METAL ASSISTED CYCLOADDITIONS

IV. ENHANCED REACTIVITY OF CpFe(CO)(η^1-2-METHOXYALLYL) COMPLEX IN CYCLOADDITION REACTIONS WITH OLEFINS BY INTRODUCTION OF A PHOSPHITE LIGAND: SYNTHESIS OF TRISUBSTITUTED CYCLOPENTENES

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Summary

A phosphite substituted $CpFe(CO)_2[P(OCH_2)_3CCH_3](\eta^1$-2-methoxyallyl) complex (II) was prepared by irradiation of dicarbonyl(η^5-cyclopentadienyl) (η^1-2-methoxyallyl)iron (I) together with cyclic phosphite. This complex II was reacted with various electron deficient olefins to yield the corresponding cyclopentenyl-Fp adducts. In these reactions complex II was found to be more reactive and more selective in formation of cyclic adducts when compared to I. High yields of cyclic adducts were obtained exclusively in reactions of II with dimethyl 1-cyanoethylene-1,2-dicarboxylate and 2-cyanocinnamonitrile. Ethyl 1-cyano-4,4-trimethylene-dithiocrotonate also yielded cyclic adduct exclusively in contrast to formation of a linear product from the reaction with complex I. Trisubstituted cyclopentenes were obtained from these adducts by demetallation.

Introduction

The replacement of CO by phosphite ligands in $CpFe(CO)_2(\eta^1$-allyl) and $CpFe(CO)_2(\eta^1$-methallyl) complexes by a photochemically initiated radical chain reaction has been achieved recently [1]. It has been well established that such ligand substitution results in increased electron density at the metal and remaining carbonyl ligands, thus enhancing the reactivity of η^1-allyl ligands in phosphite substituted complexes towards electrophiles in cycloaddition reactions [1]. As part of a continuing interest in the synthesis of substituted cyclopentane derivatives via (3 + 2)
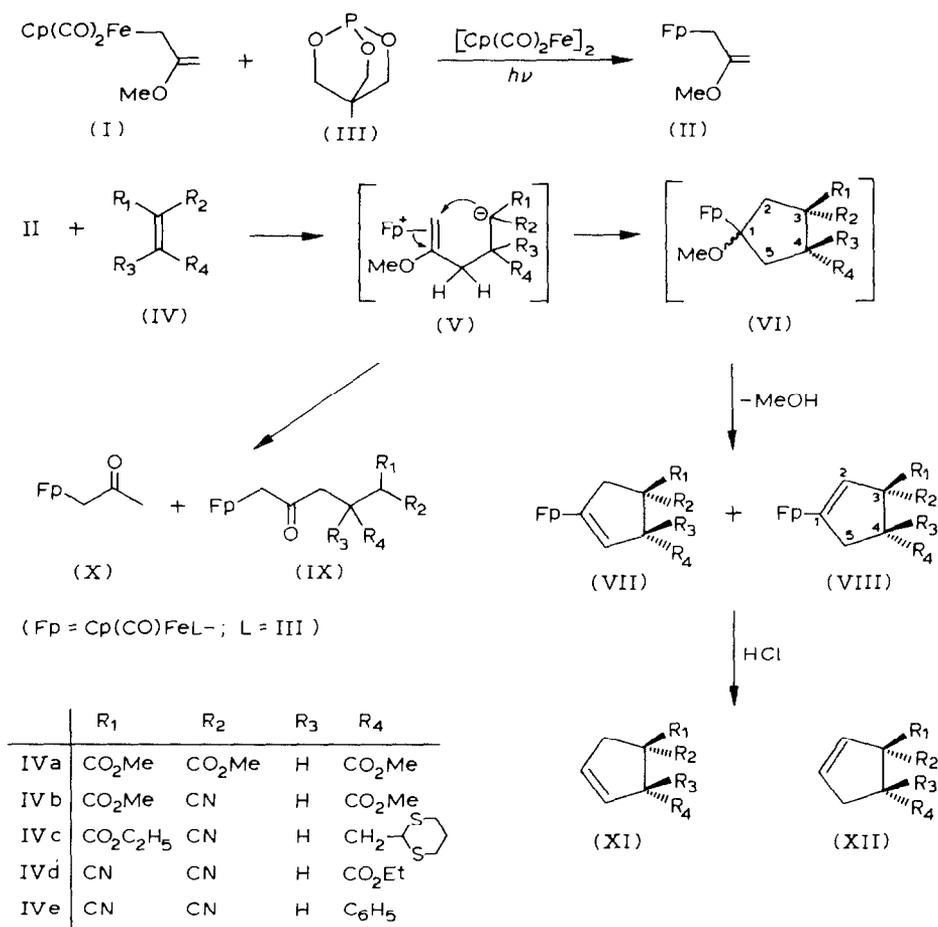
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cycloaddition reactions, we have earlier reported [2] reaction of dicarbonyl(η^5-cyclopentadienyl)(η^1-2-methoxyallyl)iron (I) with various electron deficient olefins and acetylenes [2,3]. In many cases, this complex (I) yielded linear adducts by H-transfer in competition with formation of cyclic adducts [3]. In a search for a more reactive (η^1-2-methoxyallyl)Fp complex to achieve the exclusive formation of cyclic adducts, we have now prepared a new phosphite substituted complex (II) and the results of its cycloaddition reactions with various electron deficient olefins is now reported.

Results and discussion

The phosphite substituted $CpFe(CO)[P(OCH_2)_3CCH_3](\eta^1$-2-methoxyallyl) complex (II) was prepared by brief irradiation of a pentane solution of dicarbonyl(η^5-cyclopentadienyl)(η^1-2-methoxyallyl)iron (I) and 4-methyl-2,6,7-trioxa-1-phosphatricyclo [2.2.2]octane (III) [4] in presence of a catalytic amount of $[CpFe(CO)_2]_2$. The cyclic phosphite III was employed due to its strong σ-donor ability [5] and its rigid cage structure. This product II was found to be an air stable crystalline solid in

SCHEME 1

	R_1	R_2	R_3	R_4
IVa	CO_2Me	CO_2Me	H	CO_2Me
IVb	CO_2Me	CN	H	CO_2Me
IVc	$CO_2C_2H_5$	CN	H	CH_2-⟨S S⟩
IVd	CN	CN	H	CO_2Et
IVe	CN	CN	H	C_6H_5

constrast to I which is an unstable amber oil. Reactions of Fp complex II with various electron deficient olefins (IVa–IVe) was studied (Table 1). Reaction of II with trimethyl ethylenetricarboxylate (IVa) [6] (Scheme 1) in dichloromethane for 5 h yielded after column chromatography, two 1/1 adducts in a ratio of 2/1. In this reaction, it is feasible that the collapse of intermediate zwitterion (V) could follow several routes [3] to yield cyclic and H-transfer linear adducts. From the spectral and analytical data, the two products obtained were assigned the structures (VIIa + VIIIa) and (IXa). The cyclopentenyl complexes were isolated as a mixture of positional isomers (VIIa and VIIIa) and were found, by HPLC analysis, to be present in equal proportions. The methylene protons of the cyclic adducts resonated at δ 2.7–2.98 ppm (m) and the methine proton was found at δ 3.6–3.7 ppm (m) (Table 2). The loss of elements of methanol was observed to occur during the cycloaddition reactions, since the NMR spectrum of the crude reaction mixture did not show any peaks due to methoxyl protons. This is in contrast to the reactions of I [3], where the methoxyl group is present in the cyclic adducts and in the present reactions the loss of methanol may be due to the presence of a bulky cyclic phosphite ligand in the intermediate cyclic adduct VI. The spectral features of complex IXa were similar to that of $FpCH_2COCH_3$ (X) which was always isolated as a side product in these reactions of complex II, due to its hydrolysis, during column chromatography.

Cyclopentenyl-Fp adducts (VIIb and VIIIb) were the sole products (with some of the hydrolysed product X) obtained from the reaction of II with dimethyl 1-cyanoethylene-1,2-dicarboxylate [7]. These two diastereomeric cyclopentenyl complexes (VIIb and VIIIb) were separable by column chromatography on neutral alumina and were found to be in a ratio of 1/1.

Reaction of complex II with ethyl 1-cyano-4,4-trimethylenedithiocrotonate (IVc) in dichloromethane at room temperature for 20 h afforded a single cyclic adduct and was assigned structure (VIIIc) from ^{1}H NMR spectral data. Similarly a single adduct

TABLE 1

REACTION OF COMPLEX II WITH ELECTRON DEFICIENT OLEFINS

Olefin	Amount of olefin (mol equiv)	Reaction time (h)	Product yield [h] (%)	Product ratio (%)			% Yield of X
				VII	VIII	IX	
IVa	2.0	5	75 [e] (56)		64 [a] (40)	36 [d] (60)	
IVb	1.2	14	33 [e] [i]	50 [a]	50 [a]	—	20 [d]
IVc	1.1	20	52 [e] (53)	— —	100 [a] —	— (100)	28 [d]
IVd	1.1	20	70 [g] (58)	—	100 [c]	—	—
IVe	1.5	14	98 [f] [j]		100 [b]	—	—

[a] Eluant: petroleum ether/diethyl ether 1/3. [b] Eluant: Petroleum ether/diethyl ether 1/1. [c] Eluant: Petroleum ether/diethyl ether 7/3. [d] Petroleum ether/ethyl acetate 1/1. [e] Column chromatography was carried out with neutral alumina, Act III. [f] Act IV. [g] Florisil. [h] The product yields given in the parentheses are from the reaction of complex I with olefins. [i] No identifiable products were isolated [10]. [j] No reaction [10].

TABLE 2

PHYSICAL AND SPECTRAL DATA OF ADDUCTS (VII, VIII, IX AND X)

Product	M.p. (°C)	ν_{max} (cm^{-1})	^{1}H NMR chemical shifts (δ values in ppm)	m/e	HPLC t_R (min)	HRMS Formula	Found (calcd.)
VIIa + VIIIa	144–145 (d)	1950s (C≡O), 1730s (C=O), 1610w (C=C)	0.74 (s, 3H, CCH$_3$), 2.70–2.98 (m, 2H, CH$_2$), 3.60, 3.66, 3.70 (each s, each 3H, 3 × CO$_2$CH$_3$), 3.6–3.70 (m, 1H, CHCO$_2$CH$_3$), 4.12 (d, 6H, J 5 Hz, (OCH$_2$)$_3$), 4.59 (s, 5H, Cp), 5.32 (m, 1H, =CH).	538 (0.2%, M$^+$), 510 (12.8, M$^+$ – CO), 362 (100, M$^+$ – CO, L), 302 (39.9).	VIIa 5.2 VIIIa 4.8	C$_{22}$H$_{27}$O$_{10}$FeP	538.1577 (538.0691)
IXa^a	Yellow gummy solid	1940s (C=O), 1740s (C=O, ester) 1635s (C=O. ketone)	0.80 (s, 3H, CCH$_3$), 1.13–1.39 (m, 1H, FpCH), 1.54–1.66 (m, 1H, FpCH), 2.80–3.15 (m, 2H, COCH$_2$), 3.44–3.66 (m, 1H, CHCO$_2$Me), 3.68 (s, 3H, CO$_2$CH$_3$) 3.76 (s, 6H, 2×CO$_2$CH$_3$, 3.92 (d, 1H, J 8 Hz, CH(CO$_2$CH$_3$)$_2$, 4.10 (d. 6H, J 5 Hz, (OCH$_2$)$_3$, 4.54 (s, 5H, Cp).	556 (0, M$^+$), 408(0.2, M$^+$ – L), 297 (0.8, Fp), 269(5.3).	–	–	–
VIIb	74–76	2250w (C≡N), 1945s (C=O), 1740s (C=O), 1610w (C=C)	0.74 (s, 3H, CCH$_3$), 2.72–3.04 (m, 2H, CH$_2$), 3.62 (m, 1H, CHCO$_2$CH$_3$), 3.74–3.84 (each s, each 3H, 2×CO$_2$CH$_3$), 4.16 (d, 6H, J 4 Hz, (OCH$_2$)$_3$), 4.60 (s, 5H, Cp), 5.05 (m, 1H, =CH)	505 (1.0, M$^+$), 478 (5.9, M$^+$ – HCN), 477 (26.2, M$^+$ – CO), 329 (100, M$^+$ – L, CO), 302 (83.5), 269 (20)	5.0	C$_{21}$H$_{24}$NO$_8$FeP	505.0365 (505.0588)
VIIIb	150–151	2240 w C≡N, 1940s (C=O)	0.74 (s, 3H, CCH$_3$), 2.74–3.14 (m, 2H, CH$_2$), 3.62(m, 1H, CHCO$_2$CH$_3$), 3.68–3.72 (each s.	505 (0.5, M$^+$), 477 (12.7, M$^+$-	5.6	C$_{21}$H$_{24}$-NO$_8$FeP	505.0365 (505.0588)

Compound	m.p. (°C)	IR	^{1}H NMR	MS	%	Molecular formula	HRMS found (calcd)
		1738s (C=O), 1600w (C=C)	each 3H, $2 \times CO_2CH_3$), 4.16 (d, 6H, J 4 Hz, $(OCH_2)_3$), 4.60 (s, 5H, Cp), 5.13 (m, 1H, =CH).	CO), 329(100, M^+ − L, CO), 302 (23.7), 269 (22.0).			
VIIIc	85–86	2236w (C≡N), 1950s (C=O), 1735s (C=O), 1610w (C=C)	0.76 (s, 3H, CCH_3), 1.35 (t, 3H, J 8 Hz, OCH_2CH_3), 1.70–2.54 (m, 5H, CCH, $CHCH_2$ SCH_2−CH_2S), 2.60–3.20 (m, 6H, ring CH_2, $SCH_2CH_2CH_2S$), 4.18 (d, 9H, J 4 Hz, $(OCH_2)_3$, OCH_2CH_3, $SCHS$), 4.61 (s, 5H, Cp), 5.16 (m, 1H, =CH).	593 (0.1, M^+), 566 (0.8, M^+ − HCN), 417 (12.5), 390 (22.5, M − L,CO, HCN), 343 (2.3).	3.7	$C_{25}H_{32}$-NO_6S_2FeP	593.0700 (593.0758)
VIIId	149(d)	2235w (C≡N), 1950s (C=O), 1735s (C=O), 1605w (C=C)	0.78 (s, 3H, CCH_3), 1.36 (t, 3H, OCH_2CH_3), 2.90 (bd, 2H, J 8 Hz,CH_2), 3.52 (bt, 1H, $CHCO_2CH_2CH_3$), 4.18 (d, 6H, J 4 Hz $(OCH_2)_3$), 4.14–4.50 (m, 2H, OCH_2CH_3), 4.55 (s, 5H, Cp), 5.18 (m, 1H, =CH).	486 (0.1, M^+), 459 (1.6, M^+ − HCN), 458 (6.3, M^+ − CO), 310 (12.6, M^+ − L, CO), 283 (52.5).	3.6	$C_{21}H_{23}$-N_2O_6FeP	486.1587 (486.0643)
VIIe + VIIIe	114–115 (d)	2240w (C≡N), 1950s (C=O), 1615,1600m (C=C)	0.80 (s, 3H, CCH_3), 3.0 (bd, 1H, CH_2), 3.52 (bs, 1H, CH_2), 3.90 (t, 1H, J 8 Hz, $CHPh$), 4.23 (d, 6H, J 4 Hz, $(OCH_2)_3$), 4.68 (s, 5H, Cp), 5.26 (m, 1H, =CH), 7.50 (bs, 5H, C_6H_5)	490 (0.3, M^+), 463 (0.2, M^+ − HCN), 462 (1.1, M^+ − CO), 314 (2.5, M^+ − L, CO), 77 (11.3)	3.0	$C_{24}H_{23}$-N_2O_4FeP	490.1866 (490.0744)
X[a]	171–172 (d)	1945s (C=O), 1628s (C=O)	0.80 (s, 3H, CCH_3), 1.15–1.35 (m, 1H, $CHCOCH_3$), 1.6 (6, 1H, $CHCOCH_3$), 2.06 (s, 3H, $COCH_3$), 4.20 (d, 6H, J 5 Hz, $(OCH_2)_3$), 4.53 (s, 5H, Cp).	354 (0.2, M^+), 326 (0.4, M^+ − CO), 297 (0.3, M^+ − C_3H_5O), 269 (5.9), 178 (5.8), 186 (45.9), 121 (56.6).	–	$C_{14}H_{19}$-O_5FeP	354.1718 (354.0319)

[a] Mass spectrum recorded at 25 eV.

TABLE 3

HCl CLEAVAGE OF CYCLOPENTENYL Fp ADDUCTS (VIIa–VIIe, VIIIa–VIIIe)

Fp Adducts	Product	Yield (%)	ν_{max} (cm^{-1})	^{1}H NMR spectral data (δ values in ppm)	m/e	GLC t_R (min)	HRMS Formula	Found (calcd.)
VIIa + VIIIa	XIa + XIIa	48	1740s (C=O)	2.83–2.98 (2H, m, CH$_2$), 3.68 3.71, 3.76 (each s, each 3H, 3×CO$_2$CH$_3$), 3.90 (t, 1H, J 8 Hz, CHCO$_2$CH$_3$), 5.60–6.06 (m, 2H, CH=CH).	242 (0.38, M^+), 211 (14.4, M^+ − OMe), 210(28.5), M^+ − MeOH), 183 (31.6), 182 (89) 151 (100),	3.0 and 3.2^a	C$_{11}$H$_{14}$O$_6$	242.1034 (242.0891)
VIIb	XIb	84	2245w (C≡N), 1750s (C=O), 1620w (C=C)	3.06–3.22 (m, 2H, CH$_2$), 3.83 and 3.93 (each s, each 3H, 2×CO$_2$CH$_3$), 3.68–4.06 (m, 1H, CHCO$_2$CH$_3$), 5.90 (s, 2H, CH=CH).	209 (1.9, M^+) 182 (8.7), 150 (31.7), 106 (100), 91 (23.7).	3.0^a	C$_{10}$H$_{11}$NO$_4$	209.0596 (209.0688)
VIIIb	XIIb	72	2245w (C≡N), 1750s (C=O), 1620w (C=C)	2.6–3.08 (m, 2H, CH$_2$), 3.64–3.96 (m, 1H, CHCO$_2$CH$_3$), 3.76 and 3.80 (each s, each 3H, 2×CO$_2$CH$_3$), 5.66–6.26 (m, 2H, CH=CH)	209 (1.85, M^+) 182 (3.6, M^+ − HCN), 150 (28.2, M^+ − CO$_2$CH$_3$), 91 (29.9, M^+ − 2CO$_2$CH$_3$).	3.5^a	C$_{10}$H$_{11}$NO$_4$	209.0504 (209.0688)
VIIIc	XIIc	46	1735s (C=O)	1.36 (t, 3H, OCH$_2$$CH_3$), 1.60–2.5 (m, 5H, C$CHCH_2CH_3$; SCH$_2$$CH_2CH_2$S), 2.70–	297 (53.6, M^+), 224	8.0^b	C$_{14}$H$_{19}$NO$_2$S$_2$	297.0613 (297.0857)

			IR (cm⁻¹)	¹H NMR (δ)		MS, m/z (rel. int.)	Formula	Found (Calc.)
				3.0 (m, 4H, SCH₂CH₂CH₂S), 3.0–3.2 (m, 2H, ring CH₂), 3.90–4.54 (m and q, 3H J 8 Hz, OCH₂CH₃ and SCHS), 5.6–5.84 (m, 2H, CH=CH).		(15.5, M⁺ – CO₂CH₂CH₃)		
VIIId	XIId	60	2260w (C≡N) 1720s (C=O) 1620w (C=C)	1.38 (t, 3H, J 8 Hz, OCH₂CH₃), 2.80 – 3.10 (bd, 2H, J 7 Hz, CH₂), 3.78 (t, 1H, J Hz, CHCO₂C₂H₅), 4.20–4.60 (m, 2H, OCH₂CH₃), 5.60–5.60 (m, 2H, CH=CH, with a bs at 6.0).	3.0 ᵃ	190 (0.4, M⁺), 163 (6.4, M⁺ – HCN), 145 (33.8, M⁺ – OCH₂CH₃), 118 (10.3 CH₃), 117 (45.1), 91 (100), 90 (20.4).	C₁₀H₁₀N₂O₂	190.0870 (190.0742)
VIIe+ VIIIe	XIe+ XIIe	81	2260w (C≡N) 1610, 1600, 1500w (C=C)	3.32 (bs, 2H, CH₂), 4.62 (bd, 1H, CHPh), 5.03 (m, 2H, CH=CH), 7.42 (m, 5H, C₆H₅).	9.6 ᵃ	194 (11.9, M⁺), 167 (6.4, M⁺ – HCN), 140 (4.0, M⁺ – 2HCN), 116 (100), 77 (15.8)	C₁₃H₁₀N₂	194.1054 (194.0844)

ᵃ Column A. ᵇ Column B.

(VIIId) was isolated in the reactions of II with ethyl 3,3-dicyanoacrylate [8] with a minute amount of its other isomer (VIId) (about 1% from HPLC analysis). The ^{1}H NMR spectrum of this adduct showed a broad doublet at δ 2.90 ppm assignable to methylene protons of C(5) coupled with the C(4) hydrogen (VIIId) which resonated at δ 3.25 ppm (broad t). Irradiation of the peak at δ 3.52 ppm resulted in collapse of the peak at δ 2.90 ppm (d) to a singlet and irradiation of the peak assigned to CH_2 caused collapse of the triplet of the CH to a singlet. The olefinic proton resonated as a broad peak at δ 5.18 ppm.

Reaction of II with 2-cyanocinnamonitrile (IVe) [9] yielded quantitatively the cyclic adducts (VII + VIIIe) as an inseparable mixture. From ^{1}H NMR spectral data, these adducts were found to occur in equal proportions.

From the above described results, it is evident that the introduction of the cyclic phosphite ligand in dicarbonyl(η^5-cyclopentadienyl)(η^1-2-methoxyallyl) iron (I) enhanced its reactivity to a substantial extent (Table 1). Complex II was found to be both more reactive and more selective in formation of cyclic adducts. The greater reactivity of II is most clearly indicated by its reaction with dimethyl 1-cyanoethylene-1,2-dicarboxylate (IVb) and 2-cyanocinnamonitrile (IVe) since no products were obtained on their reaction with complex I (Table 1). The selectivity of cycloaddition of reactions of II compared to I is shown by exclusive formation of VIIIc from reaction of II with ethyl 1-cyano-4,4-trimethylene dithiocrotonate (IVc) in contrast to the linear adduct obtained from complex I [10].

Formation of isomeric cyclopentene complexes (VIIa + VIIIa, VIIb + VIIIb and VIIe + VIIIe) in the reactions of II with olefins (IVa, IVb and IVe respectively) must be due to the comparable cleavage of a C–H bond from the two available methylene groups in intermediate cyclopentyl complexes (VIa, VIb and VIe). However, the presence of two highly electron withdrawing groups in complexes VIc and VId appears to facilitate a more selective elimination of methanol due to the differing acidities of the protons at C(2) and C(5). This results in exclusive formation of only one adduct (VIIIc and VIIId) in the reactions of II with IVc and IVd.

Demetallation

For the cycloaddition reactions to be of synthetic use in organic chemistry, the Fp-moiety from the cyclopentenyl complexes VII and VIII has to be eliminated by a suitable method. We have earlier reported [8] cleavage of the Fp-moiety with hydrogen chloride gas. Treatment of a dichloromethane solution of the cyclopentenyl-Fp complexes (VIIa + VIIIa) with hydrogen chloride gas for 1 h at 0°C resulted in the exclusive formation of trimethyl cyclopentenetricarboxylates (XIa + XIIa) in 48% yield. From GLC studies the two cyclopentenes were found to be present in equal ratio. Attempts to separate these compounds by column chromatography with $AgNO_3$ impregnated silica gel were partly successful on a small scale.

Dimethyl 1-cyanocyclopent-3-ene-1,2-dicarboxylate (XIb, 84%) and dimethyl 1-cyanocyclopent-4-ene-1,2-dicarboxylate (XIIb, 72%) were obtained by treatment of VIIb and VIIIb respectively with hydrogen chloride. The authenticity of XIb was proved by comparison of the spectral and analytical data with a sample prepared by an earlier reported procedure [11]. Similarly, the other cyclopentenyl adducts (VIIIc, VIIId and VII + VIIIe) were subjected to acid cleavage and cyclopentene derivatives thus obtained characterized by spectral and analytical data (Table 3).

Experimental

All operations were carried out as described earlier [8]. HPLC was carried out on a Dupont instrument with Zorbax sil. (25 × 0.46 cm, normal phase column) at ambient temperature, 140 bar pressure with a flow rate of 1.5 ml min^{-1} and UV detector. The mobile phase used was 50% heptane, 47% CH_2Cl_2, 2% MeOH and 1% H_2O. GLC were carried out on PYE 104 gas chromatograph, with 10%FFAP (3 m × 2 mm, Column A), 5% OV-101 (3 m × 2 mm, Column B) isothermally at 240°C with nitrogen as carrier gas at a flowrate of 25 ml min^{-1}.

Preparation of CpFe(CO)[P(OCH$_2$)$_3$CCH$_3$](η^1-2-methoxyallyl) (II)

A solution of I (8.5 mmol) [2], 4-methyl-2,6,7-trioxa-1-phosphatricyclo [2.2.2]octane (III)(1.3 g, 8.5 mmol), [CpFe(CO)$_2$]$_2$ (20 mg, 0.06 mmol) in pentane (80 ml) was irradiated with a 200 W table lamp while stirring for 30–45 min. Complex II began to separate as a yellow solid. This mixture was left at room temperature for a further 30 min until no more solid separated. This was filtered under nitrogen to give pure yellow crystalline compound II (2.2 g, 70%), dec. 124°C; ν_{max} (CH_2Cl_2) 1940s (C≡O); NMR (CDCl$_3$) δ (ppm) 0.75 (s, 3H, C CH$_3$) 1.10 1.90 (m, 2H, CH$_2$), 3.50 (s, 3H, OCH$_3$), 3.65 (m, 1H, CH=), 3.75 (m, 1H, =CH), 4.15 (d, 6H, J 5 Hz, (OCH$_2$)$_3$) and 4.45 (s, 5H, Cp). m/e 368 (M^+, 0), 340 (M – CO, 3.9%) 220 (M – L, 1.5) and 192 (M – CO, L, 18.3).

Reaction of Fp complex II with olefins (IVa–IVe), (general procedure)

To a solution of the Fp complex II (ca. 1 mmol) in CH_2Cl_2 (5–10 ml) was added olefin IV dissolved in the same solvent (2–3 ml). The reaction mixture was then stirred at room temperature for the reaction times indicated (Table 1). After removal of the solvent under reduced pressure, the crude product was chromatographed on a 1.5 × 20 cm column. The residue was, in general, applied to the column as a benzene solution. The products were then eluted with petroleum ether (40–60°)/diethylether and petroleum ether/ethyl acetate mixtures. Separation of the cyclic and linear adducts was effectively carried out with appropriate solvents and the adducts were purified by rechromatography. All the products showed satisfactory spectral and analytical data (Table 2). Unreacted II has been isolated in the form of FpCH$_2$COCH$_3$ (X) (Table 1) from column chromatography.

Preparation of ethyl-1-cyano-4,4-trimethylene dithiocrotonate (IVc)

A solution of 3,3-trimethylenedithiopropanal [12] (6.6 g, 41 mmol), ethyl cyanoacetate (3.88 g, 34 mmol), acetic acid (0.7 ml) and β-alanine (20 mg, 0.2 mmol) in benzene (40 ml) was heated to reflux for 20 h. The water produced in the reaction was removed azeotropically using a Dean and Stork apparatus. After removal of the solvent in vacuo the residue was partitioned between ether (150 ml) and water (50 ml) and the aqueous layer discarded. The organic layer was then washed with saturated aqueous sodium chloride solution (50 ml), dried over anhydrous sodium sulphate, filtered through celite and the solvent removed in vacuo. Rapid chromatography [13] of the above crude product (7.2 g), eluting with diethyl ether/petroleum ether (3/2) afforded an inseparable mixture of ethyl 1-cyano-4,4-trimethylene dithiocrotonate (IVc) and ethyl cyanoacetate (as a yellow oil, 6.47 g, ca. 78% yield) in a ratio of approximately 9/1. Distillation resulted in considerable decomposition of

the olefinic product, although it could be isolated in low yield (45% crude, b.p. 160–170°C at 0.2 mmHg), ν_{max} (CHCl$_3$), 2235w (C≡N), 1735s (C=O) and 1665m (C=C). ^{1}H NMR, δ (ppm) 1.36 (t, 3H, J 7 Hz, CH$_3$), 1.71–2.31 (m, 2H, SCH$_2$CH$_2$CH$_2$S), 2.80–3.14 (m, 6H, SCH$_2$CH$_2$S and CHCH$_2$CH=C), 4.20 (t, 1H, J 8 Hz, CH$_2$CHS), 4.34 (q, 2H, J 7 Hz, OCH$_2$) and 7.67 (t, 1H, J 7.5 Hz, C=CH). m/e 257 (5, M^+), 122 (5), 121 (9), 119 (100, M − CH=C(CN)CO$_2$Et), 106 (8), 75 (4) and 73 (6).

Demetallation of cyclopentenyl-Fp adducts (VIIa–VIIe and VIIIa–VIIIe), (General procedure)

The cyclic adducts (VIIa–VIIe, VIIIa–VIIIe) (0.14–0.6 mol) were dissolved in CH$_2$Cl$_2$ (30 ml) and dry hydrogen chloride gas was bubbled through at 0°C for one hour. The reaction mixture was then set aside in a well stoppered flask for 20 h at room temperature. The solvent was removed under reduced pressure, after which the residue was dissolved in CCl$_4$ (30 ml) and exposed to sunlight for 4–5 h to decompose any FpCl present. The separated green solid was filtered and the filtrate concentrated to give the crude products which were purified by rapid chromatography [13] on silica gel (1.5 × 15 cm). The isomeric olefins in some cases (XIa and XIIa) were obtained as inseparable mixtures and the ratios were determined by GLC analysis and ^{1}H NMR spectral data (Table 3).

Acknowledgements

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