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Tricarbonylbis(η^2-*cis*-cyclooctene)iron: Photochemical Synthesis of a Versatile $Fe(CO)_3$ Source for Olefin Isomerization and Preparative Applications

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Abstract: The photoreaction of pentacarbonyliron and *cis*-cyclooctene in alkane solvent at −40 °C results in high yield formation of tricarbonylbis(η^2-*cis*-cyclooctene)iron (**1**). Solid **1** can be handled at room temperature. In solution at $\gtrsim -35$ °C the complex is substitutionally labile and serves as a versatile source of the $Fe(CO)_3$ unit. The thermal reaction of **1** with 1-pentene results in extensive isomerization of the alkene with turnover numbers up to 2000, thus establishing the role of $Fe(CO)_3$ as the repeating unit in the catalytic alkene isomerization. Turnover rates are 0.48 min^{-1} at −20 °C, 12.2 min^{-1} at 0 °C, and 173 min^{-1} at 20 °C. Ligand exchange with 1,3-dienes and vinyl-substituted aromatic compounds provides excellent yields of the corresponding (η^4-organic ligand)$Fe(CO)_3$ complexes. The reaction of **1** with 2-butyne demonstrates that alkyne coupling products are accessible under remarkably mild conditions.

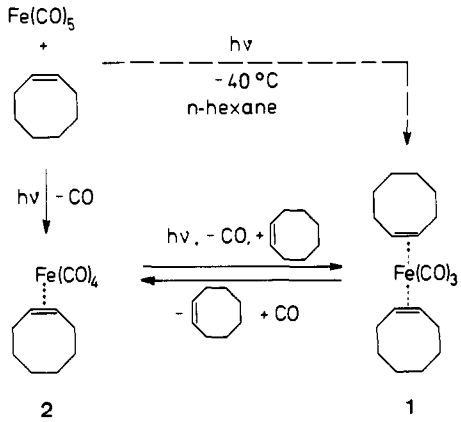
The carbonyliron catalyzed isomerization of alkenes is known for some time to proceed photochemically under mild conditions.[1-3] Quantum yields for 1-pentene to *cis*- and *trans*-2-pentene isomerization, photocatalyzed by pentacarbonyliron at ambient temperature, have been reported to exceed unity by 2 or 3 orders of magnitude.[4,5] These and other findings are consistent with the notion of a thermal catalytic process subsequent to the photochemical generation of the actual catalyst. Efforts were made[4-8] toward establishing plausible mechanistic schemes. Two rather different species have been suggested to carry the catalytic cycle: a carbonyl-bridged diiron complex[7] and, alternatively, a mononuclear tricarbonyliron unit, presumably present as a substitutionally labile (η^2-alkene)$_2$Fe(CO)$_3$ complex.[4,5] However, there has been no unequivocal proof for any of these species, and the active catalyst has not yet been identified conclusively.

Our interest in the preparation and properties of bis(η^2-olefin)(carbonyl)metal compounds[9-11] led us to attempt, by analogy with (η^2-methyl acrylate)$_2$Fe(CO)$_3$,[9] the photochemical synthesis and isolation of (η^2-olefin)$_2$Fe(CO)$_3$ complexes of simple alkenes. One particular aim of this work is to study the substitutional behavior of such compounds and to elucidate their conceivable role in the above-mentioned catalysis. Anticipating that linear alkenes would yield mixtures of isomeric (η^2-alkene)(η^2-alkene′)Fe(CO)$_3$ complexes, we have chosen a cycloalkene as the olefinic ligand.

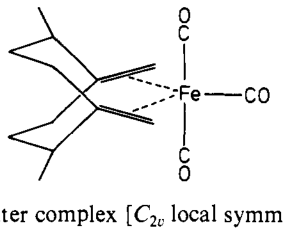
Results and Discussion

(η^2-*cis*-Cyclooctene)$_2$Fe(CO)$_3$ (1). Extended photolysis of pentacarbonyliron in the presence of excess *cis*-cyclooctene in hexane −40 °C results in the formation of (η^2-*cis*-cyclooctene)$_2$Fe(CO)$_3$ (**1**). The primary photoproduct, as detected by infrared spectroscopy, is (η^2-*cis*-cyclooctene)Fe(CO)$_4$[12] (**2**), which upon further irradiation is converted to **1** (Scheme I). Complex **1** crystallizes upon cooling the reaction mixture to −78 °C and can be isolated as yellow crystals in 85–90% yield. Solid **1** can be handled at room temperature whereas solutions of **1** in an inert solvent such as hexane are unstable. Decomposition starts slowly above −35 °C, whereby (η^2-*cis*-cyclooctene)Fe(CO)$_4$ (**2**)[12] and a brown, insoluble material are formed. Treatment of **1** with carbon monoxide, by warming a hexane solution of **1** to room temperature under CO atmosphere, immediately gives the tetracarbonyliron complex **2** (Scheme I) together with small amounts of Fe(CO)$_5$. This displacement reaction is significantly retarded if carried out in neat *cis*-cyclooctene, thus pointing toward a dissociative mechanism. Accordingly, the aforementioned decomposition of **1** is suppressed in the presence of excess *cis*-cyclooctene: the complex is stable for hours in neat *cis*-cyclooctene at room temperature.

Scheme I



The infrared spectrum of **1** in the metal carbonyl region [$\tilde{\nu}$(CO) 2044.5 (m) and 1966 (vst) cm^{-1}, in *n*-hexane at −50 °C] is in agreement with a trigonal-bipyramidal structure where the C=C double bonds of the two cyclooctene ligands lie in the equatorial plane (Figure 1). Such a structure was verified by X-ray crystallography in the case of (η^2,η^2-1,5-dimethylene-2,6-dimethylcyclooctane)Fe(CO)$_3$ (**3**).[13] The metal carbonyl infrared bands of the latter complex [C_{2v} local symmetry of the Fe(CO)$_3$



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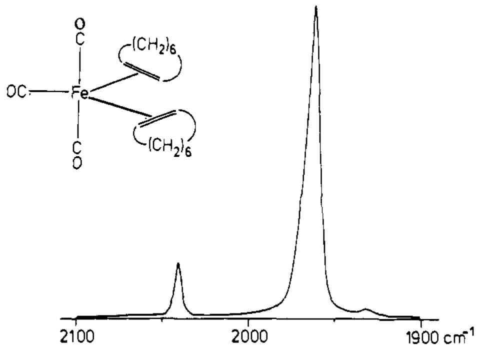
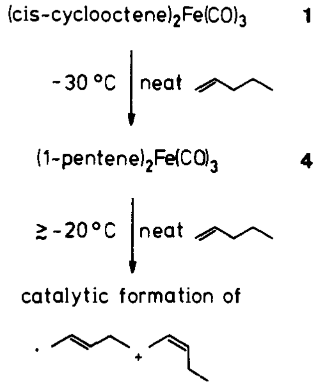


Figure 1. Infrared carbonyl stretching bands of complex 1, in *cis*-cyclooctene at room temperature.

Scheme II



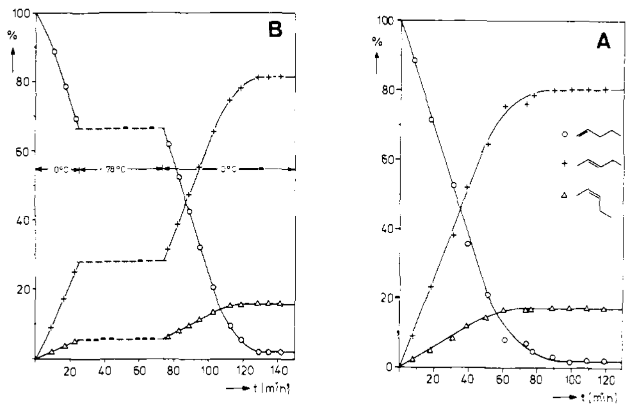


Figure 2. Catalytic isomerization of 1-pentene (○) → *cis*-2-pentene (△) and *trans*-2-pentene (+); 0.012 M solution of complex 1 in neat 1-pentene (9.14 M). (A) at 0 °C (experiment 7, Table I). (B) At 0 °C/−78 °C/0 °C (experiment 9, Table I).

fragment; $\bar{\nu}$(CO) 2042.5 (m, A_1) and 1959 (vst, A_1 and B_1) cm^{-1}, in *n*-hexane] are quite similar to those of **1** with regard to the frequencies as well as to the relative intensities. Thus it seems justified to assume an analogous coordination geometry around the metal atom. In contrast to the 1,5-dimethylene-2,6-dimethylcyclooctane complex **3**, which is rigid at room temperature,[13] **1** appears to be fluxional even at 198 K. The ^{13}C NMR spectrum of **1** (in *cis*-cyclooctene/toluene-d_8 mixture) exhibits only one CO signal (214.6 ppm) at 228 K, which slightly broadens upon cooling down to 198 K; the cyclooctene ligand signals (63.1, 32.9, and 31.7 ppm; one missing line may be hidden by a cyclooctene solvent signal; cf. ^{13}C NMR data of **2**[12]) remain sharp over this temperature range.

Tricarbonyliron Catalyzed Isomerization of 1-Pentene. (η^2-*cis*-Cyclooctene)$_2$Fe(CO)$_3$ (**1**) readily undergoes olefin exchange, as monitored by infrared spectroscopy. When a solution of **1** in neat 1-pentene is warmed from −50 to −30 °C, the CO stretching bands of **1** (2042 and 1962 cm^{-1}) gradually disappear in favor of two new bands at 2050 (m) and 1971 (vst) cm^{-1}. Taking into account that the shape of the new spectrum is quite similar to that of **1**, we assign these bands to the analogous complex (η^2-1-pentene)$_2$Fe(CO)$_3$ (**4**), particularly as the shift to higher frequencies is consistent with the substitution of *cis*-cyclooctene for 1-pentene [cf. the infrared data of the corresponding (η^2-olefin)Fe(CO)$_4$ complexes[4,12]].

A further rise in temperature to −20 °C or above leaves the spectrum virtually unchanged, at least for a certain period of time. However, analysis by means of gas chromatography shows that under these conditions 1-pentene undergoes catalytic isomerization, yielding *cis*- and *trans*-2-pentene (Scheme II). Turnover numbers up to ~2000 are achieved, without irradiation, in the dark. Hence it follows that *substitutionally labile (η^2-olefin)$_2$Fe(CO)$_3$ plays a key role in the carbonyliron catalyzed alkene isomerization.* It is demonstrated that a complex of this type, photochemically generated from pentacarbonyliron, provides an entrance to the catalytic cycle, the particular steps of which do not require the action of light.

In this context it is of interest to note that in a very recent communication[14] on the low-temperature photochemistry of Fe(CO)$_4$(olefin) complexes the formation of "*trans*-Fe(CO)$_3$(1-pentene)$_2$" and "Fe$_2$(CO)$_6$(1-pentene)$_2$" has been reported. In view of our own observations it seems indispensable to point out that (i) the infrared data stated for "Fe$_2$(CO)$_6$(1-pentene)$_2$" (2048 and 1972 cm^{-1}) are in excellent agreement with our data for (1-pentene)$_2$Fe(CO)$_3$ (**4**, see above) and are comparable with those of **1**, **3**,[13] and (η^2-*trans*-cyclooctene)$_2$Fe(CO)$_3$ (**5**)[15] [$\bar{\nu}$(CO) 2046 (m, A_1), 1982 (st, A_1), and 1971 (vst, B_1) cm^{-1}, in *n*-hexane], which has been proven by X-ray analysis to possess a trigonal-bipyramidal structure with the two olefinic ligands in a cis-equatorial arrangement; (ii) the whole series of (η^2-olefin)$_2$M(CO)$_3$ complexes (M = Fe,[9,13,15] Ru,[11] and Os[16]) there is no precedent of *trans*-(olefin)$_2$M geometry. Quite possibly "*trans*-Fe(CO)$_3$(1-pentene)$_2$" [$\bar{\nu}$(CO) *1925* cm^{-1}] may be reformulated either as *trans*-Fe(CO)$_2$(1-pentene)$_3$ [cf. (η^2-*trans*-cyclooctene)$_3$Os(CO)$_2$,[16] $\bar{\nu}$(CO) 1935 cm^{-1}] or as Fe(CO)$_2$(1-pentene)$_2$ [cf. the complex fragments of the type (η^2-olefin)$_2$Fe(CO)$_2$, generated by low-temperature photolysis[17] of **3** and **5**, $\bar{\nu}$(CO) ~1990 and ~*1930* cm^{-1}]. Adscititiously, attention should be directed toward a paper[8] on FT-IR measurements during and after the photolysis of pentacarbonyliron and excess 1-pentene stating that the active isomerization catalyst exhibits a strong absorption at 1969 cm^{-1}, in agreement with the intense band of **4** (see above).

The velocity of 1-pentene isomerization with complex **1** as the Fe(CO)$_3$ source is negligible at ≲−30 °C. At 0 °C a 0.012 M solution of **1** in neat 1-pentene (catalyst/substrate ratio = 1/750) approaches the equilibrium of the three pentene isomers after 80–100 min (Figure 2A). The catalysis can be halted by cooling the reaction mixture and continues to proceed with the same velocity upon warming up again. Figure 2B displays an experiment performed at 0 and −78 °C, respectively. Another experiment (Table I, no. 10) with 10 days interruption at −78 °C shows that the catalyst is stable at low temperature for an extended period of time without any loss of activity.

It is of particular advantage that complex **1** is stable enough to be weighed on a balance. This enables us to use well-defined catalyst concentrations, contrary to the in situ generation of the active species from pentacarbonyliron under photocatalytic conditions, and to evaluate accurate turnover rates from the initial slope of concentration vs. time curves (Figure 2). At various temperatures we find the following turnover rates (average values from Table I): 0.48 min^{-1} (mol of 1-pentene/mol of catalyst) at −20 °C, 12.2 min^{-1} at 0 °C, and 173 min^{-1} at +20 °C. The series of experiments at 0 °C (Table I, no. 4–13) with varying amounts of complex **1** reveals a linear relationship between the complex concentration and the velocity of 1-pentene isomerization (Figure

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Table I. Tricarbonyliron Catalyzed Isomerization of 1-Pentene (neat, 9.14 M)

						pentene isomers[c]		
expt	1, mM	*t*, °C	1-pentene conversion, mM min	turnover rate,[a] min^{-1}	method[b]	% 1-pentene	% *trans*-2-pentene	% *cis*-2-pentene
1	9.13	−20	4.10	0.45	A	4.2	81.4	14.4
2	9.12	−20	5.11	0.56	A	1.9	83.9	14.2
3	9.13	−20	3.97	0.43	B	2.3	84.2	13.5
4	6.09	0	74.9	12.3	A	*d*		
5	6.09	0	72.5	11.9	B	2.4	81.2	16.4
6	6.09	0	83.1	13.6	B	5.2	78.3	16.5
7	12.0	0	145	12.1	A	1.9	81.2	16.9
8	12.1	0	176	14.5	A	1.9	81.4	16.7
9	12.1	0[e]	140	11.5	A	1.8	82.3	15.9
10	12.2	0[e]	136	11.2	B	*d*		
11	36.5	0	425	11.6	A	1.7	82.6	15.7
12	36.6	0	391	10.8	B	*d*		
13	36.5	0	457	12.5	B	1.4	82.4	16.2
14	12.1	20	2280	188	B	5.2	75.5	19.3
15	12.2	20	1760	144	B	*d*		
16	12.2	20	2290	188	B	5.7	76.3	18.0

[a] (mol of 1-Pentene/mol of complex 1) min^{-1}. [b] A: Samples drawn by condensation from the gas phase; B: samples quenched with triphenylphosphine; for details see exptl part. [c] Final product distribution. [d] Conversion not monitored up to completion. [e] After 25-min catalysis interrupted for 50 min (expt 9, Figure 2B) and 10 days (expt 10), respectively, by cooling to −78 °C.

Table II. Quenching of the Tricarbonyliron Catalyzed[a] Isomerization of 1-Pentene[b]

			pentene isomers[c]		
expt	*t*, °C	quenching reagent (M)	% 1-pentene	% *trans*-2-pentene	% *cis*-2-pentene
1	0	air	32.3	55.3	12.4
2	0	air	33.4	54.3	12.3
3	20	air	14.1	67.6	18.3
4	20	air	14.6	67.1	18.3
5	0	CO	55.5	36.7	7.7
6	0	CO	46.8	43.2	10.0
7	0	CO	42.5	46.5	11.0
8	20	CO	39.3	48.6	12.1
9	20	CO	38.0	49.7	12.3
10	0	1,3-cyclooctadiene (0.6)	95.2	4.0	0.8
11	0	1,3-cyclooctadiene (0.6)[d]	86.9	10.8	2.3
12	0	1,3-cyclooctadiene (0.6)[e]	72.8	22.6	4.6
13	0	$P(C_6H_5)_3$ (0.06)	98.2	1.5	0.3
14	0	$P(C_6H_5)_3$ (0.06)	98.7	1.1	0.2
15	0	$P(C_6H_5)_3$ (0.06)	98.6	1.2	0.2
16	20	$P(C_6H_5)_3$ (0.06)	99.2	0.7	0.1
17	0	$P(C_6H_5)_3$[d] (0.054)	89.5	8.7	1.8
18	0	$P(C_6H_5)_3$[e] (0.06)	78.2	18.0	3.8

[a] 0.012 M Complex 1, catalysis started in the presence of the quenching reagent unless noted otherwise. [b] Neat, 9.14 M. [c] Final composition of the reaction mixture. [d] Added 5 min after catalysis started. [e] Added 15 min after catalysis started.

3) or, in other words, a constant turnover rate based on the respective amounts of complex **1**. These results confirm the role of the *mononuclear* tricarbonyliron species as the repeating unit, contradictory to the alternative mechanistic proposal,[7] which involves a dinuclear, carbonyl-bridged iron complex as the actual catalyst. Although infrared spectroscopy does not provide evidence for such a species, one might argue that it could exist in small concentration in equilibrium with the mononuclear complex. However, this is not consistent with the relationship displayed in Figure 3.

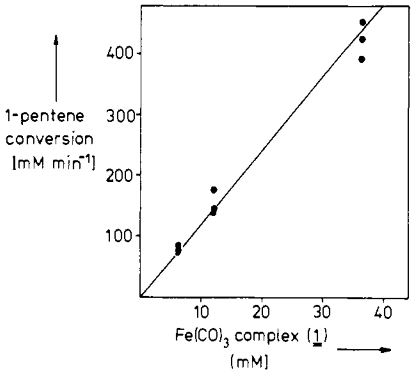

Figure 3. Rates of 1-pentene isomerization at various tricarbonyliron complex concentrations at 0 °C.

Previously reported turnover rates of in situ photogenerated catalyst are substantially larger (≥3700 min^{-1} [6] and 4000 s^{-1} [5]), by orders of magnitude, than our results. Apparently these discrepancies originate from the estimation of extremely short lifetimes for the active catalyst (<5 s[6] and 0.2 s[5]), which are in contrast to our observation that at room temperature the catalytic activity persists for ~15 min.[18] The possible reaction of the active catalyst with carbon monoxide[4–6] back to inactive (pentene)Fe(CO)$_4$ seems not to account for a very short lifetime: even when the isomerization of neat 1-pentene with 0.012 M complex **1** is started and performed in CO-saturated solution under an atmosphere of carbon monoxide we still observe 40–60% conversion (Table II, experiment 5–9). Hence several hundred turnovers (corresponding to an average catalyst lifetime of ~2 min) take place before the active species is completely converted to (pentene)Fe(CO)$_4$ [mixture of isomers;[4,19] $\tilde{\nu}$(CO) 2082, 2079, 2000 (sh),

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[18] The gradual decomposition of the catalyst results in a complicated mixture of products that is still under investigation.

1997, and 1976 (br) cm^{-1}, in pentene].

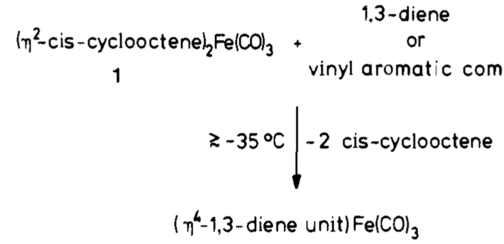
In this connection it should be emphasized that instantaneous deactivation of the catalyst in the samples drawn from reaction mixtures is not a trivial problem. Oxidative decomposition of the catalyst by exposing the samples to the air, analogous to the treatment of samples from photocatalytic runs,[6] cannot be recommended as a reliable, instantly effective method: when a solution of complex **1** is prepared in air-saturated 1-pentene and subsequently left in contact with air we still find extensive isomerization in the range of 500–600 turnovers (Table II, experiments 1–4) before the catalytic activity ceases. 1,3-Dienes have been reported to be very effective in quenching the carbonyliron photocatalyzed 1-pentene isomerization[4] due to the formation of stable (η^4-1,3-diene)Fe(CO)$_3$. In agreement with these previous results we observe merely 5% conversion of 1-pentene (~40 turnovers) if an excess of 1,3-cyclooctadiene is present in a solution of **1** in 1-pentene (Table II, experiment 10). The tricarbonyliron unit is trapped as (η^4-1,3-cyclooctadiene)Fe(CO)$_3$ (**6**) [$\bar{\nu}$(CO) 2045 and 1975 (br) cm^{-1}, in pentene], identified by comparison with an authentic sample.[20] Likewise the quenching is delayed by 30–40 turnovers if 1,3-cyclooctadiene is added sometime after the catalysis is started (Table II, experiments 11 and 12). Phosphines seem to be almost instantaneously effective in quenching the catalytic activity. Addition of triphenylphosphine to a catalytic run (Table II, experiments 17 and 18) results in a mixture of the pentene isomers, which corresponds, within an experimental error of ≲2%, to that expected at the particular moment of the catalysis (cf. Figure 2A). The extent of isomerization is almost negligible if triphenylphosphine is originally present (Table II, experiments 13–16). The infrared spectrum of the solution indicates the formation of an (η^2-olefin)(triphenylphosphine)Fe(CO)$_3$ complex [$\bar{\nu}$(CO) 2015, 1952, and 1923.5 cm^{-1}, in pentene; cf. data reported[19] for (η^2-1-pentene)(PPh$_3$)Fe(CO)$_3$] rather than (PPh$_3$)$_2$Fe(CO)$_3$.

These results led us to use triphenylphosphine as a quenching reagent when samples were drawn during the course of a catalytic run. The samples were mixed with a large excess of the reagent, thus immediately terminating the catalytic reaction at the particular moment (method B, Table I). In the other series of experiments, samples were condensed, via the gas phase, in a cooled trap, leaving the catalyst behind in the reaction mixture (method A, Table I). This technique implicates a certain, albeit small, systematic error as the vapor pressures of the pentene isomers are slightly different and the catalyst concentration increases according to the amount of material distilled off. Nevertheless, the results are comparable with those obtained with method B.

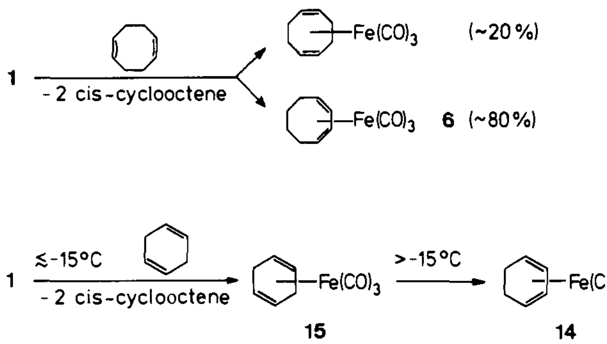
Not unexpectedly, the reactions of *cis*- and *trans*-2-pentene with complex **1** yield the same mixture of pentene isomers. Further investigations, including studies on the higher *n*-alkene homologues and on nonconjugated alkadienes are under way in order to gain further insight into the mechanism, beyond the involvement of the (η^2-alkene)$_2$Fe(CO)$_3$. At the present stage, for lack of experimental evidence, we prefer not to speculate extensively about the particular steps of the catalytic cycle, although we are not in doubt about a (η^3-allyl)metal hydride species as a key intermediate.[14,21-23]

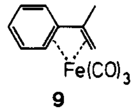
Tricarbonyliron Transfer Reactions. (Benzylideneacetone)Fe(CO)$_3$ has been recommended as a tricarbonyliron transfer reagent[24,25] and was used to prepare, e.g., a variety of (η^4-diene)Fe(CO)$_3$ complexes.[26,27] These reactions require warming to ~60 °C for several hours. By contrast, bis(η^2-*cis*-cyclooctene)tricarbonyliron (**1**) undergoes exchange of *cis*-cyclooctene for other ligands at temperatures below 0 °C; at room temperature the reactions have gone to completion within a few minutes. It was those mild reaction conditions that led us to explore the versatility of complex **1** as a convenient source for the tricarbonyliron unit. As monitored by infrared spectroscopy, the ligand exchange reactions of complex **1** with a variety of acyclic and cyclic dienes, heterodienes, and vinyl-substituted aromatic compounds result in nearly quantitative formation of the corresponding (η^4-1,3-diene unit)Fe(CO)$_3$ complexes (Scheme III). Examples that have been performed on a preparative scale include (η^4-1,3-cyclooctadiene)Fe(CO)$_3$ (**6**),[20] (η^4-1,3-cyclopentadiene)Fe(CO)$_3$ (**7**),[28] (η^4-styrene)Fe(CO)$_3$ (**8**), (η^4-α-methylstyrene)Fe(CO)$_3$ (**9**),[29] (η^4-1,1-diphenylethene)Fe(CO)$_3$ (**10**), (η^4-2-vinylnaphthalene)Fe(CO)$_3$ (**11**),[30] (η^4-*E*-1-naphthyl-2-phenylethene)Fe(CO)$_3$ (**12**), and (2-vinylpyridine)Fe(CO)$_3$ (**13**). Isolated yields are in the range of ≳70%.

Scheme III



Scheme IV





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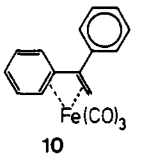

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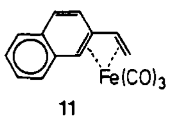

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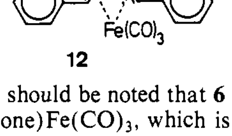
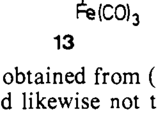


12



13

It should be noted that **6** was not obtained from (benzylideneacetone)Fe(CO)$_3$, which is reported likewise not to react with 1,4-cyclohexadiene and 1,5-cyclooctadiene.[27] In these cases, too, complex **1** serves as a useful Fe(CO)$_3$ source. However, as a result of double bond migration the corresponding (η^4-1,3-cyclodiene)Fe(CO)$_3$ complexes **6** (together with minor amounts of 1,5-cyclooctadiene complex) and **14** are formed (Scheme IV). (η^4-1,4-Cyclohexadiene)Fe(CO)$_3$ (**15**) is observed by infrared spectroscopy at −15 °C as an intermediate product [$\bar{\nu}$(CO) 2030 and ~1958 (br) cm^{-1}, in *n*-hexane] and upon slightly warming undergoes rearrangement[21] to **14**. This facile rearrangement may

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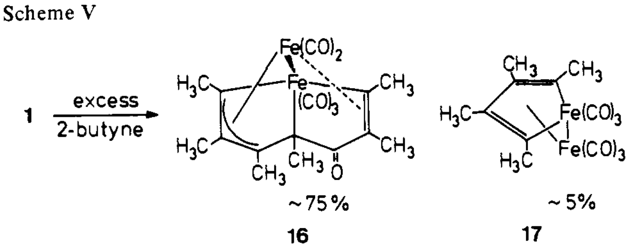
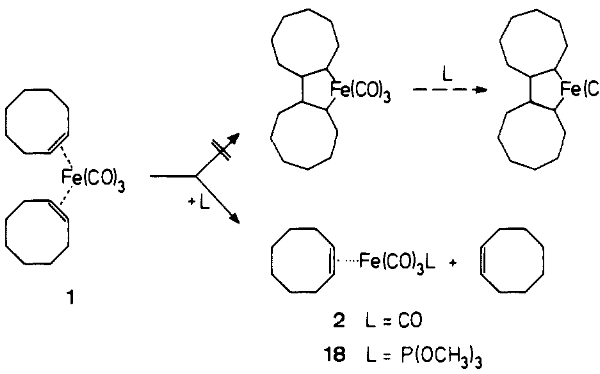
Scheme V



Scheme VI



be of interest in the conversion of specifically substituted nonconjugated cyclohexadienes to the corresponding (η^4-1,3-cyclohexadiene)Fe(CO)$_3$ complexes, which are extensively used[31,32] in organoiron syntheses.

In view of the rich carbonylmetal chemistry with alkynes,[33,34] it seemed worthwhile to ascertain whether complex **1** could furnish a convenient approach to this field, taking advantage of the mild reaction conditions. In fact, the reaction of **1** with 2-butyne, as a first example, is terminated within a few minutes after warming to room temperature, resulting in ~75% yield of the coupling product **16**[35] together with a small amount of **17**[35] (Scheme V). Exploratory experiments indicate that, depending on the complex concentration and other conditions, the reaction can be directed toward other products such as (η^4-tetramethylcyclopentadienone)Fe(CO)$_3$.

Finally, it is of utmost interest to note that in none of the reactions of complex **1** do we find any indication of coupling of the two olefinic ligands along the lines of ferracyclopentane formation, as it has been observed[9,36] or proposed to intermediately occur[37] in the reactions of some olefins with iron carbonyls. The addition, to complex **1**, of an ancillary ligand such as carbon monoxide or trimethyl phosphite (which would be necessary to form a stable complex from the presumed primary cyclization product) does not result in the formation of a ferracyclopentane complex (Scheme VI). Instead, one of the olefinic ligands is displaced, even when an excess of *cis*-cyclooctene is present in order to suppress the dissociation of the bis(olefin) complex (cf. Scheme I). Furthermore, various attempts to bring about the cyclization of **3** and **5** have so far failed, notwithstanding that these compounds are much more stable than **1** with respect to metal–olefin bond dissociation, and although the X-ray structure analyses of **3**[13] and **5**[15] reveal that the bis(η^2-olefin)iron geometry is quite suitable for the ring closure. Hence it appears that, at least with simple olefins, the oxidative cyclization of (η^2-olefin)$_2$Fe(CO)$_3$ complexes is not a facile reaction but is probably a symmetry-forbidden process.[38]

Conclusion

Tricarbonylbis(η^2-*cis*-cyclooctene)iron (**1**) is the first example of an isolated (η^2-olefin)$_2$Fe(CO)$_3$ complex with a simple olefin. The complex is readily accessible in high yield. In the solid state it can be handled at room temperature, but it is highly substitutionally labile in solution. It serves as an excellent, versatile tricarbonyliron transfer reagent promising a wide range of applications. In particular it has been applied in mechanistic studies on the carbonyliron catalyzed isomerization of alkenes, establishing the role of the Fe(CO)$_3$ moiety as the repeating unit in the catalytic cycle. Similar investigations on alkene hydrogenation and hydrosilation are in progress.

Experimental Section

All reactions and manipulations were carried out, unless noted otherwise, under argon and in argon-saturated solvents. Spectra were recorded by using the following instruments: IR, Perkin-Elmer 580; UV-vis, Cary 17; NMR, Bruker WH 270. A modified variable-temperature infrared cell (Beckmann VLT-2K) was used to run infrared spectra in solution at low temperature. Melting points were determined on a Reichert Kofler apparatus. Microanalyses were performed by Dornis & Kolbe, Mülheim a.d. Ruhr. Analytical grade solvents (Merck) and reagents (Merck, Fluka) were used as received. *cis*-Cyclooctene and 1-pentene (Merck z.S.) were purified by means of preparative gas chromatography (Gerstel Labormechanik, AMPG 60 preparative gas chromatograph): *cis*-cyclooctene (20% Carbowax 20 M/Chromosorb P 60–80 mesh, 6 m, o.d. 40 mm, 650 mL min^{-1} N$_2$, 150 °C) was 97–99% (cyclooctane, 1–3%; 1,3- and 1,5-cyclooctadiene, <0.01%); 1-pentene (20% SE 30/Chromosorb P 60–80 mesh, 6 m, o.d. 40 mm, 700 mL min^{-1} N$_2$, 50 °C) was $\gtrsim$99.5% (2-methyl-1-butene, <0.4%; 2-methyl-2-butene, <0.1%; pentadienes, <0.005%).

Tricarbonylbis(η^2-*cis*-cyclooctene)iron (**1**). *cis*-Cyclooctene (55 g, 0.50 mol) and pentacarbonyliron (4.90 g, 0.025 mol) in *n*-hexane (400 mL) are irradiated at -40 °C in an immersion lamp apparatus (inner and outer cooling jacket, solidex glass, $\lambda \gtrsim 280$ nm; Philips HPK 125-W mercury lamp) while the solution is purged with argon in order to remove liberated carbon monoxide. A second portion of pentacarbonyliron (4.90 g, 0.025 mol) is added after 3–5 h, according to the extent of conversion as monitored by infrared spectroscopy. Irradiation is continued (~24 h) until pentacarbonyliron and intermediately formed tetracarbonyl(η^2-*cis*-cyclooctene)iron (**2**) have largely disappeared. The solution is concentrated in vacuo at -20 °C to ~200 mL, filtered if necessary, and cooled to -80 °C whereupon complex **1** precipitates. Inverse filtration at -80 °C and drying under vacuum at $\lesssim$0 °C yields yellow crystals of **1**, 10.15 g (56.3%), mp 54–57 °C dec. Anal. Calcd for $C_{19}H_{28}FeO_3$: C, 63.34; H, 7.83; Fe, 15.50. Found: C, 63.38; H, 7.64; Fe, 15.48. After evaporation of the mother liquor under vacuum at $\lesssim$-10 °C a second crop of **1** (5.86 g, 32.5%) is obtained which is contaminated with a trace amount of **2**; recrystallization from hexane/*cis*-cyclooctene (9/1) yields pure **1**.

Isomerization of 1-Pentene. (A) (Table I, Experiments 1, 2, 4, 7–9, and 11). Complex **1** (18–36 mg, 0.05–0.1 mmol) is placed in a Schlenk tube and cooled to -78 °C. The appropriate amount of precooled 1-pentene, deoxygenated by three freeze–pump–thaw cycles, is added. The Schlenk tube is transferred into a bath held at constant temperature (-20, 0, and +20 °C, respectively). While the solution is stirred in the dark, samples of the resulting mixture of pentene isomers are drawn via the gas phase by connecting evacuated traps, cooled to liquid nitrogen temperature, with the Schlenk tube. Ten to twelve samples, each ~0.1 mL, are condensed in the cooled traps during the course of a catalytic run and analyzed by gas chromatography (Varian 1400; capillary column, 64 m, OV1, film thickness 1 µm, 50 °C, 0.6 atm of N$_2$, 0.1 µL, FID).

(B) (Table I, Experiments 3, 5, 6, 10, and 12–16). The reaction mixture is prepared as described above. A precooled pipette is used to draw 0.1-mL samples from the solution. Instantaneous deactivation of the catalyst is achieved by mixing the samples with an excess of triphenylphosphine (10–20 mg). The volatiles are stripped off under vacuum, condensed in a cooled trap, and analyzed by gas chromatography as described above.

Isomerization of 1-Pentene in the Presence of Quenching Agents (Table II). The reaction mixtures, prepared as described above and kept at -78 °C, are saturated with air (experiments 1–4) and carbon monoxide

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(experiments 6–9), respectively, or mixed with an excess of 1,3-cyclooctadiene (experiment 10) and triphenylphosphine (experiments 13–16), respectively, before or after (experiments 11, 12, 17, and 18) the catalysis is started by placing the Schlenk tube into a bath held at the desired temperature. After 1 h the volatiles are stripped off and analyzed as described above.

Reactions of Complex 1 with Dienes or Vinyl-Substituted Aromatic Compounds. General Procedure. Complex 1 and the respective organic compound (molar ratio 1:2) are dissolved at <−40 °C in *n*-hexane or *n*-pentane (10 mL/1 mmol of 1) that may contain 2–5% *cis*-cyclooctene. The solution is stirred while being allowed to warm up to 0 °C or to room temperature for 10–30 min, concentrated and filtered if necessary, and then cooled to −78 °C in order to crystallize the resulting (η^4-1,3-diene unit)Fe(CO)$_3$ product. Products that do not crystallize directly, due to their high solubility, are purified, after evaporation of the reaction solution to dryness, by column chromatography using silica gel and *n*-pentane eluent.

(**a**) **(η-^{4}-1,3-Cyclooctadiene)Fe(CO)$_3$ (6)**: yield 79.8%, yellow crystals, mp 32–34 °C; identified by comparison with an authentic sample;[20] ^{1}H NMR, δ 4.75 (2 H), 3.0 (2 H), 1.85 (4 H), 1.1 (4 H), in toluene-d_8; mass spectrum, *m/e* 248 (M$^+$, w), 220, 192, 164, 162, 136, 134, etc.; IR, $\bar{\nu}$(CO) 2045.5, 1978 :5, 1974 cm^{-1}, in *n*-hexane.

(**b**) **(η^4-1,3-Cyclopentadiene)Fe(CO)$_3$ (7)**:[28] yield 80%, yellow oil; ^{1}H NMR, δ 2.01 (dm, 12 Hz), 2.43 (dm, 12 Hz), 2.51 (m, 2 H), 5.08 (m, 2 H), in toluene-d_8; mass spectrum, *m/e* 206 (M$^+$), 178, 150, 122, etc.; IR, $\bar{\nu}$(CO) 2048.5, 1980.5, 1973 cm^{-1}, in *n*-hexane.

(**c**) **(η^4-Styrene)Fe(CO)$_3$ (8)**: yield 90.2%, orange-yellow crystals, mp 60–62 °C dec, recrystallized from *n*-pentane/styrene (19/1) at −78 °C. Anal. Calcd for $C_{11}H_8FeO_3$: C, 54.14; H, 3.30; Fe, 22.89. Found: C, 53.86; H, 3.37; Fe, 22.99. ^{1}H NMR, δ −0.18 (dd, 2.2 Hz, 8.8 Hz), 1.41 (dd, 2.2 Hz, 6.6 Hz), 2.70 (d, 5.5 Hz), 5.50 (dd, ~9 Hz, ~7 Hz), ~6.6 (m, 3 H), 6.90 (d, 8 Hz), in toluene-d_8; mass spectrum, *m/e* 244 (M$^+$), 216, 188, 160, 104, etc.; IR, $\bar{\nu}$(CO) 2045.5, 1982.5, 1972 cm^{-1}, in *n*-hexane; UV–vis, 440 (ϵ 485 L mol^{-1} cm^{-1}), 337 (3150), 243 nm (18 300), in *n*-hexane.

(**d**) **(η^4-α-Methylstyrene)Fe(CO)$_3$ (9)**:[29] yield 84.5%, red-purple crystals, mp 55–57 °C dec, recrystallized from *n*-hexane/α-methylstyrene (49/1). Anal. Calcd for $C_{12}H_{10}FeO_3$: C, 55.85; H, 3.91; Fe, 21.64; M_r 258.1. Found: C, 55.70; H, 3.88; Fe, 21.25; M_r 260 (cryoscopic in benzene). ^{1}H NMR, δ −0.15 (d, 2.2 Hz), 1.47 (d, 2.2 Hz), 2.14 (s, 3 H), 2.45 (d, ~5 Hz), ~6.6 (m, 3 H), 7.12 (d, ~8 Hz), in toluene-d_8; ^{13}C NMR, δ 20.1 [q, ^1J(CH) = 126 Hz], 40.3 (t, 154 Hz), 66.3 (d, 161 Hz), 88.0 (s) 104 (s), 124.0 (d, 160 Hz), 124.6 (d, 160 Hz), 128.6 (d, 160 Hz), 137.1 (d, 160 Hz), 213.3 (s), in toluene-d_8, ~35 °C; mass spectrum, *m/e* 258 (M$^+$), 230, 202, 174, etc.; IR, $\bar{\nu}$(CO) 2043, 1980, 1968 cm^{-1}, in *n*-hexane; UV–vis, 446 (ϵ 510 L mol^{-1} cm^{-1}), 338 (3500), 244 nm (18 800), in *n*-hexane.

(**e**) **(η^4-1,1-Diphenylethene)Fe(CO)$_3$ (10)**: yield 61.7%, red-purple crystals, mp 86–88 °C, recrystallized from *n*-pentane. Anal. Calcd for $C_{17}H_{12}FeO_3$: C, 63.78; H, 3.78; Fe, 17.45. Found: C, 64.20; H, 3.70; Fe, 17.25. ^{1}H NMR, δ 0.14 (d, 2 Hz), 1.85 (d, 2 Hz), 2.63 (m), ~6.6 (m, 3 H), ~7.1 (m, 3 H), 7.36 (m), 7.53 (m, 2 H), in toluene-d_8; IR $\bar{\nu}$(CO) 2045.5, 1980.5, 1975 cm^{-1}, in *n*-hexane; UV–vis, 445 (ϵ 690 L mol^{-1} cm^{-1}), 341 (3380), 236 nm (sh, 23 100), in *n*-hexane.

(**f**) **(η^4-2-Vinylnaphthalene)Fe(CO)$_3$ (11)**:[30] yield 80%, red-purple crystals, mp 76–78 °C, recrystallized from *n*-pentane. Anal. Calcd for $C_{15}H_{10}FeO_3$: C, 61.26; H, 3.43; Fe, 18.99. Found: C, 61.12; H, 3.64; Fe, 18.86. ^{1}H NMR, δ −0.11 (dd, 2.5 Hz, 9 Hz), 1.36 (dd, 2.5 Hz, 7 Hz), 2.85 (s), 5.27 (dd, 7 Hz, 9 Hz), 6.70 (d, 9 Hz), 6.78 (d, 9 Hz), ~7.0 (m, 2 H), 7.12 (m), 7.36 (m), in toluene-d_8; mass spectrum, *m/e* 294 (M$^+$), 266, 238, 210, 154, etc.; IR, $\bar{\nu}$(CO) 2047, 1986, 1976.5 cm^{-1}, in *n*-hexane; UV–vis, 349 (ϵ 3180 L mol^{-1} cm^{-1}), 263 nm (22 300), in *n*-hexane.

(**g**) **(η^4-2-Styrylnaphthalene)Fe(CO)$_3$ (12)**: yield 85%, red-purple crystals, mp 138–141 °C dec, recrystallized from *n*-hexane. Anal. Calcd for $C_{21}H_{14}FeO_3$: C, 68.14; H, 3.81; Fe, 15.09. Found: C, 67.96; H, 4.11; Fe, 15.03. ^{1}H NMR, δ 1.79 (d, 9 Hz), 3.23 (s), 5.88 (d, 9 Hz), 6.86 (2 H), ~6.93 (m), ~7.07 (m, 4 H), ~7.16 (m, 3 H), 7.47 (m), in toluene-d_8; mass spectrum, *m/e* 370 (M$^+$), 342, 314, 286, etc.; IR, $\bar{\nu}$(CO) 2044, 1983, 1977 cm^{-1}, in *n*-hexane.

(**h**) **(2-Vinylpyridine)Fe(CO)$_3$ (13)**: yield 70.4%, yellow-brown crystals, recrystallized from *n*-pentane. Anal. Calcd for $C_{10}H_7FeNO_3$: C, 49.02; H, 2.88; Fe, 22.79; N, 5.72. Found: C, 48.76; H, 3.20; Fe, 22.82; N, 5.68. ^{1}H NMR, δ 2.47 (d, 6.5 Hz), 3.23 (d, 8 Hz), 3.65 (dd, 6.5 Hz, 8 Hz), 5.76 (d, 8 Hz), 5.86 (m), 6.41 (m), 6.52 (d, 5 Hz), in toluene-d_8; mass spectrum, *m/e* 245 (M$^+$), 217, 189, 161, etc.; IR, $\bar{\nu}$(CO) 2037.5, 1964, 1956.5 cm^{-1}, in *n*-hexane.

(**i**) **1,4-Cyclohexadiene Yields (η^4-1,3-Cyclohexadiene)Fe(CO)$_3$ (14)**:[39] yield 78.3%, yellow oil; ^{1}H NMR, δ 1.35 (m, 4 H), 2.82 (m, 2 H), 4.76 (2 H), in toluene-d_8; mass spectrum *m/e* 220 (M$^+$), 192, 164, 162, 134, 78, etc.; IR, $\bar{\nu}$(CO) 2048.5, 1980, 1975 cm^{-1}, in *n*-hexane.

Reaction of Complex 1 with 1,5-Cyclooctadiene. 1,5-Cyclooctadiene (1.06 g, 9.8 mmol) is added to a cold solution of complex 1 (0.177 g, 0.49 mmol) in *cis*-cyclooctene (8.8 mL). The solution is allowed to warm up to 0 °C and subsequently diluted with *n*-hexane to 100 mL. The infrared spectrum shows the formation of (η^4-1,5-cyclooctadiene)Fe(CO)$_3$[20] and (η^4-1,3-cyclooctadiene)Fe(CO)$_3$ (**6**),[20] which are quantitatively determined by using the authentic materials[20] as internal standards: 79.9% **6** and 20.1% (1,5-COD)Fe(CO)$_3$.

Reaction of Complex 1 with 2-Butyne. Complex 1 (1.80 g, 5 mmol) is added at <−40 °C to a solution of 2-butyne (2.70 g, 50 mmol) and *cis*-cyclooctene (1.3 mL) in *n*-hexane (50 mL). The solution is allowed to warm up to room temperature, filtered, and evaporated under vacuum. Column chromatography on silica gel yields $[C_4(CH_3)_4]Fe_2(CO)_6$ (**17**,[35] eluted with *n*-pentane; 0.05 g, 5%, yellow crystals. Anal. Calcd for $C_{14}H_{12}Fe_2O_6$: C, 43.34; H, 3.12; Fe, 28.79. Found: C, 43.36; H, 2.94; Fe, 28.81. ^{1}H NMR, δ 1.40 (s, 6 H), 2.01 (s, 6 H), in benzene-d_6; mass spectrum, *m/e* 388 (M$^+$), 360, 332, 304, 276, 248, 220, etc.; IR, $\bar{\nu}$(CO) 2063, 2024, 1989.5, 1983, 1939 cm^{-1}, in *n*-hexane) and $[C_6(CH_3)_6CO]Fe_2(CO)_5$ (**16**,[35] eluted with diethyl ether/pentane 1/1; 0.84 g, 76%, red crystals. Anal. Calcd for $C_{18}H_{18}Fe_2O_6$: C, 48.91; H, 4.10; Fe, 25.27. Found: C, 48.92; H, 4.28; Fe, 25.27. ^{1}H NMR, δ 0.90 (s, 3 H), 1.44 (s, 3 H), 1.48 (s, 3 H), 1.96 (s, 3 H), 2.84 (s, 3 H), 2.88 (s, 3 H), in benzene-d_6; mass spectrum, *m/e* 442 (M$^+$), 414, 386, 358, 330, 302, etc.; IR, $\bar{\nu}$(CO) 2064.5, 2017, 2010, 1998, 1962.5, 1675 cm^{-1}, in *n*-hexane).

Reaction of Complex 1 with Trimethyl Phosphite. Complex 1 (1.44 g, 4 mmol) is dissolved at <−50 °C in a solution of trimethyl phosphite (0.55 g, 4.4 mmol) and *cis*-cyclooctene (2 mL) in *n*-hexane (40 mL). The solution is allowed to warm up to room temperature, filtered, and cooled to −78 °C whereupon yellow crystals of (η^2-*cis*-cyclooctene)(trimethyl phosphite)Fe(CO)$_3$ (**18**) precipitate (yield 1.26 g, 84%), mp 50–52 °C dec, recrystallized from *n*-hexane. Anal. Calcd for $C_{14}H_{23}FeO_6P$: C, 44.94; H, 6.20; Fe, 14.93; P, 8.29. Found: C, 45.00; H, 6.14; Fe, 15.21; P, 8.38. Mass spectrum, *m/e* 374 (M$^+$), 346, 343, 318,, 304, 290, 286, 264, 236, 208, 180, etc.; IR, $\bar{\nu}$(CO) 2020, ~1960 (sh), 1955.5, 1926 cm^{-1}, in *n*-hexane.

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Registry No. 1, 88657-71-0; **6**, 33270-50-7; **7**, 40729-83-7; **8**, 75010-53-6; **9**, 33363-82-5; **10**, 88657-72-1; **11**, 12130-14-2; **12**, 88657-73-2; **13**, 88657-74-3; **14**, 12152-72-6; **16**, 70893-60-6; **17**, 12245-44-2; **18**, 88657-75-4; Fe(CO)$_5$, 13463-40-6; (η^4-1,5-cyclooctadiene)Fe(CO)$_3$, 12093-20-8; 1-pentene, 109-67-1; *trans*-2-pentene, 646-04-8; *cis*-3-pentene, 627-20-3.

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