In memory of T. A. Stephenson

Hydride Addition Reactions of the Olefin Complexes $[Fe(\eta^5-C_5H_5)(CO)_2(olefin)][BF_4]$; Formyl Formation as the Kinetically Preferred Process; Regio- and Stereo-selectivity during Addition to the Co-ordinated Olefins

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Reactions of the complexes $[Fe(cp)(CO)_2(olefin)]^+$ (cp = η^5-C_5H_5; olefin = CH_2=CH_2, CH_2=CHMe, 1-hexene, or methylenecyclohexane) with hydride donors under a variety of conditions normally yield the alkyl products of hydride addition to the olefin, and the hydride $[Fe(cp)(CO)_2H]$, a product which has not been previously noted. Detailed examination of the addition reactions of the complexes of CH_2=CHMe, 1-hexene, and methylenecyclohexane show that the reactions exhibit no recognizable patterns of regioselectivity, in contrast to many other metal–olefin systems. Addition of deuteride to $[Fe(cp)(CO)_2(C_6H_{10})]^+$ (C_6H_{10} = cyclohexene) gives only the *trans* isomer of the 2-deuteriocyclohexyl complex, consistent with *exo* attack by the nucleophile on the co-ordinated olefin. Reaction of $[Fe(cp)(CO)_2(CH_2$=$CH_2)]^+$ with $NaBH_4$ in acetone at low temperature gives an unstable formyl compound, presumably $[Fe(cp)(CO)(C_2H_4)(CHO)]$, as the kinetic product. On warming, the formyl compound converts smoothly to the above-mentioned hydride complex rather than to the corresponding ethyl complex. The mechanistic implications of these results are discussed.

Organotransition-metal complexes exhibit extensive reactivity toward a wide variety of nucleophiles, many reactions involving attack by a nucleophile (Nu) at a co-ordinated ligand. As a result, reactions of nucleophiles with transition-metal complexes of saturated and unsaturated organic ligands constitute some of the more useful procedures for both the preparation of new compounds and for the synthetic elaboration of the organic ligands concerned. Thus there have appeared several comprehensive reviews of the chemistry of a wide variety of σ-alkyl, η^2-olefin, η^3-allyl, η^4-diene, η^5-dienyl, and η^6-arene complexes with hydride sources, organolithium and Grignard reagents, and oxygen, sulphur, nitrogen, or phosphorus donors.[1–3] There are also available several monographs outlining the synthetic utility of many such reactions.[3–5]

Of particular relevance here are nucleophilic addition reactions of co-ordinated olefins, which result in the formation of new σ-alkyl complexes, equation (1). Such reactions have been

$$M(CH_2{=}CHR) + Nu \longrightarrow \underset{\textbf{(A)}}{M{-}CH_2CH(Nu)R} + \underset{\textbf{(B)}}{M{-}CHRCH_2(Nu)} \quad (1)$$

reported for a wide variety of olefin complexes, normally of metals in positive oxidation states. The alkyl products formed are often those of Markownikoff addition (**A**), although many systems are far from being regiospecific and products of anti-Markownikoff addition (**B**) are also often observed.[1–5]

Although it is generally agreed that the molecular orbital of the metal–olefin complex which receives the incoming nucleophile in reaction (1) is primarily of olefin π* character, simple olefins do not normally undergo nucleophilic addition or substitution and opinions differ with respect to the actual mechanism of activation of their complexes.[6–8] In this and a subsequent paper,[9] we present experimental and theoretical studies, respectively, of reactions of the series of cationic olefin complexes $[Fe(cp)(CO)_2(olefin)][BF_4]$ [cp = η^5-C_5H_5; olefin = CH_2=CH_2 (**1**), CH_2=CHMe (**2**), 1-hexene (**3**), methylenecyclohexane (**4**), or cyclohexene (**5**)] with a variety of hydride sources. Complexes of this type are of interest because they are known to react with a wide variety of nucleophiles to form alkyl complexes which appear generally to be stable with respect to subsequent isomerization processes,[10–14] equation (2) (olefin = CH_2=CHR or CH_2=CR_2; Nu = anionic, neutral donor).

$$[Fe(cp)(CO)_2(olefin)]^+ + Nu \longrightarrow [Fe(cp)(CO)_2(alkyl)]^{0,+} \quad (2)$$

The purpose of this investigation, therefore, was (*a*) to confirm an earlier report[14d] that hydride addition reactions to the iron–olefin system do occur *trans* to the iron, (*b*) to determine if possible the degree of regioselectivity which occurs during (2) (Nu = hydride donor), and (*c*) to determine whether the alkyl products of (2) are indeed the kinetic products. We demonstrate that addition of deuteride to (**5**) does occur *trans* to iron, thereby justifying our theoretical treatment[9] of hydride addition as occurring in that fashion. We also find that hydride additions to (**2**), (**3**), and (**4**) occur with no recognizable patterns of regioselectivity, suggesting that the differences in activation energies for the alternative modes of addition are too slight to be reflected in the calculations. Finally, consistent with calculations which suggest preferential attack at CO,[9] we show that the kinetic product of hydride addition to (**1**) at low temperature is a thermally labile formyl complex.

Experimental

Compounds (**1**),[14a] (**2**),[14a] (**3**),[15] (**4**),[15] and (**5**)[16] were prepared essentially as described in the literature; all were characterized spectroscopically. The compounds $NaBH_4$, $LiBH_4$, $NaBH_3CN$,

Table 1. Product distributions from hydride additions to the complexes $[Fe(cp)(CO)_2(olefin)][BF_4]$

					Relative proportions of products		
Expt.	Olefin	Hydride source	Solvent	Temperature (°C)	$[Fe(cp)(CO)_2$-(n-alkyl)]	$[Fe(cp)(CO)_2$-(isoalkyl)]	$[Fe(cp)(CO)_2$-H]
1	Propene	$NaBH_4$	thf	20	1	2	1.5
2	Propene	$NaBH_4$	thf	0	1	2	1.5
3	Propene	$NaBH_4$	thf	−78	1	3	0.3
4	Propene	$NaBH_3CN$	thf	20	1	1	0
5	Propene	$NaBH_3CN$	thf	0	1	1	0
6	Propene	$NaBH_3CN$	thf	−78	1	0.5	0
7	Propene	$KHB(Bu^s)_3$	thf	20	0	0	1*
8	Propene	$[Fe(cp)(CO)(PPh_3)H]$	thf	20	0	1	0
9	Propene	$NaBH_4$	MeCN	20	1	2	0
10	Propene	$NaBH_3CN$	MeCN	20	1	1	0
11	Propene	$[Fe(cp)(CO)(PPh_3)H]$	MeCN	20	0	1	0
12	1-Hexene	$LiBH_4$	thf	20	1	3	4
13	1-Hexene	$NaBH_4$	thf	20	1	1.5	4
14	1-Hexene	$NaBH_3CN$	thf	20	3	2	0
15	1-Hexene	$[Fe(cp)(CO)(PPh_3)H]$	thf	20	1	32	0
16	1-Hexene	$LiBH_4$	MeCN	20	1	2	3
17	1-Hexene	$NaBH_4$	MeCN	20	1	3	0
18	1-Hexene	$NaBH_3CN$	MeCN	20	2	1	0
19	1-Hexene	$[Fe(cp)(CO)(PPh_3)H]$	MeCN	20	1	23	0
20	Methylenecyclohexane	$NaBH_4$	thf	−60	0	0	0*
21	Methylenecyclohexane	$NaBH_4$	MeCN	0	1	2	0*
22	Methylenecyclohexane	$NaBH_4$	MeCN	−45	1	2	0*
23	Methylenecyclohexane	$NaBH_3CN$	thf	0	9	1	0
24	Methylenecyclohexane	$NaBH_3CN$	thf	−60	1	0	0
25	Methylenecyclohexane	$NaBH_3CN$	MeCN	0	1	0	0

* Major product $[\{Fe(cp)(CO)_2\}_2]$.

and $KHB(Bu^s)_3$ were purchased from the Aldrich Chemical Company, while $[Fe(cp)(CO)(PPh_3)H]$ was synthesized as in the literature.[17]

Hydride addition reactions to (**2**), (**3**), or (**4**) (0.5—1.0 g olefin complex, 1.25:1 molar ratio of hydride donor to olefin complex) were carried out in tetrahydrofuran (thf) or acetonitrile under nitrogen at various temperatures (Table 1). As the ionic hydride donors exhibit rather low solubilities in the solvents used, most of the reactions were heterogeneous, at least in the early stages. The reactions were monitored by i.r. spectroscopy in the carbonyl stretching region, and the isomeric alkyl compounds were separated chromatographically (15-cm alumina column, low boiling light petroleum eluting solvents[15]) from other products. The alkyl compounds are stable under these conditions, and are not fractionated.[15] Their relative yields were readily and fairly reproducibly determined from the ^1H n.m.r. spectra, and are shown in Table 1. Absolute yields of the alkyl compounds were not determined in all cases but, aside from major exceptions noted in Table 1, appeared to be 40—50% for reactions of $LiBH_4$, 50—60% for reactions of $NaBH_4$, 85—95% for reactions of $NaBH_3CN$, and 75—85% for reactions of $[Fe(cp)(CO)(PPh_3)H]$.

Many of the reactions resulted in the formation of the dimer, $[\{Fe(cp)(CO)_2\}_2]$, and the hydride, $[Fe(cp)(CO)_2H]$ (**6**), which is known to be labile with respect to decomposition to the dimer.[18] Yields of (**6**) were therefore estimated by comparisons of the ν(CO) of (**6**) with the ν(CO) of the alkyl compounds, although yields of the dimer could be obtained gravimetrically after elution from the column with diethyl ether.

Reactions of (**2**) and (**5**) with $NaBD_4$ were carried out in thf in the same way, the alkyl products being purified prior to n.m.r. characterization by elution from an alumina column with n-pentane. The reaction of (**1**) with $NaBH_4$ was monitored at low temperatures by adding a suspension of $NaBH_4$ in $[^2H_6]$acetone to a frozen (liquid N_2) solution of (**1**) in an n.m.r. tube in the same solvent. The n.m.r. tube was placed in the probe of an AM400 n.m.r. spectrometer at −60 °C, and the solvent was allowed to melt. ^1H N.m.r. spectra were run immediately and after 15 min, and then every 10 °C as the temperature was allowed to rise to 0 °C. The solubility of $NaBH_4$ at −60 °C is such that (**1**) was present in a solution in excess.

Results and Discussion

The theoretical investigation discussed in a subsequent paper[9] was initiated in order to gain a better understanding of the factors which lead to the often demonstrated activation of co-ordinated olefins to nucleophilic attack. Of ancillary interest were factors which influence the site of attack on an unsymmetrical olefin (degree of regioselectivity) since, as mentioned above, both Markownikoff and anti-Markownikoff attack have been observed although the former seems more prevalent. However, alkyl group isomerization *via* β-elimination processes can in principle provide a route to rearrangement of initially formed addenda,[19] a process which apparently has rarely been anticipated or considered during previous investigations of nucleophilic additions to co-ordinated olefins. It was therefore thought desirable to carry out the theoretical calculations on a system for which reliable regiochemical information was available or could be obtained. For this reason, most of our calculations involved hydride addition to olefin complexes of the type $[Fe(cp)(CO)_2(olefin)]^+$ [reaction (2), $Nu = H^-$], a system which is appropriate because the alkyl products are thermally stable and have not been observed to rearrange *via* secondary processes.[10-14] Unfortunately, for examples of hydride addition to these cationic olefin–iron complexes, there is in the literature considerable disagreement with respect to product distributions.[14] We have therefore carried out and report here a series of experiments with compounds (**2**)—(**4**),

Table 2. ^1H and $^{13}C-\{^1H\}$ n.m.r. data for $[Fe(cp)(CO)_2(cyclo\text{-}C_6H_{11})]$ (7) and (**D-7**) ($CDCl_3$)*

Compound	δ_H	δ_C
(7)	4.65 (s, 5 H, cp)	218.0 (CO)
	2.52 (tt, 1 H, H^1, *J* 12, 3.5)	85.75 (cp)
	1.86 (br d, 2 H, $H^{2,6}$, *J* 3.5)	28.29 (C^1)
	1.56 (br d, 2 H, $H^{2',6'}$, *J* 12)	44.11 ($C^{2,6}$)
	1.4—1.5 (m, 6 H, $H^{3,3'}$, $H^{4,4'}$, $H^{5,5'}$)	31.78 ($C^{3,5}$)
		27.41 (C^4)
(**D-7**)	4.65 (s, 5 H, cp)	218.0 (CO), 85.75 (cp)
	2.52 (td, 1 H, H^1, *J* 12, 3.5)	28.17 (C^1)
	1.86 (br d, 1 H, H^6, *J* 3.5)	43.67 (t, C^2, J_{CD} 19.6)
	1.56 (br d, 2 H, $H^{2',6'}$, *J* 12)	31.66 (C^3)
	1.4—1.5 (m, 6 H, $H^{3,3'}$, $H^{4,4'}$, $H^{5,5'}$)	27.37 (C^4)
		31.77 (C^5)
		44.07 (C^6)

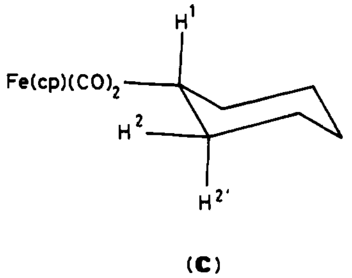
* tt = Triplet of triplets, td = triplet of doublets.

performed under standard conditions, in order to ascertain the extent of any inherent regioselectivity.

Product Distributions during Hydride Addition Reactions.—We list in Table 1 product distributions from the reactions of several hydride sources with the complexes (**2**), (**3**), and (**4**), carried out in thf or acetonitrile at several temperatures. The reaction products generally included both possible isomeric alkyl products, which were the major products except in those cases where a significant hydride, (**6**), or dimer, $[\{Fe(cp)(CO)_2\}_2]$, formed. The hydride has, interestingly, not been reported previously for this type of reaction, but was identified unambiguously by its i.r. and n.m.r. spectra, and by its facile conversion to $[Fe(cp)(CO)_2Cl]$ *via* reaction with carbon tetrachloride.[18] The dimer has often been noted, and probably forms *via* degradation of (**6**)[18] or, possibly, *via* electron-transfer processes (see below). From the data in Table 1 it is clear that hydride donors exhibit no general preference for either olefinic carbon atom of any of the complexes. Ratios of alkyl isomers vary considerably on changing the solvent and even, in those cases studied, the temperature. Furthermore, the complex of the 1,1-disubstituted ethylene, (**4**), exhibited as much variation in the position of addition as do (**2**) and (**3**), although (**4**) would be expected to exhibit the greatest degree of regioselectivity.[9]

We have also examined the addition of deuteride ($NaBD_4$) to (**2**) in order to establish that no scrambling of product occurs during the addition. If deuteride addition occurs as in equation (1), then a single deuterium atom should appear in both of the propyl–iron products, specifically in one of the methyl groups of the isopropyl compound and in the β-methylene group of the n-propyl compound. An approximately 1:3 Pr^n–Pr^i ratio of propyl products was isolated from a reaction of (**2**) with $NaBD_4$ in thf, and the sites of deuterium incorporation were determined by ^1H, $^{13}C-\{^1H\}$, and ^2D n.m.r. spectroscopy. In the ^{13}C n.m.r. spectrum, the methyl resonance of the isopropyl isomer was found to consist of a singlet (δ 32.63) and an overlapping 1:1:1 triplet (δ 32.32, J_{CD} 19.5 Hz), while the methine resonance was a singlet (δ 15.3). Similarly, the β-carbon resonance of the n-propyl isomer was a 1:1:1 triplet (δ 31.15, J_{CD} 39.4 Hz), while the α and γ-carbon resonances were singlets (δ 6.35 and 19.1, respectively). The ^1H n.m.r. spectrum of the mixture of deuteriated propyl compounds was consistent with deuteriation at the expected sites in that the various aliphatic resonances were considerably more complicated than they are in the n.m.r. spectra of the corresponding undeuteriated materials, but poor resolution and overlap of the resonances made interpretation difficult. However, the ^2D n.m.r. spectrum exhibited a single broad resonance at δ 1.44, a chemical shift corresponding to overlapping methyl and β-methylene resonances of the iso- and n-propyl compounds, respectively. Thus the addition of deuteride to (**2**) results in alkyl products in which the deuterium is incorporated only at carbon atoms β to the iron.

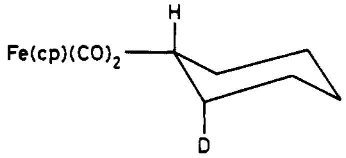
Stereochemistry of Hydride Addition.—The addition of deuteride to (**5**) was carried out to justify the assumption of *exo* attack in our calculations.[9] Previously only a single determination of the stereochemistry of hydride attack on an olefin complex of the type studied here had been reported, but that involved a strained olefin and the general implications of the result were not clear.[14d] The products of the reactions of (**5**) with $NaBH_4$ and $NaBD_4$ in thf, (**7**) and (**D-7**), respectively, were characterized utilizing ^1H, $^{13}C-\{^1H\}$, and ^2D n.m.r. spectroscopy; the pertinent chemical shift and coupling constant data are listed in Table 2. Although the nature of the preferred conformation(s) of (**5**) is not known, the $Fe(cp)(CO)_2$ moiety will certainly assume an equatorial position on a cyclohexyl ring, *i.e.* as in (**C**).



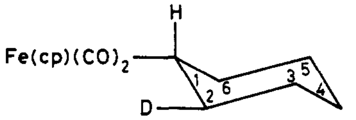
(**C**)

Space-filling molecular models show that the $Fe(cp)(CO)_2$ group is at least as bulky as is the t-butyl group, and the latter exhibits a very strong preference for an equatorial position in a cyclohexyl ring, effectively locking t-butylcyclohexane into a single conformation.[20] Consistent with this hypothesis, the aliphatic region of the ^1H n.m.r. spectrum of $[Fe(cp)(CO)_2(cyclo\text{-}C_6H_{11})]$ (**7**) exhibits resonances at δ 2.52 (1 H, triplet of triplets, *J* 3.5, 12 Hz), 1.86 (2 H, broad doublet, *J* 3.5 Hz), 1.56 (2 H, broad doublet, *J* 12 Hz), 1.5—1.4 (6 H, multiplet). We assign the resonance at δ 2.52 to H^1 because of its integrated intensity and because of the very different spin–spin couplings, 3.5 Hz to two equatorially oriented atoms, presumably H^2, 12 Hz to two axially oriented atoms, presumably $H^{2'}$.[21] It follows then that the resonances at δ 1.86 and 1.56 are to be attributed to H^2 and $H^{2'}$, respectively.

The products of deuteride addition on the same and on the opposite sides of the cyclohexene ring relative to the iron (*cis* or *endo* attack, and *trans* or *exo* attack, respectively) would be (**C**′) and (**C**″), respectively.



(**C**′)



(**C**″)

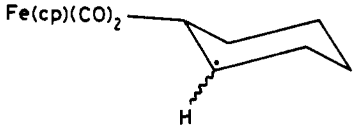
The ^1H n.m.r. spectrum of the deuteriated material obtained on treating (**5**) with $NaBD_4$ in acetonitrile exhibits for H^1 a triplet of doublets, there now being only one axial–equatorial coupling. Furthermore the intensity of the resonance at δ 1.86 has been decreased by half, a change accompanied by the appearance of a resonance in the ^2D n.m.r. spectrum *only* at δ 1.86. Thus the structure of the deuterium adduct is (**C**″), as expected for *exo* attack. Similar conclusions have been reached for interactions of other complexes of the type $[Fe(cp)(CO)_2(olefin)]^+$ with a variety of other nucleophiles.[14g]

The ^{13}C n.m.r. spectrum of deuteriated (**7**) is also consistent with deuteriation having occurred at only a single site. The spectrum of undeuteriated (**7**), assigned in part on the basis of a *J* modulated spin echo pulse sequence,[22] exhibits methylene resonances at δ 44.11, 31.78, and 27.41, and a methine resonance at δ 28.29 which is clearly to be assigned to C^1. The $^{13}C-\{^1H\}$ n.m.r. spectrum of (**D-7**) differs in that the methylene resonance at *ca.* δ 44.1 consists of a singlet at δ 44.07 and a 1:1:1 triplet (J_{CD} = 19.6 Hz) at δ 43.67, consistent with deuteriation having occurred at only a single carbon atom. Interestingly the resonance at δ 31.78 in the spectrum of (**7**) has, because of an isotope effect, become two singlets (δ 31.66 and 31.77) in the spectrum of the deuteriated compound. On careful inspection of the spectra of (**7**) and (**D-7**), it is found that all the ring carbon atoms exhibit small isotope shifts, as listed in Table 2. As can be seen, the intrinsic isotope shifts are 0.44 p.p.m. for the carbon atom to which the deuterium is attached (a one bond shift), and 0.12 p.p.m. for the carbon to which the iron is attached (C^1, presumably a two-bond shift). There is also a second isotope shift of 0.12 p.p.m., two of 0.04 p.p.m. and one of 0.01 p.p.m. Günther and co-workers[23] have carried out similar studies of cyclohexyl compounds with deuterium atoms held in equatorial orientations, finding that intrinsic isotope shifts are strongly attenuated in the order one-bond (0.39—0.46 p.p.m.) > two-bond (0.11–0.13 p.p.m.) > three-bond (0.02—0.04 p.p.m.). As these data are very similar to the various isotope shifts of (**7**), it seems likely that the shifts of 0.12, 0.04, and 0.01 p.p.m. correspond to two-, three-, and four-bond effects, especially as the last applies only to a single carbon atom. On this basis, the assignments of Table 2 have been made.

While all the evidence to this point is consistent with the anticipated nucleophilic addition of hydride to the co-ordinated olefins, we note that electron-transfer processes are being increasingly recognized as occurring during reactions of organometallic complexes.[24] A two-step mechanism such as shown by equation (3) (R = alkyl) thus seemed possible. In the case of

$$\begin{aligned}[Fe(cp)(CO)_2(olefin)]^+ + BH_4^- &\longrightarrow \\ &[Fe(cp)(CO)_2(olefin)] + \text{'}BH_4\text{'} \\ &\qquad (\mathbf{D}) \\ &\longrightarrow\longrightarrow [Fe(cp)(CO)_2R] + BH_3 \quad (3)\end{aligned}$$

hydride addition to (**5**), the reaction would then proceed *via* the 17-electron intermediates (**D**) and (**E**), the latter being a



(**E**)

carbon-centred radical. A radical such as (**E**) would be expected to racemize rapidly, leading to (**D-7**) containing both axial and equatorial deuterium. Thus the observation of a high degree of stereospecificity in the addition of deuteride to (**5**) may be taken as evidence that the reaction involves a one-step, deuteride addition process.

Low-temperature Hydride Addition.—An interesting and initially somewhat surprising result suggested by our energy level calculations[9] on (**1**) is the apparent existence of a band of low-lying, vacant orbitals, most of them of carbonyl π*, C_5H_5*, and/or iron character and only one of predominantly ethylene π* character, the latter lying *ca.* 0.3 eV above the lowest unoccupied molecular orbital in the INDO approximation.[9] In addition, both INDO and extended-Hückel molecular orbital calculations of the charge distribution of (**1**) suggested that, while there is a slightly negative charge on the ethylene carbon atoms, the charge is positive on the carbonyl carbon atoms and possibly positive on the iron atom and the cp carbon atoms. Although we do not believe that the relative energies of the vacant orbitals can be calculated with any useful degree of confidence, considerations of both orbital and charge control would suggest that hydride addition might well occur preferentially at carbon monoxide and iron rather than at ethylene. Thus the formation of (**6**) during many of the hydride addition reactions (Table 1) seemed possibly to be a result of secondary processes or even of direct attack at iron. In an attempt, therefore, to learn more about the hydride addition process(es), we utilized ^1H n.m.r. spectroscopy to monitor the low-temperature reaction of (**1**) with $NaBH_4$. As described in the Experimental section, we allowed a solution of (**1**) in $[^2H_6]$-acetone to mix briefly with a deficiency of the hydride source in the same solvent in the temperature range −95 °C (the melting point of acetone) to −60 °C. The first ^1H n.m.r. spectrum was taken at the latter temperature, a considerable amount of (**1**) and identifiable but relatively minor amounts of (**6**), $[Fe(cp)(CO)_2Et]$ (**8**), and ethylene (but no BH_4^-) being observed. In addition, there were new resonances at δ 5.05 and 15.2, in the cp and the formyl[25] regions, respectively. On standing at −60 °C for 15 min, followed by warming to −40 and −20 °C, the resonances at δ 5.05 and 15.2 disappeared while the resonances of (**6**) and free ethylene grew in. During this time, the intensities of the resonances of (**8**) did not change significantly.

These observations seem best rationalized in terms of preferential attack of hydride at carbon monoxide to give a formyl complex which is thermally unstable with respect to conversion to (**6**) and free ethylene, *i.e.* equation (4). Neither a

$$[Fe(cp)(CO)_2(C_2H_4)][BF_4]\ (\mathbf{1}) + NaBH_4 \longrightarrow [Fe(cp)(CO)(C_2H_4)(CHO)] \longrightarrow [Fe(cp)(CO)_2H]\ (\mathbf{6}) + C_2H_4 \quad (4)$$

formyl compound nor (**6**) has been previously reported from hydride addition reactions of the types of olefin complexes discussed here. However, Brown *et al.*[26] have reported that hydride addition to the cationic complex $[Fe(cp)(CO)_3]^+$ occurs at −80 °C to give the formyl complex $[Fe(cp)(CO)_2(CHO)]$, which rearranges at higher temperatures to (**6**). Davies *et al.*[27] have similarly reported a number of similar iron and ruthenium formyl complexes.

As the first low-temperature ^1H n.m.r. spectrum taken already exhibited small amounts of (**6**), we cannot rule (**6**) out as a possible primary product, formed *via* direct attack at iron. Small amounts of (**8**) had also formed prior to the first n.m.r. spectrum being run, but the concentration of (**8**) did not increase significantly as the reaction mixture warmed up. Thus (**8**) was not formed as a secondary product from the decomposition of the formyl compound, but rather was formed simultaneously with the formyl compound. Therefore it would seem that hydride attack on (**1**) occurs competitively at the two sites, with addition to carbon monoxide being somewhat preferred kinetically in acetone at low temperature. This conclusion is consistent with the suggested[9] molecular orbital scheme for (**1**), in which the lower-lying vacant molecular orbitals are closely grouped in energy such that several would interact competitively with an incoming nucleophile. Interestingly, no evidence was found for attack at the cp ring of (**1**), although there is a vacant orbital of significant cp π^* character which may be energetically accessible[9] and attack at the cp ring has been noted previously for related cationic alkyne–iron complexes.[28]

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