Pergamon

Tetrahedron Letters 39 (1998) 2325–2326

TETRAHEDRON LETTERS

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

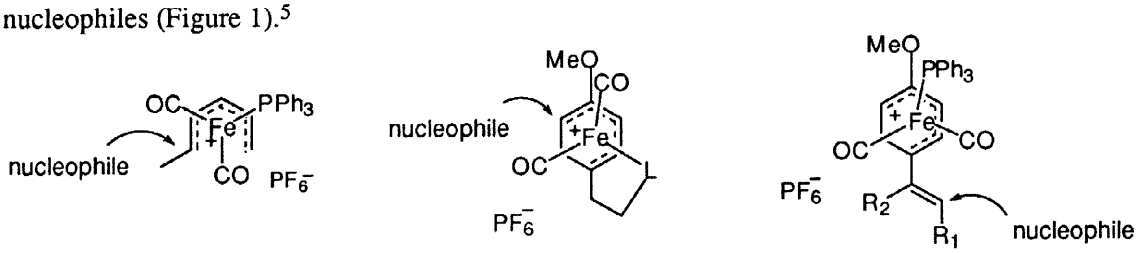
Nicolas Millot, Catherine Guillou* and Claude Thal

Institut de Chimie des Substances Naturelles, C.N.R.S., 91198 Gif-sur-Yvette (France)

Received 17 December 1997; accepted 19 January 1998

Abtract : Nucleophilic addition of malonate anion to cationic 1-substituted (η^5-4-methoxycyclohexadienyl)Fe(CO)$_2$PPh$_3$ complexes **6e-g** proceeds predominantly at the more substituted cyclohexadienyl terminus to afford 1,1-disubstituted (η^4-4-methoxy-2,4-cyclohexadiene)Fe(CO)$_2$PPh$_3$ complexes **7e-g** in good yields. © 1998 Elsevier Science Ltd. All rights reserved.

Cationic tricarbonyl(η^5-cyclohexadienyl) iron complexes are useful synthons in organic synthesis as they undergo regio- and stereoselective nucleophilic addition reactions.[2] Their reactivity depends from the substituent attached to the dienyl system as well as the ligand attached to the iron atom. Recently, it was shown that nucleophiles react at the more substituted C1 terminus of the dienylium ligand in the (pentadienyl) Fe(CO)$_2$PPh$_3$ series[3] and at the less substituted C5 terminus of the dienylium ligand in the chelated (η^5-4-methoxycyclohexadienyl)Fe(CO)$_2$L series.[4] The nucleophiles enter *trans* to the PPh$_3$, OPPh$_2$ and PPh$_2$ ligands of complexes **1**, **2**, **3** respectively. Cations **4** and **5** on the other hand allow conjugate addition of nucleophiles (Figure 1).[5]



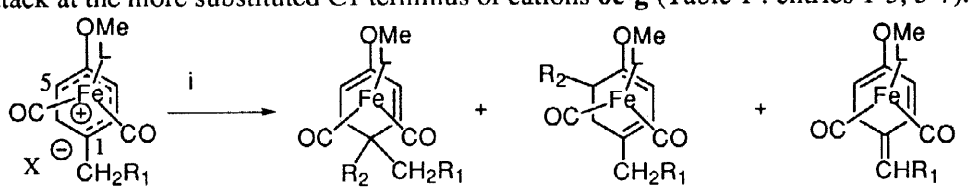
1

2 : L = OPPh$_2$
3 : L = PPh$_2$

4 : R$_1$ = CH$_3$; R$_2$ = H
5 : R$_1$ = H; R$_2$ = CO$_2$Me

Figure 1

We now report the reaction of cationic 1-substituted(η^5-4-methoxycyclohexadienyl)Fe carbonyl complexes **6e-g** (L = PPh$_3$) with sodio dimethyl malonate. The reaction of the tricarbonyl complexes **6a-d** (L = CO) with NaCH(CO$_2$Me)$_2$ gave mixtures of the diene complexes **7**, **8** and sometimes **9** (scheme 1) (Table 1).[1, 2, 6] On the other hand, replacement of a carbonyl ligand by a triphenylphosphine ligand improved the yield of attack at the more substituted C1 terminus of cations **6e-g** (Table 1 : entries 1-3, 5-7).[7]



6 **7** **8** **9**

i : NaCH(CO$_2$CH$_3$)$_2$; THF; 0°C; 5 min. R$_2$: CH(CO$_2$CH$_3$)$_2$

Scheme 1

* Fax : (+33) 1 69 07 72 47; E-mail : Guillou@icsn.cnrs-gif.fr

0040-4039/98/$19.00 © 1998 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(98)00191-9

Entry	Cations	L	X -	R_1	7#	8#	9#
1	**6a**	CO	PF_6^-	CH_2OCH_3 (ref. 6)	56	22	-
2	**6b**			CH_2NPhth (ref. 1)	55	24	-
3	**6c**			CO_2CH_3 (ref.1)	35	35	5
4	**6d**		BF_4^-	CO_2CH_3 (ref. 6)	10	7	30
5	**6e**	PPh_3	PF_6^-	CH_2OCH_3	70	-	-
6	**6f**			CH_2NPhth	70	20	-
7	**6g**			CO_2CH_3	46	-	30
8	**6h**		BF_4^-	CO_2CH_3	-	-	70

#: isolated yields **Table 1**

A competitive deprotonation reaction was observed when the acidity of hydrogens α to the C1 position increased (entry 7). This pathway became predominant when the counter ion PF_6^- of **6g** was replaced by BF_4^- (entry 8). Moreover, nucleophilic addition occurred to a minor extent at the less substituted C5 terminus of the dienylium ligand of cation **6f** which possesses a bulky phthalimido-protected aminoethyl side-chain (entry 6).

The structures of complexes **7e-g** were assigned on the basis of their ^1H NMR and ^{13}C NMR spectral data.[8] The P-CO coupling constants have been reported to provide a reliable aid to structure elucidation of simple (diene)$Fe(CO)_2L$ complexes (L = phosphine, phosphite).[9] The ^{13}C NMR spectra of complexes **7e-g** present two CO chemical shifts at 221-220 (CO axial; J (Pbasal-COaxial) ≃ 6.5 - 11.9 Hz) and 219-217 ppm (CO basal; J (Pbasal-CObasal) ≃ 17-20 Hz). Moreover, the tendency of phosphine ligands to occupy basal sites in (dienyl)$Fe(CO)_2L$ has been reported.[10] We propose that complexes **7e-g** have the phosphorus ligand in the basal position. Thus, cations **6e-g** most probably have the structures indicated in scheme 1. Nucleophiles therefore attack the more substituted termini of the dienyl cations *trans* to the bulky phosphine ligand.

In conclusion, we have shown that replacement of a carbonyl ligand in the 1-substituted (η^5-4-methoxycyclohexadienyl)$Fe(CO)_3$ iron series by a triphenylphosphine ligand favors nucleophilic attack of malonate anion at C1, leading to quaternary carbon derivatives. These results could have interesting synthetic applications.

REFERENCES AND NOTES

1) Preliminary results concerning this work were presented at the 6th Belgian Organic Synthesis Symposium (BOSS) , Gent July 8-12, 1996.
2) Pearson, A.J. *Iron Compounds in Organic Synthesis, Best Synthetic Methods* ; Academic Press **1994**, pp. 97-138.
3) Donaldson, W. A.; Shang, L. *Tetrahedron Lett.* **1995**, *36*, 1575-1576.
4) Millot, N.; Guillou, C.; Thal, C. *Tetrahedron* **1997**, *53*, 12553-12564.
5) a) Hudson, R.D.A.; Osborne, S.A.; Roberts, E.; Stephenson, G.R. *Tetrahedron Lett.* **1996**, *37*, 9009-9012.
b) Hudson, R.D.A.; Osborne, S.A.; Stephenson, G.R. *Tetrahedron* **1997**, *53*, 4095-4104.
6) Pearson, A.J. ; Chandler, M. *J. Chem. Soc. Perkin Trans 1*, **1980**, 2238-2243.
7) Complexes **6e-g** have been previously prepared.
Guillou, C.; Millot, N. ; Reboul, V.; Thal, C. *Tetrahedron Lett.* **1996**, *37*, 4515-4518.
8) **7e:** Anal. Calcd for $C_{35}H_{37}FeO_8P$: C, 62.51; H, 5.55. Found : C, 62.77; H, 5.58.^1H NMR (C_6D_6 ; 250 MHz) δ : 7.67 (6H; t; $J_{ortho} = J_{\beta\text{-}P} = 8.0$ Hz ; Hβ); 7.05-6.96 (9H ; m ; Hγ, Hδ); 4.44 (1H; m; H3); 3.77 (1H; s; H7'); 3.34 (3H; s; CO_2CH_3); 3.30 (3H; s; CO_2CH_3); 3.31-3.21 (3H ; H5, H8); 3.10 (3H; s; OCH_3); 2.98 (3H; s; OCH_3); 2.99-2.92 (1H ; H6endo); 2.41 (1H; t ; $J_{vic} = 6.3$ Hz ; H7endo); 2.30 (1H; t ; $J_{vic} = 5.8$ Hz ; H7exo); 2.21 (1H; t ; $J_{2\text{-}3,P} = 6.2$ Hz; H2); 2.04 (1H; dt ; $J_{gem} = 15.0$ Hz, $J_{6exo\text{-}5,P} = 3.0$ Hz ; H6exo). ^{13}C NMR (C_6D_6 ; 50.29 MHz) δ : 221.4 (d ; $J_{CO\text{-}P} = 8.7$ Hz; COaxial); 215.1 (d; $J_{CO\text{-}P} = 19.0$ Hz; CObasal); 169.3 and 169.0 (CO_2CH_3); 138.5 (C4); 136.2 (d; $J_{P\text{-}C\alpha} = 38.7$ Hz; Cα); 133.2 (d; $J_{P\text{-}C\beta} = 10.3$ Hz; Cβ); 129.7 (Cδ); 128.3 (d; $J_{P\text{-}C\gamma} = 9.1$ Hz; Cγ); 69.2 (C3, C8); 60.4 (C7'); 58.8 (C2); 58.4 (OCH_3); 54.8 (OCH_3); 52.0 (CO_2CH_3); 47.3 (d; $J_{5\text{-}P} = 9.2$ Hz; C5); 42.8 (C1); 40.5 (C7); 39.4 (C6).
9) Howell, J.A.S.; Walton, G.; Tirvengadum, M.C.; Squibb, A.; Palin, M.G. *J. Organomet. Chem.* **1991**, *401*, 91-123.
10) Whitesides, T.H; Budnik, R.A. *Inorg. Chem.* **1975**, *174*, 664-673.