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Tricarbonyl(η^6-arene)chromium and ferrocene complexes linked with aromatic spacers

Zoi F. Plyta, Damien Prim, Jean-Philippe Tranchier, Françoise Rose-Munch and Eric Rose *

Laboratoire de Synthèse Organique et Organométallique, UMR CNRS 7611, Tour 44, 4 place Jussieu, 75252 Paris, Cedex 05, France

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Abstract

The synthesis of alkenyl arenic bridged dinuclear complexes is performed by reacting aromatic ferrocenyl substituted aldehydes with tricarbonylchromium-complexed benzylphosphonates. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: tricarbonylarenechromium complexes; ferrocene; ferroceneboronic acid; coupling reaction; olefination reaction.

Syntheses of new conjugated organometallic compounds have attracted much interest due to their potential application in electro-optical and non-linear optical (NLO) materials.[1] In particular, metallocene type complexes linked with alkenes[2] and (or) arenes[3] as a spacer have been described. With some of them, high levels of NLO efficiencies are reached; indeed high sizable second harmonic generation (SHG) χ^2 have been observed.[1] We were interested in preparing Cr–Fe dinuclear complexes where (η^6-arene) chromium moiety would be linked to the ferrocene moiety by conjugated spacers. An elegant study of the Horner–Emmons–Wadsworth olefination with tricarbonylchromium benzyl phosphonates was published by Müller,[4] describing an easy way to synthesise alkenyl-substituted chromium complexes. We decided to address the potentiality of this approach for elaborating conjugated dimetallic complexes. While we were preparing the manuscript of this study, the same author[5] reported the reaction of $Cr(CO)_3$-complexed benzylphosphonates with organometallic aldehydes. This prompts us to report our own results in the same field as a preliminary communication.

Thus, the phosphonate complex **1**, treated with NaH in THF, reacts readily with different electrophilic ferrocenyl substituted aldehydes (Scheme 1). By using the ferrocenyl aldehyde **2a**, *para* and *meta* ferrocenyl benzaldehydes **2b**[6a,9–11] and **2c**,[6a,9] complexes with only *trans* configurated double bonds **3a**,[5] **3b** and **3c** were formed in 70, 75 and 64% yield, respectively, showing characteristic vicinal coupling constants of 16 Hz by ^{1}H NMR. More interestingly, the same strategy allowed us to obtain a dimetallic complex whose bridge included an heteroatomic ring such as thiophene.[7] Indeed, by reacting 5-ferrocenyl

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* Corresponding author. E-mail: rose@ccr.jussieu.fr

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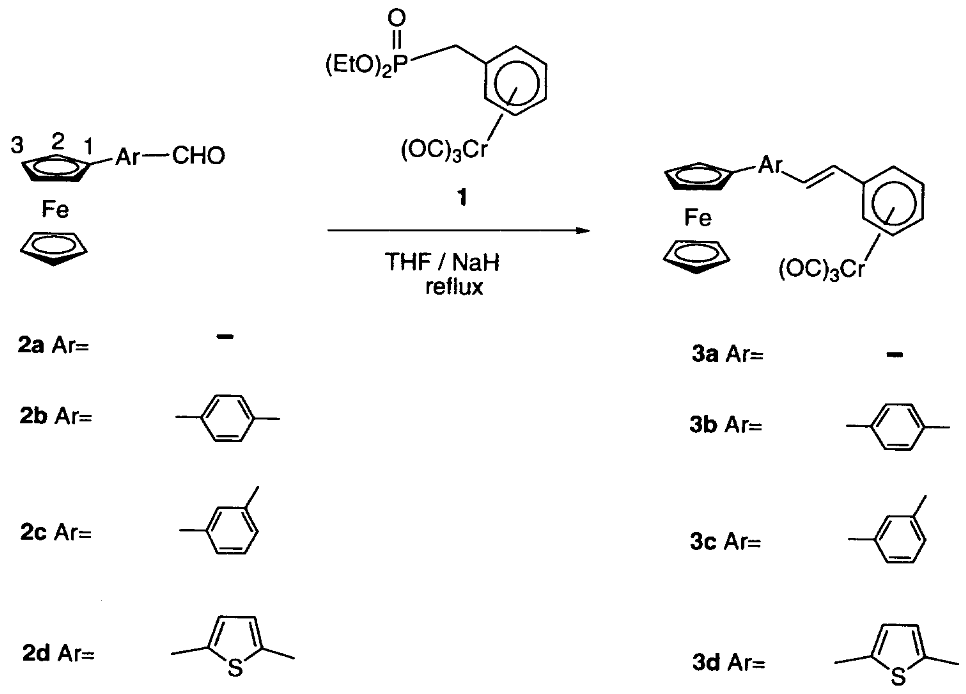
thiophene-2-carboxaldehyde **2d**,[6a] with complex **1**, the expected compound **3d**[6b] was obtained in 90% yield.



Scheme 1.

It is worthy to note that the conformation of the $Cr(CO)_3$ entity of all these dinuclear complexes is in good agreement with an *anti*-eclipsed conformation of the double bond with respect to the Cr–CO bond in solution. Indeed, the two protons of the phenyl ring *ortho* to the double bond appeared at the lowest field as a doublet.[8a] These observations are well precedented in the literature.[8b,c]

In conclusion, these results show that the reaction recently described for the synthesis of alkenyl arene–$Cr(CO)_3$ complexes can be extended to the synthesis of original alkenyl arenic, or alkenyl thienyl bridged dinuclear complexes by using an olefination with $Cr(CO)_3$-complexed benzyl phosphonates and organometallic aldehydes. These aldehydes were prepared by Suzuki coupling from commercially available ferroceneboronic acid.

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6. (a) Aldehydes **2b**, **2c** and **2d** have been prepared by a Suzuki reaction.[9] Aldehydes **2b** and **2d** have been obtained in the literature using more tedious procedures.[10,11] Typical procedure for aldehyde **2d**: a mixture of $Pd(PPh_3)_4$ (41 mg, 0.35 mmol), 5-bromo thiophene-2-carboxaldehyde (226 mg, 1.18 mmol) in dry DME (1 ml) was stirred at room temperature for 10 min under N_2. Ferroceneboronic acid (354 mg, 1.53 mmol) was added sequentially and then aqueous Na_2CO_3 (2 M, 2.37 mmol). The reaction was heated for 24 h. After filtration and extraction of the organic phase, the reaction mixture was evaporated under reduced pressure and purified by silica gel chromatography column using a (9:1) petroleum ether:ether mixture. Recrystallisation in CH_2Cl_2 and pentane afforded red crystals of **2d** in 21% yield. Mp: 101°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.81 (s, 1H, C*H*O), 7.58 (d, 1H, J=4 Hz, C*H*=CS), 7.08 (d, 1H, J=4 Hz, C*H*=CS), 4.68 (bs, 2H, C_5H_4), 4.42 (bs, 2H, C_5H_4), 4.10 (bs, 5H, C_5H_5); ^{13}C NMR ($CDCl_3$) δ 182.4 (CHO), 156.2 (C Ar), 141.0 (C Ar), 137.6 (*C*H=CS), 123.0 (*C*H=CS), 78.0 (C_1), 70.9 (C_5H_5), 70.6, 68.1 (C_2, C_3); IR (CH_2Cl_2) cm^{-1}: 3095, 3090, 1658. (b) All new compounds showed satisfactory spectral and analytical data. Typical procedure for product **3d**: A solution of phosphonate complex **1** (86 mg, 0.245 mmol) in dry THF (3 ml), was treated with NaH 60% (9 mg, 0.225 mmol) under N_2. After stirring for 10 min at room temperature, a solution of the aldehyde **2d** (40 mg, 0.135 mmol) in dry THF was added. The reaction mixture was refluxed for 3 h. Then the mixture was evaporated under reduced pressure and the residue purified by silica gel chromatography using a mixture of petroleum ether:ether (6:4) as eluant to afford complex **3d** (60 mg) in 90% yield. Recrystallisation from dichloromethane and pentane gave orange-red crystals, mp: 189°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.03 (d, 1H, J=16 Hz, C*H*=CH), 6.88 (s, 2H, C*H*=CS), 6.33 (d, 1H, J=16 Hz, CH=C*H*), 5.51 (d, 2H, J=6 Hz, H*o*), 5.42 (t, 2H, J=6 Hz, H*m*), 5.28 (t, 1H, J=6 Hz, H*p*), 4.57 (bs, 2H, C_5H_4), 4.31 (bs, 2H, C_5H_4), 4.11 (bs, 5H, C_5H_5); ^{13}C NMR ($CDCl_3$) δ 233.1 (CO), 138.5 (C Ar), 129.0 (CH), 124.7 (CH), 123.9 (C Ar), 123.1 (CH), 122.7 (CH), 92.8 (CH C_6H_5), 91.3 (C C_6H_5), 90.4 (CH C_6H_5), 78.0 (C_1), 70.2 (C_5H_5), 69.1, 67.0 (C_2 C_3); IR (CH_2Cl_2) cm^{-1}: 1973, 1900.
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8. (a) Even in the case of complex **3a**,[5] we obtained a well first order resolved NMR spectrum in C_6D_6 and the arene–$Cr(CO)_3$ protons exhibit signals at 4.62 (d, 2H, J=6 Hz, H*o*), 4.54 (t, 2H, J=6 Hz, H*m*), 4.31 (t, 1H, J=6 Hz, H*p*). (b) Rose-Munch, F.; Gagliardini, V.; Renard, C.; Rose, E. *Coord. Chem. Rev.* **1998**, *178–180*, 249–268. (c) Rose-Munch, F.; Rose, E. *Current Org. Chem.* **1999**, *3*, 493–515.
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