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THE REACTION OF BENZYLIDENEACETONEIRON TRICARBONYL WITH DIENES; MEASUREMENT OF RELATIVE REACTIVITIES USING COMPETITION EXPERIMENTS *

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Summary

Benzylideneacetoneiron tricarbonyl (BDAFe(CO)$_3$) reacts with acyclic conjugated dienes to give good to moderate yields of dieneiron tricarbonyl complexes. Competition experiments demonstrate that there is a large difference in relative reactivities among a series of acyclic and cyclic dienes. Certain cyclic and nonconjugated dienes are essentially inert. These differences are rationalized primarily on the basis of the conformation of the diene. Results of the reaction of cycloheptatriene with BDAFe(CO)$_3$/BDA mixtures support a mechanism of BDAFe(CO)$_3$ selectivity previously postulated.

Introduction

Benzylideneacetoneiron tricarbonyl (BDAFe(CO)$_3$) was first used as an iron tricarbonyl transfer reagent by Lewis and Johnson [1,2]. They showed, for example, that BDAFe(CO)$_3$ reacts thermally in toluene with 8,8'-diphenylheptafulvene [1] and cycloheptadiene [2] to form the corresponding dieneiron tricarbonyl complexes in 70 and 78% yield, respectively. Since these initial reports, we have shown that this exchange reaction is highly selective in that BDAFe(CO)$_3$ traps, as iron tricarbonyl complexes, bicyclic diene tautomers present in low concentrations in 1,3,5-cyclooctatriene-bicyclo[4.2.0]octadiene type equilibria [3—7]. For example, thermal reaction of BDAFe(CO)$_3$ with cyclooctatriene, bicyclo[6.2.0]deca-2,4,6-triene, and *syn*-1-methylbicyclo-[6.1.0]nona-2,4,6-triene results in trapping of the diene tautomers and formation of complexes I, II, and III, respectively, in good yields [3,4,7]. Reaction

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* Reported in part at the New York Academy of Sciences Meeting on "The Place of Transition Metals in Organic Synthesis", New York, Nov. 10—12, 1976 [7].

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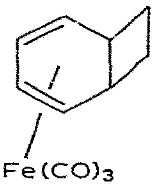

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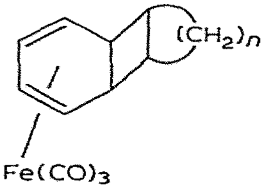

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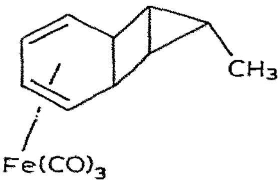
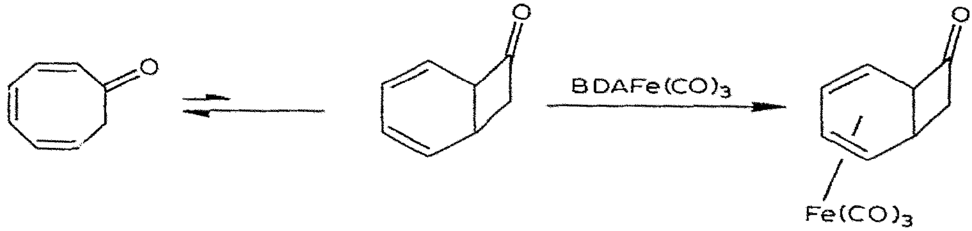


(III)

of the $Fe(CO)_3$ transfer reagent with bicyclo[6.1.0]nona-2,4,6-triene results in formation of tricyclic complex IV along with other iron complexes arising from trapping of the thermal rearrangement products of the starting triene [4,7]. Work in these laboratories [5,6] and by Lewis and Johnson [8] has shown that bicyclo[4.2.0]octa-2,4-dienoneiron tricarbonyl can be prepared from the thermal reaction of $BDAFe(CO)_3$ with cyclooctatrienone. Oxidative cleavage of iron tricarbonyl complexes II—V proves to be a synthetically useful route to isolation of pure samples of these high energy diene valence tautomers [3—7]. Johnson and Lewis have also used $BDAFe(CO)_3$ to synthesize acetylergosteroliron tricarbonyl for the purpose of protecting the diene unit in further synthetic transformations [9].



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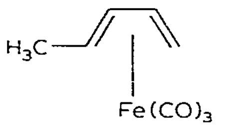
Although $BDAFe(CO)_3$ has been clearly demonstrated to have synthetic utility as a mild, highly selective reagent for the transfer of the iron tricarbonyl moiety to dienes, it is interesting to note that in all reactions reported, the diene is either a cyclohexadiene derivative or a cyclic system containing a nearly planar diene unit. With these factors in mind, the goals of the present work were to (1) survey reactions of $BDAFe(CO)_3$ with a variety of acyclic and cyclic dienes in order to assess further the synthetic utility of this reagent and (2) gain further insight into the selectivity of $BDAFe(CO)_3$ through competition studies of the various cyclic and acyclic diene substrates with a standard diene such as cyclohexadiene.

Results and discussion

Reactions with acyclic dienes

Four acyclic dienes, *trans*-1,3-pentadiene, *trans,trans*-2,4-hexadiene, 2,3-dimethylbutadiene, and *trans,trans*-2,4-hexadienal were treated with $BDAFe(CO)_3$ and moderate to good yields of the corresponding dieneiron tricarbonyl complexes VI—IX were realized (Table 1). The product complexes were purified by column chromatography and identified by ^{1}H NMR. From the results obtained with these four dienes, it can be concluded that BDAFe(CO)$_3$ is a synthetically useful reagent for the trapping of acyclic dienes and conversion to iron tricarbonyl complexes.



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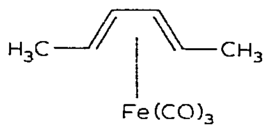

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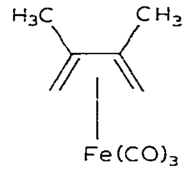

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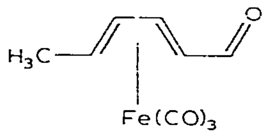

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Reactions with cyclic dienes

As noted above, BDAFe(CO)$_3$ reacts selectively with planar 1,3-cyclohexadiene derivatives to form dieneiron tricarbonyl complexes. From information obtained through kinetic studies with cyclooctatriene and cyclohexadiene we have proposed the transfer mechanism to be that shown in Scheme 1 [4,7]. Presumably, once the reaction with a bicyclic (or tricyclic) isomer containing an essentially planar diene unit has reached the stage of intermediate X, loss of benzylideneacetone (BDA) and full complexation of the diene unit to form the Fe(CO)$_3$ complex takes place rapidly. In contrast, in the case of the tub-shaped cyclooctatriene derivatives, a significant energy barrier for the conversion of XI to product exists since the *dihapto*-bound, tub-shaped triene must very substantially distort to chelate the second double bond. Thus, in this case the reaction is reversible by coordination of free BDA with XI to return to X which then may return to BDAFe(CO)$_3$ and free triene. The reversible nature of the X to XI conversion and the overall higher free energy of activation for the conversion of XI to product in the case of conjugated dienes which are twisted out of a planar configuration very likely plays the major role in governing the high selectivity of BDAFe(CO)$_3$ [4,7].

This supposition is qualitatively confirmed by the lack of reactivity of various nonplanar cyclic dienes with BDAFe(CO)$_3$ (Table 2). Reaction of 1,3- and 1,5-cyclooctadiene with BDAFe(CO)$_3$ under typical conditions (48 h, 60°C) in benzene gave no dieneiron tricarbonyl complexes and led only to

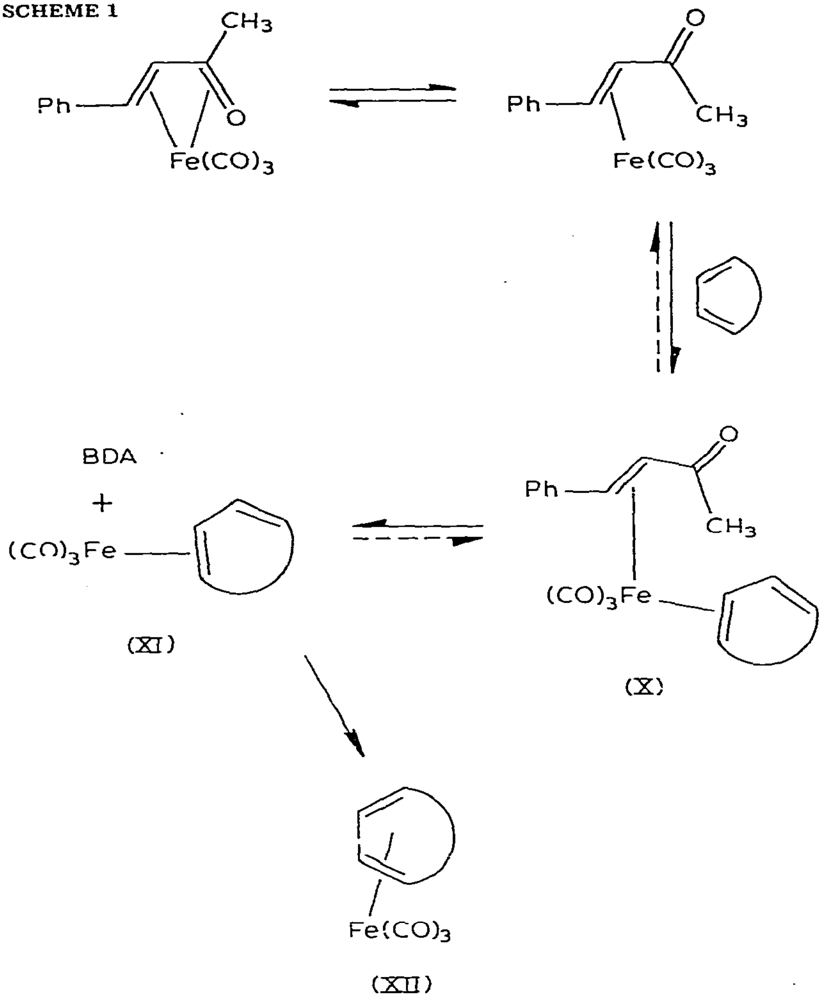
TABLE 1

REACTION OF BDAFe(CO)$_3$ WITH ACYCLIC DIENES [a]

Diene	Diene/BDAFe(CO)$_3$ (molar ratio)	Isolated yield (%) of diene complex [b]
trans,trans-2,4-Hexadiene	1/1	54
trans-1,3-Pentadiene	5/1	84
2,3-Dimethylbutadiene	2/1	72
trans,trans-2,4-Hexadienal	1/1	96

[a] All reactions carried out in benzene at 55—60°C for 24—72 hours. [b] Based on BDAFe(CO)$_3$.

SCHEME 1



recovery of unisomerized starting diene and BDAFe(CO)$_3$ (see Table 2). Both the 1,3- and 1,5-dieneiron tricarbonyl complexes can be prepared photochemically from Fe(CO)$_5$ and should be isolable under the reaction conditions

TABLE 2

REACTION OF BDAFe(CO)$_3$ WITH CYCLIC DIENES [a]

Diene	Diene/BDAFe(CO)$_3$ (molar ratio)	Isolated yield (%) of diene complex [b]
1,3-Cyclohexadiene	1/1	>95
1,4-Cyclohexadiene	4/1	0
Norbornadiene	3/1	9
1,3-Cyclooctadiene	1.2/1	0
1,5-Cyclooctadiene	1.3/1	0
Cycloheptatriene	1/1	50
Cyclooctatetraene	1/1.1	74

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[a] All reactions carried out in benzene at 55—60°C for 24—72 h. [b] Based on BDAFe(CO)$_3$.

[10]. The 1,5-cyclooctadieneiron tricarbonyl has been shown to thermally decompose to 1,5-cyclooctadiene-bis(iron tetracarbonyl) [10], but this stable complex was not recovered from any reaction mixture. Therefore, the non-planar, tub-shaped 1,3- and 1,5-dienes are completely unreactive toward BDAFe$(CO)_3$ and support the above conformational argument. Similarly, 1,4-cyclohexadiene also reacts with pure iron carbonyl reagents thermally or photolytically to give good yields of 1,3-cyclohexadieneiron tricarbonyl [11]. (These latter rearrangements likely proceed through a metal hydride intermediate). However, as in the 1,5-cyclooctadiene case, 1,4-cyclohexadiene does not undergo reaction of any kind, either isomerization or formation of a complex, when heated with BDAFe$(CO)_3$ (see Table 2). Reaction of norbornadiene, another 1,4-diene, leads to a very low yield of the known diene complex [12]. In this case, the diene unit is constrained in a somewhat better, although not ideal, geometry for chelation. Cycloheptatriene and cyclooctatetraene react with BDAFe$(CO)_3$ to form the corresponding stable 1,3-dieneiron tricarbonyl complexes (Table 2). These reactions will be discussed in more detail below.

Competition experiments

Further insight into the selectivity of the BDAFe$(CO)_3$ reagent was obtained through competition studies in which mixtures of cyclohexadiene and a second diene were allowed to compete for small amounts of BDAFe$(CO)_3$. By analyzing the ratios of the two diene complexes produced, a reasonable estimate of the relative reactivities of the dienes could be made. Results are summarized in Table 3. A considerable range in relative reactivities was noted. None of the dienes studied was more reactive than the reference diene, 1,3-cyclohexadiene. The difference of ca. 35 in the relative reactivities of 2,3-dimethylbutadiene and *trans,trans*-2,4-hexadiene may be due to the fact that the hexadiene prefers a planar *s-trans* configuration whereas the ground-state conformation of the 2,3-dimethylbutadiene is likely to be closer to the required planar *s-cis* geometry required for binding to iron. The higher reactivity of the *trans,trans*-hexadienal

TABLE 3

COMPETITION REACTIONS OF VARIOUS DIENES WITH 1,3-CYCLOHEXADIENE (CHD)

Diene	Molar ratios Diene/CHD/BDAFe$(CO)_3$	T (°C)	Reactivity ratio [a] Diene/CHD
2,3-Dimethylbutadiene	20/6/1	60	0.25
trans,trans-2,4-Hexadiene	40/6/1	59	0.0072
trans,trans-2,4-Hexadienal	40/6/1	56	0.14
	12/6/1	60	0.13
Cyclooctatetraene (COT)	40/6/1	58	0.06
	40/6/1	57	0.07
	CHT/COT/BDAFe$(CO)_3$		
Cycloheptatriene (CHT)	12/6/1	60	ca. 0.003 [b]

[a] Corrected for the difference in initial ratios of Diene/CHD. [b] Corrected assuming a CHD/COT reactivity ratio of 16/1.

is probably in part related to the greater backbonding ability of this diene and the resulting increase in stability of the dieneiron tricarbonyl complex.

The conformational argument discussed earlier is further supported here by the low reactivity of tub-shaped cycloheptatriene with BDAFe(CO)$_3$ compared to cyclohexadiene. The fact that the cycloheptatriene complex is formed is probably because conformational restraints are not as pronounced in the cyclic seven-membered triene as compared to, for example, the inert eight-membered 1,3-cyclooctadiene.

One surprising observation was the relatively high reactivity of cyclooctatetraene, which is 21 times more reactive than cycloheptatriene. Just as in the case of cyclooctatriene and the cyclooctadienes, cyclooctatetraene exists in a tub conformation. The half-life of reaction of cyclooctatetraene (0.34 molar) with BDAFe(CO)$_3$ (0.3 molar) at 60°C in benzene was found to be 85 min. This is faster than the ring closure of cyclooctatetraene to its bicyclic triene isomer at this temperature [13], and therefore no bicyclic dieneiron tricarbonyl complex is formed. Although cyclooctatetraene possesses several unique structural features in comparison with cycloheptatriene and cyclooctatriene, the precise reason for its high reactivity relative to these systems cannot be specified at this time.

Reaction of cycloheptatriene with BDAFe(CO)$_3$/BDA mixture

As noted earlier, it was felt that an important feature of the reaction of BDAFe(CO)$_3$ with dienes was the loss of BDA to form the 16 electron intermediate, XI [4,7]. It was proposed that for nonplanar diene units (i.e. in cyclooctatriene, cyclooctadiene, etc.) a significant energy barrier exists for the chelation of the second double bond and conversion of XI to product. This feature apparently gives rise to the high selectivity of the BDAFe(CO)$_3$ reagent. A confirmation of the reversible nature of the reaction (XI → X) would be provided by demonstrating that the rate of formation of product is suppressed by addition of free BDA. Since cycloheptatriene is nonplanar and reacts slowly with BDAFe(CO)$_3$ to give cycloheptatrieneiron tricarbonyl, this system represented an attractive case to examine for rate suppression by free BDA.

Cycloheptatriene was treated with BDAFe(CO)$_3$ in degassed benzene for 24 h at 67°C in the presence of varying amounts of BDA as shown in Table 4. That the presence of free BDA does affect the reaction rate is indicated by the

TABLE 4

YIELD OF CYCLOHEPTATRIENEIRON TRICARBONYL FROM THE REACTION OF CYCLOHEPTATRIENE WITH BDAFe(CO)$_3$ AS A FUNCTION OF ADDED FREE BDA [a]

Molar ratios CHT/BDAFe(CO)$_3$/BDA	Yield (%) CHTFe(CO)$_3$
1.5/1/0	50
1.5/1/2	20
1.5/1/5	13
1.5/1/10	<1

[a] All reactions carried out for 24 h at 67°C.

corresponding lower yields of cycloheptatrieneiron tricarbonyl isolated after the standard 24 h reaction period with the addition of increasing amounts of BDA. Apparently with the addition of free BDA, reversible reaction of XI back to X via BDA trapping competes with collapse of XI to the final iron tricarbonyl complex. Thus these fidings are consistent with and lend support to the reaction mechanism proposed earlier [4,7] and shown in Scheme 1.

Experimental

General

All ^{1}H NMR spectra were recorded on a Varian XL-100 FT or a Jeol-C60HL NMR spectrometer. Infrared spectra were recorded on a Perkin-Elmer 421 spectrophotometer. All NMR samples of iron complexes were prepared under nitrogen using degassed solvents. Reactions were performed under dry, oxygen-free nitrogen gas. Nitrogen was dried by passing through concentrated H_2SO_4 followed by KOH. Traces of oxygen were removed by passage through a heated BASF catalyst-R3-11 column.

Preparation of benzylideneacetoneiron tricarbonyl

Benzylideneacetone (4.0 g, 27 mmol) and $Fe(CO)_5$ (10 ml, 75 mmol) were photolyzed in a Pyrex well in benzene (150 ml) for 8 h using a 450 W Hanovia lamp. The dark red solution was filtered, concentrated under reduced pressure, and then heated in benzene for several hours at 60° C until the 2095 cm^{-1} band in the infrared spectrum of benzylideneacetoneiron tetracarbonyl disappeared. The solution was refiltered, concentrated, and then chromatographed on silica gel eluting with 5% ethyl acetate in benzene. The material was collected, concentrated, and rechromatographed to give dark red crystals, 4.6 g (m.p. 88—89° C), identical to the material reported by Lewis [1,2]. The overall yield was 60%. ^{1}H NMR (C_6D_6): δ 2.6 (s, 3H, CH_3), 3.03 (d, 1H), 5.35 (d, 1H), 6.88 ppm (m, C_6H_5).

Reaction of dienes with BDAFe(CO)$_3$

All reactions were carried out in degassed benzene at 55—60° C for 24—72 h under a nitrogen atmosphere. In general, after completion of the reaction, the cooled benzene solution was concentrated in vacuo and the resulting oil was chromatographed on a short alumina column (basic, III) eluting with distilled, degassed hexane. The hydrocarbon complexes always eluted rapidly and after removal of the hexane eluant gave pure complex. In each case the dieneiron tricarbonyl complex was identified by its ^{1}H NMR spectrum.

trans,trans-2,4-Hexadieneiron tricarbonyl. BDAFe$(CO)_3$ (1.0 g, 3.5 mmol) and *trans,trans*-2,4-hexadiene (0.22 g, 3 mmol) were heated in benzene at 60° C for 72 h. Purification as above gave 359 mg (54% yield) of the *trans,trans*-2,4-hexadieneiron tricarbonyl complex as a yellow oil. The ^{1}H NMR in $CDCl_3$ was identical to that previously reported for this compound [14].

trans-1,3-Pentadieneiron tricarbonyl. BDAFe$(CO)_3$ (0.125 g, 4 mmol) and *trans*-1,3-pentadiene were heated at 54° C in benzene for 72 h. Work up as above gave 0.07 g (84%) of the pale yellow *trans*-1,3-pentadieneiron tricarbonyl as an oil. The ^{1}H NMR of the yellow oil in $CDCl_3$ was identical to that previously reported for this complex [14].

2,3-Dimethylbutadieneiron tricarbonyl. BDAFe$(CO)_3$ (0.150 g, 0.5 mmol) and 2,3-dimethylbutadiene (0.082 g, 1 mmol) were heated in benzene for 48 h at 57° C. Work up led to isolation of 0.080 g (72% yield based on BDAFe$(CO)_3$) of 2,3-dimethylbutadieneiron tricarbonyl as a pale yellow oil, identified by its ^{1}H NMR spectrum.

trans,trans-2,4-Hexadienaliron tricarbonyl. BDAFe$(CO)_3$ (0.5 g, 1.7 mmol) and *trans,trans*-2,4-hexadienal (0.19 g, 2 mmol) were heated in benzene at 60° C for 72 h. The cooled solution was filtered, concentrated and the residue was passed down a short alumina column (III). Elution with benzene afforded a yellow band which contained 650 mg of material which by ^{1}H NMR was a mixture of free BDA, *trans,trans*-2,4-hexadienal and *trans,trans*-2,4-hexadienaliron tricarbonyl. The molar amounts of these compounds were calculated by integration of the aldehydic proton signals of the free aldehyde (d, δ 9.53 ppm) the complexed aldehyde (d, δ 9.24 ppm) [15], and the methyl singlet (δ 2.5 ppm) for free BDA. From this measurement it was calculated that 400 mg of the mixture was *trans,trans*-2,4-hexadienaliron tricarbonyl (96% yield).

1,3-Cyclohexadieneiron tricarbonyl. The synthesis of 1,3-cyclohexadieneiron tricarbonyl using BDAFe$(CO)_3$ has been reported [4].

Attempted reaction of 1,4-cyclohexadiene with BDAFe(CO)$_3$. Reaction of 1,4-cyclohexadiene (0.24 g, 3 mmol) with BDAFe$(CO)_3$ (0.2 g, 0.7 mmol) for 72 h at 58° C in benzene followed by the usual work up did not furnish any cyclohexadieneiron tricarbonyl complex and led to recovery of only a small amount of BDAFe$(CO)_3$.

Attempted reaction of 1,3- and 1,5-cyclooctadiene with BDAFe(CO)$_3$. In both cases a 2/1 excess of diene was allowed to react with BDAFe$(CO)_3$ (1.4 mmol) of diene and 0.7 mmol of BDAFe$(CO)_3$ in 50 ml of benzene) for 96 h at 60° C. Only BDA, BDAFe$(CO)_3$ and free diene ligand were recovered from both reactions.

Norbornadieneiron tricarbonyl. Norbornadiene (0.193 g, 2.1 mmol) and BDAFe$(CO)_3$ (0.2 g, 0.7 mmol) were stirred for 72 h at 60° C in benzene. Work up as above gave 15 mg of a pale yellow oil which ^{1}H NMR showed to be norbornadieneiron tricarbonyl [12] (9% yield).

Cycloheptatrieneiron tricarbonyl

Cycloheptatriene (0.13 g, 1.4 mmol) and BDAFe$(CO)_3$ (0.2 g, 0.7 mmol) were heated together at 60° C in benzene for 72 h. Work up as usual led to isolation of 80 mg (50% yield based on BDAFe$(CO)_3$) of cycloheptatrieneiron tricarbonyl identified by its ^{1}H NMR spectrum [16].

Cyclooctatetraeneiron tricarbonyl

Reaction of cyclooctatetraene (0.156 g, 1.5 mmol) with BDAFe$(CO)_3$ (0.5 g, 1.7 mmol) at 57° C for 48 h in benzene led to isolation after work up of 270 mg (74% yield based on cyclooctatetraene) of the red crystalline cyclooctatetraeneiron tricarbonyl identified by its distinctive singlet at δ 4.94 ppm in the ^{1}H NMR spectrum [17].

Reaction of BDAFe(CO)$_3$ with cycloheptatriene in the presence of free BDA

Cycloheptatriene (0.138 g, 1.5 mmol) was heated with BDAFe(CO)$_3$ (0.3 g, 1 mmol) for 24 h in degassed benzene at 62° C. Following work up as described above, 75 mg (50%) of cycloheptatrieneiron tricarbonyl was isolated. The yield of this reaction was reproducible (3 times) to within a few percent. The experiment was repeated 3 times adding respectively 2, 5, and 10 mmol of free BDA to the initial reaction mixture. After work up 30 mg (20%), 20 mg (13%), and ca. 1 mg ($<1\%$) of the product complex were isolated, respectively. Each of these runs was duplicated giving isolated yields of cycloheptatrieneiron tricarbonyl within 1—2 mg of that obtained in the first run.

Competition reactions

These reactions were designed to compare the reactivity of other dienes with cyclohexadiene in competition for reaction with BDAFe(CO)$_3$. In general, a 6/1 ratio of cyclohexadiene to BDAFe(CO)$_3$ was always used to insure an approximately constant ratio of concentrations of cyclohexadiene/diene throughout the course of the reaction. Table 4 lists the ratio of diene to cyclohexadiene to BDAFe(CO)$_3$ used in the individual experiments. In general, a large excess of competing diene over cyclohexadiene was required in order for dieneiron tricarbonyl complex other than $C_6H_8Fe(CO)_3$ to be formed. Each reaction was run in 50 ml degassed benzene at 55—60° C (see Table 4) for about 24 h. These were worked up as described earlier for the diene reactions, and the mixture of complexes was isolated by column chromatography. Each reaction was repeated at least once. ^{1}H NMR measurements were used to determine the molar ratio of product complexes, and this became the reactivity ratio once it was corrected for the molar ratios of starting dienes.

Due to its comparatively low reactivity, it was very difficult to obtain accurate, reproducible results comparing cycloheptatriene directly to cyclohexadiene. Therefore cycloheptatriene was allowed to compete directly with cyclooctatetraene and the reactivity ratio obtained was then corrected to cyclohexadiene using the known cyclohexadiene/cyclooctatetraene reactivity ratio.

Qualitative rate of reaction of cyclooctatetraene with BDAFe(CO)$_3$

BDAFe(CO)$_3$ (0.5 g, 17 mmol) and cyclooctatetraene (0.17 g, 15 mmol) were heated to 59° C in degassed benzene (ca. 50 ml) under a nitrogen atmosphere. At 0, 1, 2, 3, and 4 h reaction time, 2 ml samples were withdrawn from the solution and frozen at 0° C. Each of these solutions was filtered into an NMR tube under nitrogen and the ^{1}H NMR spectrum was recorded. At zero time the NMR spectrum clearly showed the singlet for free cyclooctatetraene at δ 5.69 ppm and the methyl singlet for BDAFe(CO)$_3$ (the other signals for BDAFe(CO)$_3$ were not seen due to the highly dilute nature of the samples). After 1 h the signal for $C_8H_8Fe(CO)_3$ had begun to grow along with the methyl signal for free BDA. After 2 h the ratios for the signals of $C_8H_8Fe(CO)_3$ (δ 4.94 ppm) to free cyclooctatetraene was 1.5. Using the 1 and 2 h spectra, the half-life was estimated to be ca. 85 min.

Acknowledgment

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References

1 J.A.S. Howell, B.F.G. Johnson, P.L. Josty, and J. Lewis, J. Organometal. Chem., 39 (1972) 329.
2 A.J.P. Domingos, J.A.S. Howell, B.F.G. Johnson, and J. Lewis, Inorg. Synth., 16 (1976) 103.
3 G. Scholes, C.R. Graham, and M. Brookhart, J. Amer. Chem. Soc., 96 (1974) 5665.
4 C.R. Graham, G. Scholes, and M. Brookhart, J. Amer. Chem. Soc., 99 (1977) 1180.
5 M.Brookhart, G.O. Nelson, G. Scholes, and R.A. Watson, J. Chem. Soc., Chem. Commun., (1976) 195.
6 M. Brookhart, G.W. Koszalka, G.O. Nelson, G. Scholes, and R.A. Watson, J. Amer. Chem. Soc., 98 (1976) 8155.
7 M. Brookhart, C.R. Graham, G.O. Nelson, and G. Scholes, Ann. N.Y. Acad. Sci., 295 (1977) 254.
8 B.F.G. Johnson, J. Lewis, and D. Wedge, J. Chem. Soc. Dalton, (1976) 1874.
9 G. Evans, B. Johnson, and J. Lewis, J. Organometal. Chem., 102 (1975) 507.
10 E. Koerner von Gustorf and J.C. Hagen, Tetrahedron Lett., (1968) 3191.
11 (a) J.E. Arnet and R. Pettit, J. Amer. Chem. Soc., 83 (1961) 2954; (b) A.J. Birch, P.E. Cross, J. Lewis, D.A. White, and S.B. Wild, J. Chem. Soc. A, (1968) 332; (c) H. Alper, P.G. LaPort, and S. Wolfe, J. Amer. Chem. Soc., 91 (1969) 7553.
12 (a) R. Pettit, J. Amer. Chem. Soc., 81 (1959) 1266; (b) M.L.H. Green, L. Pratt, and G. Wilkinson, J. Chem. Soc., 81 (1959) 1266.
13 R. Huisgen, F. Mietzsch, G. Boche, and H. Seidl, Chem. Soc., Spec. Publ., No. 19 (1965) 3.
14 G.F. Emerson, J.E. Mahler, R. Kochlar, and R. Pettit, J. Org. Chem., 29 (1964) 3620.
15 M. Brookhart and D.L. Harris, J. Organometal. Chem., 42 (1972) 441.
16 R. Burton, L. Pratt, and G. Wilkinson, J. Chem. Soc., 89 (1967) 24.
17 T.A. Manuel and F.G.A. Stone, J. Amer. Chem. Soc., 82 (1960) 366.