of the values obtained for 3 where only B sites are present. The alternate assignment leads to isomer shift values showing no obvious relationship to those found in 1, 4, and 5.

If the above assignments are accepted, it is then possible to reach some interesting additional conclusions about the bonding in these materials. Table IX contains a summary of the bond distances found in several of the compounds under study. The most striking feature of this table is the lack of variation in these distances in spite of distinct changes in the ligands. This is particularly true of the iron–iron bond distance which varies only 1.4% over the compounds studied. If **3a** is excluded (see below), the variation is less than 0.5%. This seems surprising in view of the changes in the iron Mössbauer effect isomer shift with changing ligand. We believe that this lack of variation in the iron–iron bond distance is further evidence for the lack of direct iron–iron bonding in these compounds. If there were such a bond, it seems reasonable that its bonding order and hence bond length should reflect the s-electron density variation at the iron. The lack of any such variation implies that the distance is really determined by the steric constraints imposed by the ideal bonding of the two bridging carbonyl groups. Recent ab initio molecular orbital studies[20] have revealed that the iron–iron interaction in *trans*-$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (**6**) was either nonbonding or partially antibonding. The iron atom–iron atom spin coupling is apparently accomplished through a multicentric molecular orbital derived from the iron d orbitals and the π-antibonding orbitals of the bridging carbonyl ligands. The absence of iron–iron bonding in *trans*-$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (**6**) was also revealed by both X-ray and neutron diffraction results.[21,22] The X–N derived electron density deformation maps indicate virtually no increase in electron density between the iron atoms. The different isomer shift values found for the A and B sites in **2a**, **2b**, **4b**, and **4c** provides further experimental support for the lack of direct iron–iron bonding in these compounds. We have observed a similar isomer shift difference in a related η^3-allyl organoiron complex.[5] It is interesting to note that **3a**, with the shortest diphosphine ligand, $Ph_2PCH_2PPh_2$, also has the shortest iron–iron distance. In this case the short bridging phosphine ligand apparently is responsible for shortening the iron–iron bond.

Acknowledgment. G.J.L. thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this research. G.O.N. gratefully acknowledges partial funding of this work by the NSF through Grant CHE-8102918.

Registry No. 1, 42830-83-1; **2a**, 99797-91-8; **2b**, 99797-92-9; **3a**, 78373-20-3; **3b**, 78357-02-5; **3c**, 87174-20-7; **4b**, 78357-01-4; **4c**, 87156-99-8; 5, 12154-95-9; Fe, 7439-89-6.

Supplementary Material Available: Tables of anisotropic thermal parameters and bond lengths and angles, a crystallographic report, and a listing of structure factors (23 pages). Ordering information is given on any current masthead page.

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(20) Bénard, M. *Inorg. Chem.* **1979**, *18*, 2782.

(21) Mitschler, A.; Rees, B.; Lehmann, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 3390.

(22) Bénard, M. In "Electron Distributions and the Chemical Bond"; Coppens, P., Hall, M. B., Eds.; Plenum Press: New York, 1982; p 221.

Studies of Deuterium Exchange in Alkenes Added to Iron–Ethylene-d_4 Matrices

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When iron atoms are cocondensed with C_2D_4 at 77 K and alkenes are added to the resulting matrix, a selective exchange of deuterium into the alkene is observed. Both propene and 1-butene preferentially exchange the H at C_2 while the predominant reaction of (*E*)- or (*Z*)-2-butene is exchange of the H at C_2 with *E*–*Z* isomerization. Cyclopentene exchanges all hydrogens at equal rates and is postulated to undergo exchange of allylic hydrogen followed by a more rapid allylic rearrangement. Norbornadiene does not undergo exchange. These results have been rationalized by an associative mechanism involving addition of an Fe–D to the double bond followed by rotation about either a C–C or an Fe–C bond and cis elimination of Fe–H. The reactivity of the Fe–C_2D_4 matrix is different from that of either Fe–C_2D_2 or Fe–D_2 matrices.

Hydrogenation catalyzed by mono- and polynuclear metal complexes and finely divided metals is perhaps the most common reaction in organometallic chemistry. Many studies of these hydrogenations have sought to elucidate the mechanism of the first step of the reaction by investigating the reversible exchange of deuterium into alkenes.[1]

In a recent investigation of the reactivity of the complex formed when iron atoms are cocondensed with ethylene at 77 K, we have reported that condensation of Fe with a mixture of C_2H_4 and C_2D_4 results in statistical scrambling of the label in the ethylene recovered upon warming.[2] In order to rationalize this rapid exchange of vinylic hydrogens, we proposed that an initial iron–ethylene complex, **1**, undergoes insertion into a C–H bond to generate vinyl hydride **2** which can insert another ethylene into the Fe–H bond to give **3** as shown in eq 1. If this reaction is rapid and reversible, substitution of C_2D_4 for one C_2H_4 will lead

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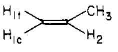
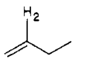
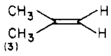
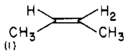
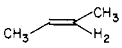
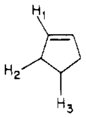
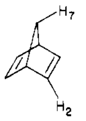
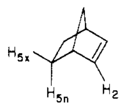
[†] Permanent address: Departamento de Quimica, Universidad de Concepcion, Casilla 3-C, Concepcion, Chile.

(1) For leading references see: Atsumu, O. "Isotopic Studies of Heterogeneous Catalysis"; Academic Press: New York, 1977.

(2) Cardenas T, G.; Shevlin, P. B. *J. Org. Chem.* **1984**, *49*, 4726.

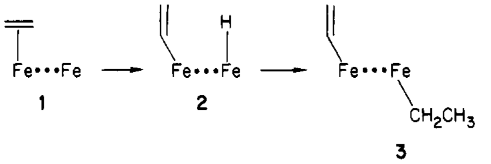
0276-7333/86/2305-0784$01.50/0

Table I. Extent of D Exchange of Alkenes on Fe-R-D Matrices

substr	matrix	time,[a] h	rel amount of D at each position	molar equiv of D in total sample × 10^2: in alkene	in alkane
	Fe–C_2D_4	0	$H_{1t} = 1.47$, $H_{1c} = 1.47$, $H_2 = 2.70$, $H_3 = 1.0$	4.23	0.25
	Fe–C_2D_2	0	$H_{1t} = 1.00$, $H_{1c} = 1.00$, $H_2 = 1.00$, $H_3 = 1.00$	1.03	4.86
	Fe–D_2	0	$H_1 = 1.0$, $H_2 = 4.2$		37.6
	Fe–C_2D_4	0	exchange only detectable at H_2	0.5 4.4[b]	1.65
	Fe–C_2D_4	0	$H_1 = 2.0$, $H_3 = 1.0$	4.5	6.4
	Fe–C_2D_4	0.25	$H_1 = 1.0$, $H_2 = 2.7$	190.0	0.19
	Fe–C_2D_2	0	$H_1 = 1.0$, $H_2 = 1.25$	3.92	3.92
	Fe–D_2	17	$H_1 = 1.0$, $H_2 = 1.87$		2.16
	Fe–C_2D_4	17	$H_1 = 1.0$, $H_2 = 1.3$	106.0	12.4
	Fe–C_2D_2	17	$H_1 = 1.0$, $H_2 = 1.0$	6.6	5.8
	Fe–C_2D_4	0	$H_1 = 1.0$, $H_2 = 1.1$, $H_3 = 1.1$	59.5	37.2
	Fe–C_2D_4	17	no exchange observed		
	Fe–C_2D_2	17	$H_1 = O$, $H_{2,3} = 2.78$, $H_7 = 1.0$	1.76	3.13
	Fe–C_2D_4	17	$H_2 = 1.5$, $H_{5n} = 1.0$, $H_{5x} = 3.4$	16.4	15.4
	Fe–C_2D_2	17	$H_2 = 0.0$, $H_{5n} = 1.0$, $H_{5x} = 9.5$, $H_{7s} = 14.5$	15.1	
	Fe–D_2	17	exchange only Detectable at H_2	trace	1.48 (exo/endo = 11.7)

[a] Time that the substrate was allowed to remain in contact with the matrix after warming to room temperature. When $T = 0$ the volatiles were removed as they warmed to room temperature. [b] This is the molar equiv of D in the (*E*)- and (*Z*)-2-butenes.

to a statistical mixture of deuterated and protiated ethylenes.[3]



(1)

The fact that iron inserts into a C–H bond of ethylene is consistent with numerous spectroscopic studies of ethylene on the surface of iron[4] and other metals[5] in which loss of hydrogen to generate a surface-bound acetylene invariably occurs. A logical first step in such a process is the C–H insertion to generate a σ-vinyl intermediate as depicted in eq 1. The fact that fast exchange between C_2D_4 and C_2H_4 is observed indicates that this reaction is rapidly reversible. When this reaction was carried out with propene as the hydrogen acceptor by condensing C_2D_4 with Fe and adding propene after condensation, it was observed that D exchange into the propene had occurred.[2] The extent of exchange was dependent on the time that the olefin–Fe matrix was allowed to stand before pumping out. When the propene and ethylene were removed by pumping as the matrix was allowed to warm, incomplete exchange of D into the propene was observed and the protons on C_2 were exchanged more rapidly than those on C_1 which, in turn, exchanged faster than the protons on C_3. To explain the observed preference for D exchange at C_2, we proposed the mechanism in Scheme I in which a propene is reversibly inserted into the Fe–D bond. If, for either steric or electronic reasons, the Fe in **2** preferentially adds to the C_1 of propene to give **4** ($k_1 > k_2$), the observed preference of exchange at C_2 may be rationalized. Addition of Fe at C_2 generates **5** which can exchange D at C_1 and C_3. The fact that exchange occurs more rapidly at C_1 than C_3 indicates that the methyl groups in **5** are nonequivalent. It is possible that rotation about the C_2–Fe bond in **5** must occur before a hydrogen on C_3 can be transferred. If this is the case and $k_3 > k_4$, the preference for exchange at C_1 over C_3 may be rationalized.

In order to learn more about the reactivity of the iron–ethylene species and to amplify the mechanism in Scheme I, we have extended this deuterium exchange reaction by the Fe–C_2D_4 matrix to a number of other alkenes. In particular, we have cocondensed Fe and C_2D_4, added various alkenes, and used NMR spectroscopy to determine the relative amount of deuterium exchange at the various hydrogens of the added alkene. We have also compared these results with those obtained when alkenes are added to a C_2D_2–Fe matrix and when they are reacted with D_2 over freshly deposited Fe. These reactions are similar to those reported by Touroude and Gault, who observed vinylic hydrogen exchange between propene-d_6 and a number of 1-alkenes on an iron surface at 236 K.[6] However in the present work, we have cocondensed the deuterated alkene with the metal and used[2] NMR to determine the specific position of deuterium incorporation in the olefin added after cocondensation.

Results and Discussion

The Reactions of Alkenes with the Fe–C_2D_4 Matrix. These studies have been carried out by cocondensing iron and C_2D_4 at 77 K, adding the alkene substrate, and allowing the mixture to warm to room temperature and to

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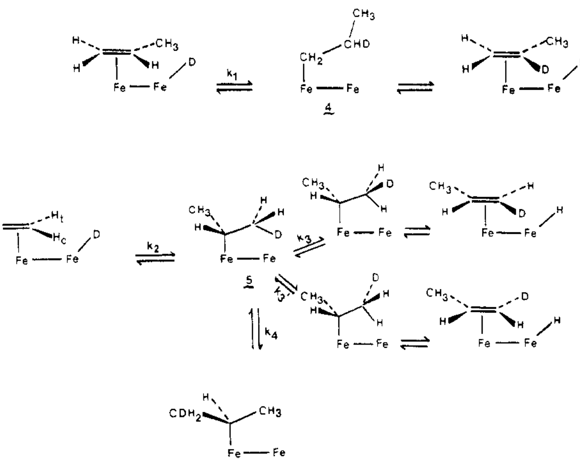
(3) The mechanistic equations in which reactions are depicted as occurring on two iron centers are meant to be schematic representations of the mechanisms only. No firm evidence as to the nuclearity of the reactions has been obtained.

(4) Earley, W.; Basso, A. M.; Ibach, H. *Sur. Sci.* **1982**, *120*, 273.

(5) Lehwald, S.; Ibach, H. *Sur. Sci.* **1979**, *89*, 425 and references cited therein.

(6) Touroude, R.; Gault, F. G. *J. Catal.* **1974**, *32*, 288.

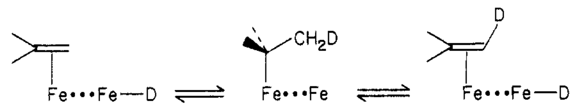
Scheme I



stand for a given period. Although the state of aggregation of the active Fe in this system is not known, it is probable that an iron–ethylene cluster of low nuclearity is formed initially.[7] As the matrix warms, larger clusters undoubtedly form.[8] The olefins which have been used as substrates in these studies are propene (**6**), 1-butene (**7**), (*E*)- and (*Z*)-2-butene (**8a** and **8b**), 2-methylpropene (**9**), cyclopentene (**10**), norbornadiene (**11**), and norbornene (**12**). Of these substrates, only **11** failed to undergo exchange of hydrogen with the Fe–C_2D_4 matrix. Table I shows the relative amount of deuterium exchange (per H) of the labile hydrogens and the total amount of D incorporated for alkenes **6**–**12** calculated from the ^2H NMR spectrum. In order to ensure that the results reflect a kinetic rather than an equilibrium effect, the reactions were generally allowed to proceed to only a few percent exchange. In all cases, a competing reaction was the formation of the deuterated reduction product. The yields of these deuterated alkanes are also shown in Table I.

Table I demonstrates that **7** shows the same preference for exchange at C_2 as does **6**. In fact, ^2H NMR reveals only deuterium incorporation at C_2. However, this result is complicated by the fact that a competing isomerization to (*E*)- and (*Z*)-2-butene without exchange also occurs. The isomerization of 1-butene on Fe surfaces has been previously reported and is thought to proceed via a surface-catalyzed migration of allylic hydrogen.[9]

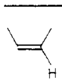
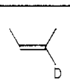
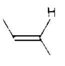
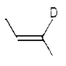
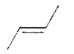
The use of alkene **9** as a substrate provides further evidence for an intermediate in which the methyl groups are nonequivalent. If rotation about the Fe–C bond in intermediate **13** were rapid compared to D exchange, the methyl and olefinic hydrogens should exchange at equal rates per H. However, Table I shows that the olefinic protons are exchanged twice as fast as those on the methyl. Since it is probable that a degenerate allylic isomerization analogous to that observed for **7** is occuring in deuterated **9**, the numbers in Table I may represent a lower limit of the preference for olefinic hydrogen exchange.

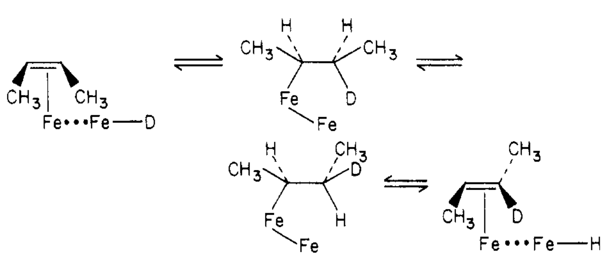


13

The mechanism in Scheme I makes certain stereochemical predictions which can easily be tested by using other alkenes as the substrate. Scheme I postulates that rotation about the C_1–C_2 bond in **4** and **5** must occur before D exchange will take place. This postulate can be tested by using either (*E*)- or (*Z*)-2-butene as the D acceptor. As shown in eq 2, addition of the Fe–D bond to **8b** will only lead to D exchange after a rotation about the central C–C bond has occurred. However, this rotation is just what is required to effect geometrical isomerism of the 2-butene after it eliminates the iron hydride. Thus the proposed mechanism predicts that the Fe–C_2D_4 matrix will bring about *E*–*Z* isomerism of the 2-butenes and that the isomerized butene will contain D at C_2 while the nonisomerized alkene will contain little D.

Table II. Deuterium Incorporation and Isomerization of 2-Butenes by Fe–C_2D_4

		product ratio			
substr	reactn time				
	15 min	3.22	1	1.5	2.7
	17 h	1	2.34	3.8	1.25



(2)

In these experiments, deuterium incorporation into the butenes was followed by NMR spectroscopy. Although (*E*)- and (*Z*)-2-butene have similar proton and deuterium spectra, the ^{13}C spectra of the (*E*)- and (*Z*)-2-butenes-*2-d*$_1$ have been reported and these compounds are easily distinguishable from one another and from their undeuterated counterparts.[10] Table II shows the isomer distribution as well as the deuterium content at C_2 of the butenes recovered after addition of (*E*)- or (*Z*)-2-butene to the Fe–C_2D_4 matrix. These results demonstrate that the isomerized 2-butene bears the majority of the deuterium at C_2 as predicted by the mechanism in Scheme I. For example, when (*Z*)-2-butene is added to the Fe–C_2D_4 matrix at 77 K, the matrix is allowed to warm to room temperature for 15 min and the volatile gasses are pumped out, the recovered (*Z*)-2-butene contains 23.6% *2-d* while the (*E*)-2-butene produced contains 64.3% *2-d*.

Although these results demonstrate that rotation about the C_2–C_3 followed by exchange of vinylic hydrogen in 2-butene is the most rapid process, there are obviously a number of other reactions occurring. In particular, *E*–*Z* isomerization without exchange as well as exchange of vinylic hydrogen without isomerization both occur. In addition, a slower exchange of the methyl hydrogens is observed. The mechanism in Scheme I may be considered to be an intramolecular cis addition followed by a cis elimination. A competing process may be the intermolecular trans addition followed by cis elimination (eq 3) or intramolecular cis addition followed by intermolecular trans elimination (eq 4). Both of these mechanisms would produce exchange without isomerization. Entropy considerations dictate that these intermolecular mechanisms would be slower than the mechanism in Scheme I.

The isomerization without exchange is probably an *E*–*Z* isomerization of the butenes catalyzed by the Fe surface,

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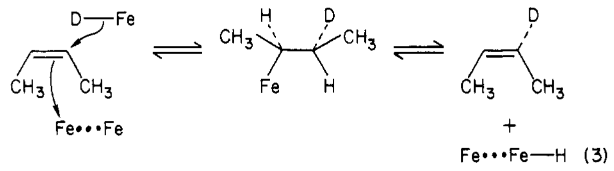
[7] Hanlan, A. J.; Ozin, G. A.; Power, W. J. *Inorg. Chem.* **1978**, *17*, 3648 have reported a dimeric cobalt–ethylene complex at 77 K.

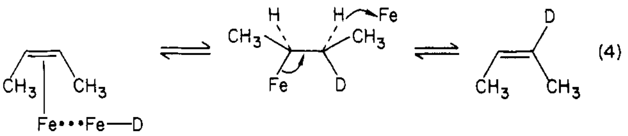
[8] Klabunde, K. J.; Murdock, T. O. *J. Org. Chem.* **1979**, *44*, 3901.

[9] Touroude, R.; Gault, F. G. *J. Catal.* **1974**, *32*, 294.

[10] Bigley, D. B.; Brown, C.; Weatherhead, R. H. *J. Chem. Soc., Perkin Trans. 2* **1976**, 701.



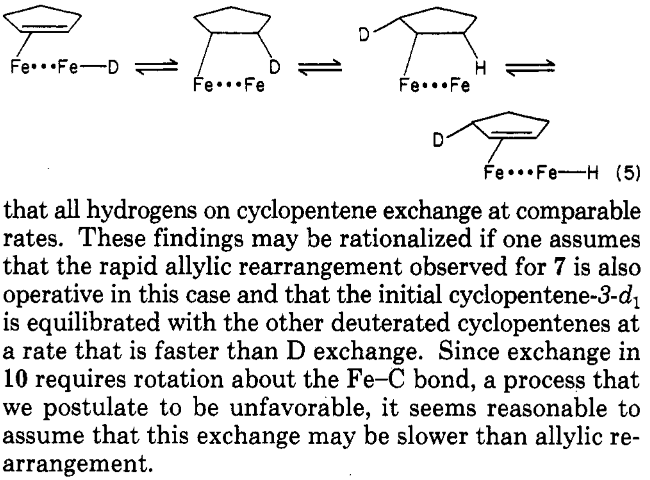
(3)



(4)

a process which is well documented.[1,11] The slower exchange of deuterium into the methyl groups may be explained by the reversible allylic isomerization of deuterated **8a** and **8b** analogous to that observed for **7**. It is interesting that **8a** is far more reluctant to undergo the exchange reaction than is **8b**. Thus, pumping **8b** from the Fe–C_2D_4 matrix immediately upon warming results in substantial exchange while **8a** must be allowed to stand in contact with the Fe–C_2D_4 for a far longer time before exchange can be detected. Although the reason for this great difference in exchange rates is not known, we may speculate that the unfavorable energetics of the C_2–C_3 rotation which eclipses the methyl groups, perhaps enhanced by the proximity of the Fe, is responsible.

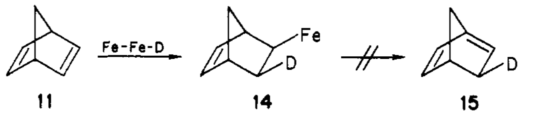
It was of interest to extend these studies to a cyclic alkene such as cyclopentene (**10**), in which rotation about the C_1–C_2 bond is precluded. The mechanism in Scheme I predicts that the lowest energy pathway for deuterium exchange will be addition of Fe–D to C_1 and C_2 of cyclopentene followed by rotation about the Fe–C bond and transfer of the H on C_5 back to Fe generating cyclopentene-*3*-d_1 (eq 5). However, the results in Table I reveal



(5)

that all hydrogens on cyclopentene exchange at comparable rates. These findings may be rationalized if one assumes that the rapid allylic rearrangement observed for **7** is also operative in this case and that the initial cyclopentene-*3*-d_1 is equilibrated with the other deuterated cyclopentenes at a rate that is faster than D exchange. Since exchange in **10** requires rotation about the Fe–C bond, a process that we postulate to be unfavorable, it seems reasonable to assume that this exchange may be slower than allylic rearrangement.

Another substrate of interest is norbornadiene, **11**, which is expected to undergo initial exo addition of the Fe–D bond to generate intermediate **14**. However, rotation about the C_2–C_3 is precluded, and rotation about the Fe–C bond followed by elimination of Fe–H_1 is impossible as the highly strained bridgehead alkene **15** would result. Thus, we expect **11** to be unreactive toward deuterium exchange, and this is the case. When **11** added to the Fe–C_2D_4 matrix and the mixture allowed to stand for 16 h, no deuterium could be detected in either the ^{2}H NMR or the IR spectrum of recovered **11**.



11 **14** **15**

A qualitatively similar result is obtained when norbornene, **12** is used as the substrate in these investigations in that **12** is sluggish toward exchange requiring 17 h in contact with the Fe–C_2D_4 matrix before appreciable exchange is observed. However, the deuterium distribution in recovered **12** is interesting in that the exchange is into the exo-5,6-, endo-5,6-, and 2,3-positions of **12**.[12] While the reason for this labeling pattern is not clear, the fact that D exchange in **12** is so much slower than in the other substrates indicates that a different mechanism may be operative in this case.

An examination of the ^{2}H NMR spectrum of the norbornane reduction product from **12** shows peaks at δ 1.47 and 1.23 in a 12:1 ratio. Since the signal at δ 1.47 is due to the exo-2,3 protons,[13] we conclude that the norbornene is reduced mainly by exo addition of D. Other investigations have demonstrated the preferences for coordination to the exo face of **12**[14] and exo reduction.[15] When norbornane or norbornadiene is added to the Fe–C_2H_4 matrix, no **12** is observed. This fact rules out a hydrogenation–dehydrogenation mechanism for generating labeled **12**.

Although deuterium exchange between deuterated and protiated alkenes occurs on an iron surface,[6] the species generated in the present work by cocondensing the deuterated alkene with iron is more active toward exchange. This fact is demonstrated by condensing iron at 77 K, warming to room temperature, recooling to 77 K, and adding ethylene-d_4 and propene. When the alkenes are pumped from the reactor upon warming, no exchange is detected. In contrast, Table I demonstrates that significant exchange occurs when propene is added to the Fe–C_2D_4 cocondensate at 77 K and pumped from the reactor upon warming.

Addition of Alkenes to Fe–D_2 and Fe–C_2D_2 Matrices. A major point that has not yet been considered is the question of whether the exchange reactions that we observe here are simply those of Fe–D bonds formed upon cocondensation or are unique to the Fe–C_2D_4 matrix. In order to address this point, we have cocondensed Fe and acetylene-d_2 and added alkenes to the Fe–C_2D_2 matrix thus generated. The results of these experiments, which are included in table I, indicate that generally much less D is incorporated into the alkene and that its distribution is different from that observed after reaction over the Fe–C_2D_4 matrix. For example, propene shows a very small amount of total deuterium incorporation and all of the protons exchange at roughly equal rates (per H). While **11** shows no deuterium exchange on the Fe–C_2F_4 matrix, the Fe–C_2D_2 brings about exchange of the vinylic protons and the protons on C-7 (Table I).

The results obtained when **12** is added to the Fe–C_2D_2 matrix are interesting in that the majority of the deuterium is incorporated into the 7-syn position with smaller amounts in the 5,6-exo and the vinyl positions (Table I). This result, which is quite different from that obtained with **12** on the Fe–C_2D_4 matrix, may be rationalized by assuming a mechanism involving initial electrophilic addition of a deuteron to give the norbornyl cation, **16** which can add Fe to give **17** and **18**. While compound **17** cannot undergo a syn elimination of Fe–H, **18** should do so with ease generating **12** labeled with D at the 7-syn position.

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(11) Mintsa-Eya, W.; Touroude, R.; Gault, F. G. *J. Catal.* **1980**, *66*, 412.

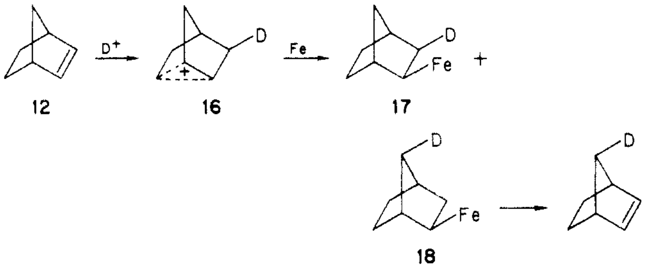
(12) The proton chemical shifts of 12 have been assigned by Marchand, A. P.; Rose, J. E. *J. Am. Chem. Soc.* **1968**, *90*, 3724.

(13) Marchand, A. P.; Marchand, N. W. *Tetrahedron Lett.* **1971**, 1365.

(14) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495.

(15) Franzus, B.; Baird, W. C., Jr.; Surridge, J. H. *J. Org. Chem.* **1968**, *33*, 1288.

The addition of D^+ to **12** followed by rearrangement to place D at the 7-exo position is well-known.[16] The increase in acidic character of the Fe–C_2D_2 matrix as compared to the Fe–C_2D_4 matrix may be attributed to the acetylenic residue in which there is more π-bonding character of the end on bond in C_2H than in the C_2H_3 of the ethylenic residue.



Yet another type of reactivity is observed when either **6**, **8b**, or **12** and D_2 are added to freshly condensed Fe at 77 K and the mixture allowed to warm to room temperature. In this case, the only deuterium that is incorporated is found in the reduction products propane, butane, and norbornane. Again, the majority of the reduction of **12** is from the exo face giving norbornane deuterated in the 2,3-exo positions.

Thus, although these experiments provide evidence for the formation of M–H bonds when acetylene is cocondensed with Fe or hydrogen is deposited on an iron surface, the hydrides generated differ from one another in their chemistry and show quite different reactivities from the species produced by the condensation of iron with ethylene.

Conclusion. These investigations demonstrate a rich and somewhat unique chemistry for the species formed upon cocondensation of Fe with ethylene. In addition to the previously reported dimerization and reduction reactions,[2] selective exchange of hydrogens with added alkenes may also take place.

Experimental Section

Starting Materials. Deuterium, ethylene, propene, and the butenes were obtained from Matheson Gas Products. Norbornene and norbornadiene were from Aldrich Chemical Co. Ethylene-d_4 was purchased from Merck and Co. Acetylene-d_2 was prepared by the addition of D_2O to calcium carbide which had been heated under vacuum at 500 °C for 14 h. All substrates were degassed by freeze–thaw cycles and vacuum transferred into the reactor.

Deuterium Exchange Studies. Iron atoms (4–15 mmol) and deuterated substrate (5 mmol) were cocondensed at 77 K in a reactor based on that designed by Timms[17] and previously described by us.[2] After condensation, the alkene substrate (1 mmol) was distilled into the reactor and the contents were allowed to warm to room temperature. The alkenes were allowed to remain in contact with the Fe–deuterated substrate matrix until their IR spectrum showed C–D stretch. Contact times are given in Table I where $T = 0$ indicates that the contents of the reactor were pumped out as they warmed to room temperature. Volatile products were pumped from the reactor through a trap at 146 K which passed the deuterated ethylene or acetylene but not the exchanged alkene. The contents of the 146 K trap were analyzed by ^2H NMR.

Analysis of Deuterium in Exchanged Alkenes. The exchanged alkenes were distilled into a 5-mm NMR tube containing $CDCl_3$ (6.23×10^{-2} mmol) in $CHCl_3$. The tubes were sealed and their ^2H spectra recorded at 61.4 mHz on a Bruker AM 400 NMR spectrometer. The amount of deuterium exchange at each position was determined from the relative areas of the peaks, and the amount of total deuterium incorporation was calculated by using the $CDCl_3$ peak as an internal standard. In all cases, the δ values for ^2H were the same as those in the corresponding ^1H spectra. The results of these analyses for ^2H are given in Table I.

Analysis of the Deuterated (*E*)- and (*Z*)-2-Butenes. The relative amounts of the 2-d_1 compounds and their protiated counterparts were determined from the relative intensity of the ^{13}C NMR signals (at 100.6 mHz) for C_3 in each compound. The chemical shifts (ppm) of the C_3 in the four compounds were as follows: (*E*)-2-butene, δ 125.92; (*E*)-2-butene-2-d_1, δ 125.83; (*Z*)-2-butene, δ 124.69; (*Z*)-2-butene-2-d_1, δ 124.52. These values are similar to those which have been reported.[12] As a standard, a mixture of (*E*)- and (*Z*)-2-butene-2-d_1 was prepared[18] and the *E*:*Z* ratio determined by gas chromatography. This mixture was combined with known amounts of (*E*)- and (*Z*)-2-butene and the resulting mixture used as a standard for the ^{13}C integration ratios in the NMR analysis. The results are given in Table II.

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Registry No. **6**, 115-07-1; **7**, 106-98-9; **8a**, 624-64-6; **8b**, 590-18-1; **9**, 115-11-7; **10**, 142-29-0; **11**, 121-46-0; **12**, 498-66-8; Fe, 7439-89-6; C_2D_4, 683-73-8.

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[16] Brown, H. C.; Liu, K.-T. *J. Amer. Chem. Soc.* **1975**, *97*, 2469 and references cited therein.

[17] Timms, P. L. *J. Chem. Educ.* **1972**, *49*, 782.

[18] Caldwell, R. A. *J. Org. Chem.* **1970**, *35*, 1193.