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$Cr(CO)_3$-Complexed Benzylphosphonates - A Horner-Emmons-Wadsworth Approach To Alkenyl Substituted Tricarbonylchromium Arene Complexes

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Summary: The Horner-Emmons-Wadsworth reaction of η^6-benzylphosphonate complexes **1** with aldehydes, dialdehydes and ketones **2** with sodium hydride as a base in boiling THF gives rise to arene$Cr(CO)_3$ substituted *trans*-alkenes **3** in moderate to good yields.
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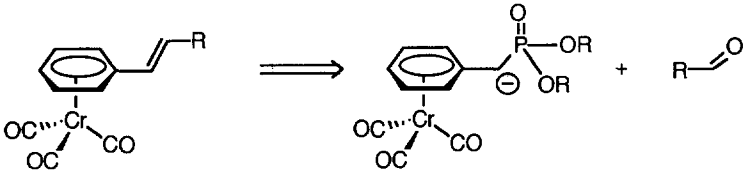
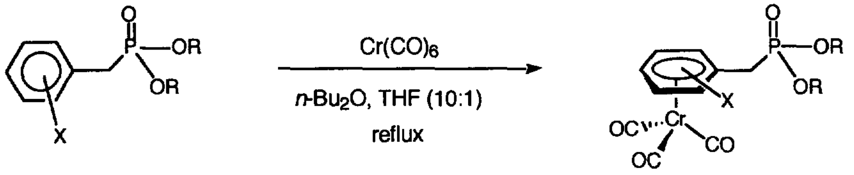
The Wittig and the Horner-Emmons-Wadsworth (HEW) reactions are the most reliable and efficient olefination processes in organic synthesis.[1] Not only the chemoselectivity is very high but also the stereoselectivity can be predicted and controlled in numerous examples.[1c] As a part of our program[2] initiated to synthesize and to study conjugated organometallic π-systems and to investigate their optical and electronical properties as well as their synthetic potential there was need for a facile and regioselective introduction of strongly electron withdrawing $Cr(CO)_3$-complexed arene fragments into an alkenyl-bridged conjugated π-system. Furthermore, alkenyl substituted chromium arene complexes are known to react either with stabilized carbanions or electrophiles such as acyl halides selectively in the β-position to give α-stabilized benzylic anions or cations, respectively.[3] This allows a sidechain activation of styrene derivatives which is unprecedented with the corresponding free ligands. Retrosynthetically, a methodology using the Wittig or the HEW reaction lies at hand (Scheme 1). Unfortunately, the Wittig reaction using $Cr(CO)_3$-complexed benzaldehydes and phosphorus ylides often leads to a mixture of *E* and *Z* stereoisomers.[4] Therefore, taking advantage of the ability of tricarbonyl chromium arene complexes to stabilize benzylic anions[3] it can be expected that $Cr(CO)_3$-complexed benzyl phosphonates should react stereoselectively with aldehydes in a HEW reaction to give alkenylsubstituted arene$Cr(CO)_3$ complexes in *trans*-configuration.



Scheme 1

The phosphonate complexes can be prepared from the corresponding free ligands by thermal complexation with hexacarbonyl chromium[5] and are obtained as light yellow crystalline solids[6] in 40-70 %

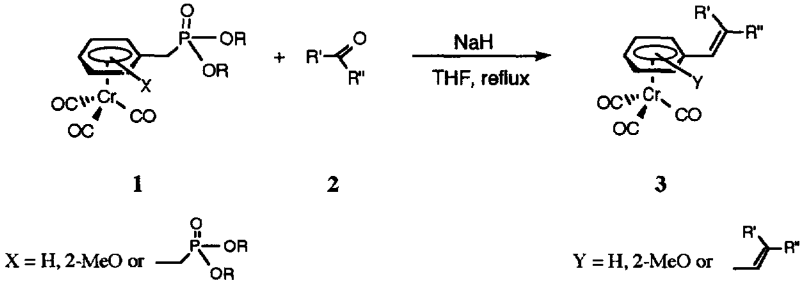
yield (see Scheme 2). The η^6-arene complexation is supported by the considerable upfield shift of the arene proton and carbon resonances in the ^1H and ^{13}C NMR spectra, respectively.



1a X = H, R = CH_3
1b X = 4-$CH_2P(O)(OCH_2CH_3)_2$, R = CH_2
1c X = 2-OCH_3, R = CH_3

Scheme 2

After deprotonation with sodium hydride the phosphonate complexes **1** react smoothly in boiling THF with a number of aldehydes, dialdehydes or ketones **2** to give the desired alkenylsubstituted areneCr(CO)$_3$ complexes in moderate to good yields[7] (see Scheme 3 and Table 1). The complexes **3** are obtained as yellow to orange crystalline solids.

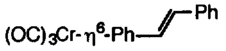
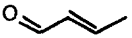
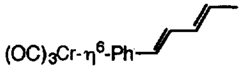
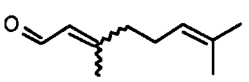
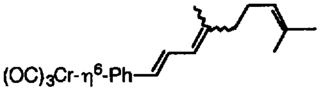
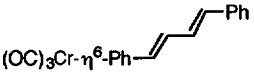
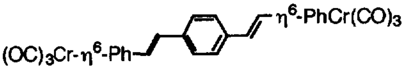
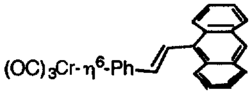
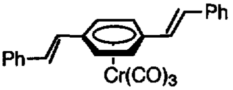
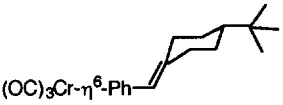
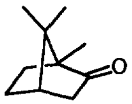
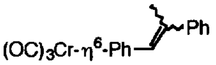
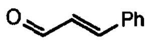
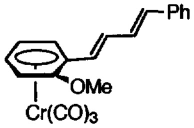
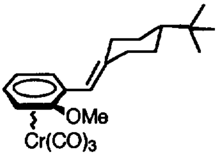


Scheme 3

The Cr(CO)3 complexed arene fragments can be easily identified due to the upfield shift of the arene proton and carbon resonances in the NMR spectra. Expectedly, only the *trans*-configuration of the double bond is formed from aliphatic and aromatic aldehydes as indicated by the vicinal coupling constants (J = 14.6-16.6 Hz) in the proton NMR spectra. For the unsymmetrical ketone acetophenone a 1:1 mixture of E and Z isomers is formed (entry 10). The racemic complex **1c** reacts with the prochiral 4-*tert.*-butylcyclohexanone to give rise to the formation of a 1:1 racemic mixture of diastereomers (entry 12) that can be identified by two distinct sets of signals in the carbon NMR spectrum. The NOESY NMR spectrum of the condensation product of **1c** and cinnamic aldehyde (entry 11) shows that only the drawn conformer is populated in solution. Compared to even sterically crowded aldehydes like 9-anthracenyl carbaldehyde (entry 6) the reactivity of ketones is considerably lower as reflected by the lower yields obtained under otherwise similar conditions. A clear limitation of the HEW with phosphonate complexes are sterically demanding ketones like camphor (entry 9) which do not react even after prolonged heating in THF.

The UV/VIS spectra show strong metal-to-ligand charge transfer (MLCT) bands[8] in the region between 390 and 430 nm. In agreement with the electron-withdrawing nature of the alkenyl substituent the MLCT bands are shifted bathochromically in comparison to the parent complex tricarbonyl-η^6-benzenechromium.

Table 1. Alkenyl substituted areneCr(CO)$_3$ complexes **3**[a] by HEW reactions of the phosphonate complexes **1** with the carbonyl compounds **2**.

entry	phosphonate complex **1**	carbonyl compound	alkenyl complex **3**	isolated yield (%)
1	**1a**	PhCHO		57
2	**1a**			39
3	**1a**	 *E*/*Z* = 60:40		91 *E*/*Z* = 60:40
4	**1a**			89
5	**1a**	OHCC$_6$H$_4$CHO		42
6	**1a**	9-anthracenyl carbaldehyde		78
7	**1b**	PhCHO		40
8	**1a**			75
9	**1a**		—	0
10	**1a**	acetophenone		49 *E*/*Z* = 1:1
11	**1c**			81
12	**1c**			79 racemic mixture of diastereomers

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[a] all complexes **3** are spectroscopically characterized and give satisfactory elemental analyses

Intense MLCT bands can be accounted on a strong polarizability of the chromophore.[9] Therefore, alkenyl substituted arene complexes also can be promising chromophores for displaying optical nonlinearities.[10]

In conclusion, compared with the direct complexation of alkenyl arenes the HEW reaction of benzylphosphonate complexes represents a superior methodology for the selective introduction of Cr(CO)$_3$ tripods to a π-system. The selective synthesis of the centrally singly complexed styrenylstilbene (entry 7) exemplifies the major advantages of the HEW in comparison to complexation, which undoubtedly leads to a statistical mixture of complexes. Further methodological studies on the chemical behavior (cycloadditions, reactions with nucleophiles and electrophiles) of areneCr(CO)$_3$ substituted dienes and the utility of the HEW of phosphonate complexes in the synthesis of organometallic polyphenylenevinylenes and extended π-systems are currently underway.

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6. Analytical data of the phosphonate complexes **1**: **1a**: mp = 115 °C (dichloromethane/pentane), ^{1}H NMR ([D$_6$]DMSO, 300 MHz): d = 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, 2 H), IR (KBr): n = 1964 cm^{-1}, 1887, anal. calcd. for $C_{12}H_{13}CrO_6P$: C 42.87, H 3.90, found: C 42.97, H 3.85; **1b**: mp = 106-107 °C (dichloromethane/pentane), ^{1}H NMR ([D$_6$]DMSO, 300 MHz): d = 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), IR (KBr): n = 1963 cm^{-1}, 1876, anal. calcd. for $C_{19}H_{28}CrO_9P_2$: C 44.37, H 5.49, found: C 43.77, H 5.20; **1c**: mp = 100-101 °C (dichloromethane/pentane), ^{1}H NMR ([D$_6$]DMSO, 300 MHz): d = 2.91 (dd, *J* = 15.0, 21.0 Hz, 1 H), 3.21 (dd, *J* = 15.0, 19.8 Hz, 1 H), 3.64 (d, *J* = 10.9 Hz, 3 H), 3.66 (d, *J* = 10.9 Hz, 3 H), 3.76 (s, 3 H), 5.33 (t, *J* = 6.2 Hz, 1 H), 5.75 (d, *J* = 6.9 Hz, 1 H), 5.87 (m, *J* = 1.2, 6.6 Hz, 1 H), 6.00 (d, *J* = 6.4 Hz, 1 H), IR (KBr): n = 1957 cm^{-1}, 1874, anal. calcd. for $C_{13}H_{15}CrO_7P$: C 42.63, H 4.13, found: C 42.53, H 4.02.
7. Typical experimental procedure. To a degassed solution of 1 mmol of the phosphonate complex **1a** in 15 ml of THF 1.1 mmol of sodium hydride (97 %) is added under argon. After stirring for 10 min at r.t. 1 mmol of cinnamic aldehyde in 2 ml of THF is added to the suspension. The reaction mixture is heated to reflux temperature for 12 h. After cooling to r.t. the mixture is diluted with 20 ml of ether and filtered through a short plug of silica gel to remove the precipitated salts. The solvents are removed from the clear solution in vacuo to give the crude product **3** (entry 4) in 89 % yield. Further purification can be achieved by recrystallization from dichloromethane/pentane. Analytical data of **3** (entry 4): mp = 159-160 °C, ^{1}H NMR ([D$_6$]DMSO, 300 MHz): d = 5.67 (t, *J* = 6.3 Hz, 1 H), 5.83 (pt, *J* = 6.5 Hz, 2 H), 6.01 (d, *J* = 6.5 Hz, 2 H), 6.40 (d, *J* = 14.6 Hz, 1 H), 6.80 (d, *J* = 14.7 Hz, 1 H), 7.08 (m, *J* = 10.5, 14.7 Hz, 1 H), 7.10 (m, *J* = 10.5, 14.8 Hz, 1 H), 7.28 (t, *J* = 7.2 Hz, 1 H), 7.38 (pt, *J* = 7.2, 7.6 Hz, 2 H), 7.54 (d, *J* = 7.4 Hz, 2 H), IR (KBr): n = 1955 cm^{-1}, 1887, anal. calcd. for $C_{19}H_{14}CrO_3$: C 66.67, H 4.12, found: C 66.52, H 4.07.
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