Redox active alkenyl-bridged bi- and trinuclear arene–Cr(CO)₃-complexes by Horner–Emmons–Wadsworth olefinations

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Dedicated to Professor Dr Wolfgang Steglich on the occasion of his 65th birthday

Abstract

Alkenyl-bridged arene–Cr(CO)₃-complexes **2** are readily synthesized in good yields by Horner–Emmons–Wadsworth (HEW) olefinations from Cr(CO)₃-complexed benzylphosphonates **1** and organometallic aldehydes. The resulting bi- and trinuclear homo- and heterometallic complexes display a strong electronic coupling between the metal fragments as shown by a strong correlation of the CO resonances in the carbon NMR spectra and the chromiumcarbonyl metal–ligand charge transfer (MLCT) bands in the UV/vis spectra. Furthermore, the electrochemistry of the oligonuclear complexes **2** was investigated by cyclic voltammetry. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Alkenes; Arene complexes; Chromium; Cyclic voltammetry; Ferrocene; Iron

1. Introduction

The increasing demand for conjugated organic/organometallic structures in the rapidly developing field of electro optical and nonlinear optical materials has initiated an eager search for syntheses and structures of novel molecule based materials [1]. In particular, metallocene type structures play a key role in the search for organic–inorganic hybride motifs [2]. Structurally, these organometallic building blocks are linked either directly [3] or with a spacer, preferentially a conjugating π-bridge such as alkynes [4], alkenes [5] or arenes [6]. Since the direct complexation of organometallic fragments to an unsaturated organic ligand containing more than one benzene or cyclopentadienide ring is not efficient, i.e. either low yielding or unselective, the synthetic strategy suggests a convergent approach. Therefore, small mononuclear and easily accessible metallocenes bearing reactive functional groups for condensation or cross coupling reactions allow the application of well-established organic synthetic methodology for a chemo- and regioselective construction of polynuclear metallocene framework. The most simple representatives of polymeric metallocene chains are triads of changing or identical sandwich or half sandwich fragments. Here, the synthesis and the cyclic voltammetry of ferrocenyl and benchrotrenyl triads crosslinked by ethenyl bridges will be described and discussed.

2. Results and discussion

Recently, we found a facile and general access to alkenyl substituted arene–Cr(CO)₃-complexes based upon the Horner–Emmons–Wadsworth (HEW) olefination of η⁶-Cr(CO)₃-benzyl phosphonates [7]. This approach takes advantage from the activation of the benzylic position by stabilization of negative charges
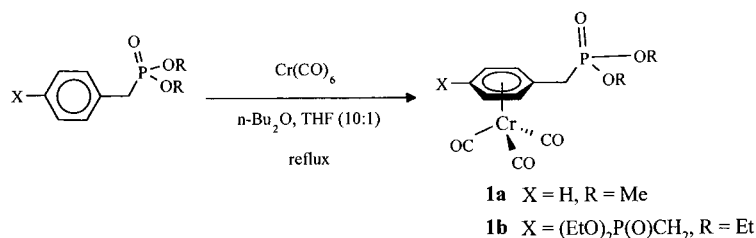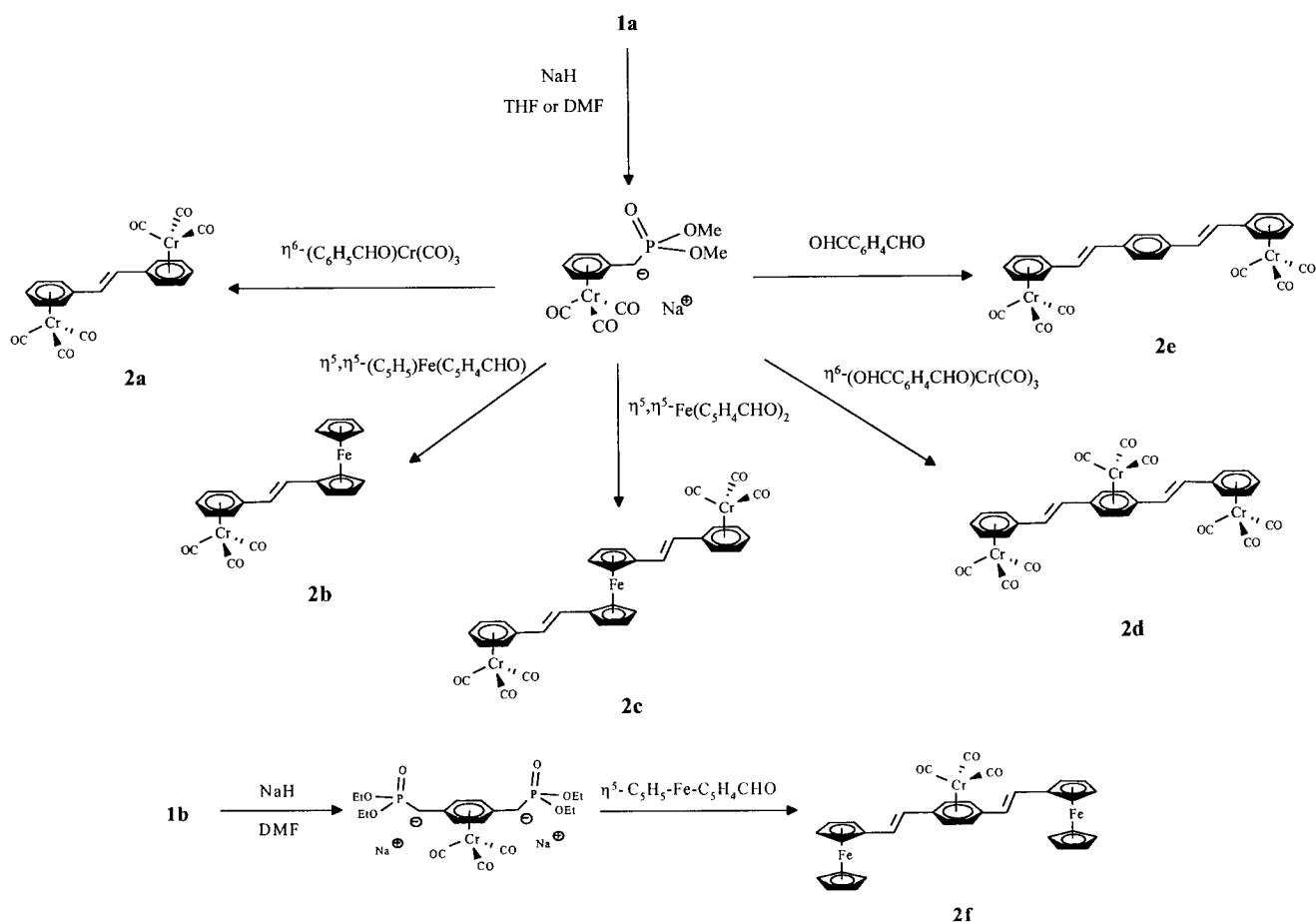
Scheme 1.

due to the net electron withdrawing chromium carbonyl tripod [8]. Furthermore, the HEW reaction overcomes a severe stereochemical ambiguity of Wittig olefinations, i.e. the formation of a mixture of *cis*- and *trans*-stereoisomers. Thus, HEW olefinations stereoselectively lead to the formation of double bonds in the *E*-configuration [9].

The phosphonate complexes **1** can be easily prepared from the corresponding free ligands by thermolysis of hexacarbonyl chromium and are obtained as light yellow crystalline solids in 68 and 40% yield (Scheme 1). The η^6-arene complexation is supported by the considerable upfield shift of the arene proton and carbon resonances in the ^1H and ^{13}C spectra, respectively. Even the rather

remote phosphorus nuclei at the benzylic carbon atoms experience a slight shift to higher field in the ^{31}P spectra. Thus, the phosphorus resonances of the free ligands, benzyl dimethyl phosphonate and *p*-xylenyl bis(diethyl) phosphonate, appear at $\delta = 28.9$ and 26.4, those of the complexes **1a** and **1b** at $\delta = 26.3$ and 23.6, respectively.

After deprotonation with sodium hydride in THF or DMF the complexes **1** react smoothly in boiling THF or at room temperature in DMF with organometallic mono- and dialdehydes to give the alkenyl bridged bi- and trinuclear complexes **2** (Scheme 2) in moderate to excellent yields as orange–red crystalline solids.

As expected, only *trans*-configured double bonds are formed in the HEW-olefination as indicated by the

Scheme 2.

characteristic vicinal coupling constants ($J = 16.0$–16.6 Hz) in the ^{1}H-NMR spectra. The chromiumcarbonyl complexed arene moieties and the ferrocenyl fragments are identified due to the upfield shift of the arene proton and carbon resonances and the typical carbonyl resonances of the CO ligands appear between $\delta = 233.6$ and 234.8 (Table 1). In recent studies on alkynyl substituted chromiumcarbonyl arene complexes [4f,h] we have applied the shift of the carbonyl resonances to probe the relative electron density on the metal center, i.e. the increasing electron richness, with the down field shift [10]. Since no discrete charges are involved these effects are rather small but they still give a qualitative impression of the electron density distribution on the chromium atom(s). Thus, the ferrocenyl moiety (**2b**, **2c**, **2f**) acts as an electron donor by transmitting its substituent effect via the alkenyl bridge to the arene–Cr(CO)$_3$-fragment by resonance and inductive mechanisms [11]. In turn, the low donor capacity of the phenylene bridge (**2e**) and the strong electron withdrawal of the arene–Cr(CO)$_3$-substituents (**2a**, **2d**) is reflected in the upfield shift of the CO signals. Obviously, the electron density on the chromium can be fine tuned by attaching electron donating or withdrawing organometallic substituents at the β-carbon atom of the alkenyl bridge. A closer inspection of the UV/vis absorption bands reveals a similar dependence of the electron density on the chromium atom (Table 1). All electronic spectra display similar features [1d,12]: a short wave length absorption between 305 and 340 nm which can be assigned to π–π* transitions and ligand–metal (LM) charge transfer (CT) bands and a longer wave length band between 377 and 436 nm arising from metal–ligand (ML) CT bands from the chromiumcarbonyl fragments. Those compounds with ferrocenyl

Fig. 1. δ(CO) vs. λ_{max} plot (regression analysis: λ_{max} [nm] $= -51.635$ nm ppm^{-1} δ(CO) [ppm] $= 12505$ nm; $r = 0.9677$).

substituents (**2b**, **2c**, **2f**) additionally display a long wave length absorption band between 450 and 475 nm which clearly can be assigned to 3d–3d transitions in the ferrocenyl moiety [12a,13]. Interestingly, there is a strong correlation of the chromiumcarbonyl MLCT bands in the UV spectra and the CO resonances in ^{13}C-NMR spectra as indicated by the regression analysis of λ_{max} vs. δ(CO) plot ($r = -0.97$) (Fig. 1): the lower the electron density on the chromium atom the stronger the red shift of the MLCT band of chromiumcarbonyl moiety. Thus, alkenyl linked metallocene oligomers can be devised and constructed with distinct electronic properties.

This implies a major reason why transition metal complexes have been devised for tailor-made electroactive chromophores. In addition, most metallocene and half-sandwich complexes show a rich electrochemistry since the metal(s) can often be reversibly oxidized to higher or reduced to lower levels of oxidation [14]. In numerous cases the electrochemical behavior of oligonuclear metallocenes has also been studied with respect to metal–metal electron transfer [2b,4d,e,15]. The electronic synergism of two metallocenes with similar electronic configuration (d^6) was successfully applied in ligand substitution and addition reactions of arene–Cr(CO)$_3$ complexes by attaching a ferrocenyl moiety as a self-closing redox switch [16]. Behind this effect hides an ECE mechanism, i.e. the initial oxidation occurs at the ferrocene center followed by an electron transfer from the chromium to the iron center characterized by the equilibrium constant K_{eq} and finally again an iron-centered oxidation leading to a dication (Scheme 3). Based upon ligand substitution reactions the equilibrium constant K_{eq} was estimated to 2.4×10^3. As a consequence this intramolecular electron transfer can be considered as a segment model for a p-doped electrically conducting metallocene polymer.

The electrochemical behavior of the alkenyl bridged complexes **2** was investigated by cyclic voltammetry (Table 2) using dichloromethane (oxidation potentials) and THF (reduction potentials of oligo benzene–

Table 1
^{13}C-NMR CO resonances and UV/vis spectroscopic data

Compound	CO resonances	UV/vis absorptions
2a	233.93	329 (15900)
		434 (7300)[a]
2b	234.59	306 (17900)
		386 (5530, sh)[a]
		452 (2800, sh)[b]
2c	234.54	321 (29800)
		400 (10900)[a]
		475 (4200, sh)[b]
2d	233.59	306 (39100)
	233.94	436 (13700)[a]
2e	234.36	338 (43100)
		408 (16000)[a]
2f	234.83	328 (36000)
		377 (11300, sh)[a]
		461 (6500)[b]

[a] Arene–Cr(CO)$_3$-MLCT.
[b] Ferrocene-3d–3d-transition.

Scheme 3.

$Cr(CO)_3$ complexes). The communication of the two chromium atoms in the doubly complexed *trans*-stilbene **2a** is supported by the occurrence of two quasi-reversible one-electron oxidations at 782 and 900 mV. The reduction presumably starts with an irreversible formation of a stilbene dimer [17] at 1250 mV followed by two reversible reduction at the chromium centers at 1600 and 1900 mV [18]. Compared to stilbene the reduction potential is considerably lowered upon chromium carbonyl complexation but binuclear chromium arene complexes rather tend to form stabilized localized anionic cyclohexadienide complexes than highly delocalized anions [19]. The oxidation of the bimetallic binuclear complex **2b** occurs at 453 and 774 mV, respectively. Upon linking the electron withdrawing benzene–$Cr(CO)_3$ moiety to the ferrocene by a conjugating ethenyl bridge the first oxidation potential is reversible and shifted anodically indicating a strong substituent effect. According to the ECE mechanism (vide supra) the ferrocenium ion is reduced to ferrocene by an intramolecular electron transfer now giving rise to a chromium centered cation. The second oxidation potential arising from a second ferrocene centered oxidation is irreversible presumably due to a slow decomposition [20] of the dicationic species with two 17e transition metal fragments by an intermolecular CO displacement by an alkenyl ligand. The irreversible reduction potential arises from a reversible stilbene dimerization [17]. A similar cyclic voltammogramm is obtained for complex **2c** where a reversible ferrocene centered one electron oxidation occurs at 372 mV followed by a rapid decomposition at 750 mV (Fig. 2). Remarkably, the ferrocene oxidation is facilitated by linking two benzene–$Cr(CO)_3$ fragments to a ferrocene unit. Since the second oxidation potential still is lower than expected for a chromium centered oxidation another ferrocene centered oxidation can generate the dicationic species which rapidly decomposes. As expected, ferrocene donates electron density to the chromiumcarbonyl fragments causing a cathodical shift of the reduction potentials.

The cyclic voltammograms of the homometallic bi- and trinuclear benzene–$Cr(CO)_3$ complexes **2d** and **2e** display similar features: the oxidation potentials are irreversible and represent average values of the oxidation potentials of **2a**. This can be accounted to a strong interaction between the two or three metal centers transmitted through the conjugating bridge. As expected the stilbene dimerization [17] at 1200 mV precedes the reversible two electron chromium centered reduction potentials of the first chromium center at 1655 and 1662 mV, respectively, followed by a second irreversible reduction wave at about 1900 mV. The similarity of the potentials of the first chromium centered reduction can also be deduced from a strong electronic coupling by an efficient delocalizing π-bridging system. Finally, the heterometallic trinuclear complex **2f** (Fig. 3) containing one chromium and two iron centers displays electrochemical characteristics comparable to the heteronuclear complexes **2b** and **2c**. The oxidation at the ferrocene centers is facilitated compared to **2b** and **2c** and occurs reversibly as a two electron wave at 351 mV. At higher oxidation poten-

Table 2
Electrochemical potential vs. a platinum electrode, relative to Fc/ Fc^+ ($E_{1/2} = 403$ mV (CH_2Cl_2), 370 mV (THF)), scan rate 100 mVs^{-1}

Compnd	Oxidation potentials (CH_2Cl_2)	Reduction potentials (THF)
Fc	403	–
Bct	783	−1950
PhCH=CHPh	–	−2450
2a	782[a]	−1248[b]
	900[a]	−1593
		−1905
2b	453	−1146[b]
	774	
2c	372	−1638
	750	−2250
2d	882	−1174[b]
		−1655
		−1875
2e	852	−1194[b]
		−1662
2f	351	−1200[b]

[a] Scan rate = 1000 mVs^{-1}.
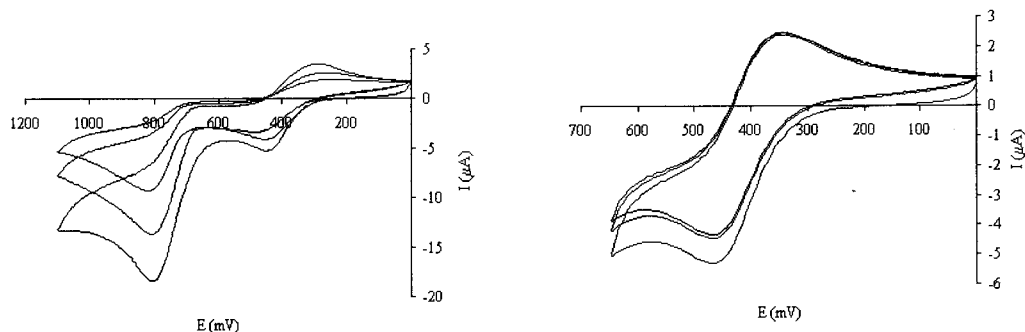[b] Stilbene-type dimerization.

Fig. 2. Cyclic voltammetric oxidation (first and second oxidation wave, left; first oxidation wave, right) in dichloromethane of **2c** (scan rate = 100 mVs^{-1}).
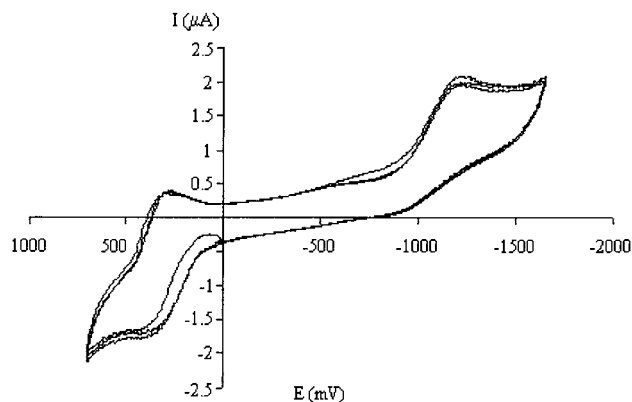

Fig. 3. Cyclic voltammetric oxidation and reduction in dichloromethane of **2f** (scan rate = 100 mVs^{-1}).

tials irreversible waves indicate a rapid decomposition. The irreversible reduction at 1200 mV again results from a reversible stilbenoid dimerization [17].

All cyclic voltammograms of homo- and heteronuclear diads and triads reveal that a strong electronic coupling of the oxidized and reduced species occurs by inductive and resonance pathways. Especially, since a stilbenoid dimerization precedes the first chromium centered reductions inductive transmission mechanisms seriously have to be taken into account. These first electrochemical studies not only encourage a more sophisticated fine-tuning of redox potentials by altering the ligand sphere of the chromium tripod but also point the way to oligo or polynuclear metallocene complexes with an extended π-conjugation.

3. Conclusion

The HEW olefination of organometallic aldehydes with Cr(CO)$_3$-complexed benzyl phosphonates represents a powerful and convergent selective synthetic access to alkenyl-bridged oligonuclear arene–Cr(CO)$_3$-complexes. Especially, heteronuclear systems like chromiumcarbonyl-ferrocene ensembles display a rich

electrochemistry also with regard to intramolecular electron transfer processes. Therefore, alkenyl-bridged arene–Cr(CO)$_3$-complexes can be promising candidates for organometallic materials such as molecular wires or switches. The possibility of fine-tuning electronical properties upon connecting electron-donating or electron-withdrawing aldehydes by a HEW olefination to arene–Cr(CO)$_3$-complexes also prompts us to design novel chromiumcarbonyl based NLO materials. The syntheses and structure-property investigations of alkenyl-bridged arene–Cr(CO)$_3$-NLO chromophores are currently underway.

4. Experimental

4.1. General

All reactions involving tricarbonylchromium complexes were carried out in flame-dried Schlenk flasks under nitrogen by using septum and syringe techniques. Solvents were dried and distilled according to standard procedures [21].—Column chromatography: silica gel 60 (0.063–0.2 mm = 70–230 mesh, Firma Merck). TLC: silica gel plates (60 F$_{254}$ Merck, Darmstadt). Melting points (uncorrected values): Reichert–Jung Thermovar.—The benzyl phosphonates [22], η^6-(benzaldehyde)Cr(CO)$_3$ [23], ferrocene carbaldehyde [24], ferrocene 1,1′-biscarbaldehyde [25], η^6-(terephthalic dialdehyde)Cr(CO)$_3$ [11] were synthesized according to published procedures. Sodium hydride (95%) and terephthalic dialdehyde were purchased from Aldrich and used without further purification.—^{1}H and ^{13}C spectra: Bruker WM 300 or Bruker AC 300, [D$_6$]DMSO.—IR: Perkin Elmer FT-IR Paragon 1000 PC. The samples were pressed into KBr pellets. UV/vis: Beckman DK-2-A or Beckman UV 5240.—MS: Finnigan MAT 311-A/100MS.—Elemental analyses were carried out in the Microanalytical Laboratory of the Institute of Organic Chemistry, Technical University of Darmstadt.

4.2. Electrochemistry

Cyclic voltammetry experiments (EG and G potentiostatic instrumentation) were performed under argon in dry and degassed dichloromethane or THF at room temperature and at scan rates of 100, 500 and 1000 mVs^{-1}. The electrolyte was 0.10 M Bu$_4$NPF$_6$. The working electrode was a 1 mm platinum disk, the counter electrode was a platinum wire, and the reference electrode was a Ag/AgCl/aqueous KCl electrode. The potential of Fc/Fc$^+$ was determined in dichloromethane ($E_{1/2} = 403$ mV) and in THF (370 mV)

4.3. Cr(CO)$_3$(η^6-C$_6$H$_5$)CH$_2$P(OCH$_3$)$_2$ (1a)

A total of 3.00 g (13.6 mmol) of hexacarbonyl chromium and 2.62 g (13.1 mmol) of dimethyl benzyl phosphonate suspended in a mixture of dibutyl ether (70 ml) and THF (7 ml) were degassed by bubbling a stream of argon for 10 min through the reaction mixture. This mixture was heated to reflux temperature (oil bath 140–145°C) for 18 h. After cooling the green solution was filtered through a short pad of celite. The filter residues were rinsed with a small amount of dichloromethane. The solvents of the combined filtrates were removed in vacuo (water bath 95°C) and the residue was triturated several times with pentane to give 3.00 g (68%) of essentially pure 1a as a yellow–green powder. Further purification was achieved by recrystallization from dichloromethane/pentane to give yellow needles.—M.p. 115°C.—^{1}H-NMR (CDCl$_3$, 300 MHz): $\delta = 2.82$ (d, $J = 20.4$ Hz, 2 H), 3.73 (d, $J = 10.7$ Hz, 6 H), 5.21 (m, 1 H), 5.26 (m, 2 H), 5.40 (m, 2H).—^{13}C-NMR (CDCl$_3$, 75 MHz): $\delta = 32.26$ (d, $J = 138.0$ Hz, CH$_2$), 53.14 (d, $J = 6.2$ Hz, CH$_3$), 90.44 (CH), 93.09 (CH), 93.61 (CH), 102.66 (d, $J = 3.7$ Hz, C$_{quat.}$), 232.46 (C$_{quat.}$, CO).—^{31}P-NMR ([D$_6$]DMSO, 121 MHz): $\delta = 26.28$.—MS (CI, 70 eV), m/z (%): 336 (M^+, 4), 308 (M^+ CO, 9), 280 (M^+ 2 CO, 12), 252 (M^+ 3 CO, 100), 52 (Cr$^+$, 52).—IR (KBr): $n = 1964$ cm^{-1}, 1887, 1463, 1267, 1225, 1062, 1039, 874, 841, 665, 628, 539, 529.—UV/vis (DMSO): $\lambda_{max.}$ (ε) = 253 nm (7100), 316 (9600).—C$_{12}$H$_{13}$CrO$_6$P (336.21) Anal. Calc. C 42.87, H 3.90; Found C 42.97, H 3.85.

4.4. (C$_2$H$_5$O)$_2$PCH$_2$(η^6-C$_6$H$_4$)Cr(CO)$_3$CH$_2$P(OC$_2$H$_5$)$_2$ (1b)

A total of 3.30 g (15.0 mmol) of hexacarbonyl chromium and 5.67 g (15.0 mmol) of phenylene 1,4-bis(diethyl phosphonate) suspended in a mixture of dibutyl ether (70 ml) and THF (7 ml) were degassed by bubbling a stream of argon for 10 min through the reaction mixture. This mixture was heated to reflux temperature (oil bath 140–145°C) for 18 h. After cooling the yellow green suspension was filtered through a

short pad of celite. The filter residues were rinsed with 100 ml of dichloromethane. The solvents of the combined filtrates were removed in vacuo (water bath 95°C) and the residue was purified by flash chromatography (1. diethyl ether, 2. ethyl acetate, 3. methanol) to give 3.05 g (40%) of essentially pure 1b as a yellow needles. Further purification was achieved by recrystallization from dichloromethane/pentane.—M.p. 106–107°C.—^{1}H-NMR ([D$_6$]DMSO, 300 MHz): $\delta = 1.20$ (t, $J = 7.0$ Hz, 12 H), 2.97 (d, $J = 20.7$ Hz, 4 H), 4.02 (m, $J = 7.2$, 7.4 Hz, 8 H), 5.75 (s, 4 H).—^{13}C-NMR ([D$_6$]DMSO, 75 MHz): $\delta = 16.35$ (d, $J = 5.7$ Hz, CH$_3$), 31.15 (d, $J = 133.1$ Hz, CH$_2$), 61.96 (d, $J = 6.2$ Hz, CH$_2$), 96.06 (CH), 104.24 (d, $J = 3.8$ Hz, C$_{quat.}$), 233.80 (C$_{quat.}$, CO).—^{31}P-NMR ([D$_6$]DMSO, 121 MHz): $\delta = 23.59$.—MS (FD, 70eV), m/z (%): 514 (M^+), 378 (M^+ Cr(CO)$_3$).—IR (KBr): $n = 1963$ cm^{-1}, 1876, 1243, 1045, 1024, 968, 852, 807, 791, 669, 629.—UV/vis (DMSO): $\lambda_{max.}$ (ε) = 318 nm (9600).—C$_{19}$H$_{28}$CrO$_9$P$_2$ (514.38) Anal. Calc. C 44.37, H 5.49; Found C 43.77, H 5.20.

4.5. Horner–Emmons–Wadsworth olefinations of phosphonate complexes: general procedure

To a degassed solution of 1 equivalent of phosphonate complex 1 in 20 ml of THF or DMF 1.1 or 2.2 equivalents of sodium hydride (95%) is added under argon. After stirring for 10 min at r.t. 0.5, 1 or 2 equivalents of the corresponding aldehyde or dialdehyde in 2 ml of THF were added to the suspension. The reaction mixture was heated to reflux temperature (THF) for 12 h or stirred at room temperature (DMF) for 2 days. After aqueous workup the mixture was extracted with dichloromethane (3 × 20 ml) several times. The organic layer was washed with 20 ml of brine and then dried over anhydrous magnesium sulfate. The solvents were removed in vacuo to give the alkenyl bridged systems 2. Further purification was achieved by recrystallization from dichloromethane/pentane.

4.6. Cr(CO)$_3$(η^6-C$_6$H$_5$)CH=CH(η^6-C$_6$H$_5$)Cr(CO)$_3$ (2a)

According to the GP 341 mg (1.01 mmol) of 1a, 47 mg (1.6 mmol) of sodium hydride and 242 mg (1.00 mmol) of benzaldehyde complex in 20 ml of THF were heated to reflux temperature for 12 h to give 420 mg (93%) of pure 2a as orange crystals.—M.p. 212°C (dec.).—^{1}H-NMR ([D$_6$]DMSO, 300 MHz): $\delta = 5.72$ (t, $J = 6.1$ Hz, 2 H), 5.84 (dd, $J = 6.1$, 6.2 Hz, 4 H), 6.01 (d, $J = 6.2$ Hz, 4 H), 6.96 (s, 2 H).—^{13}C-NMR ([D$_6$]DMSO, 75 MHz): $\delta = 93.27$ (CH), 94.23 (CH), 95.08 (CH), 105.78 (C$_{quat.}$), 127.59 (CH), 233.93 (C$_{quat.}$, CO).—MS (CI, 70 eV), m/z (%): 452 (M^+, 25), 368 (M^+ 3 CO, 14), 340 (M^+ 4 CO, 11), 312 (M^+ 5 CO,

46), 284 (M^+ 6 CO, 17), 232 (M^+ Cr(CO)$_6$, 61), 52 (Cr$^+$, 100).—IR (KBr): $n = 1959$ cm^{-1}, 1895, 1860, 659, 630, 617, 527.—UV/vis (DMSO): $\lambda_{max.}$ (ε) = 329 nm (15900), 434 (7300).—C$_{20}$H$_{12}$Cr$_2$O$_6$ (452.32) Anal. Calc. C 53.11, H 2.67; Found C 52.70, H 2.66.

4.7. Cr(CO)$_3$(η^6-C$_6$H$_5$)CH=CH(η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$) (2b)

According to the GP 341 mg (1.01 mmol) of **1a**, 46 mg (1.5 mmol) of sodium hydride and 214 mg (1.00 mmol) of ferrocene carbaldehyde in 20 ml of THF were heated to reflux temperature for 12 h to give 300 mg (70%) of pure **2b** as orange crystals.—M.p. 170°C (dec.).—^{1}H-NMR ([D$_6$]DMSO, 300 MHz): $\delta = 4.15$ (s, 5 H), 4.4 (br, 2 H), 4.5 (br, 2 H), 5.83 (m, 1 H), 5.94 (m, 2 H), 5.96 (m, 2 H), 6.41 (d, $J = 16.0$ Hz, 1 H), 7.06 (d, $J = 16.0$ Hz, 1 H).—^{13}C-NMR ([D$_6$]DMSO, 75 MHz): $\delta = 67.41$ (CH), 69.42 (CH), 69.71 (CH), 81.59 (C$_{quat.}$), 92.04 (CH), 93.04 (CH), 96.06 (CH), 109.79 (C$_{quat.}$), 121.37 (CH), 130.96 (CH), 234.59 (C$_{quat.}$, CO).—MS (CI, 70 eV), m/z (%): 424 (M^+, 45), 340 (M^+ 3 CO, 100), 284 (M$^+$ Fe(CO)$_3$, 74), 52 (Cr$^+$, 29).—IR (KBr): $n = 1957$ cm^{-1}, 1884, 1636, 660, 631.—UV/vis (DMSO): $\lambda_{max.}$ (ε) = 306 nm (17900), 386 (5500, sh), 452 (2800, sh).—C$_{21}$H$_{16}$CrFeO$_3$ (424.21) Anal. Calc. C 59.46, H 3.80; Found C 59.17, H 3.59.

4.8. Cr(CO)$_3$(η^6-C$_6$H$_5$)CH=CH(η^5-C$_5$H$_4$)-Fe(η^5-C$_5$H$_4$)CH=CH(η^6-C$_6$H$_5$)Cr(CO)$_3$ (2c)

According to the GP 336 mg (1.00 mmol) of **1a**, 26 mg (1.1 mmol) of sodium hydride and 121 mg (0.50 mmol) of ferrocenyl 1,1′-biscarbaldehyde in 10 ml of DMF were stirred at room temperature for 2 days to give 262 mg (79%) of pure **2c** as a dark red powder.—M.p. 225°C (dec.).—^{1}H-NMR ([D$_6$]DMSO, 300 MHz): $\delta = 4.4$ (br, 4 H), 4.5 (br, 4 H), 5.6 (br, 2 H), 5.8 (br, 4 H), 5.9 (br, 4 H), 6.34 (d, $J = 16.1$ Hz, 2 H), 6.93 (d, $J = 16.2$ Hz, 2 H).—^{13}C-NMR ([D$_6$]DMSO, 75 MHz): $\delta = 68.63$ (CH), 71.14 (CH), 82.56 (C$_{quat.}$), 92.04 (CH), 93.10 (CH), 95.96 (CH), 109.53 (C$_{quat.}$), 121.98 (CH), 130.08 (CH), 234.54 (C$_{quat.}$, CO).—MS (CI, 70 eV), m/z (%): 662 (M^+, 7), 578 (M^+ 3 CO, 5), 526 (M^+ Cr(CO)$_3$, 28), 494 (M^+ 6 CO, 40), 442 (M^+ Cr(CO)$_6$, 95), 391 (60), 387 (44), 52 (Cr$^+$, 100).—IR (KBr): $n = 1945$ cm^{-1}, 1869, 1631, 951, 661, 632, 534.—UV/vis (DMSO): $\lambda_{max.}$ (ε) = 321 nm (29800), 400 (10900), 475 (4170, sh).—C$_{32}$H$_{22}$Cr$_2$FeO$_6$ (662.38) Anal. Calc. C 58.03, H 3.35; Found C 57.36, H 3.29.

4.9. Cr(CO)$_3$(η^6-C$_6$H$_5$)CH=CH(η^6-C$_6$H$_4$)Cr(CO)$_3$-CH=CH(η^6-C$_6$H$_5$)Cr(CO)$_3$ (2d)

According to the GP 346 mg (1.03 mmol) of **1**, 46 mg (1.5 mmol) of sodium hydride and 139 mg (0.51 mmol)

of terephthalaldehyde complex in 20 ml of THF were heated to reflux temperature for 12 h to give 300 mg (85%) of pure **2d** an orange powder.—M.p. 190°C (dec.).—^{1}H-NMR ([D$_6$]DMSO, 300 MHz): $\delta = 5.7$ (br, 2 H), 5.9 (br, 4 H), 6.0 (br, 4 H), 6.1 (s, 4 H), 7.0 (br, 4 H).—^{13}C-NMR ([D$_6$]DMSO, 75 MHz): $\delta = 93.01$ (CH), 93.30 (CH), 94.27 (CH), 95.07 (CH), 104.78 (C$_{quat.}$), 105.80 (C$_{quat.}$), 127.32 (CH), 127.61 (CH), 233.59 (C$_{quat.}$, CO), 233.94 (C$_{quat.}$, CO).—MS (FD, 70 eV), m/z: 690 (M^+), 554 (M^+ Cr(CO)$_3$).—IR (KBr): $n = 1963$ cm^{-1}, 1877, 1637, 954, 677, 656, 625.—UV/vis (DMSO): $\lambda_{max.}$ (ε) = 306 nm (39100), 436 (13700).—C$_{31}$H$_{18}$Cr$_3$O$_9$ (690.49) Anal. Calc. C 53.92, H 2.63; Found C 54.03, H 2.65.

4.10. Cr(CO)$_3$(η^6-C$_6$H$_5$)CH=CHC$_6$H$_4$CH=CH-(η^6-C$_6$H$_5$)Cr(CO)$_3$ (2e)

According to the GP 362 mg (1.08 mmol) of **1a**, 47 mg (1.6 mmol) of sodium hydride and 72 mg (1.00 mmol) of terephthalaldehyde in 20 ml of THF were heated to reflux temperature for 12 h to give 124 mg (42%) of pure **2e** as a red powder.—M.p. 210°C (dec.).—^{1}H-NMR ([D$_6$]DMSO, 300 MHz): $\delta = 5.7$ (br, 2 H), 5.9 (br, 4 H), 6.1 (br, 4 H), 6.99 (d, $J = 16.6$ Hz, 2 H), 7.31 (d, $J = 16.2$ Hz, 2 H), 7.61 (s, 4 H).—^{13}C-NMR ([D$_6$]DMSO, 75 MHz): $\delta = 93.04$ (CH), 93.83 (CH), 95.62 (CH), 107.94 (C$_{quat.}$), 125.40 (CH), 127.49 (CH), 130.61 (CH), 136.15 (C$_{quat.}$), 234.36 (C$_{quat.}$, CO).—MS (CI, 70 eV), m/z (%): 554 (M^+, 7), 470 (M^+ 3 CO, 8), 414 (M^+ 5 CO, 14), 386 (M^+ 6 CO, 7), 362 (M^+ Cr(CO)$_5$, 17), 334 (M^+ Cr(CO)$_6$, 100), 282 (M^+ 2 Cr(CO)$_3$, 36), 52 (Cr$^+$, 92).—IR (KBr): $n = 1953$ cm^{-1}, 1867, 964, 821, 657, 629, 620, 531.—UV/vis (DMSO): $\lambda_{max.}$ (ε) = 338 nm (43100), 434 (16000).—C$_{28}$H$_{18}$Cr$_2$O$_6$ (554.45) Anal. Calc. C 60.66, H 3.27; Found C 60.75, H 3.33.

4.11. (η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$)CH=CH(η^6-C$_6$H$_4$)-Cr(CO)$_3$CH=CH(η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$) (2f)

According to the GP 257 mg (0.50 mmol) of **1b**, 26 mg (1.1 mmol) of sodium hydride and 220 mg (1.03 mmol) of ferrocene carbaldehyde in 10 ml of DMF were stirred at room temperature for 2 days to give 103 mg (32%) of pure **2f** as red crystals.—M.p. 250°C (dec.).—^{1}H-NMR ([D$_6$]DMSO, 300 MHz): $\delta = 4.17$ (s, 10 4 H), 4.4 (br, 4 H), 4.6 (br, 4 H), 6.11 (s, 4 H), 6.42 (d, $J = 16.2$ Hz, 2 H), 7.08 (d, $J = 16.2$ Hz, 2 H).—^{13}C-NMR ([D$_6$]DMSO, 75 MHz): $\delta = 67.34$ (CH), 69.19 (C$_{quat.}$), 69.41 (CH), 69.66 (CH), 92.66 (CH), 107.69 (C$_{quat.}$), 121.29 (CH), 130.29 (CH), 234.83 (C$_{quat.}$, CO).—MS (CI, 70 eV), m/z (%): 634 (M^+, 8), 549 (M^+ 3 CO–H, 44), 498 (M^+ Cr(CO)$_3$, 100), 121 (CpFe$^+$, 30), (Fe$^+$, 16), (Cr$^+$, 22).—IR (KBr): $n = 1951$ cm^{-1}, 1874, 1631, 954, 6661, 623, 504.—UV/vis

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