$[\{(\eta^5\text{-}C_5Me_5)Fe\}_2(\mu\text{-}H)_4]$: A Novel Dinuclear Iron Tetrahydrido Complex**

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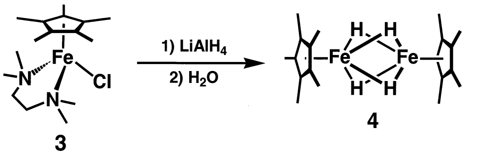
Transition metal cluster complexes have attracted attention because of their potential ability for cooperative and effective activation of substrates in a multimetallic site.[1] We have used the term "*multimetallic activation*" to refer to a mode of activation achieved as a result of cooperative action of many metal centers. Our research on multimetallic activation began as an attempt to prepare a cluster with bridging hydrido ligands. As a result, we synthesized a new class of ruthenium polyhydrido clusters, **1** and **2**, and demonstrated many examples of *multimetallic activation* through the reaction with unsaturated hydrocarbons, silanes, and phosphanes as well as alkanes.[2] According to the vertical trends associated with the transition elements, the metal–metal and metal–ligand bond enthalpies increase down a column and the complexes become more substitutionally inert. The iron analogues of these ruthenium polyhydrido clusters are, therefore, expected to be much more reactive. So far there have been no examples of an iron polyhydrido cluster which has only cyclopentadienyl derivatives (η^5-C_5R_5) as ancillary ligands. Here we report the first synthesis and brief reaction chemistry of the highly reactive and unstable dinuclear iron tetrahydrido complex $[\{(\eta^5\text{-}C_5Me_5)Fe\}_2(\mu\text{-}H)_4]$ (**4**).

$[\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu\text{-}H)_4]$ **1**

$[\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2]$ **2**

$[(\eta^5\text{-}C_5Me_5)FeCl(NMe_2CH_2CH_2NMe_2)]$ **3**

Treatment of **3**[3] with $LiAlH_4$ followed by work-up with H_2O gave the dinuclear iron tetrahydride **4** [Eq. (1)]. The tetrahydride **4** was isolated in 41% yield after purification by column chromatography on neutral alumina and was characterized on the basis of the ^1H and ^{13}C NMR data. The ^1H NMR of complex **4** in C_6D_6 exhibited two resonance signals attributable to the C_5Me_5 group and hydrido ligands at $\delta = 1.96$ and $\delta = -22.12$, respectively. The inversion–recovery T_1 measurement for the hydrido ligands was performed at 400 MHz at various temperatures. The observed T_1 value of 0.63 s at −80 °C is deemed to be sufficient to characterize the complex as a classical metal hydride with no bonding interaction between the H atoms.[4]



(1)

The molecular structure of **4** was determined by an X-ray diffraction study (Figure 1).[5] The two iron atoms are bridged by four hydrido ligands. The long H–H distance (av 1.60 (3) Å) is consistent with the results obtained based on the T_1 value. A noteworthy aspect of the structure is the very short Fe–Fe distance of 2.202(2) Å, which is shorter than those in any other organometallic iron complexes that have appeared so far in the Cambridge structural database. Since **4** is a 30-electron species, the noble gas rule requires a triple bond between the two iron centers. However, we suggest that there is no metal–metal bond since a theoretical study of dinuclear ruthenium tetrahydride **1** performed by Morokuma and Koga using an ab initio molecular orbital method showed the absence of a metal–metal bond between the two ruthenium centers in this molecule.[6]

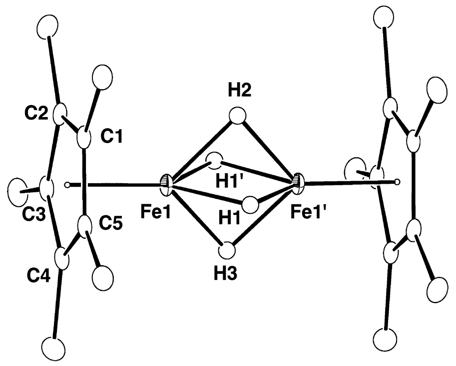
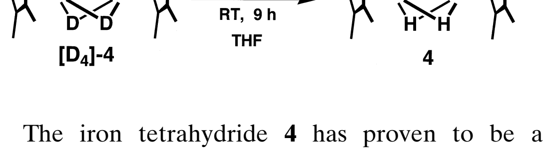


Figure 1. Molecular structure of **4** (thermal ellipsoids at 30% probability level). Selected bond lengths [Å] and angles [°]: Fe1-Fe1′ 2.202(2), Fe1-C1 2.054(2), Fe1-C2 2.058(2), Fe1-C3 2.059(2), Fe1-C4 2.058(2), Fe1-C5 2.056(2), Fe1-H1 1.57(2), Fe1-H2 1.60(2), Fe1-H3 1.56(2), H1-H2 1.60(3), H1-H3 1.60(3); Fe1-H1-Fe1 88(1), Fe1-H2-Fe1 86(1), Fe1-H3-Fe1 89(1).

The iron tetrahydride **4** has been shown to undergo intermolecular ligand exchange between hydrides and added dihydrogen. Exposure of [D$_4$]-**4** to an atmospheric pressure of dihydrogen in [D$_8$]THF at room temperature caused a gradual intensification of the hydrido resonance due to H/D exchange [Eq. (2)]. This must be an associative process because tetrahydride **4** is stable enough in solution not to release dihydrogen even under reduced pressure. The reaction proceeded much faster than the H/D exchange of the corresponding ruthenium analogue,[2e] and was complete after 9 h.



(2)

The iron tetrahydride **4** has proven to be a suitable precursor of highly reactive dinuclear species. Whereas the

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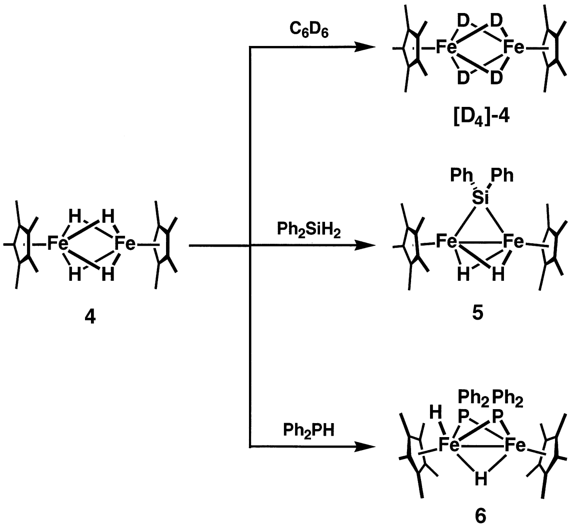
ruthenium tetrahydride **1** cannot cleave the aromatic C–H bond, **4** smoothly undergoes C–H bond activation of benzene. When the reaction of **4** with C_6D_6 was monitored by ^{1}H NMR spectroscopy at room temperature, a gradual decrease in the intensity of the hydrido resonance was observed. After 75 h, the hydrido resonance completely disappeared, leaving $[D_4]$-**4**.

The iron tetrahydride **4** readily reacted with Ph_2SiH_2 in THF below 0 °C to give a μ-silylene complex **5** by way of Si–H bond activation (Scheme 1). Complex **5** was concluded to be a μ-silylene complex based on the observation of a ^{29}Si resonance signal at $\delta = 293$. The molecular structure of **5** was determined by X-ray diffraction and the results confirm the presence of a diiron framework bridged by the μ-silylene ligand (Figure 2).[7] The Fe–Si bond lengths of 2.2582(2) and 2.2549(6) Å are comparable to those for the σ bond observed in silyl and silylene complexes of iron.[8] The Fe-Si-Fe angle is fairly acute (58.91(2)°) compared with that observed in $[\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu\text{-}H)_2(\mu\text{-}SiPh_2)_2]$ (68.70(3)°)[2d] due to the short distance between the iron centers (2.2193(5) Å).



Scheme 1.

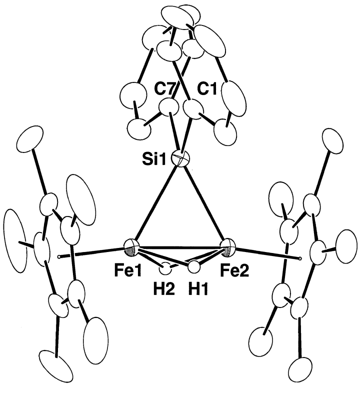


Figure 2. Molecular structure of **5** (thermal ellipsoids at 30% probability level). Selected bond lengths [Å] and angles [°]: Fe1-Fe2 2.2193(5), Fe1-Si1 2.2582(8), Fe2-Si1 2.2549(8), Fe1-H1 1.66(3), Fe1-H2 1.62(3), Fe2-H1 1.66(3), Fe2-H2 1.63(3), Si1-C1 1.884(3), Si1-C7 1.883(3); Fe1-Si1-Fe2 58.91(2), Fe2-Fe1-Si1 60.47(2), Fe1-Fe2-Si1 60.62(2), Fe1-Si1-C1 118.86(9), Fe1-Si1-C7 123.51(9), Fe2-Si1-C1 123.95(10), Fe2-Si1-C7 117.67(9).

Complex **4** also reacted with PPh_2H below 0 °C to yield the bis-μ-phosphido complex **6** (Scheme 1). The molecular structure of **6** was confirmed by an X-ray diffraction study (Figure 3).[9] One of the two hydrido ligands was located at the terminal position and the other bridged two iron atoms. This was consistent with the observation that the resonance signals for the hydrido ligands of **6** were inequivalent in the ^{1}H NMR spectrum. The four Fe–P distances are almost identical and are within the range of those reported for dinuclear iron μ-PPh_2 complexes.[10]

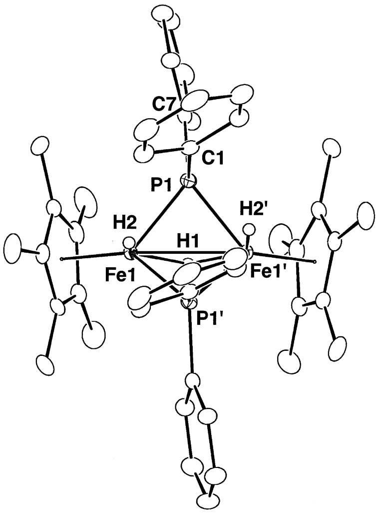
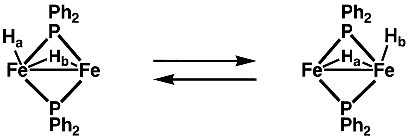


Figure 3. Molecular structure of **6** (thermal ellipsoids at 30% probability level). Selected bond lengths [Å] and angles [°]: Fe1-Fe1′ 2.6697(6), Fe1-P1 2.1935(6), Fe1′-P1 2.1989(6), Fe1-H1 1.67(2), Fe1-H2 1.40(6), P1-C1 1.838(2), P1-C7 1.843(2); Fe1-P1-Fe1′ 74.86(2), Fe1-Fe1′-P1 52.66(2), Fe1′-Fe1-P1 52.48(2), Fe1-P1-C1 122.03(7), Fe1-P1-C7 117.84(7), Fe1′-P1-C1 121.21(6), Fe1′-P1-C7 121.46(7).

The two hydrido ligands in **6** exchange coordination sites with each other [Eq. (3)]; this process was monitored by variable-temperature ^{1}H NMR spectroscopy. Two resonance signals attributed to magnetically inequivalent C_5Me_5 groups coalesced at 15 °C. The hydrido resonance signals which appeared at $\delta = -9.72$ and -16.40 at -50 °C broadened at room temperature.[11]



(3)

We have prepared a novel dinuclear iron tetrahydrido complex that is more reactive than the ruthenium analogue and effectively activates C–H, Si–H, and P–H bonds under mild conditions. This type of carbonyl-free low-valent cluster is still rare, and the reactivity study on complex **4** provides valuable insight for organometallic chemistry.

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[5] a) Diffraction measurement was made on an AFC-7R four-circle diffractometer equipped with graphite-monochromated $\mathrm{Mo_{K\alpha}}$ radiation at −180 °C. The compound crystallized in the space group $P2/c$ with $a = 9.409(7)$, $b = 8.539(3)$, $c = 12.565(6)$ Å, $\beta = 104.64(4)^\circ$, $V = 976.8(8)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.313\ \mathrm{g\,cm^{-1}}$. A total of 2396 unique reflections was recorded in the range $6^\circ \le 2\theta \le 55^\circ$, of which 1968 were used ($F > 3\sigma(F)$) for solution and refinement. In the reduction of the data, Lorentz/polarization corrections and empirical absorption corrections based on azimuthal scans were applied to the data. The structure was solved by the Patterson method (DIRDIF92, PATTY), and all hydrogen atoms were refined isotropically and all non-hydrogen atoms were refined anisotropically by using full-matrix least-squares techniques on F. The final structure of **4** was refined to $R = 0.027$, $R_w = 0.026$, for 167 parameters. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-142856 (**4**), CCDC-142858 (**5**), and CCDC-142857 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[7] Diffraction measurement was made on an AFC-7R four-circle diffractometer at −50 °C. In the reduction of the data, Lorentz, polarization, and empirical absorption corrections based on azimuthal scans were applied to the data. The structure was solved by the Patterson method (DIRDIF92, PATTY). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms except for Fe−H and Si−C_6H_5 hydrogen atoms (refined isotropically) were fixed at the calculated positions. Crystal data for **5**: monoclinic, $P2_1/a$, $a = 15.741(3)$, $b = 16.938(2)$, $c = 11.432(2)$ Å, $\beta = 102.00(1)^\circ$, $V = 2981.3(7)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.262\ \mathrm{g\,cm^{-1}}$; 8970 reflections ($6^\circ \le 2\theta \le 55^\circ$), 6318 observed with $F > 3\sigma(F)$, 364 parameters; $R = 0.041$, $R_w = 0.044$.[5b]

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[9] Diffraction measurement was made on a RAXIS-2 imaging plate area detector at −70 °C. In the reduction of the data, Lorentz and polarization corrections were applied. The structure was solved by the Patterson method (DIRDIF92, PATTY). All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were refined isotropically. Crystal data for **6**: monoclinic, $C2/c$, $a = 18.528(3)$, $b = 11.429(2)$, $c = 19.22(1)$ Å, $\beta = 112.26(2)^\circ$, $V = 3767(2)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.330\ \mathrm{g\,cm^{-1}}$; 4875 reflections ($5^\circ \le 2\theta \le 60^\circ$), 4044 observed with $F > 3\sigma(F)$, 324 parameters; $R = 0.036$, $R_w = 0.037$.[5b]

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[11] The free activation energy for this dynamic process was estimated as $\Delta G^{\neq}$ (15 °C) = 13.5 kcal mol^{-1}. This value is comparable to those for site exchange of hydrides in the diruthenium bis-μ-silylene complex $[\{(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)\}_2\{\mu\text{-}SiPh(OH)\}(\mu\text{-}SiPh_2)]$ ($\Delta G^{\neq}$ (0 °C) = 12.6 kcal mol^{-1}). T. Takao, S. Yoshida, H. Suzuki, unpublished results.

Asymmetric Alkylation of Nitroalkanes**

Barry M. Trost* and Jean-Philippe Surivet

The utility of nitro compounds as synthetic intermediates stems from the versatility of the reactivity of the nitro group.[1] One feature arises from the ease of formation of nitronate anions; however, their low reactivity generally limits the reactions they undergo to carbonyl and conjugate addition.[2] Alkylations do not normally proceed well. On the other hand, Pd-catalyzed allylic alkylations have had some success.[3] This success stimulates the search for an asymmetric allylic alkylation (AAA) which has had good results in only one case (the 1,3-diphenylallyl system) and when nitromethane was used as solvent.[4] We here report that the Pd-catalyzed AAA reaction[5] of nitroalkanes with cyclic allyl esters can proceed in high yields and enantioselectivities and provide a short asymmetric synthesis of a carbanucleoside.

Our initial studies focused on desymmetrization of *meso* diesters [Eq. (1)].[6] Our earlier results suggested the diben-

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