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Addition of organolithium compounds to tricarbonyl(tropone)iron complexes: experimental and structural studies

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Abstract

The regioselectivity (1,2 vs. 1,4) in the nucleophilic addition of organolithium reagents to tropone(tricarbonyl)iron complexes has been studied and found to be correlated with the relative hardness of the nucleophile (HSAB principle). X-ray structures of several 1,2 and 1,4 adducts are reported. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Tricarbonyl(tropone)iron complexes; Nucleophilic addition

1. Introduction

The tricarbonyl(tropone)iron complex (**1**) is a highly functionalized and reactive molecule, which has attracted the attention of both inorganic and organic chemists for more than 40 years. It was initially generated, together with other organoiron carbonyls, in the reaction of acetylene with triiron dodecacarbonyl [1] and can now be synthesized in high yield from tropone and diiron nonacarbonyl [2]. Its chemical structure was indicated in 1962 from the hydrogenation of the iron-free double bond [3] and confirmed two years later by X-ray diffraction analysis [4]. The tricarbonyl iron moiety is bonded to the carbon atoms C4 through C7 of the tropone ring, which leaves the complex **1** with an enone function. Synthetic transformations of the complex [5] have generally involved the enone unit, which manifests the reactivity expected of an isolated enone [6]. The complex undergoes, for example, a number of cycloaddition reactions with electron rich (and electron deficient) partners; in addition, various nucleophilic reagents add to the complex. Organolithium [6–8] and organomagnesium [6,7,9] reagents, as well as sodium borohydride in the presence of cerium(III) chloride [6,10], have been reported to give regio- and stereoselectively the *anti* 1,2 addition products, whereas functionalized zinc–copper reagents [11], K-Selectride® [6], and soft nucleophiles such as malonic carbanions [6] have been found to give the *anti* 1,4 addition products. We report herein complementary observations on the nucleophilic addition of organometallic reagents (mainly organolithium) to the tricarbonyl(tropone)iron complex **1** and three of its derivatives (complexes **4**, **7**, and **10**). X-ray diffraction analysis of these complexes and four representative adducts is also reported.

2. Results and discussion

During recent research in our laboratory on synthetic applications of the tricarbonyl(tropone)iron complex (**1**), we observed that the regioselectivity (1,2 vs. 1,4 adducts) in the nucleophilic addition of organolithium reagents to the complex was surprisingly dependent on the nature of the nucleophile R (Scheme 1). These results, as well as studies on the effect of changes in the solvent, counterion, and temperature, are summarized in Tables 1–4.

As can been seen in Table 1, the regioselectivity of the reaction appears, to a degree, to reflect the size of the nucleophile: small nucleophiles (entries 1, 2) gave efficiently the 1,2 addition products, whereas the bulkier ones (entries 5, 6) provided in high yield mainly or

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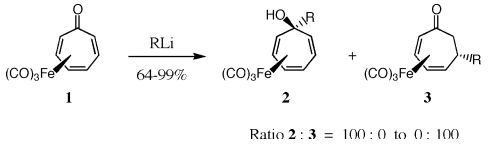


Scheme 1.

exclusively the 1,4 adducts. The regio- and stereochemical outcomes of the reactions of the complex with phenyllithium (entry 3) and *tert*-butyllithium (entry 6) were established by X-ray diffraction analysis (Figs. 1 and 2). From the X-ray structure of complex **1** (Fig. 3), it can be seen, however, that there is no significant steric difference on the *anti* face between the two electrophilic carbon atoms C1 and C3. This observation suggests that the regioselectivity of the addition of organolithium compounds to complex **1** may, in fact, be better explained by the HSAB principle [12] than by steric factors. Small alkyllithium reagents are known to be harder than those branched, and aryl- and alkynyllithium reagents are considered harder than the alkyl reagents.

The regioselectivity of the reaction is somewhat influenced by the nature of the solvent (Table 2). The best solvents for this reaction are toluene and ether. The use of more polar, complexing solvents favored, as expected, conjugate addition, but to the detriment of the yield. It is noteworthy that the reaction of the complex with Bu^tLi in the presence of HMPA (entry 6) did not yield the expected addition product, but the tricarbo-

Table 1
Nucleophilic addition of organolithium compounds to complex **1**. Regioselectivity as a function of the nucleophile.

Entry	RLi	Conditions	Products	Yield (%) [a]	Ratio **2**:**3** [b]
1	MeLi	Et_2O, −85 °C	**2a**:**3a**	95 [c]	100:0
2	$Pr^nC{\equiv}C{-}Li$	Et_2O, −85 °C	**2b**:**3b**	90 [d]	100:0
3	PhLi	Toluene, −85 °C	**2c**:**3c**	99 [e]	100:0
4	Bu^nLi	Et_2O, −85 °C	**2d**:**3d**	89	85:15
5	Bu^sLi	Et_2O, −85 °C	**2e**:**3e** [f]	68	33:67
6	Bu^tLi	Et_2O, −85 °C	**2f**:**3f**	64	0:100 [g]

[a] Based on isolated, homogeneous products.
[b] The ratio of the two regioisomers has been determined by NMR analysis of the crude mixture and confirmed by isolation of the products.
[c] Seventy-three percent in Ref. [8] and quant. in Ref. [7].
[d] Based on 12% of complex **1** recovered.
[e] Yield not given in Ref. [7].
[f] Complexes **2e** and **3e** were isolated as 1:1 mixtures of diastereomers.
[g] Trace amount of alcohol **2f** (< 1% by NMR) was detected.

Table 2
Nucleophilic addition of organolithium compounds to complex **1**. Regioselectivity as a function of the solvent.

Entry	RLi	Conditions	Products	Yield (%) [a]	Ratio **2**:**3** [b]
1	Bu^nLi	Toluene, −85 °C	**2d**:**3d**	85	87:13
2	Bu^nLi	Et_2O, −85 °C	**2d**:**3d**	89	85:15
3	Bu^nLi	THF, −85 °C	**2d**:**3d**	69	69:31
4	Bu^nLi	THF + DME (70%), −85 °C	**2d**:**3d**	47	75:25
5	Bu^nLi	THF + HMPA (10%), −85 °C	**2d**:**3d**	25	62:38
6	Bu^tLi	Et_2O + HMPA (10%), −85 °C	**3g** (R = H)	21	–

[a] Based on isolated, homogeneous products.
[b] The ratio of the two regioisomers was determined by NMR analysis of the crude mixture and/or isolation of the products.

Table 3
Nucleophilic addition of organolithium and organomagnesium compounds to complex **1**

Entry	RM	Conditions	Products	Yield (%) [a]	Ratio **2**:**3** [b]
1	MeLi	Et_2O, −85 °C	**2a**:**3a**	95	100:0
2	MeMgBr	Et_2O, −85 °C	**2a**:**3a**	78	100:0
3	Bu^nLi	Et_2O, −85 °C	**2d**:**3d**	89	85:15
4	Bu^nMgBr	Et_2O, −85 °C	**2d**:**3d**	76	80:20

[a] Based on isolated, homogeneous products.
[b] The ratio of the two regioisomers was determined by NMR analysis of the crude mixture and confirmed by isolation of the products.

Table 4
Nucleophilic addition of organolithium compounds to complex **1**. Regioselectivity as a function of the temperature.

Entry	RLi	Conditions	Products	Yield (%) [a]	Ratio **2**:**3** [b]
1	Bu^{n}Li	Et_2O, −85 °C	**2d**:**3d**	89	85:15
2	Bu^{n}Li	Et_2O, −35 °C	**2d**:**3d**	98	64:36
3	Bu^{n}Li	Et_2O, 0 °C	**2d**:**3d**	31	35:65

[a] Based on isolated, homogeneous products.
[b] The ratio of the two regioisomers was determined by NMR analysis of the crude mixture and/or isolation of the products.

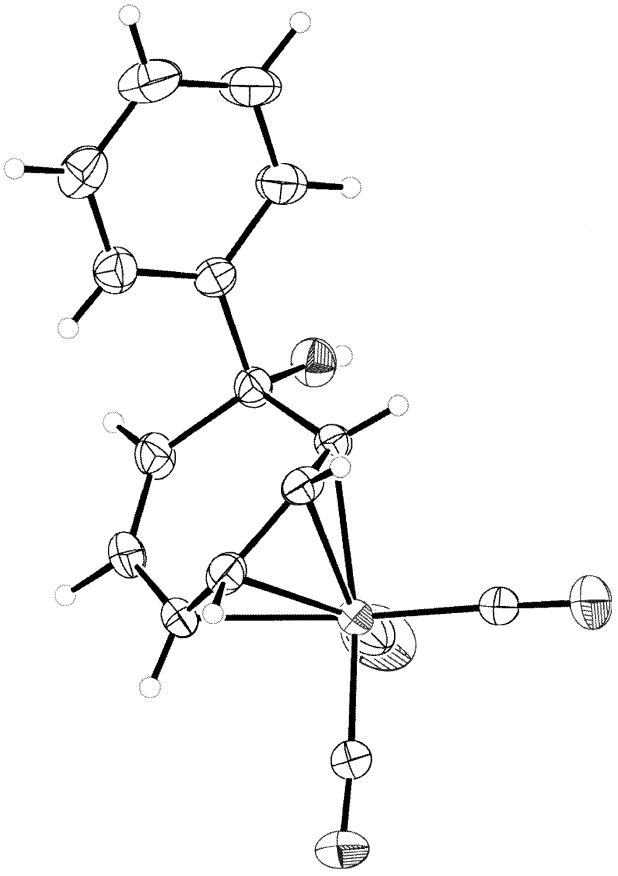


Fig. 1. ORTEP-II molecular diagram of **2c**.

nyl(dihydrotropone)iron complex **3g**, which is possibly formed through reduction by in situ generated iron carbonylates [13].

Switching the metallic counterion from lithium to magnesium did not significantly influence the regioselectivity of the reaction, but did have a deleterious effect on the yield (Table 3). The use of lithium homocuprates led only to decomposition products, which may be the result of decomplexation of the tropone, observed in a related case [14].

Augmentation of the temperature favored in the case of *n*-butyllithium in ether the formation of the 1,4-adduct, but at 0 °C there was a considerable reduction in the yield (Table 4).

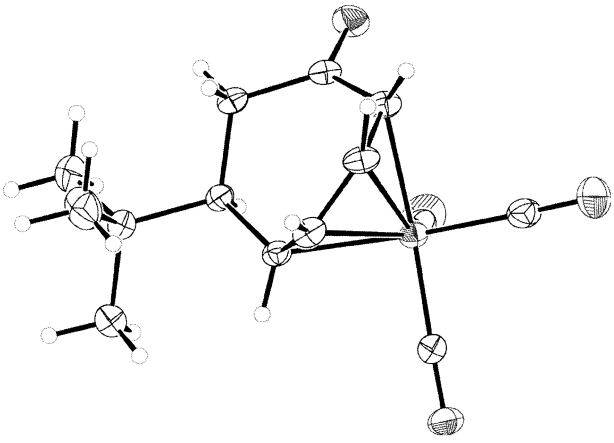


Fig. 2. ORTEP-II molecular diagram of **3f**.

The tendency for the regioselectivity of the nucleophilic addition to reflect the relative hardness of the organometallic reagent was also found with two C2-substituted tropone iron complexes. As can be seen in Table 5, with the tricarbonyl(4,5,6,7-η-2-methoxycyclo-

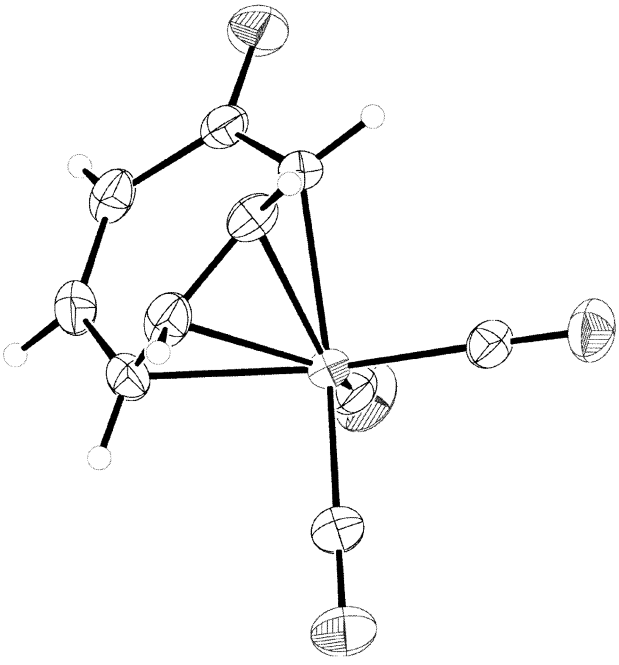


Fig. 3. ORTEP-II molecular diagram of **1**.

hepta-2,4,6-trienone)iron complex (**4**) and the tricarbonyl(4,5,6,7-η-2-methylcyclohepta-2,4,6-trienone)iron complex (**7**) (Scheme 2), as with complex **1**, hard nucleophiles gave mostly and exclusively the 1,2 addition products, whereas soft *tert*-butyllithium gave mainly the 1,4 adduct. With the larger nucleophiles, however, the yields were lower than in the additions to complex **1** (Table 1), probably due to the increased steric hindrance from the C2 substituent.

The stereochemistry of complex **9f** was determined unambiguously by X-ray diffraction analysis (Fig. 4), which showed a *trans* relationship between the substituents at C2 (methyl) and C3 (*tert*-butyl), the latter being *anti* to the iron group. Attempts to obtain the corresponding *cis* 2,3-disubstituted complex through addition of *tert*-butyllithium to complex **1**, followed by enolate quenching with iodomethane, resulted only in the formation of the non-methylated complex **3f**. The low reactivity of the lithium enolate of **3f** can probably be ascribed to steric factors as the lithium enolate of complex **3g** (Table 2, entry 6) reacted well under the same conditions [3b].

The same series of experiments has also been performed on complex **10** [15], in which the electronic density on iron has been increased relative to **1** through substitution of triphenylphosphine for a carbon monoxide ligand. Again, mixtures of 1,2 and 1,4 addition products (**11** and **12**, respectively) were obtained in various proportions as a function of the nucleophile (Scheme 3 and Table 6). The expected *anti* addition was confirmed by X-ray diffraction analysis of complex **12f** (Fig. 5).

During the attempted separation of the two isomers **11d** and **12d** on silica gel or neutral alumina, a mixture of the *Z* and *E* heptafulvene complexes **13d** ($R' = Pr^n$) was formed from dehydration of complex **11d** ($R = Bu^n$) (Scheme 3). The complex **11a** (R = Me) also suffered dehydration on alumina to give the unstable heptafulvene complex **13a** (R′ = H). Interestingly, the presence of the triphenylphosphine ligand significantly accelerates these dehydration reactions, since the corresponding tricarbonyl iron complexes **2a** and **2d** could be recovered in high yield following similar chromatographic treatment.

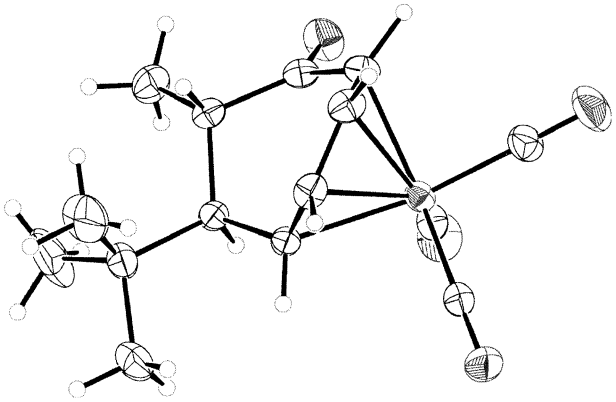
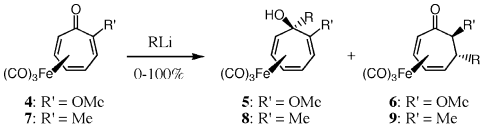
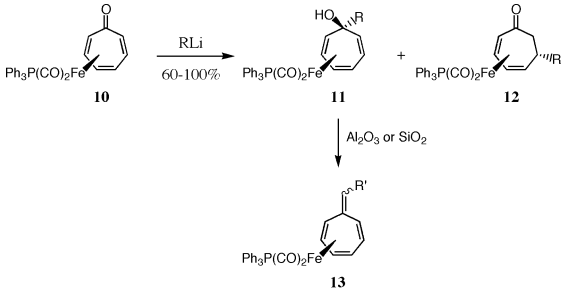


Fig. 4. ORTEP-II molecular diagram of **9f**.



Scheme 2.



Scheme 3.

Table 5
Nucleophilic addition of organolithium compounds to complexes **4** and **7**

Entry	Substrate	RLi	Conditions [a]	Products	Yield (%) [b]	Ratio **5**:**6** or **8**:**9** [c]
1	**4**	MeLi	THF, −85 °C	**5a**:**6a**	98	100:0
2	**4**	PhLi	THF, −85 °C	**5c**:**6c**	quant.	100:0
3	**4**	Bu^nLi	THF, −85 °C	**5d**:**6d**	50	89:11
4	**4**	Bu^sLi	THF, −85 °C	**5e**:**6e**	< 15	Not determined
5	**4**	Bu^tLi	THF, −85 °C	**5f**:**6f**	0	–
6	**7**	Bu^tLi	Et_2O, −85 °C	**8f**:**9f**	36	34:66

[a] THF was used because of low solubility of complex **4** in Et_2O at −85 °C.
[b] Based on isolated, homogeneous products except for entry 4.
[c] The ratio of the two regioisomers was determined by NMR analysis of the crude mixture and/or isolation of the products.

Table 6
Nucleophilic addition of organolithium compounds to complex **10**

Entry	RLi	Conditions	Products	Yield (%) [a]	Ratio **11**:**12** [b]
1	MeLi	THF, −85 °C	**11a**:**12a**	quant.	100:0
2	Bu^nLi	THF, −85 °C	**11d**:**12d**	90	69:31
3	Bu^tLi	THF, −85 °C	**11f**:**12f**	60	22:78

[a] Based on isolated, homogeneous products except for **11a** (purity > 95% by NMR without purification), **11d** (not isolated), and **11f** (isolated as a 1:1 mixture of **11f** and its decomposition product formed during purification).
[b] The ratio of the two regioisomers was determined by NMR analysis of the crude mixture and/or isolation of the products.

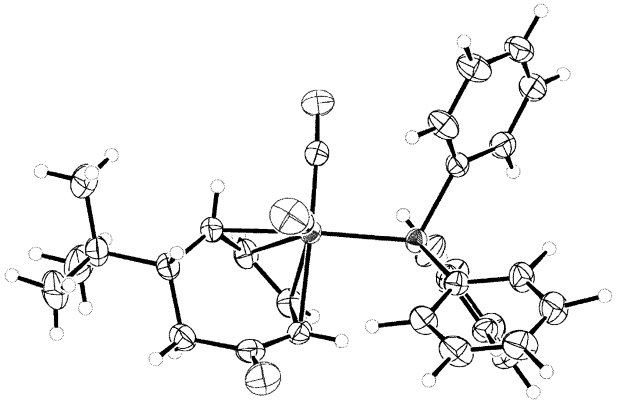


Fig. 5. ORTEP-II molecular diagram of **12f**.

3. Structural work

In order to augment the structural data available on tricarbonyl(tropone)iron complexes, X-ray diffraction analysis was also performed on complexes **1** (Fig. 3) [16], **4** (Fig. 6), and **7** (Fig. 7). The structure of complex **10** (Fig. 8) has been reproduced here for comparison [15].

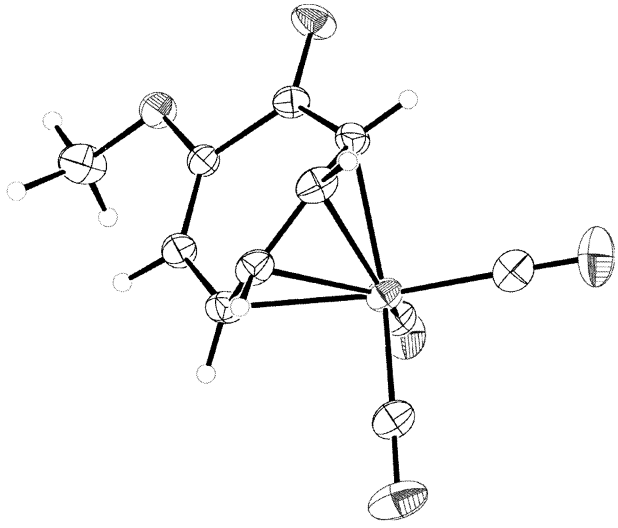


Fig. 6. ORTEP-II molecular diagram of **4**.

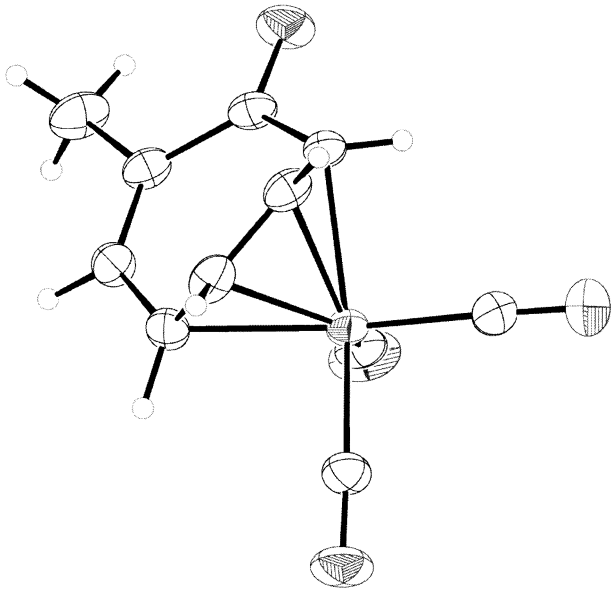


Fig. 7. ORTEP-II molecular diagram of **7**.

3.1. Structure analysis and refinement

The crystals of compounds **1**, **2c**, **3f**, **4**, **7**, **9f**, and **12f** were obtained by the slow evaporation of their chloroform solutions. Data collections were performed using an Enraf-Nonius CAD4 for compounds **2c**, **3f**, and **9f** and an Enraf-Nonius MACH 3 for compounds **1**, **4**, **7**, and **12f**, both operating with molybdenum radiation monochromated by a graphite plate (0.71073 Å). Data reductions, refinements, and drawings were performed using the teXsan software [17]. All structures were solved using the direct method SIR-92 [18]. Refinements were performed on F using a full-matrix least-squares process and anisotropic thermal parameters for all non H atoms. Crystal data and various other results are reported in Table 7.

3.2. Discussion

For structures with more than one elemental unit per cell, only mean values will be cited in the following discussion. All seven structures reported herein exhibited the distorted-square-pyramidal structure typical of

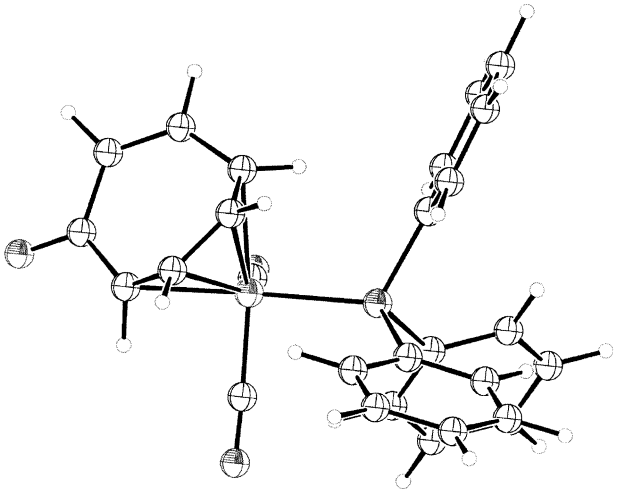


Fig. 8. ORTEP-II molecular diagram of **10**.

tricarbonyl(η^4-diene)iron complexes. The complex **1** exists in at least two distinct crystalline forms [4]. Indeed, several melting points for this complex have been reported: 63.5–64.5 °C (recrystallized from petroleum ether or benzene–petroleum ether) [3a], 83–84 °C (recrystallized from ether or benzene), 70–71 °C (not recrystallized) [2], and 76.5–77.5 °C (sublimed) [19]. Our sample, recrystallized from ethyl acetate or chloroform, exhibited a melting point of 65 °C. In Fig. 3, the X-ray structure of our material is shown. The observed space group is $P\bar{1}$ (triclinic) with two elemental units per cell. This structure differs only slightly from that previously reported (space group: $P2_1/c$, monoclinic, $Z = 4$) [4]. The seven-membered ring of the complex is non-planar, having two planes that intersect with a dihedral angle of 42.5° (ca. 47° for the previously reported structure). The shortening of the C5–C6 bond, which is a general phenomenon in this type of iron complex, is more pronounced in the present structure of the complex (1.378(4) vs. 1.396(13) Å).

In the solid state, there are no significant differences in bond lengths and angles in the four complexes **1**, **4**, **7**, and **10** (except for the greater bond-length variations of the three carbonyl ligands in the C2-substituted complexes than in the parent complex **1**). In the solid state structure of the alcohol complex **2c** (Fig. 1), there are also no significant differences in bond lengths and angles in the seven-membered ring compared with those of the parent complex **1**. In the structures of the diene complexes **3f** (Fig. 2), **9f** (Fig. 4), and **12f** (Fig. 5), the C5–C6 single bond is about 0.01 Å longer than in the

Table 7
Crystal data and structure refinement parameters for compounds **1**, **7**, **4**, **2c**, **3f**, **9f**, and **12f**

Compound	**1**	**7**	**4**	**2c**	**3f**	**9f**	**12f**
Empirical formula	$C_{10}H_6FeO_4$	$C_{11}H_8FeO_4$	$C_{11}H_8FeO_5$	$C_{16}H_{12}FeO_4$	$C_{14}H_{16}FeO_4$	$C_{15}H_{18}FeO_4$	$C_{31}H_{31}FeO_3P$
Formula weight	246.00	260.03	276.03	324.12	304.12	318.15	538.40
Temperature (K)	293	293	293	293	293	293	293
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Unit-cell dimensions							
a (Å)	6.748(4)	12.772(4)	7.390(2)	11.280(3)	6.688(4)	6.681(5)	12.946(3)
b (Å)	11.882(2)	7.700(2)	14.777(3)	11.730(5)	8.837(2)	8.915(2)	15.170(2)
c (Å)	13.087(3)	22.152(5)	20.667(4)	12.426(4)	12.439(4)	13.108(3)	14.002(6)
α (°)	99.88(2)	90	90.15(2)	86.49(3)	94.88(2)	99.34(2)	90
β (°)	101.25(3)	92.09(2)	96.51(2)	109.60(2)	104.09(4)	95.58(3)	97.73(2)
γ (°)	88.56(2)	90	90.69(2)	108.58(3)	99.85(3)	103.17(3)	90
V (Å^3)	1013.8(6)	2177.1(9)	2242.1(8)	1466(1)	696.3(5)	742.8(6)	2725(1)
Z	4	8	8	4	2	2	4
μ (mm^{-1})	1.473	1.377	1.349	1.039	1.088	1.023	0.641
$D_{calc.}$ (g cm^{-3})	1.612	1.587	1.635	1.468	1.450	1.422	1.312
$F(000)$	496	1056	1120	664	316	332	1128
Dimensions (mm)	0.25 × 0.18 × 0.17	0.29 × 0.20 × 0.15	0.29 × 0.23 × 0.18	0.35 × 0.22 × 0.21	0.40 × 0.30 × 0.30	0.33 × 0.17 × 0.15	0.32 × 0.28 × 0.22
h	−10, 9	−17, 17	−10, 10	−15, 14	−9, 9	0, 9	−18, 18
k	−17, 17	0, 10	−20, 20	−16, 16	−12, 12	−12, 12	0, 21
l	0, 19	0, 31	0, 29	0, 17	0, 17	−18, 18	0, 19
Decay (%)	8.57	20.55	2.55	2.26	2.13	6.16	0.82
Reflections	5644	4775	7112	5465	3455	3834	6140
Parameters	295	313	813	409	184	193	325
R_{int}	0.027	0.043	0.033	0.017	0.017	0.007	0.01
$R\sigma$	0.030	0.040	0.070	0.060	0.030	0.020	0.040
$R(F)$[17]	0.0454	0.0557	0.0528	0.0475	0.0306	0.0339	0.0377
wR[18]	0.0423	0.0501	0.0620	0.369	0.0372	0.0540	0.0404
Goodness-of-fit	1.921	1.913	1.956	1.892	1.801	1.946	1.793

parent triene complexes **1**, **7**, and **10**, and, in addition, the tricarbonyl iron moiety is about 0.02 Å closer to the mean plane defined by the four carbon atoms C4, C5, C6 and C7 in the diene complexes than in the triene complexes (**3f**, 1.559(1); **9f**, 1.564(1); **1**, 1.573(2); **2c**, 1.582(2); **4**, 1.586(4); **7**, 1.571(2)). In the structure of complex **12f**, it is noteworthy that the triphenylphosphine ligand, which is in the basal position *anti* to the carbonyl of the tropone ring in the complex **10**, is now in the basal position *anti* to the *tert*-butyl substituent of the tropone ring. This difference in the solid-state geometry of these two complexes can undoubtedly be attributed to steric factors.

4. Conclusion

The regioselectivity of the nucleophilic addition of a number of organolithium reagents to the tricarbonyl(tropone)iron complex and several of its derivatives can be explained by the HSAB principle. Relatively hard nucleophiles yield primarily or exclusively the 1,2 adducts, whereas those that are somewhat softer afford mainly the 1,4 adducts. Crystallographic data have led to a number of observations and complement existing data on these types of complexes.

5. Experimental

Thin-layer chromatography was performed on Merck $60F_{254}$ (0.2 mm) sheets, which were visualized with 4% molybdophosphoric acid in EtOH. Merck 40-60 silica gel 60 was employed for column flash chromatography. A Nicolet 400 spectrophotometer was used to record IR spectra. A Brucker AC 200 or Avance 300 spectrometer was employed for the NMR spectra ($CDCl_3$ solutions with Me_4Si as the reference). M.p.s were taken on a Büchi-Tottoli apparatus and are not corrected. Mass spectra were obtained on an AEI MS-30 mass spectrometer. Microanalysis were performed by the Central Service of the CNRS. THF, DME, and ether were distilled from sodium-benzophenone, and HMPA and toulene from CaH_2. All the reactions were carried in dry glassware and under an Ar atmosphere.

Complexes **1** [2], **4** [3b], **7** [20] and **10** [21] were prepared by literature procedures. Complexes **2a** [7,8], **2c** [7], and **3g** [19] exhibited physical and spectral properties identical with those reported in the literature.

The procedure for the addition of *n*-butyllithium to complex **1** is representative: To a magnetically stirred solution of 123 mg (0.50 mmol) of complex **1** in 5 mL of ether at −85 °C was added dropwise over 20 min 0.44 mL (1.0 mmol) of a 2.3 M solution of *n*-butyllithium in hexane. The solution was then diluted with ether (5 mL), treated with water (5 mL), and allowed to warm to 20 °C. The aqueous layer was extracted twice with ether–pentane (3:1) and the combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum to afford the crude product, which was purified by flash chromatography with 4–10% EtOAc in pentane to give 115 mg (76%) of alcohol complex [22] **2d**, followed by 20 mg (13%) of ketone complex **3d**. Filtration of the crude complex **11a** (purity > 95% by NMR) over silica gel or neutral alumina gave mainly a dimer of **13a**; chromatography of the crude mixture of **11d** and **12d** on silica gel or neutral alumina gave an *E*/*Z* mixture of heptafulvene complexes **13d** and the pure dienone complex **12d**; chromatography of the crude mixture of **11f** and **12f** over silica gel or neutral alumina led to partial decomposition of the complex **11f**.

5.1. *cis*-Tricarbonyl(η^4-1-*n*-pentynylcyclohepta-2,4,6-trienol)iron complex (**2b**)

Oil; IR: 3582, 2055, 1986 cm^{-1}; ^{1}H-NMR (300 MHz): δ 5.85 (dd, $J = 7.1$, 5.4 Hz, 1H), 5.58 (pseudo dd, $J =$ 4.9, 3.2 Hz, 1H), 5.40 (pseudo dd, $J = 5.3$, 3.2 Hz, 1H), 5.19 (dd, $J = 7.0$, 1.4 Hz, 1H), 3.58 (pseudo d, $J = 5.3$ Hz, 1H), 3.04 (t, $J = 5.2$ Hz, 1H), 2.16 (t, $J = 4.7$ Hz, 2H), 2.10 (s, 1H), 1.53 (hex, $J = 4.9$ Hz, 2H), 0.97 (t, $J =$ 4.9 Hz, 3H); ^{13}C-NMR (75 MHz): δ 13.6, 20.9, 22.1, 53.3, 64.3, 69.6, 82.3, 83.5, 83.8, 95.8, 128.0, 128.9, 209.8 (br); MS (DCI): *m*/*z* 297 ($[M-OH]^+$, 5%), 230 ($[M-OH+NH_3-3CO]^+$, 100%).

5.2. *cis*-Tricarbonyl(η^4-1-*n*-butylcyclohepta-2,4,6-trienol)iron complex (**2d**)

M.p. 43 °C; IR: 3606, 2049, 1973 cm^{-1}; ^{1}H-NMR (300 MHz): δ 5.84 (dd, $J = 10.7$, 8.0 Hz, 1H), 5.40–5.53 (m, 2H), 5.08 (dd, $J = 10.9$, 2.1 Hz, 1H), 3.27 (pseudo d, $J = 7.8$ Hz, 1H), 2.97 (t, $J = 7.8$ Hz, 1H), 1.77 (s, 1H), 1.47–1.72 (m, 2H), 1.06–1.47 (m, 4H), 0.90 (pseudo t, $J = 7.0$ Hz, 3H); ^{13}C-NMR (75 MHz): δ 14.1, 23.0, 26.6, 44.3, 54.2, 71.0, 71.5, 84.3, 94.1, 128.7, 131.3, 210.5 (br); MS (DCI): *m*/*z* 305 ($[MH]^+$, 3%), 287 ($[M-OH]^+$, 100%). Anal. Calc. for $C_{14}H_{16}FeO_4$: C, 55.29; H, 5.30. Found: C, 55.41; H, 5.30%.

5.3. *trans*-Tricarbonyl(η^4-3-*n*-butylcyclohepta-4,6-dienone)iron complex (**3d**)

Oil; IR: 2060, 1991, 1654 cm^{-1}; ^{1}H-NMR (300 MHz): δ 5.84 (pseudo t, $J = 5.9$ Hz, 1H), 5.49 (dd, $J = 8.0$, 5.3 Hz, 1H), 3.18 (d, $J = 7.5$ Hz, 1H), 3.11 (d, $J = 6.6$ Hz, 1H), 2.58–2.72 (m, 1H), 1.96–2.08 (m, 1H), 1.70 (t, $J =$ 11.9 Hz, 1H), 1.16–1.53 (m, 6H), 0.89 (pseudo t, $J = 6.7$ Hz, 3H); ^{13}C-NMR (75 MHz): δ 14.0, 22.6, 28.5, 41.2, 44.2, 48.0, 57.1, 65.6, 89.6, 90.9, 207.6, 208.8 (br); MS (DCI): *m*/*z* 305 ($[MH]^+$, 100%).

*5.4. cis-Tricarbonyl(η^4-1-sec-butylcyclohepta-2,4,6-trienol)iron complex (**2e**) (1:1 mixture of diastereomers)*

Oil; IR: 3605, 2049, 1974 cm^{-1}; ^{1}H-NMR (300 MHz): δ 5.80–5.95 (m, 2H), 5.42–5.57 (m, 4H), 5.03 (m, 1H), 4.99 (m, 1H), 3.10–3.22 (m, 2H), 2.88–2.99 (m, 2H), 1.84–1.98 (m, 1H), 1.74 (pseudo s, 2H), 1.32–1.64 (m, 3H), 0.71–1.12 (m, 14H); ^{13}C-NMR (75 MHz): δ 12.6, 12.7, 13.2, 14.3, 23.3, 24.9, 46.1, 46.2, 54.3, 54.3, 67.5, 67.7, 74.4, 74.4, 85.2, 85.2, 93.3, 93.3, 129.3, 129.7, 131.1, 131.4, 210.6 (br); MS (F*A*B): *m/z* 287 ($[M-OH]^+$, 13%), 259 ($[M-OH-CO]^+$, 13%), 231 ($[M-OH-2CO]^+$, 21%), 203 ($[M-OH-3CO]^+$, 100%), ($[M-OH-Fe(CO)^3]^+$, 22%).

*5.5. trans-Tricarbonyl(η^4-3-sec-butylcyclohepta-4,6-dienone)iron complex (**3e**) (1:1 mixture of diastereomers)*

Oil; IR: 2057, 1989, 1660 cm^{-1}; ^{1}H-NMR (300 MHz): δ 5.82 (pseudo t, $J = 5.9$ Hz, 2H), 5.56 (pseudo t, $J = 6.9$ Hz, 2H), 3.00–3.13 (m, 4H), 2.69–2.83 (m, 2H), 0.75–1.92 (m, 22H); ^{13}C-NMR (75 MHz): δ 12.6, 12.6, 14.6, 15.8, 26.1, 27.1, 39.4, 41.8, 43.2, 43.4, 52.8, 53.2, 57.2, 57.3, 63.1, 65.0, 90.8, 90.8, 91.0, 91.1, 207.3 (br), 208.5, 208.6, 209.2 (br); MS (DCI): *m/z* 305 ($[MH]^+$, 100%).

*5.6. trans-Tricarbonyl(η^4-3-tert-butylcyclohepta-4,6-dienone)iron complex (**3f**)*

Needles (recrystallized from $CHCl_3$), m.p. 134–135 °C; IR: 2060, 1996, 1651 cm^{-1}; ^{1}H-NMR (300 MHz): δ 5.82 (pseudo t, $J = 5.9$ Hz, 1H), 5.54 (dd, $J = 7.7$, 5.5 Hz, 1H), 3.30 (d, $J = 8.0$ Hz, 1H), 3.13 (pseudo d, $J = 6.5$ Hz, 1H), 2.47 (pseudo dd, $J = 12.4$, 4.6 Hz, 1H), 2.02–2.13 (m, 1H), 1.72 (pseudo t, $J = 12.2$ Hz, 1H), 0.91 (s, 9H); ^{13}C-NMR (75 MHz): δ 27.2, 36.4, 39.9, 57.0, 58.1, 61.3, 90.6, 90.9, 207.9, 208.9 (br); MS (DCI): *m/z* 305 ($[MH]^+$, 100%). Anal. Calc. for $C_{14}H_{16}FeO_4$: C, 55.29; H, 5.30. Found: C, 55.08; H, 5.43%.

*5.7. cis-Tricarbonyl(4,5,6,7-η-1-methyl-2-methoxycyclohepta-2,4,6-trienol)iron complex (**5a**)*

Oil; IR: 3590, 2049, 1980, 1661 cm^{-1}; ^{1}H-NMR (300 MHz): δ 5.31–5.37 (m, 2H), 4.86 (d, $J = 9.0$ Hz, 1H), 3.44 (s, 3H), 3.28–3.36 (m, 1H), 3.15 (pseudo t, $J = 9.0$ Hz, 1H), 2.40 (s, 1H), 1.41 (s, 3H); ^{13}C-NMR (75 MHz): δ 32.4, 53.9, 54.8, 69.2, 70.1, 82.9, 92.4, 96.6, 157.7, 210.4 (br); MS (DCI): *m/z* 275 ($[M-OH]^+$, 16%), 208 ($[M-OH+NH_3-3CO]^+$, 100%).

*5.8. cis-Tricarbonyl(4,5,6,7-η-1-phenyl-2-methoxycyclohepta-2,4,6-trienol)iron complex (**5c**)*

M.p. 91–92 °C; IR: 3582, 2050, 1986, 1664 cm^{-1}; ^{1}H-NMR (300 MHz): δ 7.18–7.38 (m, 5H), 5.37 (ddd, $J = 7.6$, 4.5, 1.3 Hz, 1H), 5.18 (d, $J = 9.1$ Hz, 1H), 5.13 (ddd, $J = 7.9$, 4.5, 1.3 Hz, 1H), 3.40 (s, 3H), 3.33 (pseudo d, $J = 7.9$ Hz, 1H), 3.27 (pseudo t, $J = 8.2$ Hz, 1H), 2.93 (s, 1H); ^{13}C-NMR (75 MHz): δ 53.9, 55.0, 69.9, 75.2, 83.0, 92.1, 99.6, 124.6, 127.3, 128.5, 148.4, 156.7, 210.3 (br); MS (DCI): *m/z* 337 ($[M-OH]^+$, 24%), 270 ($[M-OH+NH_3-3CO]^+$, 100%).

*5.9. cis-Tricarbonyl(4,5,6,7-η-1-n-butyl-2-methoxycyclohepta-2,4,6-trienol)iron complex (**5d**)*

Oil; IR: 3593, 2046, 1984, 1964, 1661 cm^{-1}; ^{1}H-NMR (300 MHz): δ 5.45 (ddd, $J = 8.1$, 4.5, 1.3 Hz, 1H), 5.34 (ddd, $J = 7.6$, 4.6, 1.3 Hz, 1H), 4.91 (d, $J = 9.0$ Hz, 1H), 3.43 (s, 3H), 3.15 (dd, $J = 8.1$, 1.2 Hz, 1H), 3.08 (pseudo t, $J = 7.6$ Hz, 1H), 2.31 (s, 1H), 1.60–1.75 (m, 2H), 1.19–1.46 (m, 3H), 0.80–1.04 (m, 4H); ^{13}C-NMR (75 MHz): δ 14.2, 22.9, 26.3, 43.2, 53.9, 54.9, 67.1, 73.4, 83.9, 91.5, 98.2, 156.9, 210.7 (br); MS (DCI): *m/z* 317 ($[M-OH]^+$, 22%), 250 ($[M-OH+NH_3-3CO]^+$, 100%).

*5.10. Tricarbonyl(η^4-cis-2-methoxy-trans-3-n-butylcyclohepta-4,6-dienone)iron complex (**6d**)*

Oil; IR: 2061, 1990, 1668 cm^{-1}; ^{1}H-NMR (300 MHz): δ 5.81 (pseudo t, $J = 5.9$ Hz, 1H), 5.52 (ddd, $J = 8.1$, 5.1, 0.9 Hz, 1H), 3.26 (s, 3H), 3.02–3.14 (m, 2H), 2.93 (d, $J = 10.4$ Hz, 1H), 2.50–2.61 (m, 1H), 1.48–1.76 (m, 3H), 1.24–1.43 (m, 3H), 0.93 (pseudo t, $J = 6.9$ Hz, 3H); ^{13}C-NMR (75 MHz): δ 14.2, 23.0, 27.5, 35.9, 54.4, 55.1, 58.6, 61.0, 83.2, 89.3, 90.6, 205.0, 208.6 (br); MS (DCI): *m/z* 335 ($[MH]^+$, 100%).

*5.11. cis-Tricarbonyl(4,5,6,7-η-1-tert-butyl-2-methylcyclohepta-2,4,6-trienol)iron complex (**8f**)*

Oil; IR: 3582, 2047, 1976 cm^{-1}; ^{1}H-NMR (200 MHz): δ 5.83 (dq, $J = 8.6$, 1.4 Hz, 1H), 5.57 (ddd, $J = 8.2$, 4.1, 1.4 Hz, 1H), 5.34 (ddd, $J = 7.5$, 4.5, 1.7 Hz, 1H), 3.32 (dd, $J = 8.2$, 1.4 Hz, 1H), 3.05 (ddd, $J = 8.9$, 7.5, 1.4 Hz, 1H), 1.70 (d, $J = 1.4$ Hz, 3H), 1.56 (s, 1H), 1.01 (s, 9H); ^{13}C-NMR (50 MHz): δ 22.3, 27.2, 40.7, 57.5, 72.2, 78.9, 83.8, 93.8, 128.9, 137.1, 210.8 (br); MS (DCI): *m/z* 301 ($[M-OH]^+$, 32%), 234 ($[M-OH+NH_3-3CO]^+$, 100%).

5.12. Tricarbonyl(η^4-cis-2-methyl-trans-3-tert-butylcyclohepta-4,6-dienone)iron complex (**9f**)

Prisms (recrystallized from $CHCl_3$), m.p. 100–102 °C; IR: 2062, 1999, 1648 cm^{-1}; ^{1}H-NMR (200 MHz): δ 5.71 (pseudo t, $J = 5.8$ Hz, 1H), 5.58 (pseudo dd, $J = 6.9$, 4.1 Hz, 1H), 3.27 (pseudo d, $J = 6.2$ Hz, 2H), 2.15 (dd, $J = 8.2$, 2.7 Hz, 1H), 1.85–2.03 (m, 1H), 1.10 (d, $J = 6.9$ Hz, 3H), 1.02 (s, 9H); ^{13}C-NMR (50 MHz): δ 18.0, 29.5, 37.9, 43.6, 59.7, 60.0, 62.1, 89.6, 91.4, 207.9, 209.1 (br); MS (DCI): *m/z* 319 ($[MH]^+$, 100%).

5.13. cis-Dicarbonyltriphenylphosphine(η^4-1-methylcyclohepta-2,4,6-trienol)iron complex (**11a**)

Unstable solid; IR: 3589, 1974, 1915 cm^{-1}; ^{1}H-NMR (200 MHz): δ 7.30–7.56 (m, 15H), 5.73 (dd, $J = 10.6$, 7.9 Hz, 1H), 5.05 (dd, $J = 10.3$, 2.1 Hz, 1H), 4.80–5.00 (m, 2H), 2.84–2.97 (m, 1H), 2.22–2.38 (m, 1H), 2.02 (s, 1H), 1.25 (s, 3H); ^{13}C-NMR (75 MHz): δ 32.2, 53.0, 69.2, 70.7, 83.5, 95.6, 128.3, 128.4, 129.1, 129.9, 129.9, 130.9, 133.1, 133.2, 134.6, 135.1, 217.6 [d, $J(^{31}P-^{13}C) = 16$ Hz], 218.7 [d, $J(^{31}P-^{13}C) = 14$ Hz]; MS (DCI): *m/z* 497 ($[MH]^+$, 9%), 479 ($[M-OH]^+$, 74%), 423 ($[M-OH-2CO]^+$, 55%), 263 (PPh_3+H^+, 100%), 105 ($[M-OH-Fe(CO)_2PPh_3]^+$, 100%).

5.14. trans-Dicarbonyltriphenylphosphine(η^4-3-n-butylcyclohepta-4,6-dienone)iron complex (**12d**)

M.p. 139–140 °C; IR: 1978, 1934, 1634 cm^{-1}; ^{1}H-NMR (200 MHz): δ 7.30–7.56 (m, 15H), 4.93–5.08 (m, 1H), 4.78–4.93 (m, 1H), 2.67–2.90 (m, 2H), 2.55–2.69 (m, 1H), 1.85–2.00 (m, 1H), 1.57 (pseudo t, $J = 12.0$ Hz, 1H), 1.04–1.39 (m, 6H), 0.85 (pseudo t, $J = 6.5$ Hz, 3H); ^{13}C-NMR (50 MHz): δ 14.2, 22.8, 28.8, 41.3, 44.6, 48.8, 56.7, 62.4, 89.4, 92.4, 128.6, 128.7, 130.3, 133.2, 133.4, 134.1, 134.9, 208.9, 215.8 (br), 216.4 (br); MS (DCI): *m/z* 539 ($[MH]^+$, 100%).

5.15. cis-Dicarbonyltriphenylphosphine(η^4-1-tert-butylcyclohepta-2,4,6-trienol)iron complex (**11f**)

Not isolated pure; IR: 3620, 1975, 1915 cm^{-1}; ^{1}H-NMR (200 MHz): δ 0.82 (s, 9H, *t*Bu), 0.80 (s, 9H, *t*Bu); MS (DCI): *m/z* 665 (8%), 579 (6%), 539 ($[MH]^+$, 100%), 521 ($[M-OH]^+$, 55%), 465 ($[M-OH-2CO]^+$, 10%), 435 ($[2M-2OH-3CO-2PPh_3+H]^+$, 32%), 407 ($[2M-2OH-4CO-2PPh_3+H]^+$, 2%), 351 ($[2M-2OH-4CO-2PPh_3-Fe+H]^+$, 1%), 305 ($[M-PPh_3+CO+H]^+$, 10%), 263 ($PPh_3+H^+$, 55%), 147 ($[M-OH-Fe(CO)_2PPh_3]^+$, 19%).

5.16. trans-Dicarbonyltriphenylphosphine(η^4-3-tert-butylcyclohepta-4,6-dienone)iron complex (**12f**)

Prisms (recrystallized from $CHCl_3$), m.p. 194–196 °C (dec.); IR: 1989, 1934, 1632 cm^{-1}; ^{1}H-NMR (200 MHz): δ 7.31–7.57 (m, 15H), 4.38–5.06 (m, 2H), 2.76–2.88 (m, 1H), 2.52–2.71 (m, 2H), 1.91–2.06 (m, 1H), 1.60 (pseudo t, $J = 11.7$ Hz, 1H), 0.75 (s, 9H); ^{13}C-NMR (75 MHz): δ 27.2, 36.0, 39.8, 55.9, 58.8, 90.8, 91.7, 128.4, 128.6, 130.2, 130.2, 133.1, 133.2, 134.0, 134.6, 209.0, 215.9 (br), 217.8 (br); MS (DCI): *m/z* 539 ($[MH]^+$, 100%).

5.17. The dimer of dicarbonyltriphenylphosphine(η^4-heptafulvene)iron complex (**13a**)

Not isolated pure; IR: 1978, 1915 cm^{-1}; ^{1}H-NMR (200 MHz): δ 7.30–7.58 (m, 30H), 5.74 (pseudo t, $J =$ 9.1 Hz, 2H), 5.43 (pseudo d, $J = 9.9$ Hz, 2H), 5.12–5.27 (m, 2H), 4.92 (pseudo s, 2H), 4.70–4.85 (m, 2H), 2.97 (pseudo t, $J = 7.3$ Hz, 2H), 2.46 (pseudo t, $J = 7.3$ Hz, 2H); ^{13}C-NMR (75 MHz) highly complex spectrum; MS (DCI): *m/z* 723 ($[2M+H-PPh_3+CO]^+$, 7%), 665 (23%), 583 ($[2M+H-PPh_3-4CO]^+$ or $[2M+H-Fe(CO)_2PPh_3]^+$, 16%), 479 ($[MH]^+$, 2%), 431 ($[2M+H-2PPh_3]^+$, 24%), 349 ($[2M+H-2PPh_3-3CO]^+$, 13%), 263 (PPh_3+H^+, 100%), 209 ($[2M+H-2Fe(CO)_2PPh_3]^+$, 65%), 105 ($[M+H-Fe(CO)_2PPh_3]^+$, 6%).

5.18. Dicarbonyltriphenylphosphine(η^4-8-n-propylheptafulvene)iron complex (**13d**) (1:1 mixture of *Z* and *E* isomers)

Oil; IR: 1975, 1915 cm^{-1}; ^{1}H-NMR (200 MHz): δ 7.28–7.58 (m, 30H), 5.52–5.84 (m, 3H), 5.25–5.41 (m, 3H), 5.02–5.18 (m, 2H), 4.74–4.88 (m, 1H), 4.57–4.70 (m, 1H), 3.13–3.26 (m, 1H), 2.90–3.03 (m, 1H), 2.42–2.66 (m, 2H), 1.85–2.02 (m, 2H), 1.62–1.80 (m, 2H), 1.25–1.47 (m, 4H), 0.76–0.95 (m, 6H); ^{13}C-NMR (75 MHz): δ 13.7, 13.9, 22.5, 22.8, 30.2, 30.4, 52.8, 53.8, 57.0, 66.2, 88.2, 88.3, 92.1, 92.5, 117.7, 126.2, 127.4, 128.1, 128.2, 128.3, 129.1, 129.7, 129.7, 129.8, 132.5, 133.1, 133.2, 135.2, 135.2, 135.7, 137.7, 138.7, 216.9 [d, $J(^{31}P-^{13}C) = 16$ Hz], 217.3 [d, $J(^{31}P-^{13}C) = 17$ Hz], 218.7 [d, $J(^{31}P-^{13}C) = 12$ Hz], 218.9 [d, $J(^{31}P-^{13}C) =$ 10 Hz]; MS (DCI): *m/z* 521 ($[MH]^+$, 100%), 465 ($[M+H-2CO]^+$, 33%), 147 ($[M+H-Fe(CO)_2PPh_3]^+$, 26%).

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 179617, 179836, 179893, 179725, 179684, 179989, 180095 for compounds **1**, **2c**,

3f, **4**, **7**, **9f**, **12f**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[21] Ref. [15]. Complex **10** was obtained in 91% yield following the described procedure.
[22] The neat alcohol complexes slowly decomposed on standing in the dark at −30 °C under argon.