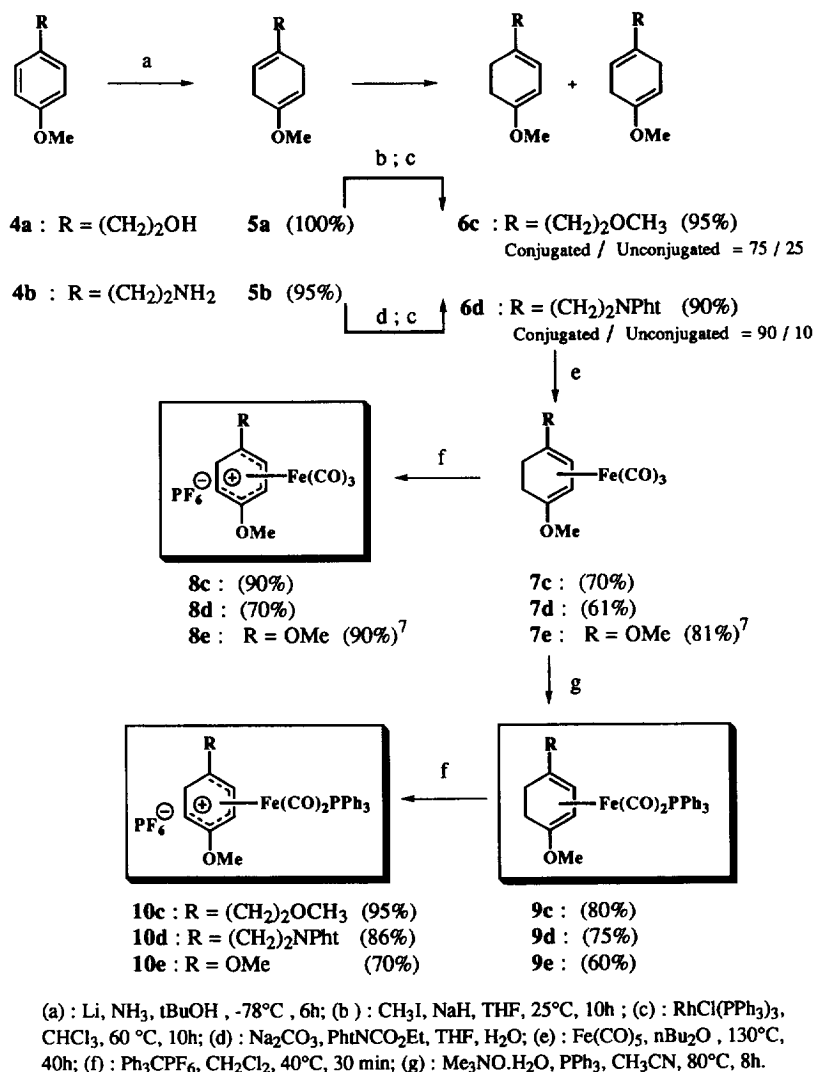


Figure 1

Up till the present, cationic 1-substituted-dicarbonyl(η^5 -4-methoxycyclohexadienyl) (triphenylphosphine)iron complexes **10** have not been prepared. Considering the potential for the use of such intermediates in natural product synthesis, we have investigated the preparation of highly functionalised cations **10** from the corresponding neutral dicarbonyl(4-methoxy-1,3-cyclohexadiene)(triphenylphosphine)iron complexes **9** (Scheme 1). The results of earlier studies show that the mono methoxy substituted dicarbonyl(1,3-cyclohexadiene)(triphenylphosphine)iron complexes **2** and **3** (Figure 1) can be prepared in moderate yields.⁴ However, their dienyl cations have not, to our knowledge, been synthesized.



Scheme 1

The new substituted cations **10c-10e** were obtained from the tricarbonyl iron complex precursors **7c-7e** (Scheme 1), themselves prepared by complexation of their corresponding cyclohexadienes with iron pentacarbonyl. We have developed a shorter and more efficient synthesis of **7c**.⁵ Thus *p*-methoxyphenethyl alcohol **4a** was converted to its unconjugated dihydro derivative **5a** by Birch reduction. Methylation of **5a** with methyl iodide followed by diene isomerization in the presence of Wilkinson's catalyst⁶ gave **6c** as an unseparable mixture of conjugated 1,3-diene (major) and unconjugated 1,4-diene isomers in a 75 / 25 ratio, respectively. Complexation of **6c** with iron pentacarbonyl in degassed di-*n*-butyl ether led in good yield to the tricarbonyl iron complex **7c** which then underwent hydride abstraction on treatment with triphenylcarbenium hexafluorophosphate in dichloromethane to give **8c**. Complex **7d**, which possesses a phthalimido protected

amino ethyl side chain, was prepared from *p*-methoxyphenethyl amine **4b** via the same route. Compounds **7e** and **8e** were prepared as described.⁷

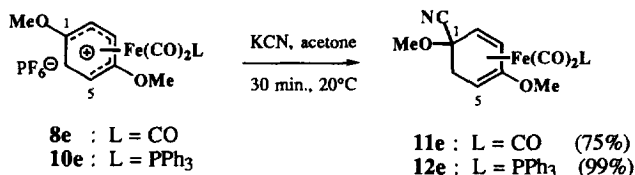
LIGAND EXCHANGE REACTIONS

Various experimental conditions were studied in order to obtain the dicarbonyltriphenylphosphine iron complex **9c**. Direct complexation of diene **6c** with $\text{Fe}(\text{CO})_4\text{PPh}_3$ ⁸ or $\text{Fe}(\text{CO})_2\text{PPh}_3$ transfer from benzylideneacetone dicarbonyltriphenylphosphine iron [η^4 -(bda) $\text{Fe}(\text{CO})_2\text{PPh}_3$]⁹ was unsuccessful. Attempts to effect ligand exchange under photochemical, thermal or classical Birch conditions (Me_3NO , PPh_3 , acetone)⁴ resulted in decomplexation and aromatisation or degradation of **7c**. New experimental conditions were thus needed in order to realise ligand exchange in high yield. We found that by slow addition (8 hours) of six equivalents of triphenylphosphine and 3.5 equivalents of trimethylamine-*N*-oxide hydrate to a solution of tricarbonyl iron complexes **7c**, **7d** or **7e** in hot (80°C) degassed acetonitrile gave satisfactory yields of **9c**, **9d** and **9e**¹⁰, respectively. Increasing the triphenylphosphine concentration improved the yield of the ligand exchange reaction and prevented the decomplexation reaction of tricarbonyl iron complexes induced by trimethylamine-*N*-oxide hydrate (see [Table 1](#)). The best results were observed with a 0.7 M concentration of triphenylphosphine in acetonitrile. Dicarbonyl (triphenylphosphine) iron complexes **9c-9e** were thus obtained in 60-80% yields after purification by flash chromatography on silica gel under medium pressure. Their corresponding cations **10c-10e** were subsequently formed upon treatment of **9c-9e** with triphenylcarbenium hexafluorophosphate in dichloromethane (45°C) followed by precipitation with anhydrous ether.

Table 1 : Effect of triphenylphosphine concentration in the ligand exchange reaction

Starting compounds	7c	7c	7d	7d	7e	7e
[PPh_3]	0.5	0.7	0.3	0.7	0.5	0.7
products	9c	9c	9d	9d	9e	9e
yield (%)	40	80	52	75	38	60

The addition of cyanide to tricarbonyl(cyclohexadienyl)iron is severely limited by undesirable side reactions and low yield.¹¹ However, we found that the corresponding reaction of cations **8e** and **10e** with cyanide ion results in regioselective reaction at the C1 terminus to give exclusively **11e** and **12e** (Scheme 2). Evidence of the regiochemistry is supported by the chemical shift and multiplicity of the H3 signal in the ¹H-NMR spectrum ($J_{2-3} = J_{3-P} = 6\text{Hz}$). Additionally, the presence of peaks at 139.7 ppm (C4), 67.3 ppm (C3) and 54.2 ppm (C2) in the ¹³C-NMR spectrum is consistent with the structure of **12e**.¹² Thus, replacement of a carbonyl ligand by triphenylphosphine improved the yield of quaternary carbon formation; compound **12e** unlike **11e**, was obtained quantitatively.



Scheme 2

In summary, new highly functionalised dicarbonyl(η^4 -4-methoxy-1,3-cyclohexadiene)(triphenylphosphine)iron complexes **9c-9e** and their cations **10c-10e** were prepared in good yields for the first time. Cation **10e** reacts quantitatively and regioselectively with KCN affording a valuable synthetic intermediate. Results of a more in-depth study of the reaction of these novel cations with nucleophiles will be reported in due course.

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- ¹H RMN (C₆D₆, 250 MHz) δ 7.74 (6H, dt, J β - γ = 8 Hz, J β - δ = 2 Hz, H β), 7.11-7.03 (9H, m, H β , H δ), 4.75 (2H, d, J $_{2-P}$ = 3.8 Hz, H 2), 3.03 (6H, s, CH₃O), 2.26 (2H, d, J $_{gem}$ = 10 Hz, H 6 endo), 1.62 (2H, dd, J $_{6-P}$ = 2 Hz, H 6 exo). ¹³C RMN (C₆D₆, 75 MHz) δ 204.0 (d, CO, J $_{C-P}$ = 16 Hz), 137.3 (d, J $_{C\alpha-P}$ = 36 Hz, C α), 133.8 (d, J $_{C\beta-P}$ = 6 Hz, C β), 129.4 (s, C δ), 128.8 (d, J $_{C\gamma-P}$ = 10 Hz, C γ), 110.8 (d, J $_{C1-P}$ = 3.4 Hz, C 1), 71.9 (C 2), 55.9 (CH₃O), 25.1 (C 6). FABMS *m/z*: 513, 485, 457. IR (CHCl₃) 1961, 1899, 1481, 1434, 1200 cm⁻¹.
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- ¹H RMN (C₆D₆, 250 MHz) δ 7.65-7.57 (6H, m), 7.3-6.92 (9H, m), 3.80 (1H, m, J $_{3-P}$ = 6 Hz, H 3), 3.21 (3H, s, CH₃O), 2.93 (3H, s, CH₃O), 2.57 (1H, sl, H 5), 2.28 (1H, dd, J $_{3-2}$ = 8 Hz, J $_{2-P}$ = 6 Hz, H 2), 2.14 (1H, ddd, J $_{gem}$ = 15 Hz, J $_{6-P}$ = 4.5 Hz, J $_{6-5}$ = 2.4 Hz, H 6 endo), 2.00 (1H, dt, J $_{6-P}$ = 3.5 Hz, J $_{6-5}$ = 3.5 Hz, H 6 exo). ¹³C RMN (C₆D₆, 75 MHz) δ 219.5 (d, CO, J $_{C-P}$ = 11 Hz), 212.0 (d, CO, J $_{C-P}$ = 22 Hz), 139.7 (C 1), 135.7 (d, J $_{C\alpha-P}$ = 37 Hz, C α), 133.3 (d, J $_{C\beta-P}$ = 11 Hz, C β), 130.1 (s, Ph, C δ), 128.5 (d, J $_{C\gamma-P}$ = 10 Hz, C γ), 121.6 (CN), 75.2 (d, J $_{4-P}$ = 11 Hz, C 4), 67.3 (C 3), 55.1 (CH₃O), 54.2 (C 2), 53.0 (CH₃O), 44.4 (C 5), 40.8 (C 6). FABMS *m/z*: 539, 513, 499, 485, 471, 457. IR (CHCl₃) 2320, 1989, 1928, 1602, 1486 cm⁻¹. Anal. Calcd for C₂₉H₂₆FeNO₄P: C, 64.58; H, 4.89; N, 2.60. Found: C, 64.17; H, 4.96; N, 2.44.

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