Hydroboration of Ferrocenylalkenes: Mechanistic and Synthetic Aspects

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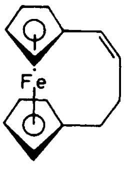
Several ferrocenylalkenes ($FcCR{=}CH_2$, $FcCH{=}CHR$, $FcCR{=}CHR$, and $FcCH{=}CHAr$) have been subjected to hydroboration–oxidation. The results show that the regioselectivity of the reaction is governed by both steric and electronic factors. Since the ferrocenyl group is particularly effective at the β-position, hydroboration–oxidation represents a convenient and general route to the preparation of 2-ferrocenylalkanols.

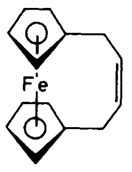
Many systematic investigations have been conducted to provide information on the factors which govern the scope, mechanism, stereochemistry, reactivity, and selectivity of the hydroboration of alkenes.[1-3] Despite its great synthetic usefulness and applicability, the detailed mechanism of hydroboration has been a matter of considerable dispute.[4-7] We have now investigated the hydroboration–oxidation of ferrocenylalkenes ($FcCR{=}CR'R''$; Fc = ferrocenyl) with a large variety of ferrocenyl derivatives, in order to examine the potential of the reaction for a new general route to 2-ferrocenylalkanols [$FcCHRC(OH)R'R''$] and to assess the influence of steric and electronic effects in mixed alkenes such as 1-ferrocenyl-2-arylethylenes.

$FcCH{=}CHC_6H_4X\text{-}p$

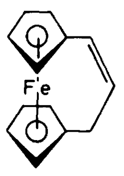
(1) a; $X = H$ d; $X = Br$
b; $X = OMe$ e; $X = NO_2$
c; $X = Me$



(2)



(3)



(4)

Results and Discussion

We have subjected to hydroboration the following major structural types: (a) terminal ferrocenylalkenes ($FcCH{=}CH_2$, $FcCR{=}CH_2$, $FcCH_2CH{=}CH_2$); (b) mono- and di-substituted ferrocenylalkenes ($FcCH{=}CHR$, $FcCH{=}CRR'$, $FcCR{=}CHR'$); (c) 1-ferrocenyl-2-arylethylenes (1); and (d) heteroannularly bridged ferrocenylalkenes (2)—(4).

The hydroboration was performed under classical conditions, i.e. with $NaBH_4$–$BF_3{\cdot}Et_2O$ mixtures,[8] and for some substrates also with borane–dimethyl sulphide (BMS). Attempts to study the rates of reaction with diborane in tetrahydrofuran revealed that these are too fast to be measured, proceeding to completion in a matter of seconds. In contrast, preliminary experiments showed that the addition of bis-(1,2-dimethylpropyl)borane is slow. The extent of alkylation of the borane was estimated from the amount of recovered alkene (see Experimental section). With terminal and monosubstituted ferrocenylalkenes ($FcCH{=}CHR$), the hydroboration step appears to proceed to the dialkylborane stage (R_2BH), whereas disubstituted ferrocenylalkenes ($FcCH{=}CRR'$) react at room temperature to utilize only one third of the active hydrogen, yielding a monoalkylborane, RBH_2. Since the corresponding common alkenes give trialkyl- and dialkyl-boranes, respectively,[8,9] the different behaviour must be ascribed to the steric hindrance exerted by the ferrocenyl group.

Owing to the well known difficulties in isolating the intermediate alkylboranes, the conversion yields were calculated on the basis of the total amounts of 1- and 2-ferrocenylalkanols [equation (i)] obtained after the alkaline peroxide oxidation step. Product analysis was performed by g.l.c. or h.p.l.c., using authentic specimens of the starting alkenes and of 1- and 2-ferrocenylalkanols as standards. Product ratios were found to be reproducible within ±2%.

$$FcCH{=}CHR \xrightarrow[H_2O_2]{(BH_3)_2} FcCH(OH)CH_2R + FcCH_2CH(OH)R \quad \text{(i)}$$

1-ferrocenylalkanol 2-ferrocenylalkanol
(α-ferrocenyl alcohol) (β-ferrocenyl alcohol)

Table 1. Regioselectivity of the hydroboration-oxidation of ferrocenylalkenes

Substrate	Products (%) [a] α-Alcohol	β-Alcohol	Total yield (%)
$FcCH_2CH{=}CH_2$	2	98	92
$FcCH{=}CH_2$	3	97	86
$FcCH{=}CHMe$	60	40	80
$FcCH{=}CHPh$	9	91	74
$FcCH{=}CMe_2$	97	3	91
$FcCH{=}CPh_2$	100		78
$FcCMe{=}CH_2$	1	99	85
$FcCBu^t{=}CH_2$		100	60
$FcCPh{=}CH_2$		100	88
$FcCMe{=}CHMe$		100	65
(2)	38	62	90
(3)		100	87
(4)	91	9	81

[a] The α and β positions refer to the Fc group.

The conversion yields of the ferrocenylalkenes fall in the range 70—90%.

Regioselective and Mechanistic Aspects.—The results for the hydroboration–oxidation of ferrocenylalkenes of the types (a) and (b) are summarized in Table 1; the literature data concerning the hydroboration–oxidation of styrenes are collected in Table 2. Comparison shows that the behaviour of the two classes of compounds, *i.e.* ferrocenyl- and phenylalkenes, is quite similar in sterically crowded systems. Thus for $FcCH{=}CMe_2$ and $FcCH{=}CPh_2$ the alcoholic function is quantitatively introduced at the α-carbon atom (just as for $PhCH{=}CR_2$). Similarly, attachment of boron to the less

Table 2. Regioselectivity of the hydroboration–oxidation of styrenes [a]

Substrate	Products (%)	
	α-Alcohol	β-Alcohol
$PhCH{=}CH_2$	20	80
$PhCH{=}CHMe$	85	15
$PhCH{=}CMe_2$	100	
$PhC(CH_3){=}CH_2$		100
$(p\text{-}ClC_6H_4)CH{=}CH_2$	35	65
$(p\text{-}MeOC_6H_4)CH{=}CH_2$	9	91
$(p\text{-}MeC_6H_4)CH{=}CH_2$	18	82

[a] Data from H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, 1960, **82**, 4708.

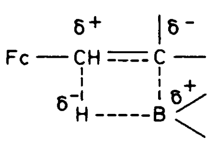
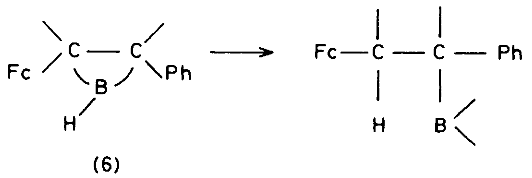

(5)

Table 3. Regioselectivity of the hydroboration of 1-ferrocenyl-2-arylethylenes: role of electronic factors

Substrate	Products (%)		Yield (%)
	α-Alcohol	β-Alcohol	
$FcCH{=}CHPh$	9	91	74
$FcCH{=}CHC_6H_4OMe\text{-}p$	30	70	88
$FcCH{=}CHC_6H_4Me\text{-}p$	18	82	81
$FcCH{=}CHC_6H_4Br\text{-}p$	6	94	78
$FcCH{=}CHC_6H_4NO_2\text{-}p$		100	70


(6)

hindered β-carbon atom is enhanced by α-branching: $FcCR{=}CH_2$ (R = Me, Bu^t, or Ph) gives 100% of the β-alcohol, and FcCMeCH(OH)Me is the only product formed by $FcCMe{=}CHMe$.

Less straightforward is the analysis of the results for the terminal and monosubstituted ferrocenylalkenes, where the directive influence of steric effects may be compounded by electronic effects. Thus, $FcCH{=}CH_2$ gives 2-ferrocenylethanol quantitatively (97%), whereas styrene affords an 80% yield of $PhCH_2CH_2OH$. Also, 1-ferrocenylpropene ($FcCH{=}CHMe$) yields $FcCH(OH)CH_2Me$ (60%) and $FcCH_2CH(OH)Me$ (40%), whereas $PhCH{=}CHMe$ gives $PhCH(OH)CH_2Me$ in 85% yield. Thus the Fc group tends to shift the regioselectivity of boron attack towards the β-carbon atom. We interpret this as due to the concomitant action of two factors, *viz.* the steric hindrance exerted by the Fc group, and its strong electron-releasing effect, which stabilizes α-carbocation formation, according to Brown's four-centre transition state [4] (5).

We have also examined the influence of electronic effects in the hydroboration by studying the dependence of regioselectivity on the polar effects of the substituents in substrates of the type $FcCH{=}CHC_6H_4X\text{-}p$. The results are shown in Table 3 and are compared with those for substituted styrenes (Table 2). On going from electron-releasing groups (OMe, Me) to electron-withdrawing ones (Br, NO_2) the amount of hydroboration at the β-carbon atom increases regularly. Even for the compound $FcCH{=}CHC_6H_4OMe\text{-}p$, the prevalent orientation is at the β-carbon atom, in agreement with the overwhelming electron-releasing effect of the Fc group. Thus, hydroboration regioselectivity is dependent on electronic factors in addition to steric ones. The electronic influence of the Fc group is in agreement with Brown's mechanism [formula (5)], but it may also be reconciled with the mechanism proposed by Jones [10] and Dewar,[11] which involves the formation of a triangular π-complex between olefin and borane, followed by a concerted symmetry-allowed conversion into products. Thus, for the hydroboration of 1-ferrocenyl-2-arylethylenes a favourable combination of electronic effects due to Fc and Ar groups strongly stabilizes the intermediate (6), and the introduction of a *p*-nitro group strengthens the ability of the aryl group to withdraw negative charge from the adjacent carbon, enhancing the attachment of boron to the carbon closer to the phenyl ring.

In the general picture of postulated mechanisms of borane addition,[12–15] the recent work of Nagase *et al.*[16] must be mentioned. They propose, on the basis of an *ab initio* MO study, that hydroboration proceeds through a two-step process: first a loose three-centre π-complex is formed, which is transformed into product *via* a four-centre transition state in the rate-determining step.

The regioselectivity of hydroboration of the bridged ferrocenylalkenes (2) and (3), where the interannular bridge does not introduce relevant strain, is in agreement with the results for the open-chain alkenes (*cf.* $FcCH{=}CHR$). Thus (2) gives [4]ferrocenophan-6-ol (38%) and [4]ferrocenophan-7-ol (62%) and (3) gives [4]ferrocenophan-7-ol in excellent yield. For these reactions the ability of the iron to stabilize carbocationoid species at the β-positions of the bridge may play a role,[17] especially if Brown's mechanism were operating.

For the alkene (4), where the strain of the bridge is relevant, hydroboration at the α-position (with the formation of [3]ferrocenophan-6-ol) is strongly favoured, despite the low stability of the α-carbocation.[18]

Finally, it is of interest to compare the behaviour of ferrocenylalkenes towards hydroboration and methoxymercuriation.[19] The rates of addition by the mercuriation reagent are lower than those of hydroboration (just as for common alkenes) and the former reaction is more sensitive to steric effects: thus (1-t-butylvinyl)ferrocene and (2-methylprop-1-enyl)ferrocene do not undergo reaction at the double bond, whereas prop-1-enylferrocene undergoes both addition and electrophilic substitution at the cyclopentadiene ring.

Synthetic Aspects.—The data in Table 1 show the great synthetic value of the hydroboration–oxidation of ferrocenylalkenes resulting from the high yields and the good regioselectivity. The reaction offers a general and convenient route to 2-ferrocenylalkanols from 1-ferrocenylalkanols, which are readily available through Friedel–Crafts acylation of ferrocene and are quantitatively dehydrated to ferrocenylalkenes. This route is particularly valuable for terminal and α-substituted ferrocenylalkenes, since the conversion into the β-alcohol is quantitative. Some typical preparative data are presented in Table 4, together with physical constants and ^{1}H n.m.r. characterization data. For example, the preparation of $FcCH_2CH(OH)R$ (R = H, Me, or Ph) by hydroboration is a convenient alternative to the procedure through ferrocenyl-

Table 4. Hydroboration–oxidation as a preparative route to ferrocenyl alcohols

		Analysis (%C) (%H)		
Alcohol obtained	M.p. (°C)	Calc.	Found	δ_H (CCl_4) (J in Hz)
$FcCH_2CH_2CH_2OH$	Liquid (red–orange)	63.95 6.6	64.05 6.6	1.6—2.0 (β-CH_2, m, 2 H), 2.2—2.4 (γ-CH_2, t, J 9, 2 H), 2.5 (OH, s, 1 H), 3.35 (α-CH_2, t, J 9, 2 H), 3.95 (Fc, m, 9 H)
$FcCH_2CH_2OH$	50 (lit.,[20] 49—51)	62.65 6.15	62.7 6.2	1.90 (OH, s, 1 H), 2.45 (α-CH_2, t, J 7, 2 H), 3.75 (β-CH_2, t, J 7, 2 H), 4.0—4.20 (Fc, m, 9 H)
$FcCH_2CH(OH)Me$	36 (lit.,[20] 36)	63.95 6.6	63.9 6.8	1.3 (CH_3, d, J 6.2, 3 H), 2.0 (OH, s, 1 H), 2.50 (CH_2, d, J 6.2, 2 H), 3.1—3.4 (CH, m, 1 H), 4.18 (Fc, s, 9 H)
$FcCH_2CH(OH)Ph$	83 (lit.,[20] 82—84)	70.6 5.9	70.45 5.8	2.20 (OH, s, 1 H), 2.90 (CH_2, d, J 8, 2 H), 4.25 (Fc, s, 9 H), 4.85 (CH, m, 1 H), 7.50 (C_6H_5, s, 5 H)
$FcCH(OH)CHMe_2$	Liquid (red–orange)	65.15 7.05	65.3 7.25	0.80 (CH_3, d, J 7.2, 6 H), 1.40—1.80 (CH, m, 1 H), 1.71 (OH, s, 1 H), 3.1 (α-CH, d, J 7.2, 1 H), 4.06 (Fc, m, 9 H)
$FcCH(OH)CHPh_2$	Liquid (red–orange)	75.4 5.8	75.2 5.91	1.7 (OH, s, 1 H), 3.8 (α-CH, d, J 7.2, 1 H), 4.05 (Fc, m, 9 H), 5.5 (β-CH, d, J 7.2, 1 H), 7.3 (C_6H_5, m, 10 H)
$FcCHMeCH_2OH$	Liquid (red–orange)	63.95 6.6	64.05 6.7	1.2—1.4 (CH_3, d, J 6, 3 H), 1.85 (OH, s, 1 H), 2.5—2.85 (CH, m, 1 H), 3.4—3.6 (CH_2, d, J 6, 2 H), 4.05—4.20 (Fc, m, 9 H)
$FcCHPhCH_2OH$	Liquid (red–orange)	70.6 5.95	70.5 5.8	1.90 (CH, t, J 6, 1 H), 2.10 (OH, s, 1 H), 3.7—3.85 (CH_2, d, J 6, 2 H), 4.05—4.20 (Fc, m, 9 H)
$FcCHBu^tCH_2OH$	Liquid (red–orange)	67.15 7.75	67.3 7.85	0.90 (Bu^t, s, 9 H), 1.95 (OH, s, 1 H), 2.48 (CH, m, 1 H), 3.55 (CH_2, d, J 6, 2 H), 4.1—4.2 (Fc, m, 9 H)
$FcCHMeCHMeOH$	Liquid (red–orange)	65.15 7.05	64.95 7.25	0.8—1.2 (CH_3, m, 6 H), 2.2 (OH, s, 1 H), 2.6—2.75 (α-CH, m, 1 H), 3.1—3.3 (β-CH, m, 1 H), 4.0—4.1 (Fc, m, 9 H)
[4]Ferrocenophan-7-ol	161 (lit.,[a] 162)	65.65 6.3	65.85 6.4	1.85 (OH, s, 1 H), 2.1—2.7 (bridge, m, 7 H), 4.1—4.3 (Fc, s, 8 H)

[a] M. Rosenblum, A. K. Banerjee, N. Danieli, R. W. Fish, and V. Schlatter, *J. Am. Chem. Soc.*, 1963, **85**, 316.

lithium and the alkene oxides, which proceeds in yields in the range 23—31%.[20]

For the systems where a mixture of 1- and 2-ferrocenylalkanols is obtained (monosubstituted ferrocenylalkenes of the type FcCH=CHR), chromatographic separation is readily achieved since 2-ferrocenylalkanols are not dehydrated on alumina. Furthermore, to the extent that 1-ferrocenylalkanols resist dehydration, they are eluted more rapidly than the 2-isomers, probably because the α-OH is hydrogen-bonded to the iron atom. In some cases the chromatographic procedure was found to dehydrate 1-ferrocenylalkanols completely.

The preparation of secondary β-ferrocenyl alcohols, FcCHRCH(OH)R′, is also of interest. The acylferrocenes, $FcCOCH_2R'$, react with Grignard reagents to give directly and predominantly ferrocenylalkenes,[21] FcCR=CHR′, which by hydroboration–oxidation form quantitatively the expected β-ferrocenyl alcohols.

The hydroboration procedure is particularly valuable with the heteroannularly bridged ferrocenylalkene (2), which allows [4]ferrocenophan-7-ol to be obtained from [4]ferrocenophan-6-ol in good yield (60%), whereas the literature procedure involves bridge enlargement of the [3]ferrocenophan-6-one. Unfortunately, hydroboration of (4) is not a convenient route to [3]ferrocenophan-7-ol, preparation of which is particularly time-consuming.[22,23]

Experimental

General Methods.—All manipulations were performed in an atmosphere of nitrogen. Glassware and syringes were oven-dried. Gas-chromatographic analyses were performed with a Hewlett–Packard 5830A apparatus, equipped with an HP 18850A integrator. H.p.l.c. measurements were made with a Waters 6000 apparatus equipped with a Hewlett–Packard 5880A integrator.

Materials.—The ferrocenylalkenes were prepared by dehydration (on alumina) of 1-ferrocenylalkanols obtained by literature methods involving Friedel–Crafts acylation of ferrocene and reduction of the ketones produced.[24,25] A typical procedure was as follows: the 1-ferrocenylalkanol (5 g) was dissolved in dry benzene (150 ml) and acidic alumina (5 g) was added. The mixture was refluxed for 4 h with continuous removal of water (Dean–Stark apparatus). The mixture was filtered and the solvent evaporated off. The crude residue was subjected to column chromatography on alumina (eluant benzene).

The ferrocenylalkenes were obtained in good yields (60—80%). The n.m.r. spectra and m.p.s were in accord with the structures assigned. The ferrocenyl alcohols formed in the hydroboration–oxidation were characterized by i.r. and n.m.r. spectroscopy, by m.p.s and by elemental analysis (Table 4). The preparations of the previously unreported ferrocenyl *p*-nitrobenzyl ketone and of 1-ferrocenyl-2-(*p*-nitrophenyl)ethene are described later.

Ferrocenyl p-*Nitrobenzyl Ketone.*—Since the direct acylation of ferrocene with *p*-nitrophenylacetyl chloride and $AlCl_3$ was unsuccessful (an extensive oxidation of ferrocene to ferricenium ion occurs) Galli's procedure was used.[26] A three-necked flask equipped with stirrer and dropping funnel was charged with *p*-nitrophenylacetic acid (Fluka, 5.43 g, 0.03 mol), ferrocene (18.1 g, 0.1 mol), 85% phosphoric acid (3.42 g, 0.03 mol), and anhydrous acetonitrile (200 ml). The mixture was stirred at 50 °C and a solution of trifluoroacetic anhydride (26.3 g, 0.125 mol) was added from the dropping funnel. After 2 h, water was added and the mixture extracted with ether. The extracts were washed with aqueous sodium hydrogen carbonate and water, dried, and evaporated and the mixture was chromatographed on silica gel with benzene. Four products were separately eluted: ferrocene, two unidentified compounds, and the expected ferrocenyl *p*-nitrobenzyl ketone (6.0 g, 18%), δ_H 4.0—4.1 (cyclopentadienyl, m, 5 H), 4.2 (CH_2, s, 2 H), 4.45 (H-2 and -5, m, 2 H), 4.72 (H-3 and -4, m, 2 H), and 7.25, 7.35, 8.0, and 8.10 (C_6H_4, q, *J* 7.8 Hz, 4 H).

*1-Ferrocenyl-2-(*p*-nitrophenyl)ethylene*.—Ferrocenyl *p*-nitrobenzyl ketone (1.35 g, 0.004 mol) was reduced with an excess of $NaBH_4$ in dry ether. After hydrolysis and extraction with ether, the solvent was evaporated off and the residue was dehydrated in benzene with alumina according to the procedure described previously. *1-Ferrocenyl-2-(*p*-nitrophenyl)ethylene* was obtained after the chromatographic purification (silica gel; benzene); yield 1.15 g (90%), m.p. 147 °C; δ_H 4.0—4.15 (cyclopentadienyl, s, 5 H), 4.2—4.3 (H-2 and -5, t, *J* 1.5 Hz, 2 H), 4.4—4.5 (H-3 and -4, t, *J* 1.5 Hz, 2 H), 6.8—6.9 (CH=CH, 2 H), and 7.2—7.6 (C_6H_4, m, 4 H) (Found: C, 61.7; H, 4.95. $C_{18}H_{17}FeNO_3$ requires C, 61.55; H, 4.9%).

Hydroboration–Oxidation Procedure.—In a three-necked flask equipped with a condenser, addition funnel, and nitrogen inlet–outlet tube, the alkene (2.5 g) was dissolved in dry tetrahydrofuran (50 ml) and $NaBH_4$ (0.85 g) was added. Boron trifluoride–ether (4.2 g) and tetrahydrofuran (10 ml) were introduced into the funnel and added dropwise to the alkene solution during 20 min. After the addition was complete, stirring was continued for an additional 1 h. The solution was cooled in an ice-bath and water (5 ml) was added dropwise to destroy the diborane in excess. A 3M-NaOH solution was added dropwise to adjust the pH to 8.0. An equal volume of 30% H_2O_2 was added and the solution was stirred for 1 h; then it was poured into water (100 ml) and extracted with ether. The combined extracts were washed with 5% $NaHCO_3$ and then with water, and dried. The crude residue was chromatographed on deactivated alumina. Light petroleum eluted unchanged alkene and traces of alkanes. Ether eluted the alcohols.

Hydroboration with Borane–Dimethyl Sulphide.—Into the glassware assembly already described were slowly injected tetrahydrofuran (5 ml) and borane–dimethyl sulphide (9 mmol). The solution was stirred for 2 h at 0 °C, and then oxidized by the concurrent addition of 3M-NaOH (1 ml) and 30% H_2O_2 (1 ml).

Product Analysis.—The crude mixtures obtained from the hydroboration–oxidation procedure were chromatographed on deactivated alumina in order to remove traces of unchanged alkene. This procedure was necessary when the 1-ferrocenylalkanols eventually formed in the reaction are dehydrated under the conditions of the g.l.c. separation. Otherwise, the crude mixtures were directly injected into the gas chromatograph. The retention times of 1-ferrocenylalkanols are much lower than those of the 2-isomers, so the relative yields can be evaluated precisely.

Extent of BH_3 *Alkylation*.—The ferrocenylalkene was treated with sufficient sodium borohydride and boron trifluoride to convert it completely into the highest alkylborane stage. At suitable time intervals samples of the reaction mixtures were removed, quenched in wet tetrahydrofuran, and analysed for residual alkene by g.l.c.

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References

1 H. C. Brown, 'Organic Synthesis *via* Boranes,' Wiley, New York, 1975.

2 G. M. Cragg, 'Organoboranes in Organic Synthesis,' Dekker, New York, 1973.

3 C. H. Mauldin, E. R. Biehl, and P. C. Reeves, *Tetrahedron Lett.*, 1972, 2955.

4 H. C. Brown, 'Hydroboration,' Benjamin, New York, 1962, p. 13.

5 D. Seyferth, *Prog. Inorg. Chem.*, 1962, 210.

6 A. Stretwieser, Jr., L. Verbit, and R. Bittman, *J. Org. Chem.*, 1967, **32**, 1530.

7 D. J. Pasto and S. Z. Kang, *J. Am. Chem. Soc.*, 1968, **90**, 3797.

8 H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, 1962, **84**, 190.

9 H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, 1959, **81**, 6428.

10 P. R. Jones, *J. Org. Chem.*, 1972, **37**, 1886.

11 M. J. S. Dewar and M. L. McKee, *Inorg. Chem.*, 1978, **17**, 1075.

12 S. Dasgupta, M. K. Datta, and R. Datta, *Tetrahedron Lett.*, 1978, 1309.

13 T. P. Fehlmer, *J. Am. Chem. Soc.*, 1971, **93**, 6366.

14 T. Clark and P. von R. Schleyer, *J. Organomet. Chem.*, 1978, **156**, 191.

15 K. R. Sundberg, G. D. Graham, and W. N. Lipscomb, *J. Am. Chem. Soc.*, 1979, **101**, 2863.

16 S. Nagase, N. K. Ray, and K. Morokuma, *J. Am. Chem. Soc.*, 1980, **102**, 4536.

17 G. Ortaggi, P. Riccio, and I. Tritto, *J. Org. Chem.*, 1979, **44**, 2920.

18 G. Cerichelli, B. Floris, and G. Ortaggi, *J. Organomet. Chem.*, 1974, **78**, 241.

19 B. Floris and G. Illuminati, *J. Organomet. Chem.*, 1979, **168**, 203.

20 W. Reeve and E. F. Group, Jr., *J. Org. Chem.*, 1967, **32**, 122.

21 W. H. Horspool, R. G. Sutherland, and J. R. Sutton, *Can. J. Chem.*, 1969, **47**, 3085.

22 M. N. Applebaum, R. W. Fish, and M. Rosenblum, *J. Org. Chem.*, 1964, **29**, 2452.

23 A. Sonoda and I. Moritani, *J. Organomet. Chem.*, 1971, **26**, 133.

24 M. Rosenblum, 'Chemistry of the Iron Group Metallocenes,' Wiley, New York, 1965.

25 D. E. Bublitz and K. L. Rinehart, Jr., *Org. React.*, 1969, **17**, 24.

26 C. Galli, *Synthesis*, 1979, 303.

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