

187. New Synthetic Routes to β -Olefinic Trialkoxyphosphonium Salts and Phosphonates: Organometallic Variants of the *Michaelis-Arbuzov* Reaction¹⁾

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The low-temperature addition of tertiary phosphites to $[(\text{allyl})\text{Fe}(\text{CO})_4]^+\text{X}^-$ complexes proceeds regio- and stereospecifically and produces metal-coordinated β -olefinic trialkoxyphosphonium ions. These can be converted by various routes into the uncomplexed phosphonium salts or phosphonates. Similar reactions of acyclic $[(\text{dienyl})\text{Fe}(\text{CO})_3]^+\text{X}^-$ compounds give metal-coordinated (2,4-dien-1-yl)trialkoxyposphonium salts or dialkyl (2,4-dien-1-yl)phosphonates. The mechanisms and their relationship to the classical *Michaelis-Arbuzov* reaction are discussed. The new compounds are characterized, if possible, by ^1H -, ^{13}C -, and ^{31}P -NMR spectra. The new phosphonium salts and phosphonates, potentially useful for *Wittig-Horner* reactions, are difficult to obtain by conventional routes.

1. Introduction. – Cationic metal- π -complexes of unsaturated organic moieties are becoming increasingly important as useful synthons in organic synthesis. This applies to even-numbered hydrocarbons like ethylene, butadiene, or benzene, where coordination to a metal cation seems, among other effects, to result in net withdrawal of electron density from the unsaturated hydrocarbon ligand leading to a higher susceptibility to nucleophilic attack by anions such as H^- , R^- , CN^- , CH_3O^- , and others [2]. In particular, it also applies to odd-numbered polyenic ligands such as allyl or dienyl, which can be regarded as stabilized (and isolable) carbocation equivalents coordinated to a transition metal. These species again are subject to attack by a wide variety of nucleophiles, and the synthetic potential of this general reaction type is considerable [3–5]. General rules for the regioselectivity of nucleophilic attack on cationic π -hydrocarbons have been developed, which make these reactions more predictable [6].

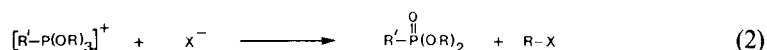
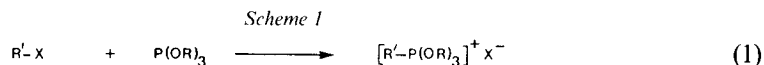
Of particular interest has been the addition of phosphorus nucleophiles like Ph_3P to metal-coordinated olefinic ligands [5], and a number of unsaturated phosphonium salts have been isolated in this manner. We had previously developed methods for decomplexation of metal-coordinated phosphonium ions [7]. When allylic complexes such as $[(\text{allyl})\text{Fe}(\text{CO})_4]^+$ were used as starting materials, free β,γ -unsaturated phosphonium salts are directly obtained in high yields, which are difficult to prepare by conventional routes [7] [8].

Phosphonium salts, when used for *Wittig* reactions, have wide synthetic use, especially in the preparation of natural products [9]. A variation of this method, the *Wittig-Horner* reaction, employs phosphonates instead of phosphonium salts, which are some-

¹⁾ Reactions with Metal-Coordinated Olefins, Part V. Part IV: see [1]. Presented in part at the XIIth International Conference on Organometallic Chemistry, Vienna, September 1985.

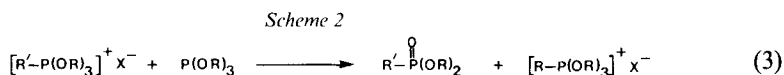
times superior in reactivity and selectivity. We, therefore, searched for general routes to prepare phosphonates and possibly their precursors, the trialkoxyphosphonium salts, starting from organometallic π -complexes.

2. Results and Discussion. – 2.1. *Formation of (2-Alken-1-yl)trialkoxyposphonium Salts and Dialkyl (2-Alken-1-yl)phosphonates.* The classical route to phosphonates, the *Michaelis-Arbuzov* reaction, generally involves the interaction between an alkyl halide $R'X$ and a phosphite $P(OR)_3$ (R = alkyl). At elevated temperatures (160–200°), an alkyl transfer takes place leading to a P(V) compound and another alkyl halide RX . There is considerable evidence for an *ionic* mechanism of this reaction, with an intermediate alkyl(trialkoxyposphonium) salt as an essential feature [10] (*Scheme 1*).



The intermediate phosphonium salt cannot be isolated under the reaction conditions, if a nucleophile X^- (Cl^- , Br^- , I^-) is present, since nucleophilic attack of X^- at $C(\alpha)$ of the phosphoric ester is more rapid than the first step [11].

In the absence of a strong nucleophile, the second step can be supplanted by an 'autocatalytic' mechanism with excess $P(OR)_3$ attacking the phosphonium salt leading to the formation of the phosphonate and another alkyl(trialkoxyposphonium) salt (*Scheme 2*). This reaction can be catalyzed by small amounts of other reagents like metal

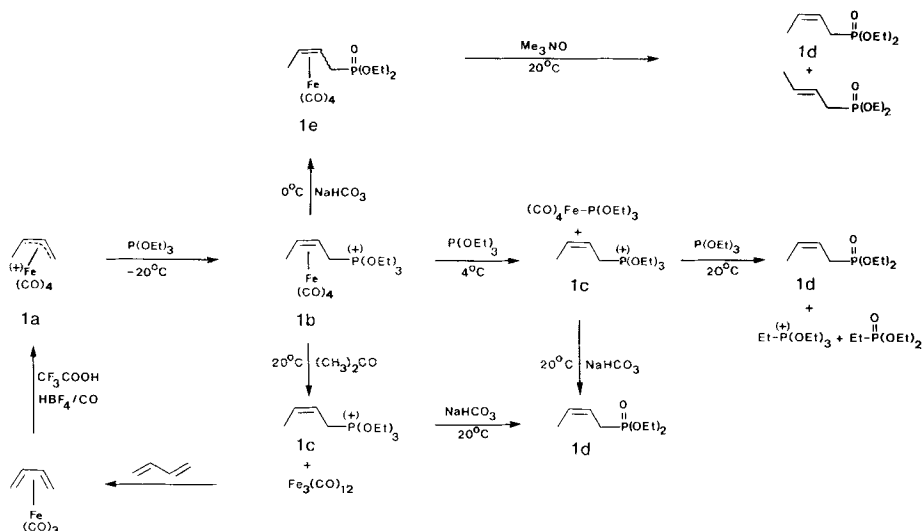


salts or metal carbonyls [12]. In this case, the intermediate trialkoxyposphonium salt can sometimes be isolated before *Reaction 3* occurs. However, this is restricted to organic molecules RX where $X = BF_4$, PF_6 , e.g. salts of stable carbonium ions, such as $[Ph_3C]BF_4$, $[(CH_3)_3O]BF_4$, or $[C_7H_7]PF_6$ [13] with non-nucleophilic counterions. Little is known about the reactivity of these trialkoxyposphonium salts in regard to their usefulness for *Wittig* reactions.

Metal-coordinated phosphites can also undergo the *Michaelis-Arbuzov* reaction, leading to metal-coordinated phosphonates. These reactions occur under much milder conditions, following the general *ionic* mechanism described above in the presence of a halide [10].

Treatment of $[(C_4H_7)Fe(CO)_4]BF_4$ (**1a**) with $P(OEt)_3$ at low temperatures ($\leq -10^\circ$) produced the expected initial addition product indicated by dissolution of the insoluble salt **1a**. Addition of Et_2O led to the quantitative precipitation of a complex of analytical composition $[(C_4H_7P(OEt)_3)Fe(CO)_4]BF_4$ (**1b**) (*Scheme 3*). If the above reaction mixture was allowed to warm to 4° , a second reaction occurred, and precipitation with Et_2O now produced nearly quantitative yields of the free phosphonium salt $[C_4H_7P(OEt)_3]BF_4$ (**1c**) (*Tables 1 and 2*). The Et_2O solution contained the iron complex $[Fe(CO)_4P(OEt)_3]$, which was identified by comparison with an authentic sample [14]. The labile mono-olefin

Scheme 3


 Table 1. ¹³C and ³¹P Chemical Shifts and J(P, C) Values of Allylic Triethoxyphosphonium Salts and Phosphonates^{a)}^{b)}

	C(1)	C(2)	C(3)	CH ₃ -C(1)	CH ₃ -C(3)	CH ₃ -C(3)	C(1')	C(2')	³¹ P
				(E)	(Z)				
1c	21.0 (129.0)	113.5 (13.0)	133.2 (15.5)	—	—	12.7 (2.5)	69.8 (8.5)	15.4 (6.0)	46.7
1d	26.0 (140.0)	120.1 (12.5)	127.8 (14.5)	—	—	12.9 (1.5)	61.5 (6.5)	16.7 (5.5)	27.8
2c	28.8 (132.0)	121.8 (10.5)	132.6 (15.8)	13.8 (7.0)	—	13.3 (1.0)	70.7 (8.0)	15.8 (5.5)	43.2
2d	31.5 (141.5)	128.0 (9.5)	126.4 (13.5)	15.3 (6.5)	—	13.3 (2.0)	61.4 (6.5)	16.7 (5.5)	31.1
3c	19.8 (128.0)	105.2 (13.0)	139.5 (16.0)	—	23.1 (3.5)	15.6 (3.0)	67.5 (7.5)	13.4 (6.0)	44.7
3d	27.0 (140.0)	114.1 (11.0)	135.3 (14.5)	—	25.8 (3.0)	17.9 (2.5)	61.4 (6.5)	16.7 (5.5)	28.5
1d'	31.2 (140.0)	121.0 (11.0)	129.8 (14.5)	—	18.1 (2.0)	—	61.5 (6.5)	16.7 (5.5)	—

^{a)} ¹³C Chemical shifts [ppm] obtained from proton-noise-decoupled spectra in (CD₃)₂CO for 1c, 2c, and 3c, all others in C₆D₆, internal reference TMS; numbers in brackets refer to P, C-coupling constants [Hz]; digital resolution and reproducibility of J(P, C) are ± 0.5 Hz.

^{b)} ³¹P Chemical shifts [ppm] obtained from proton-noise-decoupled spectra in (CD₃)₂CO for 1d, 2d, and 3d, all others in C₆D₆, external reference H₃PO₄.

Table 2. ¹H-NMR Data of Allylic Triethoxyphosphonium Salts and Phosphonates^{a)}^{b)}

	H-C(1)	H-C(2)	H-C(3)	CH ₃ -C(1)	CH ₃ -C(3) (Z)	CH ₃ -C(3) (E)	H-C(1')	H-C(2')
1c	3.61 (<i>dd</i> , <i>J</i> = 22.0, 7.75)	5.45 (<i>ddq</i> , <i>J</i> = 10.0, 7.75, 6.0, 1.0)	5.98 (<i>ddq</i> , <i>J</i> = 10.0, 5.5, 5.5)	—	1.77 (<i>ddd</i> , <i>J</i> = 5.5, 5.5, 1.1)	—	4.68 (<i>qd</i> , <i>J</i> = 7.0, 7.0)	1.44 (<i>td</i> , <i>J</i> = 7.0, 0.75)
1d	2.49 (<i>dd</i> , <i>J</i> = 22.0, 6.25)	5.42–5.67 (<i>m</i>)	5.42–5.67 (<i>m</i>)	—	1.48 (<i>dd</i> , <i>J</i> = 4.5, 4.0)	—	3.86–4.01 (<i>m</i>)	1.05 (<i>t</i> , <i>J</i> = 7.0)
2c	3.99 (<i>ddq</i> , <i>J</i> = 21.5, 10.5, 7.25)	5.33 (<i>dddq</i> , <i>J</i> = 10.5, 10.5, 5.75, 1.75)	5.93 (<i>dq</i> , <i>J</i> = 10.5, 6.75, 5.0)	1.41 (<i>dd</i> , <i>J</i> = 22.0, 7.25)	1.78 (<i>ddd</i> , <i>J</i> = 6.75, 5.0, 1.75)	—	4.69 (<i>qd</i> , <i>J</i> = 7.0, 7.0)	1.41–1.50 (<i>m</i>)
2d	3.02 (<i>ddq</i> , <i>J</i> = 20.5, 10.5, 7.0)	5.25 (<i>dddq</i> , <i>J</i> = 10.5, 10.5, 5.25, 1.75)	5.66 (<i>dq</i> , <i>J</i> = 10.5, 6.75, 4.75)	1.22 (<i>'dd'</i> , <i>J</i> = 19.0, 7.0)	1.66 (<i>ddd</i> , <i>J</i> = 6.75, 4.5, 1.75)	—	4.03–4.13 (<i>m</i>)	1.29 (<i>'t'</i> , <i>J</i> = 7.0); 1.31 (<i>t</i> , <i>J</i> = 7.0)
3c	3.54 (<i>dd</i> , <i>J</i> = 21.25, 7.75)	5.20 (<i>td</i> , <i>J</i> = 7.75, 6.0)	—	—	1.70–1.90 (<i>m</i>)	1.70 1.90 (<i>m</i>)	4.66 (<i>qd</i> , <i>J</i> = 7.0, 7.0)	1.48 (<i>td</i> , <i>J</i> = 7.0, 0.75)
3d	2.49 (<i>dd</i> , <i>J</i> = 22.0, 7.75)	5.33 (<i>tdq</i> , <i>J</i> = 7.75, 5.75, 1.25, 1.25)	—	—	1.47 (<i>dd</i> , <i>J</i> = 4.0, 1.25)	1.55 (<i>dd</i> , <i>J</i> = 5.25, 1.25)	3.83–4.08 (<i>m</i>)	1.07 (<i>'t'</i> , <i>J</i> = 7.0)

^{a)} The ¹H-NMR spectrum of **2f** was measured at 400 MHz, all others at 200 MHz.

^{b)} ¹H Chemical shifts [ppm] in C₆D₆ for **1d** and **3d**; in CD₃OD for **2d**, all others in (CD₃)₂CO; internal reference TMS; numbers in brackets refer to H, H- and P, H-coupling constants [Hz]; digital resolution and reproducibility of *J*(H, H) and *J*(P, H) are ± 0.25 Hz.

complex **1b** had, therefore, undergone a ligand substitution by excess P(OEt)₃, an expected reaction, as it is also observed with other *Lewis* bases [7]. As the counterion in our case was the non-nucleophilic BF₄[−], the free trialkoxyphosphonium salt was quite stable in the absence of P(OEt)₃. It had the expected (*Z*)-configuration of the butenyl group, apparent from the *J*(¹H, ¹H) values (Table 2).

The same phosphonium salt **1c** was formed, when previously isolated **1b** was dissolved in acetone and left at room temperature. The solution soon turned green, and after 15 h displacement of the iron group was complete; the free phosphonium salt and green Fe₃(CO)₁₂ could be separated at this stage. As Fe₃(CO)₁₂ can be used for the synthesis of the starting diolefin complex [(C₄H₆)Fe(CO)₃], this method offers the possibility for phosphonium-ion synthesis with recovery of ironcarbonyl, which can then be reintroduced into a cyclic process (Scheme 3).

The phosphonium salt **1c** can be converted into a phosphonate by two methods: *a*) The original reaction mixture of allyl complex **1a** and P(OEt)₃ is allowed to warm to room temperature. A rapid exothermal conversion into C₄H₇P(O)(OEt)₂ (**1d**) occurs above 10° and a phosphonium salt [EtP(OEt)₃]BF₄ is formed as a by-product. On prolonged reaction times, the mixture also contains another phosphonate, namely EtP(O)(OEt)₂, a clear

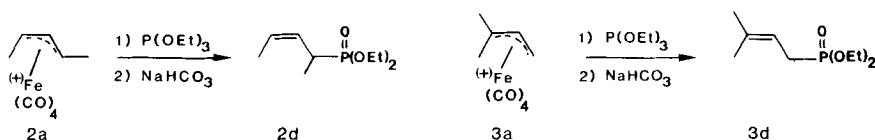
indication that the 'autocatalytic' mechanism for phosphonate formation is now predominant (*Scheme 2* and *3*). $[\text{EtP}(\text{OEt})_3]\text{BF}_4$ was identified by a comparison with an authentic sample [15]. The phosphonate formation appears to be metal-catalyzed, as the reaction occurs much more readily (15° vs. 190°) than in the absence of the by-product $[\text{Fe}(\text{CO})_4\text{P}(\text{OEt})_3]$. If the more reactive $\text{P}(\text{OMe})_3$ is used instead, the reaction becomes extremely violent and uncontrollable even with small amounts; this is most likely caused by a combination of the exothermal nature of the conversion $\text{P}-\text{O}-\text{C}$ to $\text{P}(\text{=O})-\text{C}$ [9] and decomposition of the Fe complex with CO evolution.

b) A more convenient route to the pure **1d** is the previous isolation of **1c** by precipitation with Et_2O and its conversion with aqueous NaHCO_3 solution [11]. This allows the preparation of **1d** in 90% overall yield from **1a**.

An alternative method, the previous isolation of the metal-coordinated phosphonium salt **1b** and its conversion to the metal-coordinated phosphonate **1e** by treatment with aqueous NaHCO_3 solution, and subsequent oxidation to the free phosphonate **1d** by treatment with Me_3NO , was not stereospecific. The product isolated consisted of a 1:1 mixture of **1d** and its (*E*)-isomer (*Table 1*). We are unable to account for this partial isomerization. The reaction sequence *via 1c*, on the other hand, is completely stereospecific as the (*Z*)-configuration of the diene complex is retained in the intermediate allyl species as well as the two phosphonium salts to give pure (*Z*)-butenylphosphonate. The addition of trialkylphosphites is also completely regioselective, as nucleophilic attack occurs only at the less substituted end of **1a**.

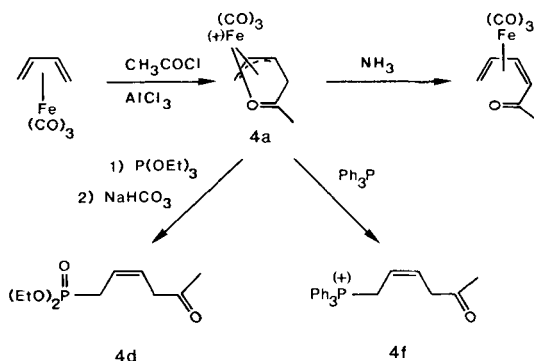
The same regioselectivity is also found in other allyl complexes. Compound **2a** adds $\text{P}(\text{OEt})_3$ with preference for the position leading to the (*Z*)-configured phosphonate **2d**, while **3a** again shows only attack at the less substituted end of the allyl complex (*Scheme 4*). The ^1H -, ^{13}C -, as well as ^{31}P -NMR data are summarized in *Tables 1* and *2*.

Scheme 4



A further extension of this method to generate other β,γ -unsaturated phosphonates was provided by the facile *Friedel-Crafts* acetylation of $[(\text{diolefin})\text{Fe}(\text{CO})_3]$ complexes. This leads to the initial formation of $[(\text{allyl})\text{Fe}(\text{CO})_3]^+$ species, where a closed-shell electronic configuration for the Fe-atom is obtained by an intramolecular σ -donation of a lone-pair of electrons from the acyl-O-atom [16]. Reaction of this intermediate cation **4a**, which we prepared from $[(\text{butadiene})\text{Fe}(\text{CO})_3]$ and $\text{CH}_3\text{COCl}/\text{AlCl}_3$ and which is normally converted by inorganic or organic bases into $[(\text{dienone})\text{Fe}(\text{CO})_3]$ compounds [17], with $\text{P}(\text{OEt})_3$ led to the free (*(Z)*-5-oxo-2-hexen-1-yl)phosphonate **4d** in 78% yield (*Scheme 5*). A similar reaction with Ph_3P under the same conditions as described before [7] allows the isolation of the corresponding triphenylphosphonium salt **4f** in 90% yield. The initial *s-cis*-conformation of $[(\text{butadiene})\text{Fe}(\text{CO})_3]$ is again retained throughout the reaction sequence and induces the formation of a (*Z*)-configured phosphonium salt or phosphonate.

Scheme 5

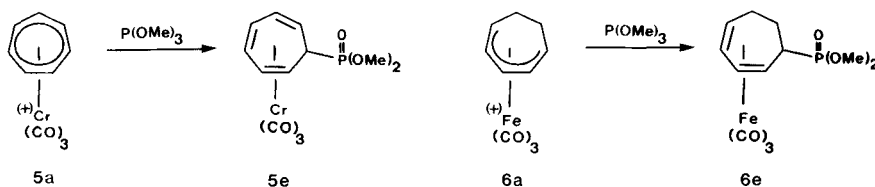


The method described here, therefore, constitutes a novel way to prepare ((*Z*)-alkenyl)phosphonates under mild conditions. It also allows the isolation of the intermediate trialkoxyphosphonium salts, e.g. **1c**, which are not accessible by any other route. Further attractive features of this method are the inexpensive starting materials, high yields, and regio- as well as stereospecific attachment of tertiary phosphites to the delocalized π -systems described above. Ironcarbonyl can in principle be recovered from the reaction mixture and reintroduced into a cyclic process to prepare the starting diolefin complex.

2.2. Formation of (2,4-Dien-1-yl)trialkoxyposphonium Salts and Dialkyl (2,4-Dien-1-yl)phosphonates. Stable tricarbonyl(dienyl)iron cations are available by a variety of preparative routes. The cations most commonly used for organic synthesis are derivatives of tricarbonyl(cyclohexadienyl)iron, which were shown to react with a variety of nucleophiles, including Ph_3P [5] and $\text{P}(\text{OMe})_3$ [18]. In the latter case, the tricarbonyl (5-phosphonio-1,3-cyclohexadiene)iron was directly obtained at ambient temperatures, and the iron group was later removed by oxidative decomplexation. The mechanism of this reaction was not further investigated, although it was proposed that the dealkylation of the initial trialkoxyphosphonium salt into the phosphonate was promoted by the solvent MeOH with formation of ' $\text{Me}_2\text{O-HBF}_4$ '. We decided to reinvestigate this reaction starting from other tricarbonyl(dienyl)iron complexes and also corresponding tricarbonyl(trienyl)chromium compounds.

The tropylium complex $[\text{C}_7\text{H}_7\text{Cr}(\text{CO})_3]\text{BF}_4$ (**5a**), although less electrophilic than the cationic Fe complexes had already been shown by *Hackett* and *Jaouen* to undergo nucleophilic attack by Ph_3P to give a stable phosphonium salt [19]. On reaction with $\text{P}(\text{OMe})_3$, we observed an instantaneous reaction and, after workup, isolated a metal-coordinated phosphonate **5e**, together with $[\text{CH}_3\text{P}(\text{OCH}_3)_3]\text{BF}_4$, which was identified by its

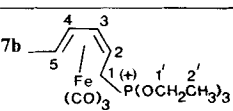
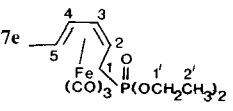
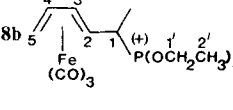
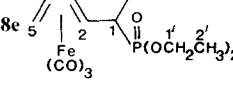
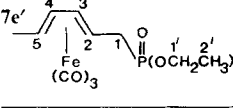
Scheme 6



^1H -NMR spectrum [20]. A similar conversion was observed with the cycloheptadienyl complex $[\text{C}_7\text{H}_9\text{Fe}(\text{CO})_3]^+$ (**6a**), which on treatment with $\text{P}(\text{OMe})_3$ generated, in quantitative yield, the phosphonate **6e** (Scheme 6). Again, a stoichiometric amount of $[\text{CH}_3\text{P}(\text{OCH}_3)_3]\text{BF}_4$ was isolated, confirming that the *Arbuzov*-type dealkylation proceeds, as in the previous cases, mainly by the 'autocatalytic' mechanism.

Of special interest to us was the formation of phosphonates derived from acyclic tricarbonyl(hexadienyl)iron complexes, such as **7a**. Preliminary results had already indicated that again metal-coordinated phosphonates were formed upon interaction with trialkyl phosphites, and that these phosphonates, generated *in situ* and directly converted into ylid-type carbanions by treatment with BuLi , reacted with aldehydes under *Wittig-Horner* olefination with high (*E*)-selectivity [21] [22]. To establish that phosphonate formation was again stereospecific, we tried to isolate and identify the intermediate phosphonium salt and the metal-coordinated phosphonate. Surprisingly, two isomeric triethoxyphosphonium salts are formed with $\text{P}(\text{OEt})_3$ at low temperatures in an approximate ratio of 5:4. The major component was the expected $[(2Z,4E)\text{-}1\text{-(triethoxyphosphonio)-2,4-hexadiene}]\text{Fe}(\text{CO})_3\text{BF}_4$ (**7b**), formed by retention of the '*cis*'-configuration of the dienyl cation and '*trans*'-addition at the sterically less hindered end. The minor component **8b** was the product derived from attack at the Me-substituted C-atom of the

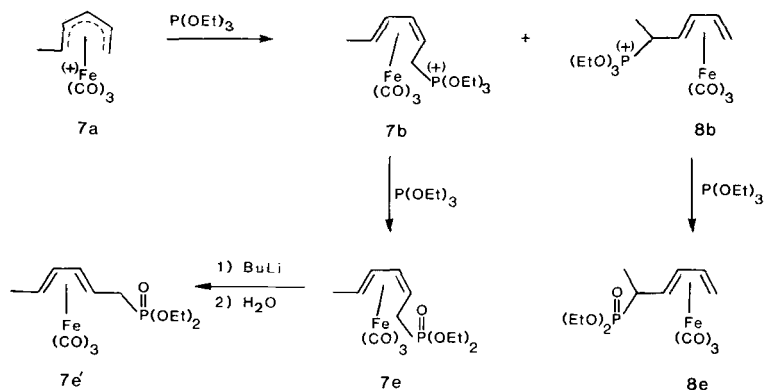
Table 3. ^{13}C and ^{31}P Chemical Shifts and $J(\text{P}, \text{C})$ Values of Acyclic $[(\text{Triethoxyphosphonio})\text{-}\eta^4\text{-hexadiene}]\text{-Fe}(\text{CO})_3$ Salts and Phosphonates^{a)}^{b)}

	C(1)	C(2)	C(3)	C(4)	C(5)	$\text{CH}_3\text{-C}(5)$	$\text{CH}_3\text{-C}(1)$	C(1')	C(2')	^{31}P
	21.6 (119.5)	39.7 (14.5)	80.0 (5.0)	96.0 —	59.9 —	19.8 —	— —	69.4 (8.0)	15.3 (5.5)	42.4
	26.5 (133.0)	47.8 (11.0)	83.4 (4.5)	96.6 —	60.2 —	20.6 —	— —	63.4 (6.5)	16.8 (5.5)	33.0
	27.9 (121.0)	50.7 (14.0)	84.4 (3.5)	93.1 —	42.5 —	— —	14.4 (4.5)	69.9 (9.5)	15.3 (5.5)	41.1
	31.1 (132.5)	59.0 (11.0)	87.5 (3.5)	93.5 —	42.9 —	— —	16.3 (5.0)	63.4 (6.5)	16.8 (5.5)	32.5
	31.3 (137.5)	51.1 (11.0)	85.2 (9.5)	87.3 —	59.3 —	19.4 —	— —	63.5 (6.5)	16.7 (3.5)	30.0

^{a)} ^{13}C Chemical shifts [ppm] obtained from proton-noise-decoupled spectra in CDCl_3 for **7b** and **8b**, all others in CD_3OD , internal reference TMS; numbers in brackets refer to $J(\text{P}, \text{C})$ coupling constants [Hz]; digital resolution and reproducibility of $J(\text{P}, \text{C}) \pm 0.5$ Hz.

^{b)} ^{31}P Chemical shifts [ppm] obtained from proton-noise-decoupled spectra in $(\text{CD}_3)_2\text{CO}$ for **7b** and **8b**, all others in CD_3OD , external reference H_3PO_4 .

Scheme 7

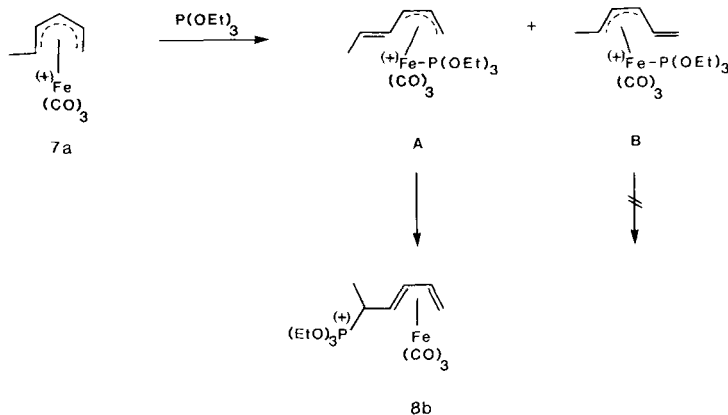


dienyl ligand which additionally had undergone a (*Z/E*)-rearrangement. When the mixture **7b/8b** with excess phosphite was allowed to warm to room temperature, an identical ratio of **7e/8e** was obtained (Scheme 7).

A similar addition at the Me-substituted end with concurrent rearrangement had previously been observed in the hydrolysis of **7a** in aqueous solution, which generated only one alcohol complex of two possible diastereoisomers [23]. This was explained by an initial attack of H_2O (or OH^-) at the metal center, which causes a rearrangement of the dienyl cation to a hydrated vinyl- π -allyl-complex with a (*E*)-configuration of the double bond. 'trans'-Addition of OH^- at this double bond then formed the observed isomer of tricarbonyl((*2E,4E*)-2,4-hexadiene-1-ol)iron.

When applying the same mechanism to the addition of phosphites and in order to explain the unusual addition at the more hindered end of **7a**, we must assume that initial attack of $\text{P}(\text{OEt})_3$ can also occur at the metal center with preferred formation of intermediate **A** over the isomeric species **B**. Isomer **A** has the most substituted olefin and the least sterically crowded π -allyl group. Further 'trans'-attack at C(2) of the intermediate

Scheme 8



and release of the metal-coordinated phosphite would then account for the formation of the observed phosphonium salt **8b** and phosphonate **8e** (Scheme 8).

Surprisingly, only phosphonate **7e** seems to undergo Wittig-Horner olefinations, as the only products formed after deprotonation of the mixture **7e/8e** with BuLi and reaction with aromatic aldehydes are derived from **7e** [22] [24]. The deprotonation of **7e** is accompanied also by a (*Z/E*)-isomerization of one double bond, as evidenced from the product configuration as well as the base-catalyzed isomerization of **7e** to **7e'**. The phosphonate **8e** on the other hand, seems to undergo mainly decomposition on treatment with base. A similar base-catalyzed (*Z/E*)-isomerization had previously been described by us with the corresponding triphenylphosphonium salts [7] [21] and appears to be an essential feature of metal-coordinated P compounds of this type. ¹³C- and ³¹P-NMR data are summarized in Table 3. The stereochemical assignments of **7e**, **8e**, and **9e** are based on off-resonance ¹³C-NMR spectra as well as ¹H, ¹H-decoupling experiments on **8e** to confirm the (*E*)-configuration at one double-bond (³*J*(H,H) = 8.5 ± 0.5 Hz).

In conclusion, the addition of P nucleophiles to cationic π -hydrocarbon ligands emerges as a valuable synthetic method for the stereospecific generation of β,γ -unsaturated organophosphorous(V) compounds. The application of these substrates in the synthesis of natural products, mainly C₁₁-oligoolefins found in various marine algae [25], is currently under investigation in our laboratory.

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Experimental Part

General. [(Butadiene)Fe(CO)₃] was purchased from Strem Chemicals. [(C₄H₇)Fe(CO)₄]BF₄ (**1a**), [(C₅H₉)Fe(CO)₄]BF₄ (**2a**), [(C₅H₉)Fe(CO)₄]BF₄ (**3a**) [7]; [(C₆H₉)Fe(CO)₃]BF₄ (**7a**) [6]; [(C₇H₉)Fe(CO)₃]BF₄ (**6a**) [26]; [(C₇H₉)Cr(CO)₃]BF₄ (**5a**) [25]; [(C₆H₉O)Fe(CO)₃]AlCl₄ (**4a**) [17] were prepared according to the procedures given in the respective references. Preparation and handling of all organometallic complexes and solvents were carried out under N₂ using Schlenk-type apparatus. ¹H-, ¹³C-, and ³¹P-NMR spectra were recorded on a Varian XL-200 at 200.1, 50.3, and 81.0 MHz, respectively, unless otherwise specified. The chemical shifts are reported in ppm relative to TMS (for ¹H-NMR and ¹³C-NMR) as internal standard. In the ¹³C-NMR data, the first letter in brackets gives the C,H-multiplicities. The ³¹P chemical shifts are reported relative to H₃PO₄ as external reference without susceptibility correction.

Tetracarbonyl [(Z)-1-(triethoxyphosphonio)-2-butene]iron Tetrafluoroborate (1b) and [(Z)-2-Buten-1-yl]-triethoxyphosphonium Tetrafluoroborate (1c). Complex **1a** (1.55 g, 5 mmol) was suspended in 8 ml of P(OEt)₃ at -30°. The mixture was allowed to heat slowly to -20° (3 h). The suspension turned dark-orange, whereas the product **1b** partly dissolved. (By adding Et₂O (25 ml), the intermediately formed cationic complex **1b**, stable to -20° in acetone, can be separated.) ¹³C-NMR (50.3 MHz, (CD₃)₂CO, -30°): 68.8 (*t*, CH₃CH₂); 56.8 (*d*, C(3)); 46.0 (*d*, C(2)); 24.0 (*td*, *J*(P,C) = 127.0, C(1)); 16.9 (*q*, CH₃-C(3)); 14.2 (*q*, CH₃CH₂). The mixture was warmed to 0° (3 h) and then stirred for another 3 h at 4°. The soln. became paler, and **1c** separated as a pale yellow oil. Complete separation and purification as described for **1b**. Yield: 1.45 g (94%). ¹H- and ¹³C-NMR: see Tables 1 and 2.

Diethyl [(Z)-2-Buten-1-yl]phosphonate (1d). A sat. aq. soln. of NaHCO₃ (15 ml) was added to **1c**. After stirring for 20 min, the mixture was extracted three times with Et₂O. Normal workup afforded 0.85 g (89%) of **1d**. Anal. calc. for C₈H₁₇O₃P (192.19): C 50.00, H 8.91, P 16.11; found: C 49.90, H 9.10, P 15.90.

Diethyl [(Z)-1-Methyl-2-buten-1-yl]phosphonate (2d) and Diethyl [(Z)-3-Methyl-2-buten-1-yl]phosphonate (3d) were synthesized using the corresponding method but further purified by chromatography (200 g SiO₂, hexane/Et₂O/MeOH 2:1:1). Yield of **2d**: 0.90 g (87%). ¹H- and ¹³C-NMR: see Tables 1 and 2. Anal. calc. for C₉H₁₉O₃P (206.21): C 52.42, H 9.29, P 15.02; found: C 52.21, H 9.42, P 15.33. Yield of **3d**: 0.88 g (85%). ¹H- and ¹³C-NMR: see Tables 1 and 2. Anal. calc. for C₉H₁₉O₃P (206.21): C 52.42, H 9.29, P 15.02; found: C 52.10, H 9.10, P 15.51.

Diethyl [(Z)-5-Oxo-2-hexen-1-yl]phosphonate (4d). Complex **4a** (1.54 mmol, 0.6 g) was suspended in 3.5 ml of $\text{P}(\text{OEt})_3$ at -30° . The soln. was allowed to warm slowly to 4° . At -5° , the suspension became oily and at 4° turned dark yellow. The mixture was stirred for 15 h at 9° . Workup as for **1d**, but CHCl_3 instead of Et_2O was used for the extraction. Purification by distillation at $132^\circ/0.1$ Torr afforded 280 mg (78%) of **4d**. $^1\text{H-NMR}$ (400 MHz, C_6D_6): 5.84 (*dt*, $J = 10.75, 7.25, 5.0, 1.5$, $\text{H-C}(3)$); 5.63 (*dt*, $J = 10.75, 7.75, 6.25, 1.5$, $\text{H-C}(2)$); 4.00–4.23 (*m*, CH_3CH_2); 3.24 (*ddd*, $J = 7.25, 3.5, 1.5$, $\text{H-C}(4)$); 2.68 (*s*, $\text{H-C}(6)$); 2.59 (*ddd*, $J = 23.0, 7.75, 1.5$, $\text{H-C}(1)$); 1.26 (*t*, $J = 7.0$, CH_3CH_2). $^{13}\text{C-NMR}$ (50.3 MHz, CDCl_3): 204.6 (*sd*, $J(\text{P},\text{C}) = 2.5$, $\text{C}(5)$); 125.2 (*dd*, $J(\text{P},\text{C}) = 14.0$, $\text{C}(3)$); 120.7 (*dd*, $J(\text{P},\text{C}) = 10.0$, $\text{C}(2)$); 62.9 (*td*, $J(\text{P},\text{C}) = 5.5$, CH_3CH_2); 41.5 (*td*, $J(\text{P},\text{C}) = 2.5$, $\text{C}(4)$); 29.1 (*q*, $\text{C}(6)$); 25.6 (*td*, $J(\text{P},\text{C}) = 140.0$, $\text{C}(1)$); 15.5 (*qd*, $J(\text{P},\text{C}) = 6.0$, CH_3CH_2). Anal. calc. for $\text{C}_{10}\text{H}_{19}\text{O}_4\text{P}$ (234.20): C 51.28, H 8.17, P 13.23; found: C 51.35, H 8.01, P 13.51.

[(Z)-5-Oxo-2-hexen-1-yl]triphenylphosphonium Tetrafluoroborate (4f). Complex **4a** (1.54 mmol, 0.6 g) was suspended in 10 ml of CH_2Cl_2 and treated at -30° with a three-fold excess of Ph_3P . The soln. was allowed to warm to r.t. and stirred overnight. After precipitation with Et_2O , a pale-yellow powder was isolated and washed with Et_2O . After drying under vacuum, this residue was extracted repeatedly with hot (60°) H_2O and filtered. The aq. extracts were collected and treated with a sat. soln. of 8 g of NaBF_4 . A crystalline white precipitate of **4f** formed immediately, which was filtered after cooling the soln. for 2 h in an ice-bath, washed with H_2O , and dried under vacuum in a desiccator. Yield: 620 mg (90%). $^{13}\text{C-NMR}$ (50.3 MHz, CD_3NO_2): 206.3 (*s*, $\text{C}(5)$); 136.4 (*dd*, $J(\text{P},\text{C}) = 3.0$); 134.8 (*dd*, $J(\text{P},\text{C}) = 9.9$); 133.2 (*dd*, $J(\text{P},\text{C}) = 13.2$, $\text{C}(3)$); 131.3 (*dd*, $J(\text{P},\text{C}) = 12.7$); 119.1 (*d*, $J(\text{P},\text{C}) = 78.0$); 117.2 (*dd*, $J(\text{P},\text{C}) = 9.0$, $\text{C}(2)$); 42.3 (*td*, $J(\text{P},\text{C}) = 2.5$, $\text{C}(4)$); 29.8 (*q*, $\text{C}(6)$); 24.2 (*td*, $J(\text{P},\text{C}) = 52.0$, $\text{C}(1)$). Anal. calc. for $\text{C}_{24}\text{H}_{24}\text{BF}_4\text{OP}$ (446.21): C 64.59, H 5.42, F 17.03; found: C 64.21, H 5.21, F 17.12.

Tricarbonyl[(1-6- η -7-(dimethylphosphonato)-1,3,5-cycloheptatrienyl)chromium (5e). $[\text{C}_7\text{H}_7\text{Cr}(\text{CO})_3]\text{BF}_4$ (**5a**) (0.7 mmol, 210 mg) was suspended in 10 ml of CH_2Cl_2 and treated with 300 mg (2.4 mmol) of $\text{P}(\text{OMe})_3$. The suspension dissolved, and a clear red soln. formed, which was stirred an additional 2 h. After precipitation of $[\text{CH}_3\text{P}(\text{OMe})_3]\text{BF}_4$ by addition of 100 ml of Et_2O and filtration, the Et_2O soln. was evaporated, and the red residue dried under vacuum. Recrystallization from toluene/hexane at -30° : 210 mg (90%). $^{13}\text{C-NMR}$ (25.2 MHz, CDCl_3): 230.9 (*s*, CO); 101.5 (*dd*, $J(\text{P},\text{C}) = 6.2$, $\text{C}(2)$, $\text{C}(5)$); 97.2 (*d*, $\text{C}(3)$, $\text{C}(4)$); 57.3 (*dd*, $J(\text{P},\text{C}) = 4.1$, $\text{C}(1)$, $\text{C}(6)$); 53.1 (*qd*, $J(\text{P},\text{C}) = 7.3$, MeO); 36.4 (*dd*, $J(\text{P},\text{C}) = 121.7$, $\text{C}(7)$). Anal. calc. for $\text{C}_{12}\text{H}_{13}\text{CrO}_6\text{P}$ (336.2): C 42.87, H 3.90, Cr 15.46; found: C 42.34, H 3.89, Cr 15.24.

Tricarbonyl[(1-4- η -5-(dimethylphosphonato)-1,3-cycloheptadienyl)iron (6e). Compound **6a** (2.44 mmol, 750 mg) was suspended in 5 ml of CH_2Cl_2 and reacted with 5 mmol (620 mg) $\text{P}(\text{OMe})_3$. The soln. became clear, and stirring was continued for 4 h. After precipitation with Et_2O and filtration as described above, Et_2O was evaporated and the residue dried under vacuum: 810 mg (96%), yellow crystals. $^{13}\text{C-NMR}$ (25.2 MHz, $(\text{CD}_2)_2\text{CO}$): 211.8 (*s*, CO); 90.3, 90.0 (*2d*, $\text{C}(2)$, $\text{C}(3)$); 60.1 (*d*, $\text{C}(1)$); 54.0, 53.1 (*2q*, $J(\text{P},\text{C}) = 7.0$, 2MeO); 52.0 (*dd*, $J(\text{P},\text{C}) = 10.0$, $\text{C}(4)$); 37.8 (*dd*, $J(\text{P},\text{C}) = 132.0$, $\text{C}(5)$); 28.0 (*td*, $J(\text{P},\text{C}) = 15.9$, $\text{C}(7)$); 23.9 (*td*, $J(\text{P},\text{C}) = 3.6$, $\text{C}(6)$). Anal. calc. for $\text{C}_{12}\text{H}_{13}\text{FeO}_6\text{P}$ (342.07): C 42.14, H 4.42, Fe 16.32; found: C 41.87, H 4.47, Fe 16.10.

Tricarbonyl[(2Z,5E)-1-(triethoxyphosphonio)-2,4-hexadiene]iron Tetrafluoroborate (7b) and Tricarbonyl[(E)-5-(triethoxyphosphonio)-1,3-hexadien-5-yl]iron Tetrafluoroborate (8b). Complex **7a** (1.62 mmol, 0.5 g) was suspended in 3.5 ml of $\text{P}(\text{OEt})_3$ at -30° . The soln. was allowed to heat slowly to 0° ($\frac{1}{4}$ h). At -4° , the mixture became oily. Purification as described for **1b** afforded **7b/8b** with a ratio of 5:4. Yield of **7b/8b**: 0.62 g (86%). $^{13}\text{C-NMR}$: see Table 3.

Tricarbonyl[(2Z,5E)-1-(diethylphosphonato)-2,4-hexadiene]iron (7e) and Tricarbonyl[(E)-5-(diethylphosphonato)-1,3-hexadiene]iron (8e). A sat. aq. soln. of NaHCO_3 was added to the mixture **7b/8b** (5:4) at 0° . Workup as described for **4d** afforded the quite instable phosphonates **7e/8e** in an unchanged ratio. Yield: 0.53 g (92%). $^{13}\text{C-NMR}$: see Table 3. The same product ratio could be observed when the reaction mixture of **7a** and excess phosphite were allowed to warm up to r.t.

REFERENCES

- [1] B. Buchmann, A. Salzer, *J. Organomet. Chem.*, **1985**, 295, 63.
- [2] O. Eisenstein, R. Hoffmann, *J. Am. Chem. Soc.* **1981**, 103, 4308.
- [3] J. P. Collman, L. S. Hegedus, 'Principles and Applications of Organotransition Metal Chemistry', University Science Books, Mill Valley, 1980.
- [4] S. G. Davies, 'Organotransition Metal Chemistry: Applications to Organic Synthesis', Pergamon Press, Oxford, 1982.
- [5] A. J. Birch, I. D. Jenkins, in 'Transition Metal Organometallics in Organic Synthesis', Ed. H. Alper, Academic Press, New York, 1976, Vol. 1.
- [6] S. G. Davies, M. L. H. Green, D. M. P. Mingos, *Tetrahedron* **1978**, 34, 3047.
- [7] A. Salzer, A. Hafner, *Helv. Chim. Acta* **1983**, 66, 1774.
- [8] T. H. Whitesides, R. W. Arhart, R. W. Slaven, *J. Am. Chem. Soc.* **1983**, 95, 5792.
- [9] H. J. Bestmann, O. Vostrowsky, in 'Topics in Current Chemistry', Springer Verlag, Berlin, 1983, Vol. 109.
- [10] T. B. Brill, S. J. Landon, *Chem. Rev.* **1984**, 84, 577.
- [11] E. S. Lewis, D. Hamp, *J. Org. Chem.* **1983**, 48, 2025.
- [12] K.-H. Worms, M. Schmidt-Dunker, in 'Organophosphorus Compounds', Eds. G. M. Kosolapoff and L. Maier, Wiley-Interscience, New York, 1976, Vol. 7.
- [13] H. R. Hudson, in 'Topics in Phosphorus Chemistry', Eds. M. Grayson and E. J. Griffith, Wiley-Interscience, New York, 1983, Vol. 11.
- [14] J. D. Cotton, R. L. Heazlewood, *Aust. J. Chem.* **1969**, 22, 2673.
- [15] K. Dimroth, R. Nürrenbach, *Chem. Ber.* **1960**, 93, 1649.
- [16] E. O. Greaves, G. R. Knox, P. L. Pauson, *J. Chem. Soc., Chem. Commun.* **1969**, 1124.
- [17] R. E. Graf, C. P. Lillya, *J. Organomet. Chem.* **1976**, 122, 377.
- [18] A. J. Birch, I. D. Jenkins, A. J. Liepa, *Tetrahedron Lett.* **1975**, 1723.
- [19] P. Hackett, G. Jaouen, *Inorg. Chim. Acta* **1975**, 12L, 19.
- [20] L. Nesterov, A. Kessel, Y. Samitov, A. Musina, *Zh. Obshch. Khim.* **1969**, 39, 1179.
- [21] A. Hafner, J. Bieri, R. Prewo, W. von Philipsborn, A. Salzer, *Angew. Chem.* **1983**, 95, 736; *ibid. Int. Ed.* **1983**, 22, 713.
- [22] A. Salzer, *Chimia* **1974**, 38, 421.
- [23] J. E. Mahler, D. H. Gibson, R. Pettit, *J. Am. Chem. Soc.* **1963**, 85, 3959.
- [24] U. Baumann, Diplomarbeit, Universität Zürich, 1984.
- [25] R. E. Moore, *Acc. Chem. Res.* **1977**, 10, 40.
- [26] R. D. King, 'Organometallic Syntheses', Academic Press, New York, 1965, Vol. 1.