171. New Synthetic Routes to β-Olefinic Triphenylphosphonium Salts *via* (Diolefin)tricarbonyliron Complexes[1])

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Summary

The regio- and stereospecific preparation of β-olefinic triphenylphosphonium salts, starting from (diolefin)tricarbonyliron compounds is described. The latter are converted by various routes into either $[(allyl)Fe(CO)_4]^+$- or $[(dienyl)Fe(CO)_3]^+$-derivatives. The allylic cations, when reacted with $P(C_6H_5)_3$, yield uncomplexed (2-en-1-yl)triphenylphosphonium salts in good yields, while treatment of the dienyl cations with $P(C_6H_5)_3$ leads to the quantitative formation of (2,4-diene-1-yl)triphenylphosphonium ions still coordinated to the $Fe(CO)_3$-moiety. A method of oxidative decomplexation is described, by which the free phosphonium salts can be obtained.

All new compounds were characterized by ^{13}C-NMR spectra and also, where necessary, by ^1H-NMR decoupling experiments to confirm the stereochemical assignments. Many of the new phosphonium salts, potentially useful as *Wittig* reagents for natural product syntheses, are difficult to obtain by conventional unequivocal routes.

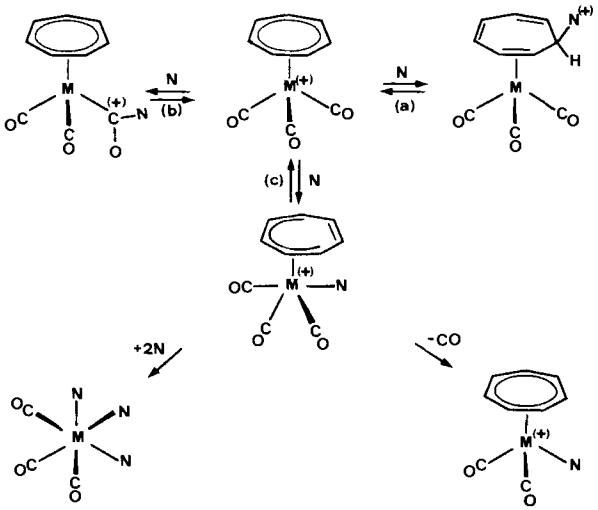
1. Introduction. – Recently the reactions of nucleophiles with $[M(\pi\text{-hydrocarbon})(CO)_X]^+$-complexes have received considerable attention [1] [2]. The synthetic potential of this reaction for organic synthesis has been explored: most notable examples include reactions of tricarbonyl(cyclohexadienyl)iron derivatives $[C_6H_6R)Fe(CO)_3]^+$ [3] as well as monoolefin complexes $[CpFe(CO)_2(olefin)]^+$ [4] with various carbanions.

In such systems several alternative reaction pathways are possible and have in fact been experimentally observed, namely nucleophilic attack at the hydrocarbon (a), at the carbonyl (b), and at the metal (c) sites *(cf. Scheme 1)*. With neutral nucleophiles, particularly tertiary phosphines, variations of experimental conditions have often led to the exclusive observation of only one reaction path [5].

All experimental results are rationalized in *Scheme 1* for the particular case of the reaction of $[(tropylium)M(CO)_3]^+$-cations with neutral monodentate nucleophiles N.

[1]) Reactions with Metal-Coordinated Olefins, Part I.

Scheme 1

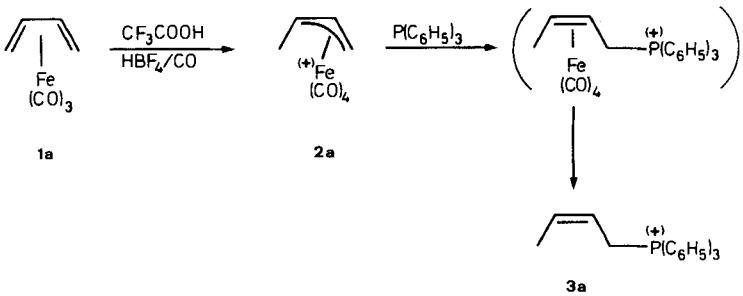


The available experimental evidence suggests that, in general, nucleophilic attack of tertiary phosphines at the hydrocarbon moiety (path a) should be the kinetically most favoured process under mild conditions [5] [6]. A number of olefinic phosphonium salts have been isolated in this manner with various metal-coordinated π-bonded hydrocarbon ligands [2].

Phosphonium salts, when used for *Wittig* reactions, have wide synthetic use [7], especially in the syntheses of natural products [8]. The above addition reactions suggest interesting alternatives for the preparation of β-olefinic phosphonium salts, which are difficult to obtain by conventional unequivocal routes. The purpose of this study was to explore the stereo- and regioselective potential of this reaction and to extend the number of metal-coordinated olefinic phosphonium salts available. A further aim was to develop methods for decomplexation and isolation of the free organic moieties.

2. Results and Discussion. – 2.1 *Formation of (2-En-1-yl)phosphonium Salts.* A preliminary communication by *Whitesides et al.* [9] reported on the formation of *cis*-allylphosphonium salts from organometallic π-complexes. The system involved the use of (1-3-η-allyl)tetracarbonyliron cations, readily available in high yield

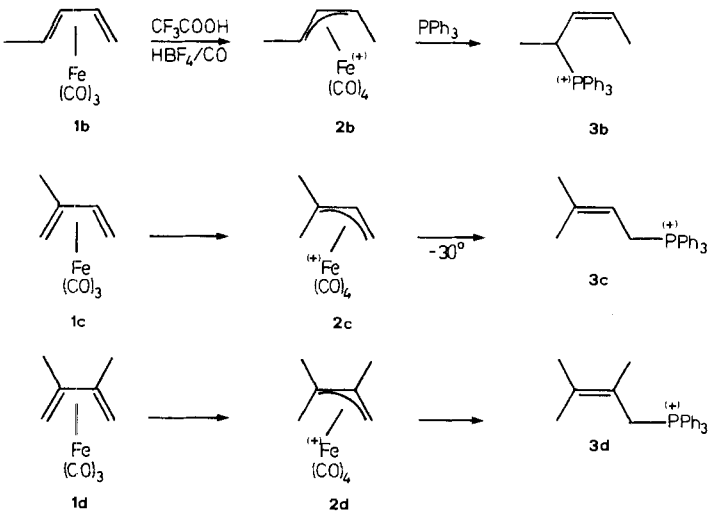
Scheme 2



from the appropriate (diene)tricarbonyliron complexes by protonation [HBF_4] in the presence of carbon monoxide. These cationic species were susceptible to attack by a variety of nucleophiles, most notably by PPh_3, with direct formation of uncomplexed *cis*-olefinic phosphonium salts, the intermediate [(monoolefin)$Fe(CO)_4$]-compounds not being isolable in most cases *(Scheme 2)*.

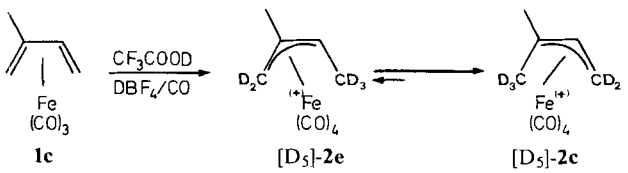
Unfortunately, no detailed preparative descriptions were given in this brief paper and no further research was apparently done on this subject. We, therefore, set out to reinvestigate this interesting reaction sequence and to develop a general preparative procedure for the isolation of the free phosphonium salts as well as to extend the number of related compounds available by the same route *(Scheme 3)*.

Scheme 3



Several features of this reaction make it highly interesting from a synthetic point of view: *a*) the *cisoid*-stereochemistry of the diene complex is retained in the intermediate allyl species (**2a–d**) as well as in the final phosphonium salts (**3a–d**); *b*) the addition of PPh_3 is regiospecific, the phosphine attacking always *1*) at the less substituted end (**2a,c**), *2*) with preference for the position leading to the (*Z*)-configurated salt (**2b**). We found that PPh_3-addition at the allyl complex **2c** at room temperature leads to a product mixture of two phosphonium salts **3c** and **3e** *(cf. Table 1)* contrary to the report by *Whitesides*. This is probably due to the fact that **2c** is in a dynamic equilibrium with an isomeric species **2e**, present in low concentration and not directly observable, but indicated by deuterium labeling during the protonation with deuterated acid [9] *(Scheme 4)*.

Scheme 4

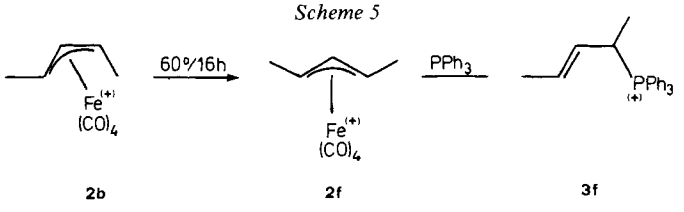


Treatment of **2c** with PPh_3 at $-30°$, however, produced only a single pure phosphonium salt **3c**. Detailed analysis of the ^{1}H-NMR spectrum of **3e**, which is present in the above mentioned mixture, revealed that its structure was indeed consistent with PPh_3-attack at the less substituted end of **2e**.

Low-temperature addition of PPh_3 led in fact to better overall yields in all cases, probably, as outlined earlier, because nucleophilic attack at the hydrocarbon site is kinetically favoured at low temperatures (phosphine addition occurs rapidly even at $-30°$, as indicated by solution of the insoluble salts **2a–d**). Yield-reducing side reactions like carbonyl substitution can be suppressed in this manner.

As the protonation of the s-*cis*-diolefin complexes always generates (allyl)-tetracarbonyliron cations having *anti*-methyl substituents, only (*Z*)-olefinic phosphonium salts are formed. It was desirable to find routes for rearrangements of the allyl complexes to the corresponding *syn*-isomers to also allow preparation of the (*E*)-olefinic phosphonium ions. Two methods were successful for this purpose. Thermal rearrangement of **2b** led to the isomeric compound **2f** [10] which, in turn, generated the phosphonium salt **3f**, isomeric to **3b** *(Scheme 5)*.

Scheme 5

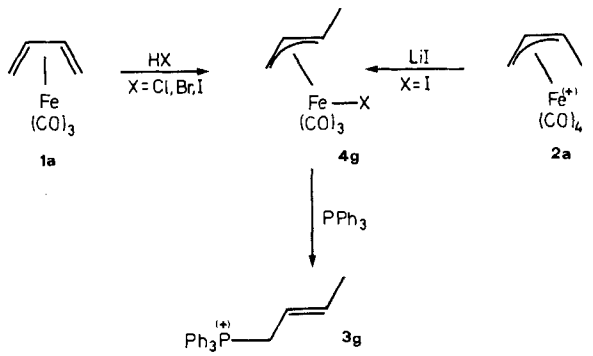


2b **2f** **3f**

It was also known that by preparation of (diene)tricarbonyliron complexes with acids like HCl instead of HBF_4 (*E*)-configurated (allyl)tricarbonyliron compounds are exclusively formed [11] [12] by an unknown rearrangement process. The yields reported are, however, very low so that an alternative route to compounds such as **4g** had to be developed.

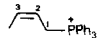
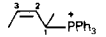
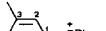
Treatment of **2a** with LiI produced the (*E*)-configurated allyl complex **4g** (X=I) in excellent yields. As we had previously extablished that neutral [(allyl)-$Fe(CO)_3X$]-complexes also reacted with PPh_3 to give free (2-en-1-yl)phosphonium salts [6], an additional route to (*E*)-olefinic phosphonium salts was now available as evidenced by the formation of pure **3g**, isomeric to **3a** *(Scheme 6)*.

Scheme 6



1a **4g** **2a** **3g**

Table 1. *^{13}C Chemical Shifts and J(P, C)-Values for Triphenylphosphonium Salts* **3a–3g**[a)][b)]

Compound		C(1)	C(2)	C(3)	CH_3–C(1)	CH_3–C(2)	CH_3–C(3) (*E*)	CH_3–C(3) (*Z*)
	**3a**	24.4 (52.5)	115.3 (9.0)	136.2 (13.0)	–	–	–	13.4 (2.5)
	**3b**	30.0 (50.0)	123.5 (5.0)	133.8 (13.5)	16.8 (3.0)	–	–	13.8 (1.5)
	**3c**	24.5 (51.0)	109.2 (9.5)	145.3 (13.0)	–	–	26.1* (3.0)	18.4* (3.5)
	**3d**	31.3 (47.0)	115.5 (11.0)	138.1 (12.0)	–	21.1 (4.5)	20.7* (2.0)	21.0* (2.0)
	**3e**	28.4 (49.0)	123.8 (9.5)	131.2 (13.0)	–	25.5 (2.5)	–	14.0 (3.0)
	**3f**	33.1 (48.0)	123.5 (6.0)	136.5 (13.5)	15.6 (3.0)	–	18.5 (2.5)	–
	**3g**	28.4 (51.0)	116.2 (10.0)	138.6 (13.5)	–	–	18.3 (3.0)	–

a) ^{13}C chemical shifts (ppm), obtained from proton-noise decoupled spectra in CD_3NO_2, internal reference TMS; numbers in brackets refer to (^{31}P, ^{13}C)-coupling constants in Hz, digital resolution and reproducibility of $J(P, C) \pm 0.4$ Hz.

b) Assignments marked with * may be reversed in particular column.

Table 2. *^{1}H-NMR Spectra for Triphenylphosphonium Salts* **3a**–**3g**[a)b)]

Compound	J(H–C(2), H–C(3))	H–C(1)	H–C(2)	H–C(3) (*E*)	H–C(3) (*Z*)	CH_3–C(1)	CH_3–C(2)	CH_3–C(3) (*E*)	CH_3–C(3) (*Z*)
3a	10.5	4.15 (*dd*) (J = 15.0 and 7.5)	5.40–5.63 (*m*) [f)]	5.85–6.08 (*m*) [f)]	–	–	–	–	1.46 (*dd*) (J = 5.5 and 5.0)
3b	10.5	4.53–4.80 (*m*)	5.31–5.50 (*m*) [c)f)]	5.78–6.07 (*m*) [d)f)]	–	1.58 (*dd*) (J = 18.5 and 7.0)	–	–	1.72 (*ddd*) (J = 7.0 and 3.0 and 2.0)
3c	–	4.08 (*dd*) (J = 15.0 and 7.5)	5.22–5.39 (*m*)	–	–	–	–	1.73 (*dd*) (J = 5.5 and 1.0)	1.35 (*dd*) (J = 4.0 and 1.0)
3d	–	4.13 (*d*) (J = 14.5)	–	–	–	–	1.67 (*d*) (J = 6.5)	1.55–1.65 (*m*)	1.08–1.18 (*m*)
3e	–	4.10 (*d*) (J = 15.0)		5.72 (*dq*) (J = 10.5 and 7.0)	–	–	1.61–1.69 (*m*)	–	1.07–1.18 (*m*)
3f	15.0	4.35–4.58 (*m*)	5.46–5.60 (*m*) [f)]	–	5.76–5.95	1.55 (*dd*) (J = 18.5 and 7.0)	–	1.65–1.75 (*m*)	–
3g	15.0	4.10 (*dd*) (J = 15.0 and 7.5)	5.43–5.62 (*m*) [f)]	–	5.75–5.98 (*m*) [e)]	–	–	1.68 (*ddd*) (J = 6.5 and 6.5 and 1.0)	–

a) All ^{1}H-NMR spectra are measured on a 200-MHz spectrometer.
b) ^{1}H chemical shifts (ppm), obtained in CD_3NO_2, internal reference TMS; numbers in brackets refer to (^{1}H, ^{1}H)- and (^{31}P, ^{1}H)-coupling constants in Hz.
c) 5.40 (*dddq*, J = 10.5, 10.5, 7.0 and 3.0).
d) 5.93 (*ddq*, J = 10.5, 7.0 and 1.0).
e) 5.86 (*ddq*, J = 15.0, 6.5 and 5.0).
f) Assignments are based on (^{1}H, ^{1}H)-decoupling experiments.

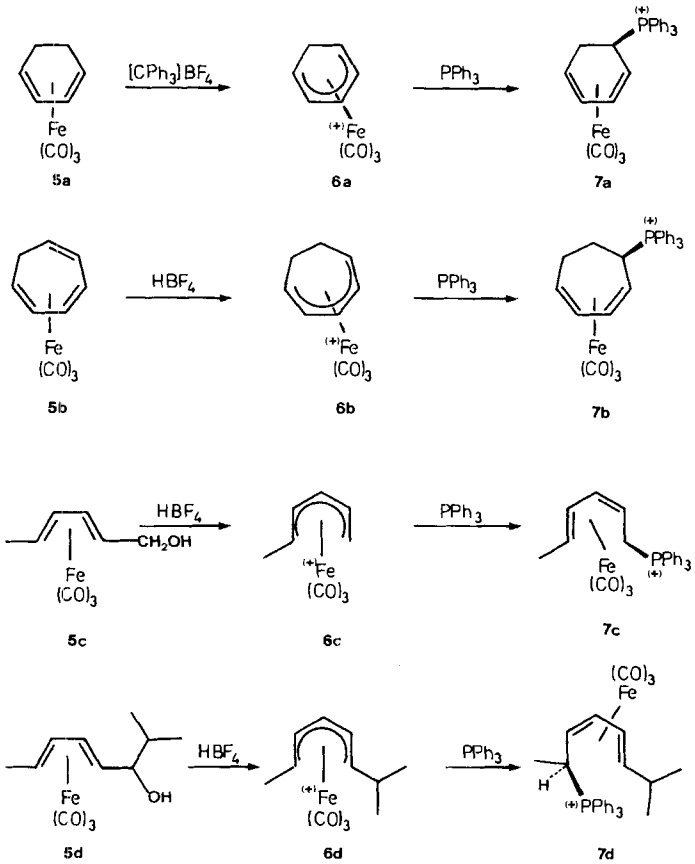
Further alternative methods are known for the formation of (1-3-η-allyl)tetracarbonyliron species, *e.g.*, starting from allylic alcohols [13]. Coupled with the possibility for either thermal or halide-induced rearrangements, phosphine addition to these compounds emerges as a versatile tool for the preparation of substituted (2-en-1-yl)phosphonium salts, superior in specificity to conventional methods [14], which quite often produce isomeric mixtures.

All phosphonium salts were characterized by ^{13}C- as well as ^{1}H-NMR spectra to confirm their stereochemical assignments (*Tables 1* and *2*). Assignments of the individual ^{13}C-resonances *(Table 1)* are based on (^{31}P, ^{13}C)-coupling constants, off-resonance spectra as well as additivity rules based on ^{13}C chemical-shift increments.

2.2. *Formation of (2,4-Diene-1-yl)phosphonium Salts.* Stable (dienyl)tricarbonyliron cations are available by a variety of preparative routes, generally starting from (diolefin)iron complexes. Principal methods include: *a*) hydride abstraction, *b*) protonation of an uncomplexed double bond and *c*) protonation of an alcohol or ether group.

All cations react readily and quantitatively with tertiary phosphines under formation of tricarbonyliron complexes with coordinated (2,4-diene-1-yl)phosphonium salts [2]. The diolefinic ligand cannot be replaced by an excess of phosphine as in the previous cases.

Scheme 7

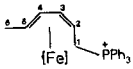
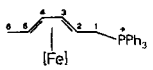
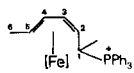
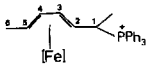
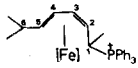


The addition of phosphines to the cations **6a–d** *(Scheme 7)* is again strictly regio- and stereospecific: *1*) the *cisoid*-stereochemistry of the dienyl cation is retained in the dienylphosphonium salts; *2*) the addition of PPh_3 proceeds *exo* to the tricarbonyl-iron group at the sterically less hindered end. Complex **7c**, which was first described by *McArdle & Sherlock* [15], rearranged to the (2*E*,4*E*)-isomer by an unknown mechanism on standing in $CDCl_3$ for 48 hours. We were unable to observe this reaction under identical conditions even after months. However, on using CD_3OD, containing catalytic amounts of base, a rearrangement took place within a few hours with formation of the (2*E*,4*E*)-isomer **7e** and deuterium incorporation at C(1). *(Scheme 8).* This rearrangement, as the previously discussed examples, appears to be metal- (as well as base-) catalyzed and is normally not observed in uncomplexed phosphonium salts [7], the driving force apparently being the higher stability of (*E*,*E*)-(diolefin)iron complexes.

Further examples of (dienyl)tricarbonyliron complexes are given in *Tables 3* and *4* together with their ^{13}C-NMR data. Assignments of individual ^{13}C-resonances are again based on the same parameters as in *Table 1.*

For use in *Wittig* reactions, the (2,4-diene-1-yl)-phosphonium complexes described above have to be either *a*) convertible into ylid complexes without previous decomplexation, *b*) isolable as free phosphonium salts by oxidative removal of the tricarbonyliron group.

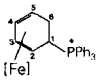
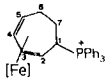
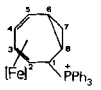
Table 3. *^{13}C Chemical Shifts and J(P,C)-Values for Non-cyclic (2,4-Dien-1-yl)tricarbonyliron-phosphonium Salts*[a][b])

Compound		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	CH_3–C(1)	CH_3–C(6)	CH_3–C(6)
	**7c**	25.2 (41.0)	44.0 (11.0)	82.4 (4.0)	96.9	60.7	20.4	–	–	–
	**7e**	28.0 (44.0)	46.5 (9.0)	85.1 (3.0)	87.3	59.8	19.1	–	–	–
		31.3 (36.0)	54.3 (10.5)	81.5 (3.0)	98.2	62.1	20.4*	18.8	–	–
		36.6 (39.5)	57.2 (6.5)	84.3 (2.5)	87.2	61.9	20.6*	19.4*	–	–
	**7d**	31.2 (35.5)	54.6 (10.5)	81.8 (3.5)	96.2	76.7 (<0.5)	36.6	18.4	24.5	26.2

[a]) ^{13}C chemical shifts (ppm), obtained from proton-noise decoupled spectra in [D_6]acetone for **7c**, **7e**, in CD_3NO_2 for all other, internal reference TMS; numbers in brackets refer to (^{31}P, ^{13}C)-coupling constants in HZ, digital resolution and reproducibility of J(P, C) ± 0,4 Hz.

[b]) Assignments marked with * may be reversed in a particular column.

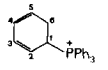
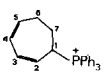
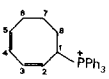
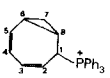
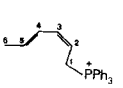
Table 4. *^{13}C Chemical Shifts and J(P, C)-Values for Cyclic (2,4-Dien-1-yl)tricarbonyliron-phosphonium Salts*[a])

Compound		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)
	**7a**	32.1 (38.0)	53.0 (10.0)	86.4	86.4	60.5 (7.0)	27.8 (5.0)	– –	– –
	**7b**	36.0 (37.0)	49.6 (6.5)	87.6 (2.0)	92.2	60.2 (1.0)	28.5 (14.0)	24.7 (1.5)	–
		35.5 (36.0)	53.1 (7.0)	89.3	89.3	63.5	14.7	14.4 (9.0)	17.2 (5.0)

[a]) ^{13}C chemical shifts (ppm) obtained from proton-noise decoupled spectra in CD_3NO_2 internal reference TMS; numbers in brackets refer to (^{31}P, ^{13}C)-coupling constants in Hz, digital resolution and reproducibility of $J(P, C) \pm 0.4$ Hz.

For the removal of tricarbonyliron groups from diolefin complexes several mild oxidation agents have been found to be effective, including $(NH_4)_2Ce(NO_3)_6$, $FeCl_3$, and $(CH_3)_3NO$ [2]. In our system, $(NH_4)_2Ce(NO_3)_6$ in methanolic solution was the reagent of choice. The uncomplexed phosphonium ions were isolable as the BF_4^-- or PF_6^--salts in about 80% yield by precipitation from aqueous solutions. Their ^{13}C-NMR spectra are listed in *Table 5.*

Table 5. *^{13}C Chemical Shifts and J(P, C)-Values for (2,4-Dien-1-yl)-phosphonium Salts*[a])[b])

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)
	29.3 (45.5)	132.1 (12.0)	116.3 (8.5)	124.2 (5.0)	125.8 (8.5)	23.6 (3.5)	–	–
	37.1 (48.0)	132.0 (16.0)	124.1 (3.5)	125.3 (2.0)	137.8	32.0 (15.0)	29.6	–
	34.5 (51.5)	135.2 (14.5)	122.3 (1.5)	125.0 (< 0.5)	134.1	29.4	22.4 (12.5)	26.8 (1.5)
	34.8 (52.5)	134.8 (18.0)	119.9 (2.0)	124.8	137.3	42.6*	18.8 (12.0)	7.8*
	24.3 (52.0)	138.6 (13.0)	111.9 (10.5)	126.2 (4.5)	131.2	18.5	–	–

[a]) ^{13}C chemical shifts (ppm), obtained from proton-noise decoupled spectra in $CDCl_3$, internal reference TMS; numbers in brackets refer to (^{31}P, ^{13}C)-coupling constants in Hz, digital resolution and reproducibility of $J(P, C) \pm 0.4$ Hz.

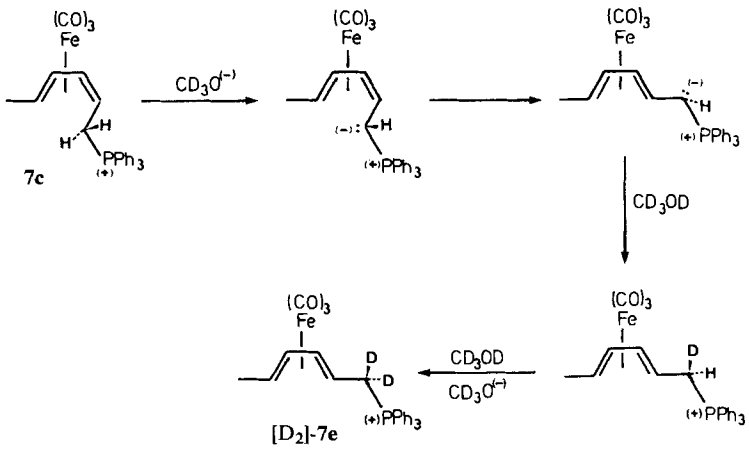
[b]) Assignments marked with * may be reversed in a particular column.

These phosphonium salts should be valuable precursors for polyene synthesis *via Wittig* olefination. The inexpensive starting materials, high yields and the regio- as well as stereospecific attachment of PPh_3 to the delocalized π-systems should make this reaction sequence an interesting alternative to conventional phosphonium-ion synthesis.

We also investigated the generation of an ylid without decomplexation. It was previously reported that attempts to produce organometallic ylids from the cyclic phosphonium ions **7a** and **7b** with strong bases were unsuccessful [16]. Reactions with BuLi gave highly unstable red solutions and addition of benzaldehyde to these solutions produced no identifiable products. In contrast, treatment of **6a** with dimethylphenylphosphine and subsequent deprotonation with sodium hydride generated a moderately stable ylid complex at low temperatures that reacted with benzaldehyde in the expected manner, as *Jaouen et al.* recently discovered [17].

The non-cyclic coordinated phosphonium ions like **7c** showed a markedly different behaviour. The base-catalyzed isomerization of **7c** to **7e** had already suggested to us that an ylid complex was formed as an intermediate, which was then reprotonated by the solvent CD_3OD. The rearrangement observed had to occur at the ylid stage proceeding faster than reprotonation *(Scheme 8)*.

Scheme 8



We conclude from this that the negative charge of the ylid C-atom in close vicinity to the $Fe(CO)_3$ group effectively destabilizes all iron complexes, if a *cisoid*-configuration is maintained. The 18-electron rule appears violated as the geometry of the molecules forces the ylid C-atom within bonding distance of the $Fe(CO)_3$-moiety. The cyclic phosphonium ions **7a** and **7b** cannot rearrange; deprotonation is, therefore, either prevented or decomposition sets in if it occurs. As yet, we have no reasonable explanation why substitution of $P(Me)_2Ph$ for PPh_3 should make such a considerable difference as observed [17]. Non-cyclic systems isomerize in any case to the more stable *transoid*-configuration; the ylid C-atom is now no longer in proximity to the $Fe(CO)_3$-group and need not be considered in the electron count.

In accordance with this we found that treatment of **7c** with stoichiometric amounts of BuLi or *t*-BuOK generated stable solutions of a dark-red organometallic ylid, which reacted readily with (sorbic aldehyde) $Fe(CO)_3$ under *Wittig* olefination. The details of this reaction together with the X-ray structure of the dimetallic product will be described elsewhere [18].

We are continuing our research on nucleophilic attack of phosphorous donors at cationic π-complexes and are currently investigating reactions of allyl complexes bearing keto-substituents as well as additions with tertiary phosphites to yield β-olefinic phosphonates.

3. Experimental. – *General.* Preparation and handling of all organometallic complexes and solvents were carried out under purified N_2-atmosphere using *Schlenk*-type apparatus.

The ^{13}N-NMR spectra were measured on a *Varian XL-100-12 FT* spectrometer at 25.2 MHz, ^{1}H-NMR spectra were recorded on a *Varian XL-200 FT* spectrometer at 200 MHz. Chemical shifts *(Tables 1–5)* of all complexes and phosphonium salts described below are given in [ppm] relative to tetramethylsilane (TMS) as internal reference.

$C_4H_6Fe(CO)_3$ (**1a**) was purchased from *Strem Chemicals*, $C_5H_8Fe(CO)_3$ (**1b**), $C_5H_8Fe(CO)_3$ (**1c**), $C_6H_{10}Fe(CO)_3$ (**1d**), $C_6H_{10}OFe(CO)_3$ (**5c**), $C_9H_{16}OFe(CO)_3$ (**5d**) [19]; $C_6H_8Fe(CO)_3$ (**5a**), $C_7H_8Fe(CO)_3$ (**5b**), $[C_7H_9Fe(CO)_3]BF_4$ (**6b**) [20]; $[C_6H_7Fe(CO)_3]BF_4$ (**6a**) [21]; $[C_6H_9Fe(CO)_3]BF_4$ (**5c**), $[C_9H_{15}Fe(CO)_3]$-BF_4 (**5d**) [22]; $[C_6H_7P(C_6H_5)_3Fe(CO)_3]BF_4$ (**7a**), $[C_7H_9P(C_6H_5)_3Fe(CO)_3]BF_4$ (**7b**) [16]; $[C_6H_9P(C_6H_5)_3$ $Fe(CO)_3]BF_4$ (**7c**), $[C_9H_{15}P(C_6H_5)_3Fe(CO)_3]BF_4$ (**7d**) [15] were synthesized according to procedures given in the indicated references.

Complex **2a**. Carbon monoxide was bubbled into a cold (0°) solution of 1.96 g (10 mmol) of complex **1a** in 3 ml CF_3COOH for 15 min. A solution of 10 mmol HBF_4, prepared by careful addition of 1.1 ml 50% aq. HBF_4 to a cold (0°) solution of 3 ml $(CF_3CO)_2O$, was added and the mixture was allowed to stand a further 45 min under a slow stream of CO. To the yellow solution 100 ml of Et_2O were added under vigorous stirring and the yellow precipitate formed was filtered, washed with Et_2O and dried under vacuum. Yield 2.8 g (90%).

Complexes **2b–d** were prepared likewise, starting from **1b–d**, yield 85–90%.

Phosphonium Salt **3a**. Complex **2a** (5 mmol, 1.55 g) was suspended in 5 ml CH_2Cl_2 at $-30°$. After addition of 4.08 g (15 mmol) of $P(C_6H_5)_3$ the solution was allowed to warm slowly to r.t. and stirred for 2 h. After addition of 100 ml Et_2O an oily precipitate formed, which was decanted 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. solution of 8 g $NaBF_4$. A crystalline white precipitate of **3a** formed immediately which was filtered after cooling the solution for 2 h in an ice-bath, washed with cold H_2O and dried under vacuum in an exsiccator. Yield 1.72 g (85%).

The phosphonium salts **3b–d** and **3f** were prepared similarly starting from **2b–d** and **2f**, yield 56–87%.

Phosphonium Salt **3g**. Complex **2a** (1 g, 3.3 mmol) was suspended in 5 ml CH_2Cl_2 ar r.t. and treated with 0.6 g (4.5 mmol) of anh. LiI. The solution was stirred until no further CO evolved. After evaporation of the solvent the residue was extracted with 25 ml hexane and filtered. The dark-brown hexane solution was evaporated under vacuum and the solid residue taken up in CH_2Cl_2. After addition of $P(C_6H_5)_3$ (2.73 g, 10 mmol) the solution was stirred for 2 h. Addition of 100 ml Et_2O produced a yellow precipitate, which was filtered and washed with Et_2O. The precipitate was extracted several times with hot (60°) H_2O and filtered. The collected filtrates were treated with $NaBF_4$ as above. Yield 0.8 g (55%).

General Procedure for Decomplexation of Metal-coordinated (2,4-Dien-1-yl)-triphenylphosphonium Salts. The metal-coordinated phosphonium salt (*e.g.* **7a–d**) (1 g) was dissolved in 10 ml MeOH. A sat. solution of $(NH_4)_2Ce(NO_3)_6$ in MeOH was added dropwise until no further CO-evolution was observed. After removal of the solvent, the residue was extracted with H_2O and filtered. After addition of a sat. solution of $NaBF_4$ the precipitate was centrifuged, decanted and dried. The solid was dissolved in acetone, filtered and precipitated with Et_2O. Yield of the uncomplexed phosphonium salt 70–80%.

Rearrangement of **7c**. Salt **7c** (1 g) was dissolved in 5 ml MeOH and treated with a few milligrams of CH_3ONa. After stirring for 6 h the rearranged complex **7e** was precipitated by addition of 100 ml Et_2O. Yield 705 mg (70%).

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