



On the role of the indenyl effect in controlling intramolecular hydride transfer in iron carbonyl complexes

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ABSTRACT

Density functional theory reveals multiple pathways for intramolecular hydride transfer in the cyclopentadienyl and indenyl species $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3\text{H}$ and $(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3\text{H}$. The ability of the indenyl ligand to undergo facile $\eta^5\text{-}$ to $\eta^3\text{-}$ ring slippage stabilises the isomer where the hydride is bonded directly to the metal, which opens up a low-energy pathway for hydride transfer from CO to metal.

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1. Introduction

The fundamental processes involved in the hydride reduction of metal carbonyl compounds continue to attract attention due to their importance in the Fischer–Tropsch process [1], the water-gas shift reaction [2] and other industrially relevant processes [3]. The unsaturated nature of ligands in typical organometallic species offers a multitude of possible sites for attack by an incoming nucleophile, including the carbonyl and other ancillary ligands such as cyclopentadienyl, as well as the metal centre itself [4,5]. In 18-electron complexes, the saturation of the metal valence shell normally precludes direct attack at the metal centre itself but ring-slippage [6], wherein a ligand reduces its hapticity and hence the number of electrons it donates to the metal, can accommodate such a direct metal-oriented attack. Complexes of the indenyl ligand offer perhaps the best characterised examples of ring slippage, the normally unfavourable shift from $\eta^5\text{-}$ to $\eta^3\text{-}$ coordination being compensated by the enhanced aromaticity of the six-membered ring (Scheme 1). The so-called ‘indenyl effect’ [7] is clearly reflected in the enhanced rates of associative ligand-substitution reactions of complexes bearing this ligand.

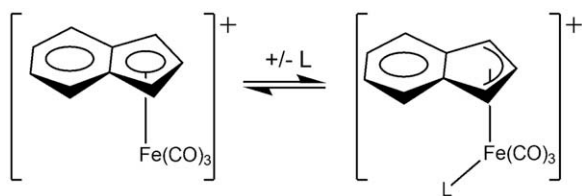
In a series of papers [8–11], Brown and co-workers have explored the reactivity of the iron carbonyl complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3]^+$ and $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3]^+$ with the hydride ion sources BH_4^- and BH_3CN^- , and observed a range of products including metal hy-

dride and metal formyl complexes as well as $\eta^4\text{-}$ cyclopentadiene complexes where the hydrocarbon ring has been reduced (Fig. 1). In the cyclopentadienyl system, addition of BH_4^- leads to two stable products, an $\eta^4\text{-}$ cyclopentadiene complex and the iron carbonyl dimer, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$. Low temperature studies, however, revealed that the dimer is formed via two distinct intermediates, the first being a metal formyl complex, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CHO})$ which subsequently decomposes to $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ via the metal hydride, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{H})$. The corresponding reaction with the milder nucleophile, BH_3CN^- , revealed an additional intermediate, with a chemical shift (δ –5.98 ppm) typical of a metal hydride, but very different from that of the dicarbonyl hydride $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{H}$ (δ –11.95 ppm) [8]. The authors proposed a structure featuring a ring-slipped $\eta^3\text{-Cp}$ ligand, although they noted that an alternative with an $\eta^5\text{-Cp}$ ligand and a weakly coordinated CO ligand could not be eliminated. Calculations performed at the MP2 level with a 3-21G basis suggested that these two alternative structures are separated by only 7 kcal mol^{–1} [12a]. Reduction of the indenyl system by BH_4^- follows a rather similar path, with the formyl complex being formed at –80 °C and subsequently decomposing to the dicarbonyl hydride (δ –15.34 ppm) above –55 °C. With BH_3CN^- , however, the formyl complex is not observed, and instead a new species is formed, the chemical shift of which (δ –8.75 ppm) again suggests that it is a hydride [9]. The authors assigned this signal to an $\eta^3\text{-}$ coordinated indenyl species, $(\eta^3\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3\text{H}$, although they noted that an alternative structure involving a ring-reduced species where a C–H bond was involved in an agostic interaction with the metal was also possible.

The data summarised above illustrate the complexity of the reaction, and also highlight the uncertainty over the identity of

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Scheme 1. The 'indenyl effect': ring slippage to accommodate additional electron pairs at the metal centre.

some of the transient species observed in solution. The evolution of the product distribution as a function of temperature in the cyclopentadienyl and indenyl cases clearly holds important clues regarding the accessible pathways for intramolecular hydride transfer. In this paper, we explore the potential energy surfaces for reduction for the two alternative ligands, cyclopentadienyl and indenyl, using density functional theory. Our purpose is first to compute the NMR chemical shifts of the various minima in order to corroborate structural assignments for the species present in solution. We then explore the various transition states that connect these minima, and establish the most favourable routes for hydride transfer. In so doing, we show that slippage of the indenyl ring opens up a low-energy pathway for hydride transfer from the carbonyl ligand to the metal, thereby reducing the kinetic stability of the formyl species.

2. Computational methodology

All calculations were performed using the B3LYP functional [13–15] with the GAUSSIAN03 series of programs [16]. Iron was described with the [6s5p3d] SDD valence basis set and the quasi-relativistic ECP28MWB effective core potential of Andrae et al. [17] while main group atoms were described using the 6-31G(d,p) basis. Full geometry optimisations with no restrictions were carried out in each case, and stationary points were confirmed to be genuine minima or transition states by analytic calculation of their harmonic vibrational frequencies. NMR chemical shifts were calculated using the GIAO formalism, along with the Wachters+f basis for Fe and 6-31G(d,p) on main group atoms [18].

3. Results

3.1. Structure of minima

3.1.1. Cyclopentadienyl complexes

The optimised structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3]^+$, **I**, a typical 18-electron complex, is shown in Fig. 2. The pseudo-octahedral geometry and Fe–C distances of 1.83 Å (CO) and 2.14 Å (Cp) are similar to crystallographically determined values for this cation [19]. We have also located four distinct isomers, **II–V**, that could arise from hydride reduction. In the most stable of these, **II**, the hydride ligand is bound directly to the 5-membered ring, giving an 18-electron cyclopentadiene complex. The reduction results in an envelope-type distortion at the saturated carbon centre, but there is no evidence for an agostic interaction between the metal and the *endo* C–H bond, the length of which is identical to its *exo* counterpart (1.09 Å). The next most stable isomer, **III**, features a formyl ligand resulting from hydride attack at one of the three carbonyl ligands. The C–O bond at this ligand is consequently somewhat longer than the others (1.21 Å versus 1.15 Å), while the Fe–C bond length increases to 1.95 Å (*c.f.* 1.77 Å for Fe–CO) as a result of the reduction in backbonding. The presence of a C=O double bond is also reflected in a much smaller $\nu(\text{C}=\text{O})$ frequency of 1768 cm^{-1} , compared to 2079 and 2122 cm^{-1} for the remaining two carbonyls (asymmetric and symmetric stretches, respectively). The third possible site of attack is the iron centre itself, and this generates two quite distinct isomers. In the first of these, **IV**, the five-membered ring slips to reduce the electron density at the metal centre as proposed by Brown et al. [8], but the structure features an η^2 -coordinated cyclopentadienyl ring rather than the η^3 -alternative, and therefore a formal electron count of only 17 at the metal. We have located a stationary point with an η^3 -coordinated cyclopentadienyl ring only 2.4 kcal/mol above **IV**, but this corresponds to a transition state rather than a minimum, with the single imaginary frequency associated with rotation of the ring about the Fe-centroid axis. Thus the $\eta^2 \rightarrow \eta^3 \rightarrow \eta^2$ -reaction coordinate defines a low-energy pathway for ring-whizzing in **IV**. Veiros has noted a similar preference for η^2 - rather than η^3 -coordination of the cyclopentadienyl ring in a survey of the reactions of phosphine-based nucleophiles [7], and argued that this reflects the high energetic cost of folding the C₅ ring along a C1–C3 axis in the η^3 -coordinated alternative which outweighs the unfavourable 17-electron count. In the limit of η^2 -coordination the system should have significant

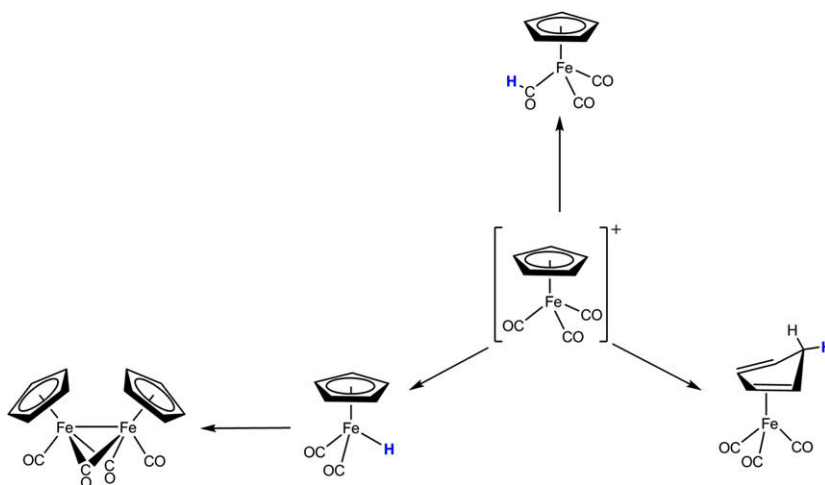


Fig. 1. Products observed from the reduction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3]^+$ by hydride.

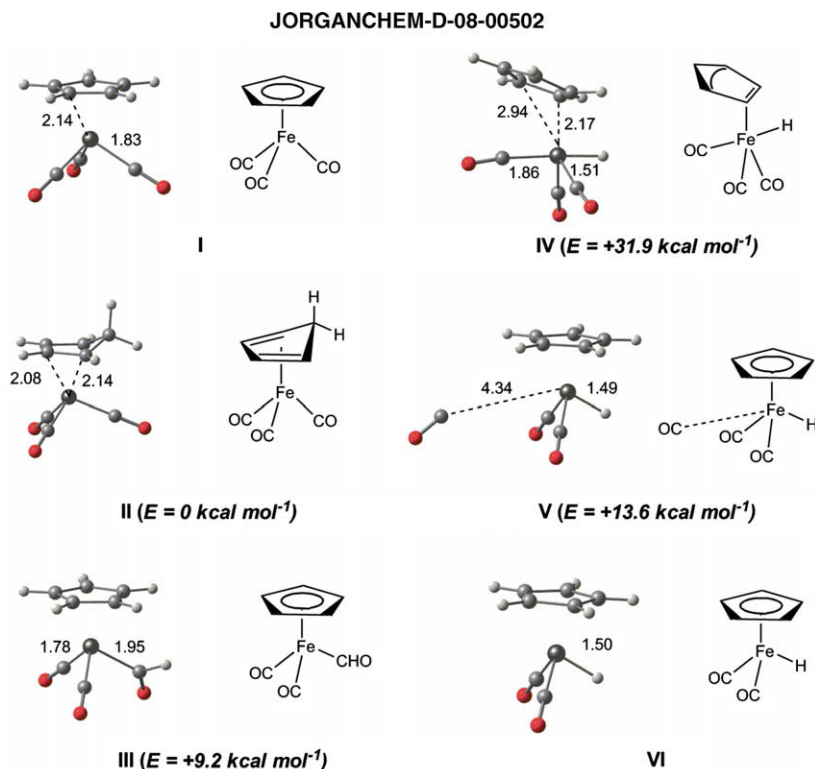


Fig. 2. Optimised structures of minima I–VI. Relative energies of the isomeric forms of $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_3\text{H}$, II–V, are shown in italics.

biradical character, with unpaired electrons localised at both the metal centre and the uncoordinated allyl unit. Our calculations, however, confirm that **IV** is a closed-shell singlet because the coordinated alkene unit of the Cp ring provides a highly effective exchange pathway between the two radical centres, resulting in strong mixing of orbitals localised on the metal and the allyl unit.

Whilst slippage of the C_5 ring provides one mechanism for reducing the electron density at the metal, the same effect can also be achieved by loss of a monodentate ligand such as CO. We have indeed located an additional isomer, **V**, where the Fe–CO separation is $>4.0 \text{ \AA}$. Brown et al. reported similar structures optimised at the HF and MP2 levels [12a]. Structure **V** is in fact only a very

shallow minimum, lying just $1.5 \text{ kcal mol}^{-1}$ below the dissociation asymptote, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{H}$ (**VI**) + CO and some $18.4 \text{ kcal mol}^{-1}$ below **IV**. The relative stability of **V** clearly reflects the unfavourable nature of ring slippage in cyclopentadienyl complexes.

3.1.2. Indenyl complexes

Structures of the parent indenyl cation, $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3]^+$ and its hydride-reduced derivatives are shown in Fig. 3. For the cation (**VII**), the ring-reduced species (**VIII**), the formaldehyde species (**IX**) and the dicarbonyl hydride (**XI**), the hapticity of the hydrocarbon ring is identical to that in the cyclopentadienyl analogues (**I**, **II**, **III** and **VI**, respectively), and the structures and relative energies

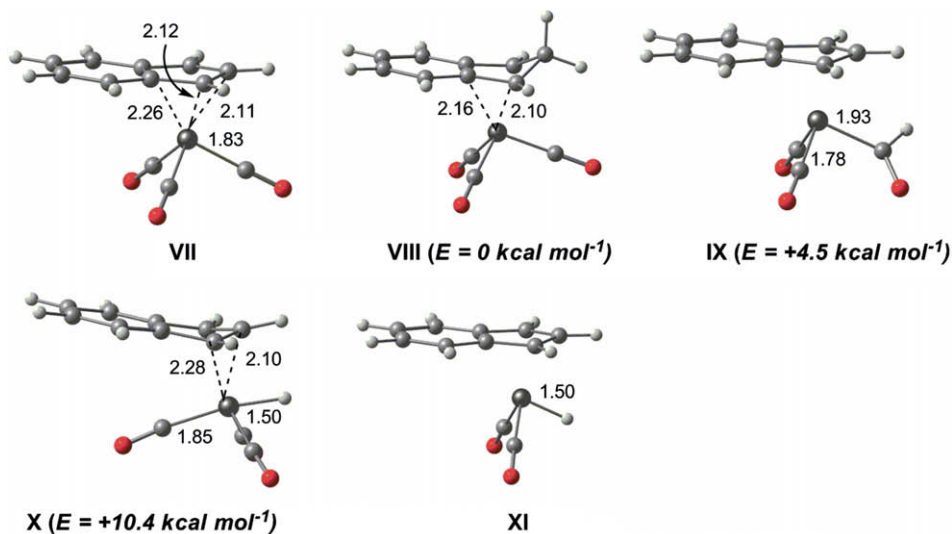


Fig. 3. Optimised structures of minima VII to XI. Relative energies of the isomeric forms of $(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3\text{H}$, VIII–X, are shown in italics.

are also very similar. The most significant difference between the ligand sets comes in the species where the hydride is directly bound to the metal, where we have been able to locate only a single minimum, **X**, in the indenyl case. All three carbonyls remain strongly bonded to the metal in **X**, and the indenyl ligand shows clear signs of an η^5 - to η^3 -ring slippage: three Fe–C bonds are in the range 2.1–2.28 Å, while the other two are significantly longer at 2.96 Å. This ring-slipped isomer is some 20 kcal mol⁻¹ more stable, relative to the global minimum, than the corresponding species with a η^2 -coordinated ring in the cyclopentadienyl case (**IV**), reflecting the strong thermodynamic driving force provided by the aromatisation of the six-membered ring. In fact, the relative stability of **X** is very similar to that of **V**: in both cases the ligand set has undergone a facile rearrangement to remove two electrons from the metal valence shell.

3.1.3. Computed NMR chemical shifts

Many of the species discussed in the previous paragraph represent transient intermediates, identified only through their spectroscopic signatures. This necessarily leaves some ambiguities concerning the exact structures of the species present in solution. The putative iron-hydride (**IV** or **V**) has been particularly difficult to pin down, and Brown et al. have suggested that the transient signal at δ –5.98 ppm could be due to either of these two species [8]. By way of precedent, the corresponding indenyl hydride species, **X**, has been reported to have a signal in the same region (δ –8.75 ppm), although this assignment is itself based only on comparison with chemically related species, and our calculations suggest that any resemblance between **X** and **IV** or **V** is in any case superficial. In light of these uncertainties, we have computed the absolute shielding parameters for the hydrogen nuclei in the cyclopentadienyl species **II**, **III**, **IV**, **V** and **VI**, along with their indenyl analogues, **VIII**, **IX**, **X** and **XI**. In Fig. 4 the computed isotropic shielding for protons in the various species is plotted against the chemical shifts reported in the literature [8–11]. The species for which the assignments are unambiguous (the stable metal hydride dicarbonyls **VI** and **XI**, the cyclopentadiene species, **II** and the formyl species, **III** and **IX**) are plotted as blue circles in the Figure, and the remarkably small deviations from the line of best fit through these points confirm that the methodology accurately models the change in the environment of the nucleus across the entire range from hydridic to covalently bound limits. For the cyclopentadiene species, even subtle differences such as the chemical shifts of the *endo* (29.42 ppm) and *exo* (29.99 ppm) hydrogens are reproduced with encouraging accuracy. The proposed indenyl hydride inter-

mediate **X** (red square) lies close to this line of best fit, suggesting that the assignment of the peak at δ –8.75 ppm to this structure is secure. We have found no evidence for the agostic cyclopentadiene species identified as an alternative origin for this peak: the cyclopentadiene complex, **VIII**, is completely non-agostic, and its computed shielding constant of 29.56 ppm is 12 ppm greater than **X**. Assignment of the peak at –8.75 ppm to this structure would therefore imply an unacceptably large deviation from the line of best fit. The hydride resonance for the putative intermediate **IV** (green triangle) also lies rather close to the line of best fit, and is clearly a much more realistic assignment for the signal at –5.98 ppm than the alternative **V** which has a much higher shielding constant, very similar to that of the hydride product, **VI**. Thus the computed NMR parameters support the proposal that intermediate **IV** has a finite lifetime in solution, despite the fact that it is some 18.3 kcal mol⁻¹ higher in energy than the iron-hydride species where a CO ligand is lost.

3.2. Interconversion pathways

We noted in the introduction that these organometallic species offer a number of alternative sites to an incoming nucleophile, and indeed the position of initial reduction appears to be dependent both on the substrate and the reducing agent. Thus for $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3]^+$ reduction by BH_4^- at –50 °C, the initial products are the formyl and cyclopentadiene products, **III** and **II**, respectively, and the former rearranges at higher temperatures to give the dicarbonyl hydride, **VI**. The milder reducing agent, BH_3CN^- , also provides evidence for a transient intermediate, **IV**, formed from decomposition of **III** to **V**. Similarly for the indenyl analogue, BH_4^- reduction generates the formyl species, **IX**, which subsequently decomposes to the dicarbonyl hydride, **XI**, while BH_3CN^- generates the η^3 -tricarbonyl hydride, **X**, and the formyl species **IX** is not observed. These observations have encouraged us to explore the various rearrangement pathways connecting the different minima, which are summarised in Fig. 5.

For the cyclopentadienyl system, we have located three distinct transition states corresponding to the transfer of a hydride between metal, carbonyl and ring. The barrier associated with direct transfer of hydride from CO to the cyclopentadienyl ring (**TS_{II-III}**) is very high (+69.5 kcal mol⁻¹ relative to **II**), suggesting such a process is unlikely to contribute to the observed dynamic behaviour. The origins of the high barrier are clearly apparent in the transition structure, where both (CO)–H and (Cp)–H bonds are greater than 1.3 Å. The large separation between CO and the π system of the ring means that bond cleavage has to be well advanced before any bond-making begins to stabilise the system. The remaining two transition states, **TS_{II-IV}** and **TS_{III-IV}**, relate to the transfer of hydride from either cyclopentadiene or CO to the metal centre, respectively. We noted in the previous section that there are two distinct isomers corresponding to the metal hydride, one where the cyclopentadienyl ring adopts an η^2 -coordination mode (**IV**), the other with a very long Fe–CO bond (**V**). The transition states for hydride transfer to the metal from either ligand connect to the less stable η^2 -Cp structure, **IV**. By Hammond's postulate, the structures of **TS_{II-IV}** and **TS_{III-IV}** should resemble **IV**, and indeed the optimised structures shown in Fig. 6 confirm the short Fe–H separation and distorted Fe–Cp coordination in both transition states. The very long C–H bond at the transition state is consistent with Berke's observation of a large kinetic isotope effect in the decomposition of manganese formyl complexes [20]. Decomposition of **IV** to **V** then proceeds via an additional low-lying transition state, **TS_{IV-V}** (13.5 kcal mol⁻¹ above **IV**) that also resembles **IV** rather closely, both structurally and energetically.

Turning to the indenyl system, the potential energy surface linking the cyclopentadiene and formyl isomers, **VIII** and **IX**, is

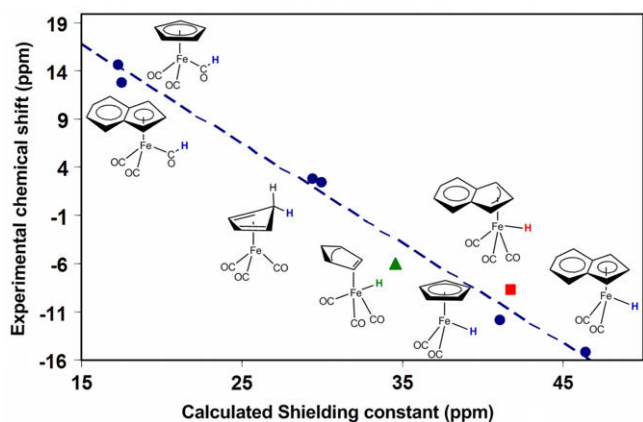


Fig. 4. Comparison of experimental chemical shifts with computed shieldings (both in ppm) for hydride, formyl and cyclopentadiene reduction products. The line of best fit is generated using only secure assignments (blue circles). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

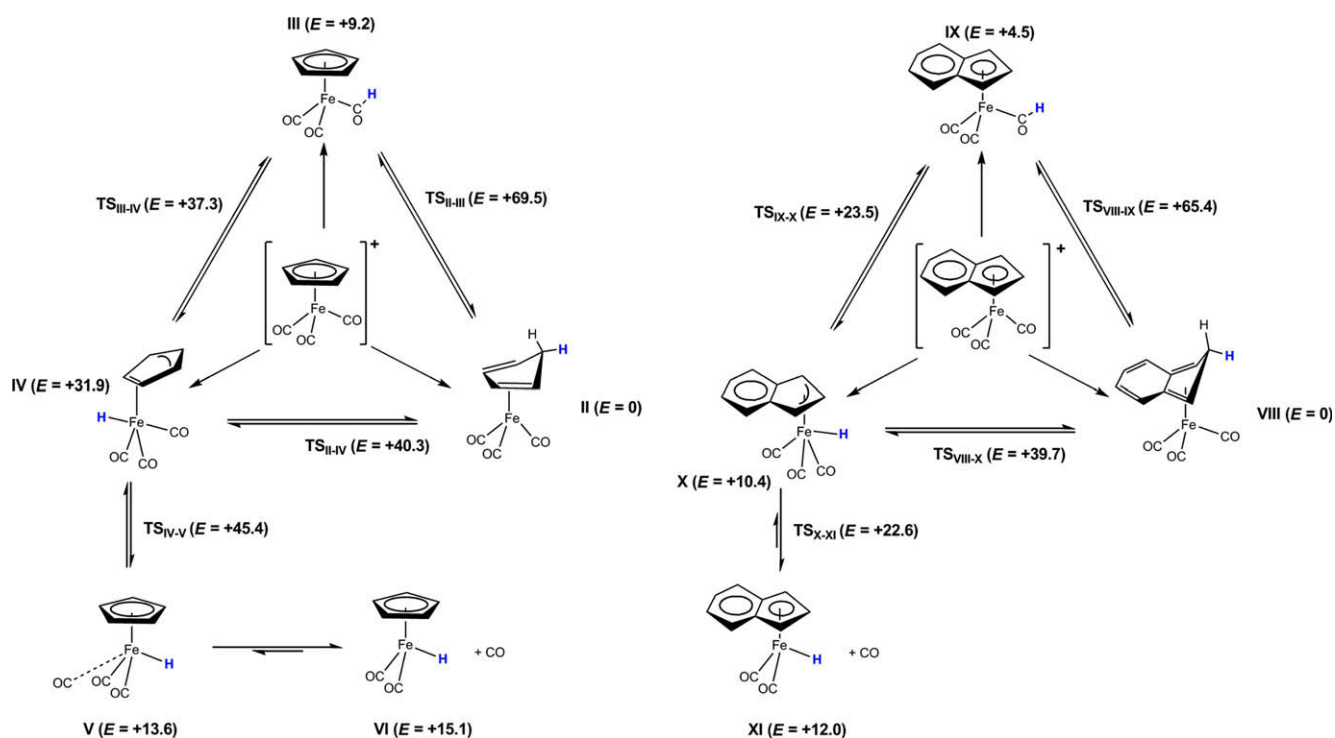


Fig. 5. Summary of rearrangement pathways for isomers of $(C_5H_5)Fe(CO)_3H$ and $(C_9H_7)Fe(CO)_3H$.

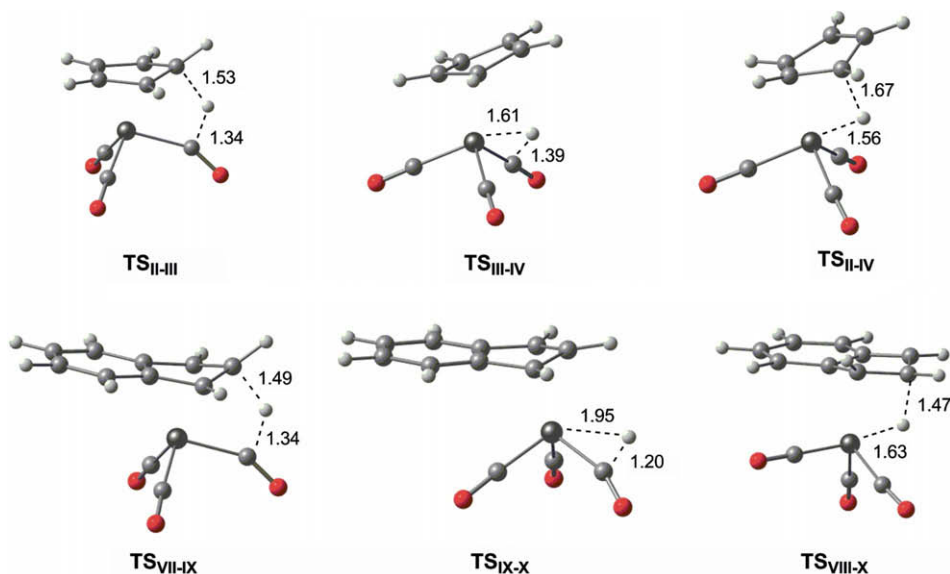


Fig. 6. Structures of transition states shown in Fig. 5.

qualitatively and quantitatively very similar to the cyclopentadienyl system, with a rather high-lying transition state that effectively blocks direct inter-ligand hydride transfer. The metal hydride region is, however, very different due to the accessible η^3 -coordination mode of indenyl, which strongly stabilises **X** relative to its cyclopentadienyl counterpart, **IV**. On this basis, we might therefore anticipate lower barriers to hydride transfer to the metal, and this proves to be the case for transfer from carbonyl (TS_{IX-X}) where the computed value of $+19.0$ kcal mol $^{-1}$ (relative to **IX**) suggests that the process should be accessible. The comparison with the corresponding process for the cyclopentadienyl ligand, where

the barrier (relative to **III**) was 28.1 kcal mol $^{-1}$, provides a striking illustration of the importance of the indenyl effect in intramolecular rearrangements. Perhaps surprising, the barrier to hydride transfer from the ring to the metal is almost unaffected by the switch from cyclopentadienyl to indenyl ($TS_{II-IV} = +40.3$ kcal mol $^{-1}$, $TS_{VIII-X} = +39.7$ kcal mol $^{-1}$), despite the much greater stability of the iron-hydride product. The structures of **TS_{II-IV}** and **TS_{VIII-X}**, offer an insight into the origin of this high barrier: in both cases, the iron centre has to move away from the centre of the C_5 ring in order to bring the Fe–H bond into a parallel alignment with one C–C bond. A simple ring slippage cannot bring these bonds into

the necessary geometry, and so a substantial barrier to direct transfer from ring to metal associated with the disruption of the Fe–C bonding persists in both ligand systems.

4. Links to experiment

The computed rearrangement pathways provide a framework for understanding the wealth of experimental data available on these two systems. Our calculations clearly indicate that barriers to transfer of a hydride to the hydrocarbon ligand, whether from metal or CO, are high, and therefore any ring-reduced product formed must arise from direct nucleophilic attack by the hydridic reducing agent. Indeed, both formyl and iron-hydride isomers are kinetically but not thermodynamically stable, and their very presence in solution is a clear reflection of these high barriers. In the cyclopentadienyl case, decomposition of the formyl species, **III**, occurs *via* the rather unstable hydride, **IV**, and the resultant high barriers retard transfer of the hydride from CO to metal. The computed barrier of 28.1 kcal mol⁻¹ for the decomposition of **III** is rather high for a process that is still rapid at relatively low temperature, but the simplicity of our model precludes quantitative agreement between experiment and theory: specifically, we do not include the boron-containing species BH₃ or BH₂CN or the solvent, all of which may influence the exact barrier heights. Nevertheless, the comparison between cyclopentadienyl and indenyl system highlights clear differences between the cyclopentadienyl and indenyl systems which can be attributed directly to the ‘indenyl effect’. In the indenyl system, the corresponding hydride **X** (δ –8.75 ppm) is much more stable due to the η^5 – η^3 -ring slippage, and the resultant lower barrier to hydride transfer from CO to metal allows for facile decomposition of any transient formyl species, **IX**.

References

- [1] C.K. Rofer–DePoorter, Chem. Rev. 81 (1981) 447.
- [2] (a) L.S. Sunderlin, R.R. Squires, J. Am. Chem. Soc. 115 (1993) 337;
(b) M. Torrent, M. Sola, G. Frenking, Organometallics 18 (1999) 2801.
- [3] E.L. Muetterties, J. Stein, Chem. Rev. 79 (1979) 479.
- [4] (a) C. Lapinte, D. Catheline, D. Astruc, Organometallics 7 (1988) 1683;
(b) J.A. Gladysz, Adv. Organomet. Chem. 20 (1982) 1;
(c) K. Kubo, H. Nakazawa, S. Nakahara, K. Yoshino, T. Mizuta, K. Miyoshi, Organometallics 19 (2000) 4932.
- [5] [a] D.A. Brown, J.P. Chester, N.J. Fitzpatrick, J. Organomet. Chem. 155 (1978) C21;
[b] D.A. Brown, N.J. Fitzpatrick, M.A. McGinn, J. Organomet. Chem. 293 (1985) 235.
- [6] J.M. O'Connor, C.P. Casey, Chem. Rev. 87 (1987) 307.
- [7] L.F. Veiros, Organometallics 19 (2000) 3127.
- [8] D.A. Brown, W.K. Glass, M.M. Salama, J. Organomet. Chem. 474 (1994) 129.
- [9] D.A. Brown, W.K. Glass, M.T. Ubeid, Inorg. Chim. Acta 89 (1984) L47.
- [10] H. Ahmed, D.A. Brown, N.J. Fitzpatrick, W.K. Glass, Inorg. Chim. Acta 164 (1989) 5.
- [11] H. Ahmed, D.A. Brown, N.J. Fitzpatrick, W.K. Glass, J. Organomet. Chem. 418 (1991) C14.
- [12] [a] D.A. Brown, N.J. Fitzpatrick, P.J. Groarke, N. Koga, K. Morokuma, Organometallics 12 (1993) 2521;
[b] D.A. Brown, J.P. Deignan, N.J. Fitzpatrick, G.M. Fitzpatrick, W.K. Glass, Organometallics 20 (2001) 1636.
- [13] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [14] P.J. Stevens, J.F. Devlin, C.F. Chabalowski, M.J. Frisch, J. Phys. Chem. 98 (1994) 11623.
- [15] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
- [16] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, GAUSSIAN03 Revision D.02, Gaussian Inc., Pittsburgh, PA, 2003.
- [17] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, Theor. Chim. Acta 77 (1990) 123.
- [18] A.M. Lee, N.C. Handy, S.M. Colwell, J. Chem. Phys. 103 (1995) 10095.
- [19] [a] M.E. Gress, R.A. Jacobson, Inorg. Chem. 12 (1973) 1746;
[b] S. Du, J.A. Kautz, T.D. McGrath, F.G.A. Stone, Dalton Trans. 1 (2003) 46;
[c] K.A. Pevear, M.M. Banaszak Holl, G.B. Carpenter, A.L. Rieger, P.H. Rieger, D.A. Sweigart, Organometallics 14 (1995) 512;
[d] D.L. Coombs, S. Aldridge, A. Rossin, C. Jones, D.J. Willock, Organometallics 23 (2004) 2911.
- [20] H. Berke, G. Huttner, O. Scheidsteger, G. Weiler, Angew. Chem., Int. Ed. Engl. 23 (1984) 735.