

Hydride Migration from a Triangular Face to a Tetrahedral Cavity in Tetranuclear Iron Carbonyl Clusters upon Coordination of $[\text{AuPPh}_3]^+$ Fragments**

Marco Bortoluzzi, Iacopo Ciabatti, Cristina Femoni, Mohammad Hayatifar, Maria Carmela Iapalucci, Giuliano Longoni, and Stefano Zacchini*

Abstract: Metal hydrides are of fundamental importance in chemistry, both as solid-state materials and molecular compounds. The first low-valent molecular metal cluster containing an interstitial four-coordinate hydride in a tetrahedral site is described, which undergoes hydride migration from the surface to the tetrahedral cavity of the cluster upon coordination of a $[\text{AuPPh}_3]^+$ fragment. The $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]^-$ mono-anion, which contains a surface $\mu_3\text{-H}$, was obtained from the reaction of $[\text{HFe}_4(\text{CO})_{12}]^{3-}$ with two equivalents of $[\text{Au}(\text{PPh}_3)\text{Cl}]$. This is, in turn, transformed into the neutral $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_3]$ upon addition of a third $[\text{AuPPh}_3]^+$ fragment, with concomitant migration of the unique hydride from the surface of the cluster to its tetrahedral cavity. All of these species have been fully characterized in solution by means of IR and multinuclear NMR spectroscopy, and in the solid state by single-crystal X-ray diffractometry.

Metal hydrides are of fundamental importance in chemistry, both as solid-state materials and molecular compounds.^[1–3] They are key intermediates in various catalytic reactions and have promising applications for hydrogen storage.^[4–7] Moreover, hydrogen displays a unique chemistry, in view of its small mass, the presence of a single 1s valence orbital, the absence of core and non-bonding valence electrons, and an anomalously high electronegativity.^[8]

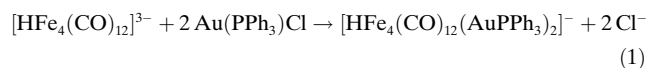
Four-coordinate hydrogen in tetrahedral sites and six-coordinate hydrogen in octahedral sites are those most commonly observed in intermetallic hydrides.^[9] The first molecular hydride complexes, $[\text{HCo}(\text{CO})_4]$ and $[\text{H}_2\text{Fe}(\text{CO})_4]$,

were reported by Hieber et al. in the 1930s,^[10] even if their nature has been fully elucidated only much later. Today thousands of molecular metal hydrides compounds are known,^[11] including mononuclear complexes, polynuclear compounds, and clusters.^[12,13]

Metal clusters and nanoparticles are intermediate species between mononuclear complexes and bulky materials.^[14] Hydride atoms in molecular clusters may display several coordination modes, as they can be coordinated to the surface of the cluster as terminal, edge or face bridging ligands, as well as located in semi-interstitial, for example, $[\text{H}_2\text{Rh}_{13}(\text{CO})_{23}]^{3-}$,^[15] or fully interstitial positions. Concerning fully interstitial hydrides, for very long-time only molecular clusters containing six-coordinate hydrogen in an octahedral cavity were known,^[16–18] and it was only in 2008 that the first molecular species containing a four-coordinate hydrogen in the tetrahedral cavity of $[(\text{C}_5\text{Me}_5\text{SiMe}_3)\text{YH}_2]_4(\text{thf})$ was fully characterized.^[19] Some other examples of tetrahedral $\mu_4\text{-H}$ are also known,^[20,21] including $[\{\text{PhP}(\text{CH}_2)_3\text{Fe}\}_4(\mu_4\text{-H})]^-$,^[22] but they are all compounds containing metals in positive oxidation states.

Herein, we report the first example of a low-valent transition-metal cluster containing an interstitial hydride enclosed within a tetrahedral cavity, namely $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_3]$. This species originates from the addition of a $[\text{AuPPh}_3]^+$ fragment to $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]^-$ with concomitant migration of the unique hydride from a triangular face of the Fe_4 cage to the interstitial tetrahedral cavity. Hydride migration from the surface to the inside of the cluster may be related to the high fluxionality observed in solution for these species and, more in general, to hydrogen diffusion in metal clusters, nanoparticles, and bulk materials. All of the species reported herein have been fully characterized in solution by means of IR and multinuclear NMR spectroscopy, and in the solid state by single-crystal X-ray diffractometry. The system has been further investigated by means of DFT and deuterium-labeling studies.

The $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]^-$ mono-anion was obtained in moderate yields from the reaction of $[\text{HFe}_4(\text{CO})_{12}]^{3-}$ ^[23] with two equivalents of $[\text{Au}(\text{PPh}_3)\text{Cl}]$ (experimental details are given in the Supporting Information), according to Equation (1):



[*] Dr. M. Bortoluzzi
Dipartimento di Scienze Molecolari e Nanosistemi
Ca' Foscari University of Venice
Dorsoduro 2137, I-30123 Venezia (Italy)

Dr. I. Ciabatti, Dr. C. Femoni, Dr. M. Hayatifar, Prof. M. C. Iapalucci,
Prof. G. Longoni, Prof. S. Zacchini
Dipartimento di Chimica Industriale "Toso Montanari"
Università di Bologna
Viale Risorgimento 4, I-40136 Bologna (Italy)
E-mail: stefano.zacchini@unibo.it

[**] Funding by Fondazione CARIPOLO, Project No. 2011-0289, is heartily acknowledged. The University of Bologna is acknowledged for financial support to this work (FARB—Linea d'Intervento 2, "Catalytic transformation of biomass-derived materials into high added-value chemicals", 2014-2016). We thank one of the referees for the useful suggestions in revising the manuscript.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201403538>.

The new compound has been fully characterized by means of IR and ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, and ESI-MS. $^{13}\text{C}\{^1\text{H}\}$ NMR data were obtained on a ^{13}CO -enriched sample, $[\text{HFe}_4(^{13}\text{CO})_{12}(\text{AuPPh}_3)_2]^-$ (^{13}CO ca. 30 %), prepared from $[\text{HFe}_4(^{13}\text{CO})_{12}]^{3-}$.^[23] Moreover, its molecular structure has been fully elucidated by X-ray crystallography on single crystals of $[\text{NET}_4][\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]$ (Figure 1). The

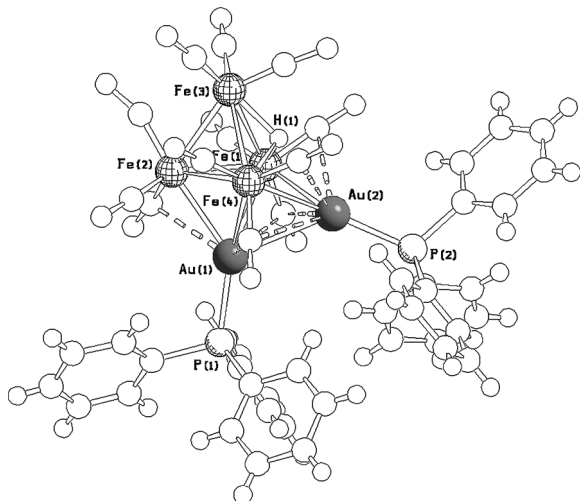


Figure 1. Molecular structure of $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]^-$ with key atoms labeled. Fe–Fe 2.648(3)–2.893(3) Å, average 2.738(7) Å; Au–Fe 2.679(2)–2.764(2) Å, average 2.727(4) Å; Fe–H 1.812(10)–1.820(9) Å, average 1.816(16) Å; Au1–Au2 2.9560(9) Å; Au...C 2.605(17)–3.010(18) Å, average 2.82(5) Å.

$[\text{HFe}_4\text{Au}_2]$ hydride-metal core with labeling is shown in Figure 2; a detailed list of the main bonding distances is included in the Supporting Information, Table S1.

The cluster is composed of a tetrahedral $[\text{HFe}_4(\text{CO})_{12}]^{3-}$ core decorated by two $[\text{AuPPh}_3]^+$ fragments. The former retains the tetrahedral structure of the parent cluster with a $\mu_3\text{-H}$ hydride. Conversely, the stereochemistry of the CO ligands is changed to permit the coordination of the two $[\text{AuPPh}_3]^+$ fragments. The hydride ligand has been located in the final Fourier difference map and its position is in correspondence with the minimum of the non-bonded potential energy surface of the cluster as located by the program XHYDEX.^[24] The hydride atom has been included in the final refinement of the structure. The hydride location

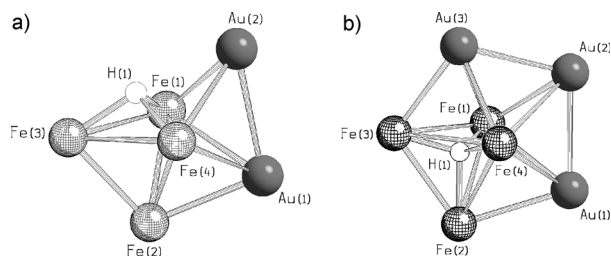


Figure 2. a) The HFe_4Au_2 hydride-metal core of $[\text{HFe}_4(\text{CO})_{12}^- (\text{AuPPh}_3)_2]^-$ and b) the HFe_4Au_3 hydride-metal core of $[\text{HFe}_4(\text{CO})_{12}^- (\text{AuPPh}_3)_3]$ with labeling.

has been also confirmed by means of geometry optimizations carried out at DFT level, starting from the experimental X-ray diffraction structure. In particular, EDF2^[25] calculations have been carried out on the $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]^-$ anion, while the hyper-GGA M06 functional^[26] has been used for the optimization of the model system $[\text{HFe}_4(\text{CO})_{12}(\text{AuPH}_3)_2]^-$. More computational details are collected in the Supporting Information. As seen from the Supporting Information, Figures S4 and S5, the computed geometries are comparable to the experimental geometry. Despite a slight underestimation of the Fe–H distances with respect to the X-ray data (Supporting Information, Table S2), DFT optimizations confirm the position of the hydride as surface $\mu_3\text{-H}$.

Au1 is μ_3 -coordinated to the Fe1-Fe2-Fe4 face of the tetrahedron, adjacent to the face capped by the $\mu_3\text{-H}$ hydride. Au2 is then added to the nearby Au1-Fe1-Fe4 face, resulting in a Fe_2Au_2 tetrahedron. In this respect, the cluster may be viewed as a Fe_4Au trigonal bipyramid capped by Au2, or as composed by three face-sharing tetrahedra (Fe_4 , Fe_3Au , and Fe_2Au_2). In all cases, it obeys to the inert gas rule, which predicts 60 cluster valence electrons (CVE) for a tetrahedron, and 84 CVE for a mono-capped trigonal bipyramid.^[27]

The 12CO ligands bonded to the four Fe atoms of $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]^-$ are all terminal, even if two may be considered as very unsymmetrically edge-bridging. By comparison, the parent $[\text{HFe}_4(\text{CO})_{12}]^{3-}$ presented 9 terminal and 3 edge bridging carbonyl ligands. Furthermore, there are seven weak Au...CO interactions (2.605(17)–3.010(18) Å, average 2.82(5) Å), represented as fragmented lines in Figure 1.

The Fe–Fe contacts are rather spread (2.6539(9)–2.9671(9) Å, average 2.795(2) Å), and a considerable swelling of the Fe_4 tetrahedron is observed after coordination of the two $[\text{AuPPh}_3]^+$ fragments; for comparison, the parent $[\text{HFe}_4(\text{CO})_{12}]^{3-}$ cluster displayed Fe–Fe contacts in the range 2.5218(12)–2.6337(12) Å (average 2.580(7) Å).^[23]

The Fe–H distances (1.812(10)–1.820(9) Å, average 1.816(16) Å) are slightly longer than in other $\mu_3\text{-H}$ -bonded Fe clusters, namely 1.71(3)–1.75(4) Å (average 1.72(9) Å) in $[\text{HFe}_4(\text{CO})_{12}]^{3-}$, 1.745(10)–1.749(10) Å (average 1.75(2) Å) in $[\text{H}_2\text{Fe}_4(\text{CO})_{12}]^{2-}$, and 1.70(3)–1.84(5) Å (average 1.75(7) Å) in $[\text{HFe}_5(\text{CO})_{14}]^{3-}$.^[23,28] It must be remarked that $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]^-$ is the fourth case of an iron cluster containing a $\mu_3\text{-H}$ ligand to be structurally characterized, whereas more than 100 examples are present within the Cambridge Crystallographic Database displaying $\mu\text{-H}$ edge-bridging hydrides.^[29]

The cluster contains five Au–Fe contacts (2.679(2)–2.764(2) Å, average 2.727(4) Å) and one Au–Au bond (2.9560(9) Å). For comparison, the sum of the covalent radii are 2.84 Å for Au–Fe and 3.00 Å for Au–Au, respectively.^[30] The tendency of Au^I ions to form interactions in the range between 2.7 and 3.3 Å is well-documented in the literature, and this phenomenon is commonly referred as “aurophilicity”.^[31–34] This phenomenon could not be explained by conventional descriptions of chemical bonding, but is now well described as dispersion-driven and enhanced by relativistic effects.^[35] Aurophilic interactions also play a fundamental role in determining the structures of molecular cluster containing two or more Au^I fragments.^[13]

The presence of a hydride ligand is confirmed by a singlet at $\delta_{\text{H}} -19.5$ ppm in the ^1H NMR spectrum of $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]^-$ in deuterated acetone. The hydride displays a long longitudinal relaxation time ($T_1 = 23$ s), as also found in the parent $[\text{HFe}_4(\text{CO})_{12}]^{3-}$ ($T_1 = 21$ s).^[23] Allowing a long delay between scans (200 s) the expected 30:1 ratio between the integrals of the phenyl protons and hydride atom has been measured (Supporting Information, Figure S2). Both $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (in the carbonyl region) show only one singlet each at all temperatures considered (193–298 K), that is, $\delta_{\text{P}} 57.3$ ppm and $\delta_{\text{CO}} 222.4$ ppm (at 298 K), indicating a very rapid exchange of the ligands at all of the temperatures. As suggested by the structure of the $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_3]$ neutral mono-hydride discussed below, this rapid exchange is likely to occur via the movement of the hydride from one triangular face to the other of the Fe_4 cage passing through its tetrahedral cavity with concomitant rearrangement of the $[\text{AuPPh}_3]^+$ fragments and CO ligands.

Aiming at preparing a purported $[\text{H}_2\text{Fe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]$ neutral di-hydride, we have investigated the reaction of $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]^-$ with one equivalent of H^+ in CH_3CN . Unexpectedly, this resulted in the $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_3]$ neutral mono-hydride species, which can be recovered in moderate yields after work-up (see the Supporting Information for details). The use of a deuterated acid such as D_2SO_4 results in the same $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_3]$ hydride and not in the $[\text{DFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_3]$ deuteride. This indicates that the hydride ligand remains bonded to the cluster during the reaction.

It is likely that the acid causes the decomposition of part of the starting cluster with release of some $[\text{AuPPh}_3]^+$ fragments, which are intercepted by the unreacted $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]^-$ cluster. The resulting $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_3]$ species is not soluble in CH_3CN and precipitates out, preventing further decomposition. The same neutral cluster may be also obtained by reacting $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]^-$ with a mild oxidant, such as $[\text{C}_7\text{H}_7][\text{BF}_4]$ in CH_3CN . Alternatively, $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_3]$ is formed after the addition of $[\text{Au}(\text{PPh}_3)(\text{NO}_3)]$ to $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]^-$, further confirming that the origin of the hydride ligand is endogenous.

The new $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_3]$ cluster has been fully characterized by spectroscopic methods (IR; ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ NMR) and its structure crystallographically determined (Figures 2b and 3). X-ray crystallographic studies have been performed both at 295 and 100 K, giving almost coincident results. As above, the presence of a hydride ligand is confirmed by a singlet at $\delta_{\text{H}} -19.1$ ppm in the ^1H NMR spectrum of $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_3]$ in CD_2Cl_2 , whereas VT $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR studies indicate fluxionality in solution, which makes the PPh_3 and CO ligands equivalent at all temperatures ($\delta_{\text{P}} 56.4$ ppm and $\delta_{\text{CO}} 218.0$ ppm at 298 K).

Dissociation to $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]^-$ and $[\text{AuPPh}_3]^+$ occurs in solution depending on the polarity of the solvent (Supporting Information, Figure S1). Thus, $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]^-$ is the main species in polar solvents such as acetone, whereas $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_3]$ is predominant in CH_2Cl_2 . A dissociative mechanism may be invoked to explain

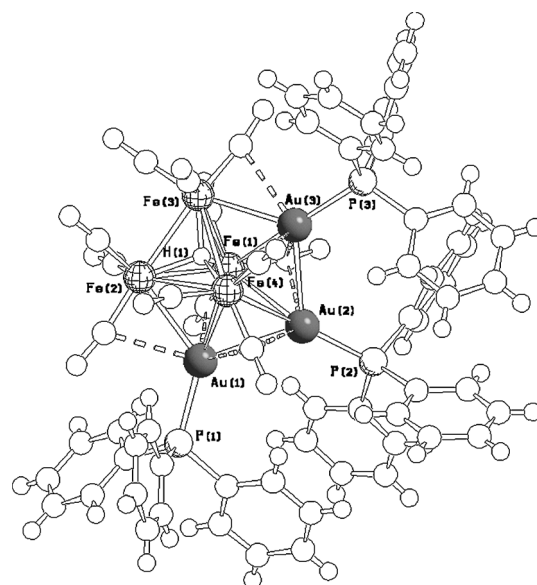


Figure 3. Molecular structure of $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_3]$ with key atoms labeled. Fe–Fe 2.6539(9)–2.9671(9) (3) Å, average 2.795(2) Å; Au–Fe 2.6655(7)–2.9193(7) Å, average 2.783(2) Å; Fe–H 1.65(5)–1.78(5) Å, average 1.72(10) Å; Au1–Au2 2.9083(3) Å; Au2–Au3 2.8766(3) Å; Au...C 2.583(5)–2.940(5) Å, average 2.718(14) Å.

the fluxionality of this neutral cluster. The hydride of $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_3]$ also shows a rather long longitudinal relaxation time ($T_1 = 16$ s), and reliable integrals between the phenyl protons and hydride (experimental 47.5:1; expected 45:1) have been obtained using 200 s delay between scans (Supporting Information, Figure S3).

The molecular structure of $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_3]$ may be derived from the one of $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]^-$ after the addition of a third $[\text{AuPPh}_3]^+$ fragment. This is μ_3 -coordinated to the Fe1–Fe3–Fe4 face, to which the hydride was coordinated in $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]^-$. As a result, the hydride ligand is forced to move in the center of the Fe_4 tetrahedron. As above, the hydride ligand has been located in the final Fourier difference map and its position is in correspondence with the minimum of the non-bonded potential energy surface of the cluster as located by the program XHYDEX.^[24] The hydride atom has been included in the final refinement of the structure. As for $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]^-$, the hydride location has been confirmed by means of DFT calculations on both $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_3]$ and $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]$. Pictures of the DFT-optimized structures are given in the Supporting Information, Figures S6 and S7. The computed Fe–H average distances are closely comparable to the experimental data (Supporting Information, Table S3).

$[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_3]$ is the first low-valent cluster that contains a hydride ligand within a tetrahedral cavity. The Fe–Fe (Fe–Fe 2.6539(9)–2.9671(9) Å, average 2.795(2) Å) and Fe–H contacts (1.65(5)–1.78(5) Å, average 1.72(10) Å) are very similar to those previously reported for $[\{\text{PhP}(\text{CH}_2)_3\text{Fe}\}_4(\mu_4\text{-H})]^-$ (Fe–Fe 2.78–2.82 Å; Fe–H 1.71 Å),^[22] even if the latter contains Fe^{II} ions whereas the oxidation state of Fe is formally negative in the present case.

The addition of a third $[\text{AuPPh}_3]^+$ fragment as well as the presence of an interstitial $\mu_4\text{-H}$ causes a further swelling of the Fe_4 tetrahedron compared to the parent anion $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]^-$.

$[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_3]$ shows two Au–Au bonding contacts (Au1–Au2 2.9083(3) Å; Au2–Au3 2.8766(3) Å) as well as eight weak Au $\cdots$ CO interactions (2.583(5)–2.940(5) Å, average 2.718(14) Å). 11 CO ligands are terminal, one edge-bridging. The coordination site of Au3 is dictated by steric effects as well as aurophilic interactions.

If partitioned into a $[\text{HFe}_4(\text{CO})_{12}]^{3-}$ tetrahedron decorated by three $[\text{AuPPh}_3]^+$ fragments, the former possesses 60 CVE as expected for a tetrahedral cluster. Alternatively, $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_3]$ may be viewed as composed of five tetrahedra (Fe_4 , Fe_3Au , Fe_2Au_2 , Fe_2Au_2 , Fe_3Au) sharing five triangular faces and resulting in a pentagonal bipyramid. It displays 96 CVE, as previously found in the isostructural $[\text{Ru}_5(\text{CO})_{15}\text{Au}_2(\text{dppm})]^{[36]}$, $[\text{Ru}_3\text{Ir}(\text{CO})_{12}(\text{AuPPh}_3)_3]^{[37]}$, $[\text{Os}_5(\text{CO})_{15}\text{Au}_2(\text{dppm})]$, and $[\text{Os}_4\text{Ru}(\text{CO})_{12}(\text{C}_6\text{H}_6)\text{Au}_2(\text{dppm})]^{[38]}$.

In conclusion, we have reported the first example of a low-valent transition-metal cluster containing an interstitial four-coordinate hydrogen in a tetrahedral site, namely $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_3]$. It originates from the addition of a $[\text{AuPPh}_3]^+$ fragment to $[\text{HFe}_4(\text{CO})_{12}(\text{AuPPh}_3)_2]^-$, which causes the migration of the unique hydride atom from the surface to the inside of the tetrahedral Fe_4 cage of the cluster. This point has been corroborated by means of deuterium-labeling studies. Steric effects as well as aurophilicity seem to play a fundamental role in this process. The presence of hydride atoms in the tetrahedral cavities of low-valent transition-metal clusters and hydride migration on and through their metal cages may help the understanding of the structures of larger clusters and nanoparticles, as well as the mechanism of their interaction with hydrogen.

Received: March 20, 2014

Revised: April 18, 2014

Published online: May 21, 2014

Keywords: aurophilicity · carbonyl ligands · cluster compounds · hydride ligands · iron

- [1] T. Shima, Y. Luo, T. Stewart, R. Bau, G. J. McIntyre, S. A. Mason, Z. Hou, *Nat. Chem.* **2011**, 3, 814–820.
- [2] a) *Transition Metal Hydrides* (Ed.: A. Dedieu), VCH, New York, **1992**; b) M. A. Esteruelas, L. A. Oro, *Chem. Rev.* **1998**, 98, 577–588; c) A. J. Hoskin, D. W. Stephan, *Coord. Chem. Rev.* **2002**, 233–234, 107–129; d) M. Konkol, J. Okuda, *Coord. Chem. Rev.* **2008**, 252, 1577–1591; e) P. K. Liao, C. S. Fang, A. J. Edwards, S. Kahlal, J. Y. Saillard, C. W. Liu, *Inorg. Chem.* **2012**, 51, 6577–6591.
- [3] a) *Recent Advances in Hydride Chemistry* (Eds.: M. Peruzzini, R. Poli), Elsevier, New York, **2001**; b) R. Bau, M. H. Drabnis, *Inorg. Chim. Acta* **1997**, 259, 27–50.
- [4] a) *Homogeneous Hydrogenation* (Ed.: B. R. James), Wiley, New York, **1973**; b) W. L. Gladfelter, K. J. Roessel in *The Chemistry of Metal Cluster Complexes* (Eds.: D. F. Shriver, H. D. Kaesz, R. D. Adams), VCH, New York, **1990**, chap. 7.

- [5] a) *Catalysis by Di- and Polynuclear Metal Cluster Complexes* (Eds.: R. D. Adams, F. A. Cotton), Wiley-VCH, New York, **1998**; b) S. Doherty, *Annu. Rep. Prog. Chem. Sect. A* **1996**, 93, 395–432; c) H. Suzuki, *Eur. J. Inorg. Chem.* **2002**, 1009–1023.
- [6] a) M. Ephritikhine, *Chem. Rev.* **1997**, 97, 2193–2242; b) Z. Hou, M. Nishiura, T. Shima, *Eur. J. Inorg. Chem.* **2007**, 2535–2545; c) G. J. Kubas, *Chem. Rev.* **2007**, 107, 4152–4205.
- [7] a) L. Schlapbach, A. Züttel, *Nature* **2001**, 414, 353–358; b) M. Takimoto, Z. Hou, *Nature* **2006**, 443, 400–401; c) F. Schüth, B. Bogdanović, M. Felderhoff, *Chem. Commun.* **2004**, 2249–2258.
- [8] G. S. McGrady, G. Guiller, *Chem. Soc. Rev.* **2003**, 32, 383–392.
- [9] A. J. Maeland in *Recent Advances in Hydride Chemistry* (Eds.: M. Peruzzini, R. Poli), Elsevier, New York, **2001**, pp. 531–556.
- [10] a) W. Hieber, *Naturwissenschaften* **1931**, 19, 360–361; b) W. Hieber, F. Leutert, *Z. Anorg. Allg. Chem.* **1932**, 204, 145–164.
- [11] a) G. G. Hlatky, R. H. Crabtree, *Coord. Chem. Rev.* **1985**, 65, 1–48; b) G. Süss-Fink, L. Plasseraud, A. Maisse-François, H. Stoeckli-Evans, H. Berke, T. Fox, R. Gautier, J. Y. Saillard, *J. Organomet. Chem.* **2000**, 609, 196–203.
- [12] a) S. Aime, M. Botta, R. Gobetto, L. Milone, D. Osella, R. Gellert, E. Rosenberg, *Organometallics* **1995**, 14, 3693–3703; b) A. P. Humphries, H. D. Kaesz, *Prog. Inorg. Chem.* **1979**, 25, 145–222.
- [13] a) *Metal Clusters in Chemistry* (Eds.: P. Braunstein, L. A. Oro, P. R. Raithby), Wiley-VCH, Weinheim, **1999**; b) *Clusters and Colloids* (Ed.: G. Schmid), Wiley-VCH, New York, **1994**.
- [14] a) S. Zacchini, *Eur. J. Inorg. Chem.* **2011**, 4125–4145; b) C. Femoni, M. C. Iapalucci, F. Kaswalder, G. Longoni, S. Zacchini, *Coord. Chem. Rev.* **2006**, 250, 1580–1604.
- [15] T. Bau, M. H. Drabnis, L. Garlaschelli, W. T. Klooster, Z. W. Xie, T. F. Koetzle, S. Martinengo, *Science* **1997**, 275, 1099–1102.
- [16] a) R. D. Köhn, Z. Pan, M. F. Mahon, G. Kociok-Köhn, *Chem. Commun.* **2003**, 1272–1273; b) S. Kamiguchi, H. Imoto, T. Saito, T. Chihara, *Inorg. Chem.* **1998**, 37, 6852–6857; c) R. D. Adams, J. E. Babin, J. T. Tanner, *Organometallics* **1988**, 7, 2027–2033.
- [17] a) P. F. Jackson, B. F. G. Johnson, J. Lewis, P. R. Raithby, M. McPartlin, W. J. H. Nelson, K. D. Rouse, J. Alibon, S. A. Mason, *J. Chem. Soc. Chem. Commun.* **1980**, 295–297; b) “Transition Metal Hydrides”: B. W. Broach, L. F. Dahl, G. Longoni, P. Chini, A. J. Schultz, J. M. Williams in *Advances in Chemistry Series, Vol. 167* (Ed.: R. Bau), American Chemical Society, Washington, DC, **1978**, chap. 7.
- [18] a) D. W. Hart, R. G. Teller, C. Y. Wei, R. Bau, G. Longoni, S. Campanella, P. Chini, T. F. Koetzle, *J. Am. Chem. Soc.* **1981**, 103, 1458–1466; b) D. W. Hart, R. G. Teller, C. Y. Wei, R. Bau, G. Longoni, S. Campanella, P. Chini, T. F. Koetzle, *Angew. Chem.* **1979**, 91, 86–97; *Angew. Chem. Int. Ed. Engl.* **1979**, 18, 80–81.
- [19] M. Yousufuddin, M. J. Gutmann, J. Baldamus, O. Tardif, Z. Hou, S. A. Mason, G. J. McIntyre, R. Bau, *J. Am. Chem. Soc.* **2008**, 130, 3888–3891.
- [20] a) Y. Luo, J. Baldamus, O. Tardif, Z. Hou, *Organometallics* **2005**, 24, 4362–4366; b) T. Stewart, M. Nishiura, Y. Konno, Z. Hou, G. J. McIntyre, *Inorg. Chim. Acta* **2010**, 363, 562–566; c) J. Cheng, K. Salu, G. Y. Kiel, M. J. Ferguson, R. McDonald, J. Takats, *Angew. Chem.* **2008**, 120, 4988–4991; *Angew. Chem. Int. Ed.* **2008**, 47, 4910–4913.
- [21] a) S. Tanaka, C. Dubs, A. Inagaki, M. Akita, *Organometallics* **2005**, 24, 163–184; b) T. Shima, Z. Hou, *Dalton Trans.* **2010**, 39, 6858–6863; c) T. A. Budzichowski, M. H. Chisholm, J. C. Huffman, O. Eisenstein, *Angew. Chem.* **1994**, 106, 203–206; *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 191–193; d) T. A. Budzichowski, M. H. Chisholm, J. C. Huffman, K. S. Kramer, O. Eisenstein, *J. Chem. Soc. Dalton Trans.* **1998**, 2563–2568.
- [22] C. B. Serrano, R. J. Less, M. McPartlin, V. Naseri, D. S. Wright, *Organometallics* **2010**, 29, 5754–5756.
- [23] C. Femoni, M. C. Iapalucci, G. Longoni, S. Zacchini, S. Zarra, *Inorg. Chem.* **2009**, 48, 1599–1605.

- [24] A. G. Orpen, *J. Chem. Soc. Dalton Trans.* **1980**, 2509–2516.
- [25] C. Y. Lin, M. W. George, P. M. W. Gill, *Aust. J. Chem.* **2004**, *57*, 365–370.
- [26] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- [27] a) *The Chemistry of Metal Cluster Complexes* (Eds.: D. F. Shriver, H. D. Kaesz, R. D. Adams), VCH, New York, **1990**; b) D. M. P. Mingos, D. J. Wales, *Introduction to Cluster Chemistry*, Prentice Hall, Englewood Cliffs, **1990**; c) D. M. P. Mingos, *Acc. Chem. Res.* **1984**, *17*, 311–319.
- [28] C. Femoni, M. C. Iapalucci, G. Longoni, S. Zacchini, *Dalton Trans.* **2011**, *40*, 8685–8694.
- [29] ConQuest, *New software for searching the Cambridge Structural Database and visualising crystal structures*, I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson, R. Taylor, *Acta Crystallogr. Sect. B* **2002**, *58*, 389–397.
- [30] a) B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echevarría, E. Cremades, F. Barragán, S. Alvarez, *Dalton Trans.* **2008**, 2832–2838; b) A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451.
- [31] a) H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2012**, *41*, 370–412; b) Z. N. Chen, N. Zhao, Y. Fan, J. Ni, *Coord. Chem. Rev.* **2009**, *253*, 1–20; c) A. Laguna, *Modern supramolecular gold chemistry: gold-metal interactions and applications*, Wiley-VCH, Weinheim, **2008**; d) P. Pykkö, *Chem. Rev.* **1997**, *97*, 597–636.
- [32] a) H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2008**, *37*, 1931–1951; b) M. J. Katz, K. Sakai, D. B. Leznoff, *Chem. Soc. Rev.* **2008**, *37*, 1884–1895; c) H. Schmidbaur, *Gold Bull.* **2000**, *33*, 3–10; d) P. S. G. Kim, Y. Hu, M. C. Brandys, T. J. Burchell, R. J. Puddephatt, T. K. Sham, *Inorg. Chem.* **2007**, *46*, 949–957.
- [33] a) C. Voß, R. Pattacini, P. Braunstein, *C. R. Chim.* **2012**, *15*, 229–236; b) J. Zank, A. Schier, H. Schmidbaur, *J. Chem. Soc. Dalton Trans.* **1998**, 323–324; c) J. P. Fackler, *Inorg. Chem.* **2002**, *41*, 6959–6972.
- [34] a) H. Schmidbaur, *Gold: Progress in Chemistry, Biochemistry and Technology*, Wiley, Chichester, **1999**; b) F. Scherbaum, A. Grohmann, B. Huber, C. Krüger, H. Schmidbaur, *Angew. Chem.* **1988**, *100*, 1600–1602; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1542–1544; c) H. Schmidbaur, *Chem. Soc. Rev.* **1995**, *24*, 391–400.
- [35] a) J. Muñoz, C. Wang, P. Pykkö, *Chem. Eur. J.* **2011**, *17*, 368–377; b) P. Pykkö, *Chem. Soc. Rev.* **2008**, *37*, 1967–1997; c) P. Pykkö, *Angew. Chem.* **2004**, *116*, 4512–4557; *Angew. Chem. Int. Ed.* **2004**, *43*, 4412–4456; d) P. Pykkö, J. Li, N. Runeberg, *Chem. Phys. Lett.* **1994**, *218*, 133–138.
- [36] P. J. Bailey, M. A. Beswick, J. Lewis, P. R. Raithby, M. C. R. de Arellano, *J. Organomet. Chem.* **1993**, *459*, 293–301.
- [37] R. D. Adams, P. J. Pellecchia, M. D. Smith, Q. Zhang, *J. Organomet. Chem.* **2012**, *706*, 20–25.
- [38] M. R. A. Al-Mandhary, R. Buntent, C. L. Doherty, A. J. Edwards, J. F. Gallagher, J. Lewis, C. K. Li, P. R. Raithby, M. C. Ramirez de Arellano, G. P. Shields, *J. Cluster Sci.* **2005**, *16*, 127–150.