Sidechain Functionalizations by Cuprate Additions to Phosphorylallenyl-Substituted Arenetricarbonylchromium Complexes

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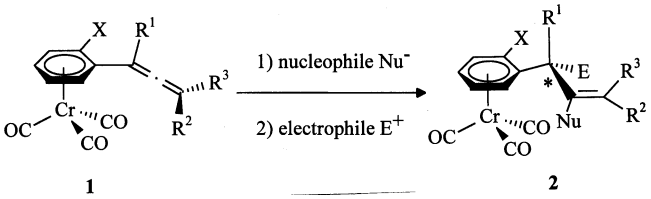
The cuprate addition to (arene)$Cr(CO)_3$-substituted phosphorylallenes **1** gives rise to the regioselective formation of complexed allylphosphane oxide derivatives **3a–c** and allylphosphonate derivatives **3d–j** in good yields. In the case of racemic planar chiral *ortho*-substituted complexed (arylallenyl)phosphonates **1c**, **d** the protonation of the intermediate allyl anion proceeds diastereoselectively due to the hindered rotation around the C_{ipso}–C_α bond. This diastereoselective protonation is discussed on the basis of the conformational analysis as deduced from the X-ray structure analyses of the allenylphosphonate **1d** and the allylphosphonates **3i**, **j**.

Introduction

Planar chiral (arene)$Cr(CO)_3$ complexes bear a plethora of opportunities for diastereoselective transformations and thus have become well-established building blocks in natural products syntheses.[1,2] Besides stereochemical issues the carbonylchromium complexation alters the reactivity of the arene ligands significantly and therefore opens new reaction pathways. In particular, the activation of the benzylic position has received the most attention and has been intensively studied.[3] Complexed benzylic anions stabilized by the strong electron-withdrawing nature of the (arene)$Cr(CO)_3$ fragment[4] basically can be generated in two different ways: (a) by deprotonation of toluene complexes[5] or (b) by addition of a nucleophile to the β-position of styrene or dihydronaphthalene complexes.[1b,6] Especially, the addition of nucleophiles to an alkenyl side chain of an arene complex represents an extremely useful reaction allowing a subsequent trapping of the complexed benzylic anion by a suitable electrophile. Unfortunately, this process is only limited to stabilized carbanions.[1b,6] Presumably, the nucleophilic susceptibility of the β-carbon atom in styrene complexes is not very strong. In order to overcome these severe limitations we have started to investigate the syntheses, structure and reactivity of allenyl-substituted arene complexes[7] which upon nucleophilic addition to the β-carbon atom of the allenyl side chain give rise to (arene)$Cr(CO)_3$-stabilized allyl anions. This interesting class of ambident nucleophiles opens new opportunities to extended sidechain functionalizations (Scheme 1).

Recently, we could show that allenylphosphonate complexes **1** [R^1 = $PO(OEt)_2$, R^2 = R^3 = Me, X = H] can be successfully applied to metal-template-directed syntheses of 5- and 6-membered heterocyclic dienes by a nucleophilic addition/intramolecular olefination sequence.[7b] So far, there are only very few examples of diastereoselective functionalizations initiated by an attack on the homobenzylic position of the tricarbonylchromium-substituted arene sidechain.[1b,8] Here we report on conformational aspects of allenylphosphonate-substituted (arene)$Cr(CO)_3$ complexes **1** in the solid state, cuprate additions to these allenylphosphonates and subsequent regio- and diastereoselective protonations of the ambident planar chiral complexed arylallyl anions to give allylphosphonate-substituted (arene)$Cr(CO)_3$ complexes. The diastereoselectivity of the protonations is discussed on the basis of conformation analyses as deduced from relative stereochemistry by X-ray crystal structure analyses of the organometallic allylphosphonates.



Scheme 1

Results and Discussion

Conformational Aspects of (Arene)$Cr(CO)_3$-Substituted Phosphorylallenes

(Arene)$Cr(CO)_3$-substituted allenes have proven to be easily accessible by displacement rearrangements of the corresponding arene complex substituted propargylic alcohols.[7] Although, the structure in solution of some planar chiral organometallic allenes has been elucidated by NMR spectroscopy,[7b] conformational aspects, i.e. the mutual arrangement of the allenyl substituent and the arene(carbonyl)chromium fragment, have not been addressed yet. In the case of the allene derivatives **1a** and **1d** the crystal structures[9] have been elaborated by X-ray structure analysis.

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The linear allenyl sidechain [C10−C11−C12: 177.1(3)°] of the benzene complex substituted allenylphosphane oxide **1a** (Figure 1, Table 4) is arranged almost coplanarily with the complexed phenyl ring (torsional angle C9−C4−C10−C11: 164.9°) indicating an ideal overlap of the proximate allenic double bond and the complexed arene π-system. One of the phenyl rings on the phosphane oxide group shields the *endo* face of the allenyl substituent. Therefore, a nucleophilic attack to this conformer will occur from the *exo* face.

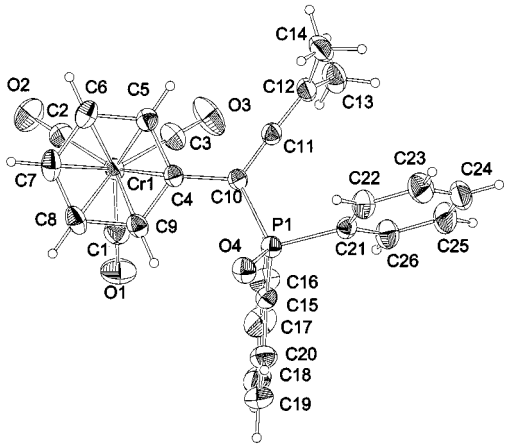


Figure 1. ORTEP plot of **1a**; selected bond lengths [Å], angles [°], and torsional angles [°]: C(10)−C(11) 1.318 (3), C(11)−C(12) 1.291 (4), C(4)−C(10) 1.489(3); C(10)−C(11)−C(12) 177.1(3), C(4)−C(10)−C(11) 122.3(2), C(4)−C(10)−P(1) 119.6(2); C(9)−C(4)−C(10)−P(1) −19.8(3), C(9)−C(4)−C(10)−C(11) 164.9 (2), C(4)−C(10)−P(1)−O(4) −47.4(2), C(7)−C(8)−C(9)−C(4) 0.5(4)

The introduction of a sterically demanding *ortho* substituent into the complexed arene causes significant changes in the mutual arrangement of the allenyl and the arene(carbonyl)chromium fragments. The X-ray structure analysis of **1d** (Figure 2 and Table 4) reveals that the torsion of the allene substructure deviates from coplanarity with the arenetricarbonylchromium fragment by almost 60° (torsional angle C9−C4−C10−C11: 59.3°). Interestingly, the phosphonate group at the linear allenyl fragment (C10−C11−C12: 178°) and carbonylchromium tripod are arranged in an *anti* conformation and the *P*-oxygen atom is arranged *anti* with respect to the acetal group. According to MM2 calculations[10] the *anti* conformer is by 1.0 kcal/mol lower in energy than the corresponding *syn* conformer and the rotation barrier can be estimated by 3.3 kcal/mol. Thus, an attacking nucleophile preferably will add in an *anti* fashion with respect to the carbonylchromium tripod and the *ortho* substituent but with only a small preference for either conformers.

Cuprate Addition and Diastereoselective Protonation

Organocuprates are known to add to allenylphosphonates in a 1,4-fashion to give allylphosphonates.[11] Thus, various Gilman and Normant cuprates easily add to the allenylarene complexes **1** to give after aqueous workup the

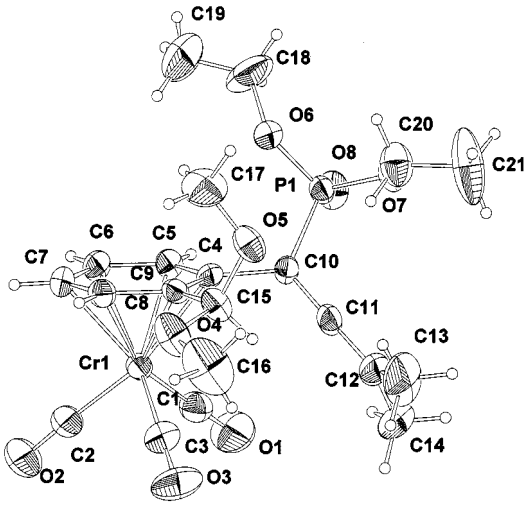
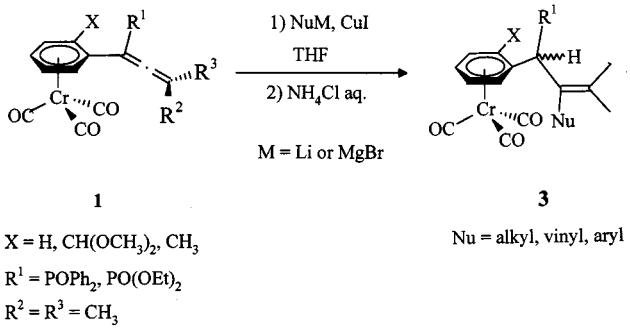


Figure 2. ORTEP plot of **1d**; selected bond lengths [Å], angles [°], and torsional angles [°]: C(10)−C(11) 1.297(9), C(11)−C(12) 1.314(11), C(4)−C(10) 1.492(9); C(10)−C(11)−C(12) 178.2(8), C(4)−C(10)−P(1) 117.9(5), C(4)−C(10)−C(11) 124.3(6); C(9)−C(4)−C(10)−C(11) 59.3(11), C(9)−C(4)−C(10)−P(1) −123.6(6), O(8)−P(1)−C(10)−C(4) −92.4(6), C(4)−C(9)−C(15)−O(5) 69.7(9), C(7)−C(8)−C(9)−C(4) 0.9(10)

regioselectively protonated allylarene complexes **3** in moderate to good yields as light yellow crystalline solids (Scheme 2 and Table 1). All transformations were performed with racemic planar chiral complexes.



Scheme 2. Cuprate addition/protonation sequence

In the NMR spectra the regioselective protonation of the allyl derivatives **3** is supported by the appearance of characteristic $^2J_{P,H}$ and $^1J_{P,C}$ coupling constants of the benzylic protons and carbon atoms. For the phosphane oxide derivatives **3a**−**3c** (R^1 = Ph, X = H) the benzylic methine proton appears in the proton NMR spectra as a doublet ($^2J_{P,H}$ = 10.0−11.6 Hz) at δ ≈ 4.6−4.7. The corresponding signals for the phosphonates **3d**−**3j** [R^1 = OEt, X = H, Me, and $CH(OMe)_2$] are found at δ ≈ 4.1−4.4 as doublets ($^2J_{P,H}$ = 25.2−27.7 Hz). In the proton-decoupled ^{13}C-NMR spectra the benzylic carbon resonances of the phosphane oxides **3a**−**3c** appear as doublets ($^1J_{P,C}$ = 63.0−67.1 Hz) at δ ≈ 46.1−46.8 and the corresponding resonances of the phosphonates **3d**−**3j** at δ ≈ 42.2−45.0 display characteristic large $^1J_{P,C}$ coupling constants (139.9−145.9 Hz).

In addition, the allylphosphonate structure was elaborated and supported by X-ray structure analyses[9] of **3f** and **3j** (Figures 3, 4 and Table 4). The benzylic carbon atom

Table 1. Summarized results of the cuprate additions protonation experiments ($R^2 = R^3 = CH_3$; E = H)

Entry	Allene R^1		Nu	X	(Phosphorylallyl)-arene complex **3** Yield[a] (ratio of diastereomers)
1	**1a**	$Ph_2P(O)$	Me	H	79% **3a**
2	**1a**	$Ph_2P(O)$	Bu	H	51% **3b**
3	**1a**	$Ph_2P(O)$	Vinyl	H	56% **3c**
4	**1b**	$(EtO)_2P(O)$	Me	H	69% **3d**
5	**1b**	$(EtO)_2P(O)$	Bu	H	57% **3e**
6	**1b**	$(EtO)_2P(O)$	Vinyl	H	79% **3f**
7	**1b**	$(EtO)_2P(O)$	Ph	H	90% **3g**
8	**1c**	$(EtO)_2P(O)$	Me	Me	68% (5:1)[b] **3h**
9	**1c**	$(EtO)_2P(O)$	Ph	Me	68% (> 15:1)[c] **3i**
10	**1d**	$(EtO)_2P(O)$	Me	$CH(OMe)_2$	85% (2:1)[d] **3j**

[a] The yields reported were determined after chromatography on silica gel. – [b] The diastereomers could be separated by chromatography. – [c] The other diastereomer was not detected by NMR spectroscopy. – [d] The major diastereomer can be enriched by recrystallization from dichloromethane/pentane (2:1 to 85:15)

C10 is pyramidalized, in agreement with the formation of an sp^3-hybridized phosphonate moiety upon regioselective protonation of an allyl anion. In the case of the planar chiral complex **3j** only the major of two possible diastereomeric racemates was crystallized and the relative configuration was determined to be (*S*,*S*) or (*R*,*R*). The benzylic and the acetal hydrogen atoms are arranged in a *syn* conformation whilst the 2-isoprenyl substituent is oriented in an antiperiplanar fashion with respect to the tricarbonylchromium tripod.

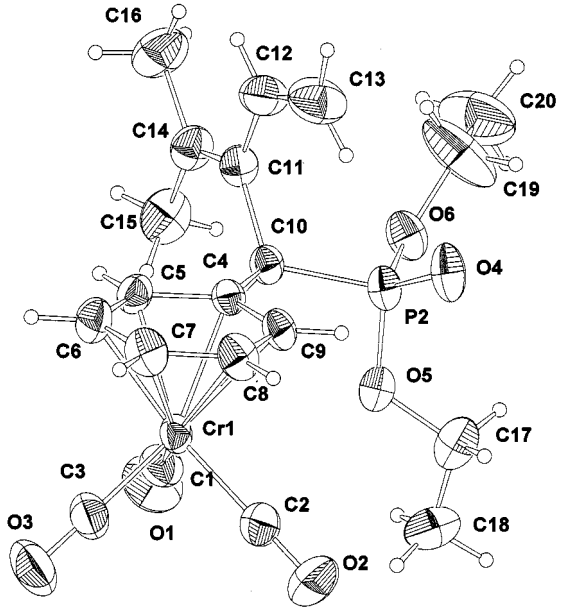


Figure 3. ORTEP plot of **3f**; selected bond lengths [Å], angles [°], and torsional angles [°]: C(4)–C(10) 1.531(4), C(10)–C(11) 1.546(5), C(11)–C(14) 1.332(5); C(4)–C(10)–C(11) 111.3(3), C(11)–C(10)–P(2) 114.2(2); C(9)–C(4)–C(10)–C(11) –122.5(3), C(9)–C(4)–C(10)–P(2) 11.0(4), C(10)–C(11)–C(14)–C(15) –2.5(6), C(6)–C(7)–C(8)–C(9) 0.5(6)

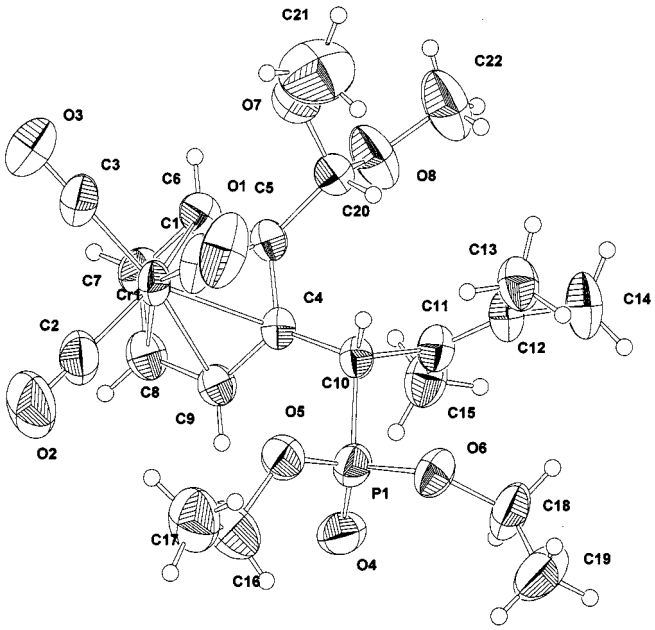
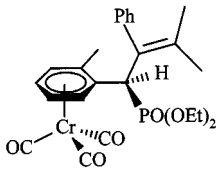


Figure 4. ORTEP plot of **3j**; selected bond lengths [Å], angles [°], and torsional angles [°]: C(4)–C(10) 1.533(6), C(10)–C(11) 1.541(6), C(11)–C(12) 1.329(7); C(4)–C(10)–C(11) 111.4(4), C(11)–C(10)–P(1) 108.5(3), C(9)–C(4)–C(10)–C(11) 110.7(5); C(9)–C(4)–C(10)–P(1) –14.0(6), C(10)–C(11)–C(12)–C(14) –0.7(10), C(7)–C(8)–C(9)–C(4) 0.9(9)

The X-ray crystal structure[9] of the pure racemic diastereomer **3i** (Figure 5 and Table 4) clearly reveals the relative configuration of the product to be (*R*,*R*) or (*S*,*S*). Unfortunately, the ethoxy group in **3i** was strongly disordered and a pentane molecule was incorporated in the crystal lattice both giving rise to an insufficient wR_2 value for all data (Table 4).

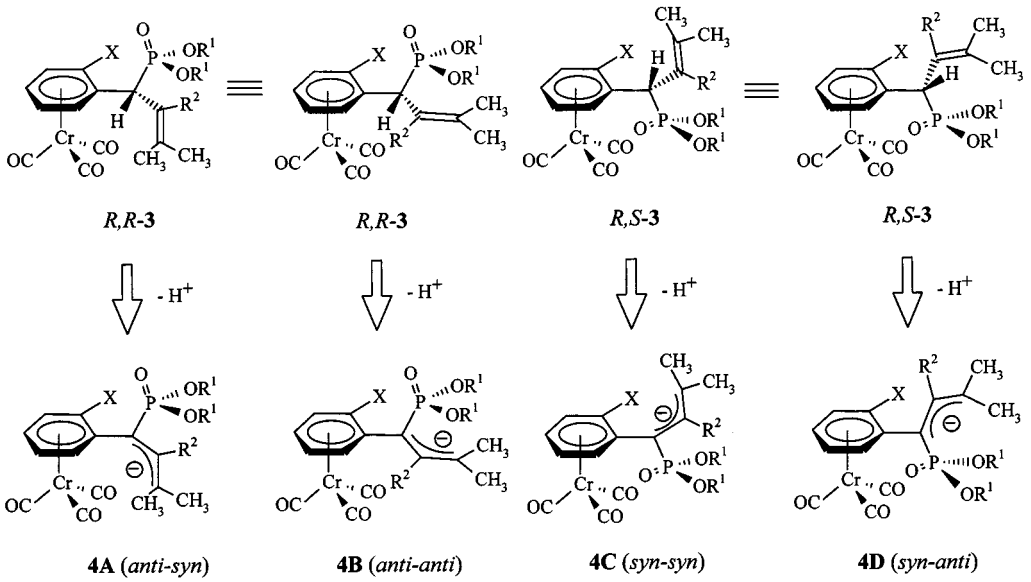


3i

Figure 5. Relative configuration of **3i**

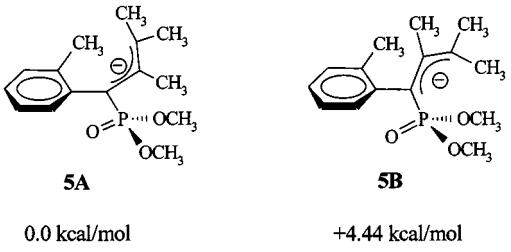
Obviously, the protonation of the allyl anions that form upon the cuprate addition to the allenyl derivatives proceeds with a facial diastereoselection. Aqueous ammonium chloride as proton source guarantees a protonation under kinetic control and excludes a base-catalyzed epimerization at the benzylic carbon atom. Based upon the relative configurations of **3i** and **3j** as established by the X-ray structure analyses the structure of the diastereomeric conformations of the allyl anions can be deduced (Scheme 3).

Assuming a diastereofacial protonation[12] of the allyl anions from the less hindered *endo* face the major diastereomer (*R*,*R*)-**3** (or *S*,*S*-**3**) can be derived from two diastereomeric allyl anions where the phosphonate group



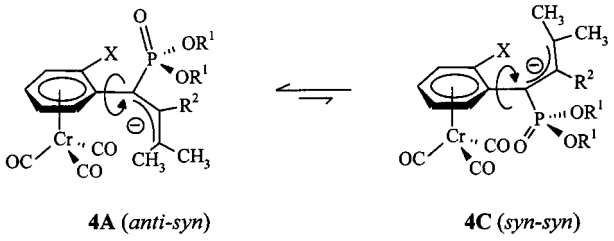
Scheme 3. Stereochemical correlation of the allylphosphonates **3** and the allylphosphonate anions **4**

orientation is *anti* to the carbonylchromium tripod and the mutual stereochemistry of the phosphonate group and the substituent R^2 is either *syn* (**4A**) or *anti* (**4B**). In analogy, the minor diastereomer (*R*,*S*)-**3** (or *S*,*R*-**3**) stems from the protonation of diastereomeric allyl anions **4C** or **4D** where the phosphonate and the chromium fragment are in a *syn* conformation whereas the substituent R^2 can be either *syn* (**4C**) or *anti* (**4D**) with respect the phosphonate group. According to PM3 calculations[10] performed on the free ligands (**5A** and **5B**, Scheme 4) the phosphonate/methyl *syn* isomer (**5A**) is by 4.44 kcal/mol lower in energy than the phosphonate/methyl *anti* isomer (**5B**). The depicted structures are also the corresponding lowest energy conformations of **5A** and **5B**, respectively.



Scheme 4. Relative energies (PM3) of the configurational isomers of the free ligand **5**

The activation enthalpy for the *anti-syn* isomerization of these allyl anions is represented by a rotation around the $C_\alpha-C_\beta$ bond and can be estimated to be 2.4 kcal/mol. This relatively low rotation barrier is caused by an efficient resonance stabilization of the benzylic phosphonate carbanion. In turn, the *anti-syn* equilibration proceeds rapidly to give the thermodynamically more stable *syn* isomer almost exclusively. Thus, it is reasonable to assume that the corresponding complexed diastereomers **4A** and **4C** (Scheme 5) with a *syn* orientation of the substituent R^2 with respect the phosphonate moiety are also low-energy isomers. Therefore, the cuprate addition to the allenylphosphonates **1** very likely leads to the formation of the diastereomers **4A** and **4C**. Since the allyl anions **4A** and **4C** are diastereomeric conformers their interconversion proceeds by a rotation around the $C_{ipso}-C_\alpha$ bond. Therefore, the temperature dependence of this rotation should be reflected in the **4A**/**4C** ratio, ultimately in the diastereomeric ratio of the protonation products **3**.



Scheme 5. The **4A/4C** equilibration by rotation around the $C_{ipso}-C_\alpha$ bond

In a number of cuprate addition/protonation sequences to planar chiral complexes the dependence on the temperature, the reaction time and the cuprate was investigated (Table 2). In case of the *ortho*-methyl-substituted complex **1c** (entries 1−4) the diastereoselectivities depend on the reaction temperature and the nature of the cuprate. Obviously, the fast cuprate addition to the allenylphosphonate **1c** predominantly leads to the kinetically controlled formation of the conformer **4A** (entries 2 and 3). The free rotation of the allyl anion moiety around the $C_{ipso}-C_\alpha$ bond is facilitated as the temperature rises and the allylanion conformers **4A** and **4B** equilibrate to give after protonation the observed thermodynamic diastereoselectivity (entry 1). This indicates that the energy difference between the allyl anion conformers **4A** and **4B** is 0.4 kcal/mol. In the case of complex **1d** (entries 5 and 6) the resulting diastereoselectivity is rather poor and not temperature-dependent. Presumably, the coordinating ability of the *ortho*-acetal facilitates the

thermodynamic equilibration very rapidly, even at low temperatures.

Table 2. Diastereotopic cuprate addition/protonation experiments

Entry	Allene	R	Temperature	Reaction time	Yield (diastereomeric ratio)
1	**1c**	Me	−40 to 20°C	3 h	68% (2:1) **3h**
2	**1c**	Me	−50 to −40°C	3 h	70% (5:1) **3h**
3	**1c**	Me	−78 to −70°C	7 h	67% (5:1) **3h**
4	**1c**	Ph	−78 to −70°C	3 h	68% (> 15:1) **3i**
5	**1d**	Me	−40 to −15°C	3 h	85% (2:1)[a] **3j**
6	**1d**	Me	−78 to −40°C	8 h	80% (2:1)[a] **3j**

[a] The major diastereomer can be enriched by recrystallization (2:1 to 85:15)

Finally, the initial step of this sequence, i.e. the cuprate addition to the allenylphosphonates **1** has to be discussed. According to MM2 calculations[10] the conformers **6A** and **6C** (Scheme 6) are almost equal in energy and are interconverted by a low rotation barrier (i.e. **6B**) indicating a rapid preequilibrium.

The cuprates add to the allenylphosphonates **1** from the *exo* face with respect to the carbonylchromium tripod and the *ortho* substituent to give preferentially the conformer **4A** under kinetic control (vide supra). Considering the bulky nature of a Gilman or Normant cuprate[13] the precoordination to the phosphonate oxygen atoms in conformer **6C** from the *exo* face with respect to the carbonylchromium fragment is sterically less biased than the corresponding attack to conformer **6A** from the *exo* face. Once the phosphonate-substituted allyl anion has formed and the organocopper group has dissociated, the conformational stability and thus the diastereoselective protonation is influenced by the temperature-dependent rotation around the $C_{ipso}-C_{\alpha}$ bond. Thus, the generation and the electrophilic trapping reactions of conformationally and configurationally stable (arene)$Cr(CO)_3$-substituted allyl anions without additional anion-stabilizing functionalities for diastereoselective side-chain functionalizations are currently under investigation.

Conclusion

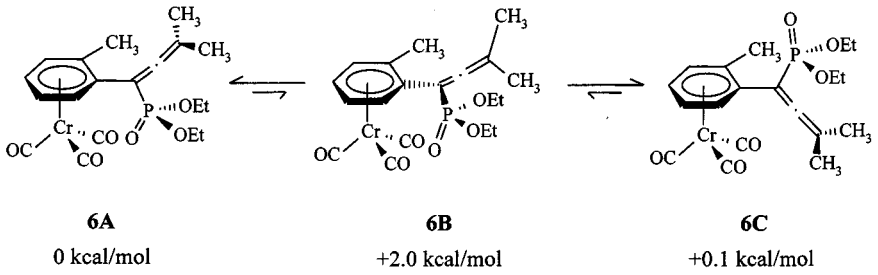
(Arene)$Cr(CO)_3$-substituted allenylphosphane oxides and allenylphosphonates readily react with organocuprates in a 1,4-addition to give after protonation 1-(arene)$Cr(CO)_3$-substituted (2-propen-1-yl)phosphane oxides and (2-propen-1-yl)phosphonates in good yields. With planar chiral *ortho*-substituted complexed allenes this cuprate addition/protonation sequence gives rise to the diastereoselective formation of complexed allylphosphane oxide and allylphosphonate derivatives. The conformation analysis of the intermediate arene complex substituted allyl anions reveals that the crucial origin of the observed diastereoselectivity stems from the hindered rotation around the $C_{ipso}-C_{\alpha}$ bond. Therefore, future studies will be directed towards the study of the reactivity and selectivity of (arene)$Cr(CO)_3$-stabilized allyl anions in intra- and intermolecular electrophilic trapping reactions.

Experimental Section

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.[14] − Column chromatography: Silica gel 60 (Merck, Darmstadt), mesh 70−230. TLC: Silica gel plates (60 F_{254} Merck, Darmstadt). Melting points (uncorrected values): Reichert-Jung Thermovar. − The *ortho*-iodobenzaldehyde dimethylacetal complex,[15] the complexed allenylphosphane oxide **1a** and the complexed allenylphosphonates **1b** and **1c** were prepared in analogy to our published procedures.[7] The organolithium and vinylmagnesium chloride solutions were purchased from Aldrich. Chlorodiethoxyphosphane (Aldrich) was used without further purification. Chlorodiphenylphosphane (Aldrich) was distilled under reduced pressure prior to use. All crystalline arenechromium complexes can be handled in air. − ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra: Bruker ARX 300, Varian VXR 400S [D_6]DMSO. The assignments of quaternary C, CH, CH_2, and CH_3 has been made by using DEPT spectra. − IR: Perkin Elmer Models Lambda 16. − MS: Finnigan MAT 90 and MAT 95 Q. − Elemental analyses were carried out in the Microanalytical Laboratory of the Institut für Organische Chemie, Ludwig-Maximilians-Universität München.

X-ray Structure Determination of Compounds 1a, 1d, 3f, 3i, and 3j: Suitable crystals were mounted on a capillary and transferred to an Enraf-Nonius CAD4 diffractometer. The structures were solved by direct methods and refined anisotropically on F^2 (G.M. Sheldrick, SHELXS-86, SHELXL-93 programs, University of Göttingen). Hydrogen atoms were found from differential Fourier synthesis and refined. The data of the X-ray structure analyses are summarized in Table 4.

Tricarbonyl{η^6-1-[3-hydroxy-3-methylbut-1-yn-1-yl]-2-(dimethoxymethyl)benzene}chromium(0): 1.00 g (2.40 mmol) of the *o*-iodobenzaldehyde dimethylacetal complex,[15] 33 mg (0.04 mmol) of bis(triphenylphosphane)palladium dichloride and 5 mg (0.02 mmol) of



Scheme 6. Relative energies (MM2) of the conformations **6A,6B** and **6C**

copper iodide were dissolved in a degassed mixture of 15 mL of THF and 7 mL of triethylamine. A solution of 0.28 mL (2.90 mmol) of 3-methylbutyn-3-ol, dissolved in 10 mL of THF, was added over a period of 1 h. After complete addition, the solution was heated to reflux temperature for 5 h and then cooled to room temperature. Diethyl ether was added, the mixture was filtered and the solvents were evaporated. Chromatography on silica gel with diethyl, ether/pentane afforded 0.65 g (73%) of the propargyl alcohol complex. Recrystallization from pentane gave yellow crystals, m.p. 68−70°C. − ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.46 (s, 6 H), 3.33 (s, 3 H), 3.53 (s, 3 H), 5.21 (s, 1 H), 5.54 (s, 1 H), 5.64 (t, *J* = 6.1 Hz, 1 H), 5.71−5.78 (m, 2 H), 5.85 (d, *J* = 6.5 Hz, 1 H). − ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 31.53 (CH$_3$), 54.01 (CH$_3$), 57.18 (CH$_3$), 63.80 (C$_{quat.}$), 74.75 (C$_{quat.}$), 91.27 (C$_{quat.}$), 91.85 (CH), 92.19 (CH), 94.67 (CH), 96.08 (CH), 99.88 (C$_{quat.}$), 101.71 (CH), 109.18 (C$_{quat.}$), 233.07 (C$_{quat.}$, CO). − MS (70 eV, FAB); *m/z* (%): 370 [M$^+$] (7), 314 [M$^+$ − 2 CO] (2), 286 [M$^+$ − 3 CO] (100), 52 [Cr$^+$] (14). − IR (KBr): $\tilde{\nu}$ = 3089 cm^{-1}, 2983, 2935, 2837, 1977, 1898, 1879, 1629, 1527, 1494, 1449, 1418, 1364, 1341, 1271, 1249, 1201, 1187, 1170, 1111, 1096, 1082, 1044, 983, 962, 912, 829, 808, 662, 624, 534, 469. − UV/Vis (DMSO): λ$_{max}$ (ε) = 325 (9500). − $C_{17}H_{18}CrO_6$ (370.31): calcd. C 55.14, H 4.89; found C 55.98, H 5.08.

Tricarbonyl{η^6-1-[1-diethoxyphosphoryl)-3-methylbuta-1,2-dien-1-yl]-2-(dimethoxymethyl)benzene}chromium(0) (1d): In a two-necked round-bottomed flask 0.49 g (1.35 mmol) of the previously prepared propargyl alcohol and 0.20 mL (1.50 mmol) of triethylamine were dissolved in 15 mL of THF under nitrogen. The resulting mixture was cooled to −78°C and 0.19 mL (1.40 mmol) of chlorodiethoxyphosphane, dissolved in 5 mL of THF, was added over a period of 5 min. After 1 h at −78°C, the cooling bath was removed and stirring was continued for further 20 h at room temperature. To the mixture was added 20 mL of water and the aqueous layer was extracted several times with dichloromethane. The combined organic phases were dried with anhydrous magnesium sulfate and the solvents were removed in a rotary evaporator under reduced pressure. After chromatography on silica gel [diethyl ether/pentane (1:1), diethyl ether, methanol/dichloromethane (1:10)], the yellow band was isolated to give 0.55 g (84%) of **1d**. Recrystallization from dichloromethane/pentane afforded yellow crystals, m.p. 70°C. − ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.21 (m, 6 H), 1.82 (m, 6 H), 3.11 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 3.98 (m, 4 H), 5.38 (s, 1 H), 5.68 (m, 2 H), 5.81 (m, 2 H). − ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 16.24 (CH$_3$, *J* = 6.1 Hz), 17.97 (CH$_3$, *J* = 6.1 Hz), 19.69 (CH$_3$, *J* = 6.1 Hz), 50.28 (CH$_3$, OMe), 56.27 (CH$_3$, OMe), 62.43 (CH$_2$, *J* = 6.1 Hz), 62.71 (CH$_2$, *J* = 6.1 Hz), 89.48 (C$_{quat}$, *J* = 191.6 Hz), 90.03 (CH), 92.12 (CH), 95.18 (CH), 97.86 (CH), 98.28 (C$_{quat}$), 98.53 (CH), 105.48 (C$_{quat}$, *J* = 15.8 Hz), 109.27 (C$_{quat}$, *J* = 4.8 Hz), 208.49 (C$_{quat}$, *J* = 4.3 Hz), 233.18 (C$_{quat}$, CO). − ^{31}P NMR ([D$_6$]DMSO, 121 MHz) : δ = 13.46. − MS (70 eV), *m/z* (%): 490 [M$^+$] (1), 434 [M$^+$ − 2 CO] (5), 406 [M$^+$ − 3 CO] (22), 354 [M$^+$ − Cr(CO)$_3$] (3), 52 [Cr$^+$] (12). − IR (KBr): $\tilde{\nu}$ = 3069 cm^{-1}, 2988, 2937, 2910, 2833, 1967, 1886, 1866, 1630, 1525, 1444, 1414, 1392, 1367, 1340, 1254, 1195, 1159, 1112, 1082, 1063, 1029, 975, 925, 907, 874, 834, 801, 753, 717, 679, 665, 627, 579, 553, 534, 479, 427. − UV/Vis (DMSO): λ$_{max}$ (ε) = 324 (8800). − $C_{21}H_{27}CrO_8P$ (490.40): calcd. C 51.43, H 5.55; found C 51.54, H 5.57.

General Procedure (GP) for the Preparation of the Complexed Allylphosphane Oxides and Allylphosphonates 3

1) Preparation of the Cuprate: A stirred suspension of 104 mg (0.550 mmol) of copper iodide in 10 mL of THF was cooled (exact conditions see below) and 1.10 mmol of a solution of a commercially available organolithium or organomagnesium halide was added over a period of 1 min by syringe. The temperature of the solution had to be adjusted exactly due to the thermal lability of some cuprates. For the preparation of the cuprates the solution was cooled to 0°C when methyllithium was used, to −60°C for butyllithium and to −78°C for phenyllithium and for vinylmagnesium chloride. The resulting cuprate solution was stirred for further 40 min at the given temperature.

2) Nucleophilic Addition/Protonation: To the stirred and cooled solution of the cuprate (temperatures see below) a solution of 0.50 mmol of **1** in 5 mL of THF was added over a period of 5 min. Stirring was continued at the indicated temperatures for 3−7 h (Tables 2 and 4). Then 20 mL of saturated ammonium chloride solution was added to the reaction mixture at the final temperature. The aqueous layer was extracted several times with diethyl ether. The combined organic phases were dried with magnesium sulfate, filtered, and concentrated in a rotary evaporator. After chromatography on silica gel (diethyl ether/pentane to diethyl ether) the yellow bands were collected to give the products **3**. The experimental details and yields are summarized in Table 3.

Tricarbonyl{η^6-[1-(diphenylphosphoryl)-2,3-dimethylprop-2-en-1-yl]benzene}chromium(0) (3a): Yellow crystals, m.p. 178−180°C. − ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.42 (s, 3 H), 1.73 (s, 3 H), 1.87 (s, 3 H), 4.60 (d, *J* = 10.3 Hz, 1 H), 5.29 (t, *J* = 6.2 Hz, 1 H), 5.51 (t, *J* = 6.3 Hz, 1 H), 5.63 (t, *J* = 6.1 Hz, 1 H), 5.76 (d, *J* = 6.2 Hz, 1 H), 6.01 (d, *J* = 6.4 Hz, 1 H), 7.48−7.88 (m, 10 H). − ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 17.22 (CH$_3$), 20.64 (CH$_3$), 21.31 (CH$_3$), 46.81 (CH, $J_{P,C}$ = 64.5 Hz), 91.07 (CH), 91.86 (CH), 96.29 (CH), 98.29 (CH, $J_{P,C}$ = 4.6 Hz), 99.72 (CH, $J_{P,C}$ = 5.6 Hz), 110.55 (C$_{quat}$), 123.62 (C$_{quat}$, $J_{P,C}$ = 5.5 Hz), 128.51 (CH, $J_{P,C}$ = 11.1 Hz), 128.74 (CH, $J_{P,C}$ = 11.1 Hz), 130.50 (CH, $J_{P,C}$ = 9.0 Hz), 131.25 (CH, $J_{P,C}$ = 9.0 Hz), 131.48 (C$_{quat}$), 131.99 (CH), 132.11 (C$_{quat}$, $J_{P,C}$ = 94.3 Hz), 132.47 (C$_{quat}$, $J_{P,C}$ = 128.3 Hz), 233.63 (C$_{quat}$). − ^{31}P NMR ([D$_6$]DMSO, 121 MHz) : δ = 31.28. − MS (70 eV, *EI*), *m/z* (%): 468 [M$^+$ − CO] (8), 440 [M$^+$ − 2 CO] (9), 412 [M$^+$ − 3 CO] (89), 360 [M$^+$ − Cr(CO)$_3$] (11), 52 [Cr$^+$] (18). − IR (KBr): $\tilde{\nu}$ = 3056 cm^{-1}, 2924, 1964, 1883, 1628, 1590, 1524, 1483, 1456, 1438, 1377, 1312, 1233, 1180, 1116, 1101, 1072, 998, 847, 816, 741, 721, 700, 660, 632, 568, 547, 534, 517, 507, 482, 427. − UV/Vis (DMSO): λ$_{max}$ (ε) = 319 (8900). − $C_{27}H_{25}CrO_4P$ (496.46): calcd. C 65.32, H 5.08; found C 65.14, H 5.10.

{η^6-[2-Butyl-1-(diphenylphosphoryl)-3-methylprop-2-en-1-yl]benzene}tricarbonylchromium(0) (3b): Yellow crystals, m.p. 157−159°C. − ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 0.76−1.74 (m, 15 H), 4.61 (d, *J* = 10.02 Hz, 1 H), 5.32 (m, 1 H), 5.49 (m, *J* = 6.1 Hz, 1 H), 5.68 (m, *J* = 6.1 Hz, 1 H), 5.88 (d, *J* = 6.1 Hz, 1 H), 6.04 (d, *J* = 5.8 Hz, 1 H), 7.50−7.91 (m, 10 H). − ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 13.86 (CH$_3$), 20.80 (CH$_3$), 21.45 (CH$_3$), 22.90 (CH$_2$), 30.55 (CH$_2$), 31.24 (CH$_2$), 46.14 (CH, d, *J* = 67.1 Hz), 90.65 (CH), 91.40 (CH), 96.52 (CH), 98.41 (CH, d, *J* = 7.6 Hz), 99.61 (CH, d, *J* = 4.6 Hz), 110.63 (C$_{quat}$), 128.44 (CH, d, *J* = 12.2 Hz), 128.69 (CH, d, *J* = 10.6 Hz), 129.43 (C$_{quat}$, d, *J* = 6.1 Hz), 130.63 (CH, d, *J* = 7.6 Hz), 131.23 (CH, d, *J* = 9.1 Hz), 131.90 (CH), 132.28 (C$_{quat}$, d, *J* = 94.6 Hz), 132.44 (C$_{quat}$), 133.03 (C$_{quat}$, d, *J* = 109.9 Hz), 233.49 (CO). − ^{31}P NMR ([D$_6$]DMSO, 121 MHz) : 30.15. − MS (70 eV), *m/z* (%): EI: 482 [M$^+$ − 2 CO] (4), 454 [M$^+$ − 3 CO] (44), 402 [M$^+$ − Cr(CO)$_3$] (36), 52 [Cr$^+$] (44); FD: 538 [M$^+$] (100), 510 [M$^+$ − CO] (5), 482 [M$^+$ − 2 CO] (25), 454 [M$^+$ − 3 CO] (5), 402 [M$^+$ − Cr(CO)$_3$] (67). − IR (KBr): $\tilde{\nu}$ = 3059 cm^{-1}, 2932, 1965, 1870, 1458, 1437, 1190, 1114, 750, 720, 700, 662, 631, 525. − UV/Vis (DMSO): λ$_{max}$ (ε) = 319 nm (9200).

Table 3. Experimental details on the cuprate addition/protonation sequence

Phosphorylallene **1** mg (mmol)	Organolithium/magnesium mL (mmol)	Temperature	Yield of **3** mg (%)
0.24 g (0.50 mmol) of **1a**	0.68 mL (1.10 mmol) of methyllithium[a]	−40°C to r.t.	0.19 g (79%) of **3a**
0.24 g (0.50 mmol) of **1a**	0.68 mL (1.10 mmol) of butyllithium[b]	−60°C to r.t.	0.13 g (51%) of **3b**
0.24 g (0.50 mmol) of **1a**	0.64 mL (1.10 mmol) of vinylmagnesium chloride[c]	−78°C to r.t.	0.14 g (56%) of **3c**
0.20 g (0.50 mmol) of **1b**	0.68 mL (1.10 mmol) of methyllithium[a]	−40°C to r.t.	0.14 g (69%) of **3d**
0.20 g (0.50 mmol) of **1b**	0.68 mL (1.10 mmol) of butyllithium[b]	−60°C to r.t.	0.13 g (57%) of **3e**
0.20 g (0.50 mmol) of **1b**	0.64 mL (1.10 mmol) of vinylmagnesium chloride[c]	−78°C to r.t.	0.15 g (70%) of **3f**
0.20 g (0.50 mmol) of **1b**	0.61 mL (1.10 mmol) of phenyllithium[d]	−78°C to r.t.	0.22 g (90%) of **3g**
a) 0.21 g (0.50 mmol) of **1c**	0.68 mL (1.10 mmol) of methyllithium[a]	−40°C to r.t.	98 mg (44%) of (*R*,*R* or *S*,*S*)-**3h** and 53 mg (24%) of (*R*,*S* or *S*,*R*)-**3h**[e]
b) 0.21 g (0.50 mmol) of **1c**	0.68 mL (1.10 mmol) of methyllithium[a]	−50°C to − 40°C	151 mg (68%) (d.r. 5:1)
0.21 g (0.50 mmol) of **1c**	0.61 mL (1.10 mmol) of phenyllithium[d]	−78°C to −70°C	0.17 g (68%) **3i** (d.r. > 15:1)
0.24 g (0.50 mmol) of **1d**	0.68 mL (1.10 mmol) of methyllithium[a]	−40°C to r.t.	0.21 g (85%, d.r. 2:1)[f] **3j**

[a] 1.6 M in diethyl ether. − [b] 1.6 M in hexanes. − [c] 1.7 M in THF. − [d] 1.8 M in cyclohexane/diethyl ether. − [e] Both diastereomers were separated by chromatography on silica gel (diethyl ether/pentane). − [f] After recrystallization from pentane: 160 mg (85:15).

− $C_{30}H_{31}CrO_4P$ (538.5): calcd. C 66.91, H 5.80; found C 66.57, H 5.76.

Tricarbonyl{η^6-[1-(diphenylphosphoryl)-2-ethenyl-3-methylprop-2-en-1-yl]benzene}chromium(0) (3c): Yellow crystals, m.p. 147−150°C. − ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.60 (d, *J* = 2.7 Hz, 3 H), 1.83 (s, 3 H), 4.68 (d, *J* = 11.6 Hz, 1 H), 5.18 (d, *J* = 17.6 Hz, 1 H), 5.30 (m, 2 H), 5.56 (m, 2 H), 5.68 (d, *J* = 6.7 Hz, 1 H), 5.91 (d, *J* = 6.0 Hz, 1 H), 6.64−6.74 (m, 1 H), 7.48−7.88 (m, 10 H). − ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 22.12 (CH_3), 22.52 (CH_3), 46.33 (CH, $J_{P,C}$ = 63.0 Hz), 91.49 (CH), 92.43 (CH), 95.59 (CH), 98.05 (CH, $J_{P,C}$ = 4.6 Hz), 98.82 (CH, $J_{P,C}$ = 3.9 Hz),

Table 4. Crystal data and structure refinements for **1a**, **1d**, **3f**, **3i**, and **3j**

	1a	**1d**	**3f**	**3i**	**3j**
Empirical formula	$C_{26}H_{21}CrO_4P$	$C_{21}H_{27}CrO_8P$	$C_{20}H_{25}CrO_6P$	$C_{25}H_{29}CrO_6P$	$C_{22}H_{31}CrO_8P$
Formula weight	480.4	490.4	444.3	547.5	506.4
Temperature	293(2) K	293(2) K	293(2) K	293(2) K	293(2) K
Radiation	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P-1$	$P2_1/n$	Pc	$P2_1/n$
Unit cell dimensions [Å]	a = 12.618(2)	a = 9.495(3)	a = 13.985(2)	a = 18.220(9)	a = 11.389(2)
	b = 10.3038	b = 16.535(4)	b = 8.977(2)	b = 11.874(4)	b = 17.153(2)
	c = 18.588(4)	c = 18.522(4)	c = 19.077(4)	c = 13.184(4)	c = 13.705(3)
[°]		α = 64.65(2)			
	β = 105.595	β = 85.68(2)	β = 110.549	β = 97.54(3)	β = 105.079
		γ = 73.77(2)			
Volume [Å^3]	2327.7(7)	2519.8(11)	2242.6(8)	2827.6(19)	2585.2(7)
Z	4	4	4	4	4
Density (calculated)	1.371 g/cm^3	1.293 g/cm^3	1.316 g/cm^3	1.286 g/cm^3	1.301 g/cm^3
Absorption correction	φ scans	φ scans	φ scans	φ scans	φ scans
Absorption coefficient	0.590 mm^{-1}	0.557 mm^{-1}	0.612 mm^{-1}	0.499 mm^{-1}	0.545 mm^{-1}
Max. and min. transmission	−	−	0.9695 and 0.9990	0.9652 and 0.9998	0.8933 and 0.9983
F(000)	992	1024	928	1148	1064
Cystal size [mm]	0.27 × 0.43 × 0.53	0.20 × 0.23 × 0.40	0.30 × 0.43 × 0.53	0.2 × 0.3 × 0.6	0.23 × 0.27 × 0.33
θ range (min./max.)	2.26 to 24.97°	2.44 to 22.55°	2.54 to 22.55°	2.49 to 21.66°	2.20 to 23.98°
Index ranges	$-14 \le h \le 14$	$-10 \le h \le 0$	$-15 \le h \le 14$	$-18 \le h \le 18$	$0 \le h \le 13$
	$-12 \le k \le 0$	$-17 \le k \le 17$	$-9 \le k \le 0$	$0 \le k \le 12$	$-19 \le k \le 0$
	$-22 \le l \le 0$	$-19 \le l \le 19$	$0 \le l \le 20$	$0 \le l \le 13$	$-15 \le l \le 15$
Reflections collected	4219	7104	3052	3500	4270
Independent reflections	4085	6625	2948	3499	4046
	[R(int) = 0.0087]	[R(int) = 0.0218]	[R(int) = 0.0105]	[R(int) = 0.0134]	[R(int) = 0.0271]
Observed reflections	3525 [$I > 2\sigma(I)$]	4675 [$I > 2\sigma(I)$]	2420 [$I > 2\sigma(I)$]	1992 [$I > 2\sigma(I)$]	2553 [$I > 2\sigma(I)$]
Refinement method	SHELXL-93 on F^2	SHELXL-93 on F^2	SHELXL-93 on F^2	SHELXL-93 on F^2	SHELXL-93 on F^2
Data/restraints/parameters	4085/0/291	6625/0/571	2948/0/257	3499/344/605	4046/60/338
Goodness of fit on F^2	1.201	1.126	1.043	1.023	1.078
Final R indices [$I > 2\sigma(I)$]					
R_1	0.0335	0.0728	0.0398	0.0834	0.0640
wR_2	0.1090	0.1496	0.1072	0.2150	0.1468
R indices (all data)					
R_1	0.0409	0.1065	0.0520	0.1368	0.1033
wR_2	0.1137	0.1651	0.1165	0.2630	0.1706
Largest diff. peak and hole (e/Å^3)	0.320 and −0.368	0.326 and −0.352	0.249 and −0.239	0.971 and −0.304	0.362 and −0.216

110.12 (C_{quat}), 120.34 (CH_2), 128.29 (C_{quat}), 128.45 (CH, $J_{P,C}$ = 11.5 Hz), 128.58 (CH, $J_{P,C}$ = 11.6 Hz), 130.64 (CH, $J_{P,C}$ = 8.9 Hz), 131.35 (CH, $J_{P,C}$ = 8.6 Hz), 131.82 (C_{quat}, $J_{P,C}$ = 94.8 Hz), 132.04 (CH), 132.10 (C_{quat}, $J_{P,C}$ = 97.1 Hz), 135.35 (CH), 135.64 (C_{quat}, $J_{P,C}$ = 10.2 Hz), 233.66 (C_{quat}, CO). − ^{31}P NMR ([D$_6$]DMSO, 121 MHz) : δ = 31.28. − MS (70 eV); *m/z* (%): 452 [M^+ − 2 CO] (7), 424 [M^+ − 3 CO] (100), 372 [M^+ − $Cr(CO)_3$] (11), 52 [Cr^+] (18). − IR (KBr): $\tilde{\nu}$ = 1964 cm^{-1}, 1881, 1628, 1524, 1457, 1437, 1383, 1181, 1116, 1073, 998, 925, 746, 722, 701, 660, 631, 545, 532. − UV/Vis (DMSO): λ_{max} (ε) = 320 (7700). − $C_{28}H_{25}CrO_4P$ (508.47): calcd. C 66.14, H 4.95; found C 66.86, H 5.36.

Tricarbonyl{η^6-[1-(diethoxyphosphoryl)-2,3-dimethylprop-2-en-1-yl]benzene}chromium(0) (3d): Yellow crystals, m.p. 100−103°C. − ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.21 (m, 6 H), 1.68 (s, 3 H), 1.70 (s, 3 H), 1.80 (s, 3 H), 4.02 (m, 5 H), 5.56 (m, 2 H), 5.69 (m, 2 H), 6.09 (d, *J* = 6.1 Hz, 1 H). − ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 16.20 (CH_3, $J_{P,C}$ = 6.1 Hz), 16.37 (CH_3, $J_{P,C}$ = 5.4 Hz), 20.83 (CH_3), 21.11 (CH_3), 45.01 (CH, $J_{P,C}$ = 140.7 Hz), 61.53 (CH_2, $J_{P,C}$ = 7.3 Hz), 62.65 (CH_2, $J_{P,C}$ = 6.9 Hz), 92.86 (CH), 93.64 (CH), 95.13 (CH), 96.75 (CH, $J_{P,C}$ = 11.9 Hz), 97.24 (CH), 109.72 (C_{quat}), 122.01 (C_{quat}), 131.49 (C_{quat}, $J_{P,C}$ = 12.9 Hz), 233.85 (C_{quat}, CO). − ^{31}P NMR ([D$_6$]DMSO, 121 MHz) : δ = 24.24. − MS (70 eV, EI); *m/z* (%): 376 [M^+ − 2 CO] (18), 348 [M^+ − 3 CO] (100), 296 [M^+ − $Cr(CO)_3$] (2), 52 [Cr^+] (5). − IR (KBr): $\tilde{\nu}$ = 3069 cm^{-1}, 2990, 2928, 1968, 1886, 1871, 1633, 1525, 1455, 1412, 1391, 1249, 1236, 1220, 1160, 1099, 1055, 1027, 974, 867, 823, 801, 761, 661, 630, 618, 586, 536, 515, 487. − UV/Vis (DMSO): λ_{max} (ε) = 316 (9900). − $C_{19}H_{25}CrO_5P$ (432.37): calcd. C 52.78, H 5.83; found C 52.97, H 5.84.

{η^6-[2-Butyl-1-(diethoxyphosphoryl)-3-methylprop-2-en-1-yl]benzene}tricarbonylchromium(0) (3e): Yellow crystals, m.p. 63−65°C.− ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 0.70−2.13 (21 H), 3.96 (m, 5 H), 5.50 (m, 1 H), 5.53 (m, 1 H), 5.70 (m, 2 H), 6.19 (m, 1 H). − ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 13.70 (CH_3), 16.15 (CH_3, $J_{P,C}$ = 7.5 Hz), 16.35 (CH_3, $J_{P,C}$ = 7.5 Hz), 20.90 (CH_3), 21.20 (CH_3), 22.70 (CH_2), 29.60 (CH_2), 31.50 (CH_2), 45.85 (CH, $J_{P,C}$ = 143.4 Hz), 61.35 (CH_2, $J_{P,C}$ = 7.5 Hz), 62.75 (CH_2, $J_{P,C}$ = 7.5 Hz), 92.90 (CH), 93.60 (CH), 94.80 (CH), 96.40 (CH), 97.30 (CH, $J_{P,C}$ = 15.1 Hz), 109.50 (C_{quat}), 127.45 (C_{quat}, $J_{P,C}$ = 7.5 Hz), 132.10 (C_{quat}, $J_{P,C}$ = 15.1 Hz), 233.90 (C_{quat}, CO). − ^{31}P NMR ([D$_6$]DMSO, 121 MHz) : δ = 23.93. − MS (70 eV); *m/z* (%): 474 [M^+] (1), 446 [M^+ − CO] (1), 418 [M^+ − 2 CO] (12), 390 [M^+ − 3 CO] (100), 338 [M^+ − $Cr(CO)_3$] (21), 52 [Cr^+] (4). − IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1}, 2929, 2858, 1966, 1887, 1731, 1601, 1524, 1495, 1455, 1414, 1391, 1249, 1163, 1098, 1055, 1028, 965, 870, 815, 747, 701, 661, 630, 560, 530, 479. − UV/Vis (DMSO): λ_{max} (ε) = 315 (5800). − $C_{22}H_{31}CrO_6P$ (474.45): calcd. C 55.69, H 6.58; found C 55.47, H 6.55.

Tricarbonyl{η^6-[1-(diethoxyphosphoryl)-2-ethenyl-3-methylprop-2-en-1-yl]benzene}chromium(0) (3f): Yellow crystals, m.p. 99−100°C. − ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.19 (m, 6 H), 1.89 (m, 6 H), 4.00 (m, 4 H), 4.29 (d, *J* = 27.7 Hz, 1 H), 5.21 (m, 2 H), 5.66 (m, 4 H), 6.10 (m, 1 H), 6.42 (m, 1 H). − ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 16.31 (CH_3), 21.76 (CH_3), 22.47 (CH_3), 43.78 (CH, $J_{P,C}$ = 139.9 Hz), 61.65 (CH_2), 62.81 (CH_2), 93.11 (CH), 93.83 (CH), 94.86 (CH), 96.67 (CH), 97.06 (CH), 109.97 (C_{quat}), 119.56 (CH_2), 126.98 (C_{quat}), 133.57 (CH), 136.24 (C_{quat}), 233.94 (C_{quat}, CO). − ^{31}P NMR ([D$_6$]DMSO, 121 MHz) : δ = 24.17. − MS (70 eV); *m/z* (%): 444 [M^+] (1), 416 [M^+ − CO] (1), 388 [M^+ − 2 CO] (10), 360 [M^+ − 3 CO] (100), 308 [M^+ − $Cr(CO)_3$] (2), 52 [Cr^+] (4). − IR (KBr): $\tilde{\nu}$ = 3084 cm^{-1}, 2982, 1971, 1886, 1867, 1629, 1528, 1458, 1393, 1248, 1221, 1177, 1049, 1026, 976, 902, 764, 668, 633, 618, 571, 529. − UV/Vis (DMSO): λ_{max} (ε) = 316 (9300). − $C_{20}H_{25}CrO_6P$ (444.38): calcd. C 54.06, H 5.67; found C 54.27, H 5.61.

Tricarbonyl{η^6-[1-(diethoxyphosphoryl)-3-methyl-2-phenylprop-2-en-1-yl]benzene}chromium(0) (3g): Yellow crystals, m.p. 146−148°C. − ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.25 (m, 6 H), 1.44 (s, 3 H), 1.97 (s, 3 H), 4.07 (m, 4 H), 4.38 (d, *J* = 25.5 Hz, 1 H), 5.36−5.66 (m, 5 H), 6.95−7.29 (m, 5 H). − ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 15.83 (CH_3, *J* = 6.2 Hz), 16.21 (CH_3, *J* = 5.7 Hz), 20.65 (CH_3), 22.89 (CH_3), 44.94 (CH, *J* = 142.3 Hz), 61.21 (CH_2), 62.41 (CH_2, *J* = 6.7 Hz), 91.82 (CH), 93.01 (CH), 94.55 (CH), 97.02 (CH), 97.69 (CH), 108.61 (C_{quat}), 126.49 (CH), 127.26 (CH), 129.30 (C_{quat}), 130.46 (CH), 134.52 (C_{quat}), 138.57 (C_{quat}), 233.91 (C_{quat}, CO). − ^{31}P NMR ([D$_6$]DMSO, 121 MHz) : δ = 23.14. − MS (70 eV); *m/z* (%): 494 [M^+] (1), 466 [M^+ − CO] (1), 438 [M^+ − 2 CO] (2), 410 [M^+ − 3 CO] (100), 358 [M^+ − $Cr(CO)_3$] (14), 52 [Cr^+] (2). − IR (KBr): $\tilde{\nu}$ = 2991 cm^{-1}, 1969, 1882, 1636, 1458, 1254, 1232, 1054, 1028, 972, 767, 702, 662, 631, 595, 531. − UV/Vis (DMSO): λ_{max} (ε) = 317 (9100). − $C_{24}H_{27}CrO_6P$ (494.44): calcd. C 58.30, H 5.50; found C 58.10, H 5.59.

(*R*,*R* or *S*,*S*)-{η^6-1-[2-Butyl-1-(diethoxyphosphoryl)-3-methylprop-2-en-1-yl]-2-methylbenzene}tricarbonylchromium(0) (3h, Major Diastereomer): Yellow crystals, m.p. 108−111°C. − ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.18 (t, *J* = 6.9 Hz, 3 H), 1.29 (t, *J* = 6,9 Hz, 3 H), 1.49 (s, 3 H), 1.69 (d, *J* = 5.3 Hz, 3 H), 1.78 (m, 3 H), 1.96 (s, 3 H), 3.73−4.15 (m, 5 H), 5.52 (d, *J* = 6.1 Hz, 1 H), 5.61 (d, *J* = 6.3 Hz, 1 H), 5.74 (t, *J* = 6.4 Hz, 1 H), 6.36 (d, *J* = 6.5 Hz, 1 H). − ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 15.71 (CH_3), 16.12 (CH_3, $J_{P,C}$ = 5.9 Hz), 16.61 (CH_3, $J_{P,C}$ = 4.6 Hz), 18.45 (CH_3), 21.01 (CH_3), 21.31 (CH_3), 42.78 (CH, $J_{P,C}$ = 144.6 Hz), 61.35 (CH_2, $J_{P,C}$ = 7.2 Hz), 63.16 (CH_2, $J_{P,C}$ = 6.6 Hz), 91.48 (CH), 95.25 (CH), 95.61 (CH), 97.30 (CH, $J_{P,C}$ = 4.6 Hz), 107.82 (C_{quat}), 109.76 (C_{quat}, *J* = 15.9 Hz), 119.60 (C_{quat}, *J* = 8.6 Hz), 132.08 (C_{quat}, *J* = 11.9 Hz), 234.25 (C_{quat}, CO). − MS (70 eV, EI); *m/z* (%): 446 [M^+] (2), 418 [M^+ − CO] (1), 390 [M^+ − 2 CO] (12), 362 [M^+ − 3 CO] (100), 310 [M^+ − $Cr(CO)_3$] (6), 52 [Cr^+] (4). − IR (KBr): $\tilde{\nu}$ = 3084 cm^{-1}, 2982, 2928, 1967, 1889, 1872, 1629, 1445, 1380, 1251, 1233, 1213, 1162, 1097, 1047, 1024, 973, 799, 754, 667, 629, 587, 538, 515, 481. − UV/Vis (DMSO): λ_{max} (ε) = 316 nm (9900). − $C_{20}H_{27}CrO_6P$ (446.39): calcd. C 53.81, H 6.09; found C 53.97, H 6.02.

(*R*,*S* or *S*,*R*)-{η^6-1-[2-Butyl-1-(diethoxyphosphoryl)-3-methylprop-2-en-1-yl]-2-methylbenzene}tricarbonylchromium(0) (3h, Minor Diastereomer): Yellow crystals, m.p. 93−95°C. − ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.06 (t, *J* = 6.9 Hz, 3 H), 1.16 (t, *J* = 7.0 Hz, 3 H), 1.66 (d, *J* = 3.3 Hz, 3 H), 1.79 (s, 3 H), 2.01 (s, 3 H), 2.28 (s, 3 H), 3.82−3.99 (m, 4 H), 4.15 (d, *J* = 26.5 Hz, 1 H), 5.44−5.49 (m, 2 H), 5.83 (t, *J* = 6.4 Hz, 1 H), 6.06 (d, *J* = 5.8 Hz, 1 H). − ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 16.30 (CH_3), 16.39 (CH_3), 17.65 (CH_3), 19.62 (CH_3), 20.96 (CH_3), 21.31 (CH_3), 40.79 (CH, $J_{P,C} \approx$ 135 Hz, under DMSO multiplet), 61.87 (CH_2, $J_{P,C}$ = 7.2 Hz), 62.57 (CH_2, *J* = 6.6 Hz), 90.16 (CH), 93.45 (CH), 97.28 (CH), 98.92 (CH, $J_{P,C}$ = 3.5 Hz), 109.83 (C_{quat}), 112.40 (C_{quat}, $J_{P,C}$ = 5.3 Hz), 122.65 (C_{quat}, $J_{P,C}$ = 5.9 Hz), 131.31 (C_{quat}, $J_{P,C}$ = 13.9 Hz), 234.01 (C_{quat}, CO). − MS (70 eV, EI); *m/z* (%): 446 [M^+] (1), 390 [M^+ − 2 CO] (12), 362 [M^+ − 3 CO] (100), 310 [M^+ − $Cr(CO)_3$] (6), 52 [Cr^+] (3). − IR (KBr): $\tilde{\nu}$ = 3090 cm^{-1}, 2988, 1955, 1873, 1631, 1444, 1386, 1251, 1213, 1191, 1163, 1097, 1047, 1033, 969, 839, 814, 797, 738, 667, 639, 628, 579, 540, 531, 497, 479. − UV/Vis (DMSO): λ_{max} (ε) = 317 nm (9000). − $C_{20}H_{27}CrO_6P$ (446.39): calcd. C 53.81, H 6.09; found C 53.92, H 6.08.

Tricarbonyl{η⁶-1-[1-(diethoxyphosphoryl)-3-methyl-2-phenylprop-2-en-1-yl]-2-methylbenzene}chromium(0) (3i): Yellow crystals, m.p. 94−97°C. − ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.30 (m, 6 H), 1.45 (d, *J* = 4.2 Hz, 3 H), 1.95 (d, *J* = 2.5 Hz, 3 H), 2.13 (s, 3 H), 4.09−4.25 (m, 4 H), 4.38 (d, *J* = 26.7 Hz, 1 H), 5.04 (t, *J* = 6.3 Hz, 1 H), 5.39 (d, *J* = 6.3 Hz, 1 H), 5.58 (t, *J* = 6.3 Hz, 1 H), 5.82 (d, *J* = 6.6 Hz, 1 H), 6.72−7.12 (m, 5 H). − ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 16.03 (CH$_3$), 16.63 (CH$_3$, $J_{P,C}$ = 5.3 Hz), 18.26 (CH$_3$), 20.78 (CH$_3$, $J_{P,C}$ = 2.6 Hz), 23.16 (CH$_3$, $J_{P,C}$ = 2.6 Hz), 42.21 (CH, $J_{P,C}$ = 145.9 Hz), 61.42 (CH$_2$, $J_{P,C}$ = 7.9 Hz), 63.14 (CH$_2$, $J_{P,C}$ = 7.3 Hz), 89.64 (CH), 93.83 (CH), 95.98 (CH), 97.95 (CH, $J_{P,C}$ = 3.9 Hz), 106.74 (C$_{quat}$, $J_{P,C}$ = 1.9 Hz), 110.37 (C$_{quat}$, $J_{P,C}$ = 15.9 Hz), 115.36 (CH), 118.91 (CH), 126.75 (CH), 127.52 (CH), 127.76 (C$_{quat}$, $J_{P,C}$ = 7.9 Hz), 129.48 (CH), 135.45 (C$_{quat}$, $J_{P,C}$ = 11.9 Hz), 139.00 (C$_{quat}$), 234.22 (C$_{quat}$, CO). − MS (70 eV, EI); *m/z* (%): 508 [M$^+$] (1), 480 [M$^+$ − CO] (1), 452 [M$^+$ − 2 CO] (2), 424 [M$^+$ − 3 CO] (100), 372 [M$^+$ − Cr(CO)$_3$] (1), 52 [Cr$^+$] (5). − IR (KBr): $\tilde{\nu}$ = 3079 cm^{-1}, 2984, 2929, 2856, 1955, 1910, 1890, 1640, 1606, 1594, 1491, 1474, 1459, 1441, 1383, 1254, 1235, 1205, 1162, 1097, 1055, 1023, 1010, 970, 830, 808, 770, 755, 723, 701, 663, 629, 596, 552, 526, 477. − UV/Vis (DMSO): λ_{max} (ε) = 317 nm (9300). − $C_{25}H_{29}CrO_6P$ (508.46): calcd. C 59.02, H 5.74; found C 60.32, H 5.84.

{η⁶-1-[2-Butyl-1-(diethoxyphosphoryl)-3-methylprop-2-en-1-yl]-2-(dimethoxymethyl)benzene}tricarbonylchromium(0) (3j): Yellow crystals, m.p. 90−96°C. − ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.19 (t, *J* = 7.0 Hz, 3 H), 1.29 (t, *J* = 6.9 Hz, 3 H), 1.48 (m, 3 H), 1.66−1.70 (m, 3 H), 1.82 (m, 3 H), 3.09 (s, 3 H, OMe), 3.42 (s, 3 H, OMe), 3.88−4.10 (m, 4 H), 4.36 (d, *J* = 25.2 Hz, 1 H), 4.91 (s, 1 H), 5.66−5.70 (m, 2 H), 5.78−5.84 (m, 1 H), 6.20−6.23 (m, 1H); additional signals (minor diastereomer): δ = 1.01 (t, *J* = 7.0 Hz, 3 H), 1.15 (t, *J* = 6.9 Hz, 3 H), 3.76−3.84 (m, 4 H), 4.74 (d, *J* = 27.9 Hz, 1 H), 5.21 (s, 1 H). − ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 16.08 (CH$_3$), 16.17 (CH$_3$), 16.66 (CH$_3$), 16.73 (CH$_3$), 21.51 (CH$_3$), 42.20 (CH, $J_{P,C}$ = 141.9 Hz), 53.62 (CH$_3$, OMe), 56.57 (CH$_3$, OMe), 61.30 (CH$_2$, $J_{P,C}$ = 7.3 Hz), 63.20 (CH$_2$, $J_{P,C}$ = 7.3 Hz), 92.74 (CH), 92.96 (CH), 93.98 (CH), 95.79 (CH, $J_{P,C}$ = 4.6 Hz), 100.48 (CH), 107.67 (C$_{quat}$, *J* = 4.6 Hz), 107.91 (C$_{quat}$), 120.79 (C$_{quat}$, *J* = 9.9 Hz), 131.09 (C$_{quat}$, *J* = 11.9 Hz), 233.53 (C$_{quat}$, CO); additional signals (minor diastereomer): δ = 49.27 (CH, $J_{P,C}$ = 141.9 Hz), 55.91 (CH$_3$, OMe), 91.03 (CH), 94.35 (CH), 98.66 (CH), 109.46 (C$_{quat}$), 233.22 (C$_{quat}$, CO). − ^{31}P NMR ([D$_6$]DMSO, 121 MHz) : δ = 23.99; additional signal (minor diastereomer): δ = 25.80. − MS (70 eV, EI); *m/z* (%): 506 [M$^+$] (1), 450 [M$^+$ − 2 CO] (21), 422 [M$^+$ − 3 CO] (100), 52 [Cr$^+$] (5). − IR (KBr): $\tilde{\nu}$ = 3084 cm^{-1}, 2984, 2931, 2832, 1965, 1888, 1635, 1525, 1444, 1416, 1391, 1347, 1252, 1238, 1204, 1162, 1101, 1055, 1024, 969, 859, 796, 762, 742, 665, 628, 586, 531, 481. − UV/Vis (DMSO): λ_{max} (ε) = 318 nm (10100). − $C_{22}H_{31}CrO_8P$ (506.44): calcd. C 52.17, H 6.17; found C 52.43, H 6.18.

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