π-Donor olefin substituents alter olefin binding to $CpFe(CO)_2^+$ †

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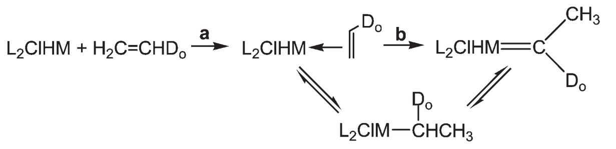
The X-ray diffraction structures of the olefin complexes $[CpFe(CO)_2(H_2CCHD_o)]PF_6$ (D_o = OEt and NMe_2) have been determined to further evaluate the previous report that the distance from Fe to the olefin carbon substituted by D_o (referred to as C_β) is long or even nonbonding. These Fe–C distances are determined here to be long [2.402(10) Å for D_o = OEt] or nonbonding [2.823(11) Å for $D_o = NMe_2$]. DFT optimization of the geometries of these, together with $CpFe(CO)_{2-n}(PH_3)_n(H_2CCHD_o)]^+$ for $n = 1$ and 2, show (a) agreement with experiment for $n = 0$, (b) a progression of Fe–C_β distances to shorter values with increasing n for D_o = OEt, (c) persistence of the Fe–C_β distance at a *nonbonding* value for all n when $D_o = NMe_2$ and (d) the shortest Fe–C_β distances for the weakest π-donor substituent, D_o = F. These results are rationalized in terms of increased localization of nucleophilicity on the olefin C_α as the π-donor ability of D_o strengthens. Therefore, not all olefins will show η^2-binding.

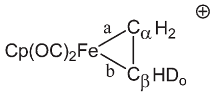
Introduction

The unsaturated monohydride fragments $MHClL_2$ (M = Ru, Os; L = P^iPr_3) first bind donor-substituted olefins (D_o = OR, O_2CR, F) [eqn. (1a)] and then isomerize them [eqn. (1b)] to heteroatom-substituted carbenes.[1,2] The thermodynamic driving force for this unusual olefin-to-carbene conversion was attributed to the electron-rich, π-basic character of the L_2ClHM fragment.[3] The facile *rate* of the conversion relies on the hydride ligand present, which permits conversion to a transient α-D_o-substituted alkyl, which can then relax to the carbene by α-H-migration [eqn. (1)].



(1)

We were interested in better understanding purely step 1a, the binding of the donor-substituted olefin to a metal. To prevent step 1b, it might be effective to avoid the presence of a hydride ligand and also to use a metal fragment that is quite Lewis acidic and minimally π-basic. These requirements might be met by the *cationic* fragment $CpFe(CO)_2^+$ (or Fp^+ for short). Compounds of this class were reported long ago by Rosenblum *et al.* and their structural characterization revealed the remarkable feature that these olefins appear not to bind in the dihapto manner so typical of olefins.[4] Instead, they bind (as in **1**, $b > a$) in a manner that could either be called "asymmetric" or η^1, *via* only C_α. Distance b was determined to be longer for the stronger donor $D_o = NMe_2$ than for D_o = OMe, which might be consistent with the electrophile $CpFe(CO)_2^+$ favoring the resonance structure **B** for the "olefinic" substrate. Such (atypical) olefins are thus to be considered as σ-donors rather than π-donors. Indeed, certain of these features had been *anticipated* in an earlier theoretical analysis.[5]



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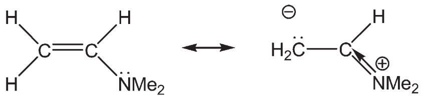

A **B**

These structural results[6] seemed sufficiently provocative to us that we wished to re-investigate them with the benefit of modern advances in crystallography at low temperature, with a fuller solution structural characterization, and with a critical evaluation of distances b in **1**, which lie in the difficult "intermediate" region where the decision "bond" or "no bond" becomes challenging to make. In addition, we wanted to apply and test the utility of density functional theory (DFT) calculations to these structures. Finally, we hoped to carry out "computational experiments" by DFT calculation of molecular structures where the electrophilicity of the metal was systematically varied *via* the series $CpFe(CO)_2^+$, $CpFe(CO)(PH_3)^+$ and $CpFe(PH_3)_2^+$.

Results

Synthesis

The synthetic route involves constructing the vinyl complexes with the carbon(s) already bound to iron [Scheme 1, where Fp = $CpFe(CO)_2$].

X-Ray structure determinations

$[CpFe(CO)_2(H_2C{=}CHNMe_2)]PF_6$. The redetermination of the crystal structure (Fig. 1 and Table 1), on crystals in the

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† Electronic supplementary information available: selected bond lengths and angles in $CpFe(CO)_2(H_2C{=}CHNMe_2)^+$ and $CpFe(CO)_2(H_2C{=}CHOEt)^+$; calculated orbital occupancies and natural charges in the iron-olefin complex and the free olefin. See http://www.rsc.org/suppdata/nj/b3/b305252d/

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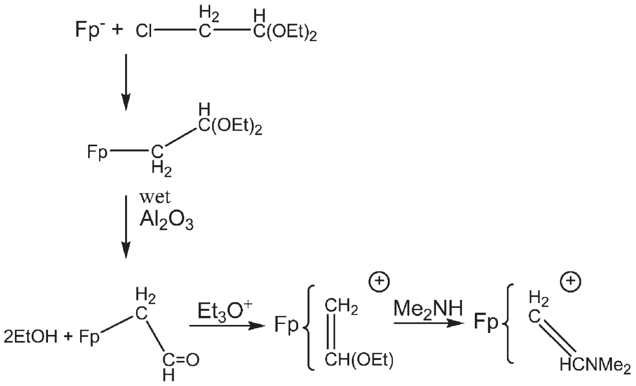


Scheme 1

same space group as before, gives esds smaller by a factor of 5–7 but showing very good agreement with the distances and angles determined earlier.[4] The solid shows no signs of disorder and even the PF_6^- anion is ordered. The linear carbonyls and one of the two vinyl amine carbons, C11, form a three-legged piano stool structure. C11 is nearly symmetrically placed with respect to the two carbonyls, the C11–Fe–C(O) angles being 87.13(4)° to C7 and 94.72(4)° to C9; the C7–Fe–C9 angle is 95.66(4)°. The angle Fe–C11–C12, 103.97(6)°, shows C11 to be nearly sp^3 hybridized. The amine nitrogen is coplanar with its attached groups (angles sum to 360.0°), the C12–N bond is short [1.302(1) Å] and the C11–C12 distance is long, 1.429(1) Å. The nonbonded Fe···C12 separation is 2.823(1) Å.

$[CpFe(CO)_2(H_2C{=}CHOEt)]PF_6$. Our crystals of the ethoxy derivative suffer the same disorder found earlier for the OMe analog. However, low temperature data collected with a CCD diffractometer enabled good resolution of the key C_α and C7 carbonyl carbons (see Experimental). These improved results permit some clear chemical conclusions (Fig. 2 and Table 2).

The Fe–C_α and Fe–C_β distances differ by 0.3 Å, but the latter distance of 2.402(10) Å cannot be dismissed as completely nonbonding. Consistent with a greater η^2-olefin character is the shorter C9–C10 distance, 1.336(14) Å, compared to the 1.429(1) Å value in the NMe_2 analog. The bonding of the vinyl ether C9 to Fe differs from the symmetric placement of C_α in the NMe_2 analog; angles from C9 to the carbonyls are 83.8(5)° and 100.1(3)°, while the intercarbonyl angle is 89.2(5)°. The corresponding angles for C10 to the carbonyls are 85.3(5)° and 113.7(4)°.

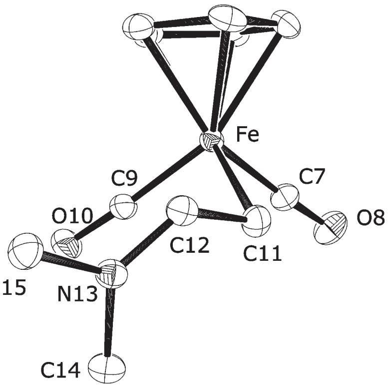


Fig. 1 ORTEP drawing (50% probability ellipsoids) of the non-hydrogen atoms of $(C_5H_5)Fe(CO)_2(H_2C{=}CHNMe_2)^+$, showing selective atom labeling.

Table 1 Selected distances (Å) and angles (deg) for $CpFe(CO)_2(H_2C{=}CHNMe_2)^+$

	X-Ray	DFT
Fe(1)–C(2)	2.0903(9)	
Fe(1)–C(3)	2.0980(10)	
Fe(1)–C(4)	2.1100(10)	
Fe(1)–C(5)	2.1230(10)	
Fe(1)–C(6)	2.0988(10)	
Fe(1)–C(7)	1.7675(10)	
Fe(1)–C(9)	1.7689(9)	
Fe(1)–C(11)	2.1143(10)	2.113
Fe(1)–C(12)	2.823(11)	2.799
C(2)–C(3)	1.4041(14)	
C(2)–C(6)	1.4334(14)	
C(3)–C(4)	1.4243(14)	
C(4)–C(5)	1.4139(15)	
C(5)–C(6)	1.4143(15)	
C(7)–O(8)	1.1449(12)	
C(9)–O(10)	1.1425(11)	
C(11)–C(12)	1.4290(13)	1.423
C(12)–N(13)	1.3015(11)	
N(13)–C(14)	1.4604(12)	
N(13)–C(15)	1.4641(12)	
C(7)–Fe(1)–C(9)	95.66(4)	
C(7)–Fe(1)–C(11)	87.13(4)	
C(9)–Fe(1)–C(11)	94.72(4)	
O(8)–C(7)–Fe(1)	176.41(9)	
O(10)–C(9)–Fe(1)	175.48(8)	
C(12)–C(11)–Fe(1)	103.97(6)	102.9
N(13)–C(12)–C(11)	127.31(8)	
C(12)–N(13)–C(14)	123.28(8)	
C(12)–N(13)–C(15)	120.80(8)	
C(14)–N(13)–C(15)	115.92(7)	
C(11)–Fe(1)–C(7)	87.13(4)	86.0
C(11)–Fe(1)–C(9)	94.72(4)	94.6

DFT calculations

$CpFe(CO)_2(H_2C{=}CHOEt)^+$. The geometry optimized structure (Fig. 3) shows near mirror symmetry of the Fp group, but the vinyl ether bonds in a distinctly asymmetric manner to iron: the Fe–C distances (Table 3) differ by more than 0.4 Å. The ethoxy substituted vinyl carbon is 2.585 Å from iron, a distance longer than all other iron–mono olefin bonds[7] and 0.4 Å longer than the Fe–C(Cp) distances in this molecule. Carbon Cα is not symmetrically placed with respect to the carbonyl carbons: ∠Cα–Fe–C3 is 82.9° while ∠Cα–Fe–C4 is 97.2°. The discrepancy in the long Fe–Cβ distance (calculated *vs.* experimental) reflects the inability of DFT to represent very

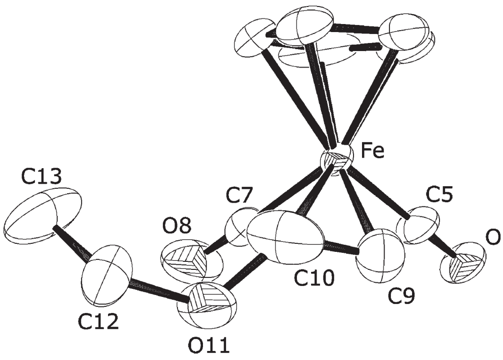


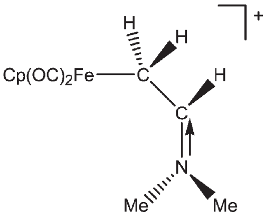
Fig. 2 ORTEP drawing (50% probability ellipsoids) of the non-hydrogen atoms of $(C_5H_5)Fe(CO)_2(H_2C{=}CHOEt)^+$, showing selective atom labeling. The view angle is chosen to allow comparison to Fig. 1 and to emphasize their similarity. This has the consequence of falsely diminishing the real difference of the angle Fe–C_α–C_β.

Table 2 Selected distances (Å) and angles (deg) for $CpFe(CO)_2(H_2C{=}CHOEt)^+$

	X-Ray	DFT
Fe(1)–C(2)	2.073(10)	
Fe(1)–C(3)	2.077(7)	
Fe(1)–C(4)	2.103(6)	
Fe(1)–C(5)	1.792(6)	
Fe(1)–C(7)	1.849(10)	
Fe(1)–C(9)	2.109(10)	2.156
Fe(1)–C10	2.402(10)	2.585
C(2)–C(3)	1.383(9)	
C(3)–C(4)	1.395(8)	
C(4)–C(4)#1	1.401(10)	
C(5)–O(6)	1.132(7)	
C(7)–O(8)	1.133(13)	
C(9)–C(10)	1.336(14)	1.391
C(10)–O(11)	1.359(12)	
O(11)–C(12)	1.448(10)	
C(12)–C(13)	1.425(12)	
C(5)–Fe(1)–C(7)	89.2(5)	
C(5)–Fe(1)–C(9)	83.8(5)	82.9
C(7)–Fe(1)–C(9)	100.1(3)	97.2
C(5)–Fe(1)–C(10)	113.7(4)	
C(7)–Fe(1)–C(10)	85.3(5)	
C(3)–C(2)–C(3)#1	109.2(9)	
C(2)–C(3)–C(4)	107.5(7)	
C(3)–C(4)–C(4)#1	107.8(4)	
O(6)–C(5)–Fe(1)	178.7(6)	
O(8)–C(7)–Fe(1)	174.8(11)	
C(10)–C(9)–Fe(1)	85.3(8)	91.0
C(9)–C(10)–O(11)	121.0(9)	
C(9)–C(10)–Fe(1)	61.1(6)	
C(13)–C(12)–O(11)	114.2(10)	

weak interactions and here we have a case where the "interactions" lie somewhere between weak and nonexistent.

$CpFe(CO)_2(H_2C{=}CHNMe_2)^+$. The amino-substituted analog (Fig. 3), however, optimizes to a structure (Table 3) that has unequivocal η^1-binding to the Fe of the $H_2C{=}CHNMe_2$ fragment: the angle Fe–Cα–Cβ is 102.9° (it is 91.0° in the vinyl ether complex) and the Fe–Cα distance is 0.04 Å shorter than in **1**, Do = NMe2, and is indistinguishable from the $Cp(OC)_2Fe{-}CH_3$ distance (2.10 Å).[7] The Fe–Cβ separation, 2.799 Å, is certainly nonbonding. Since both Cβ and N are planar (angles sum to 359.9°) and the Cβ–N distance, 1.315 Å, is short (sum of single bond radii is 1.47 Å), the structure is best represented as an iron *alkyl* complex with an iminium substituent on C1 (as in **2**). The angles from Cα to the carbonyl carbons are more symmetric than in the vinyl ether complex: ∠Cα–Fe–C3 is 86° and ∠C4–Fe–Cα is 94.6°. The Cα–Cβ distance, 1.423 Å, is long enough to be represented as a single bond between sp^2 and sp^3 carbons. For comparison, the Cα–Cβ distance in the vinyl ether complex is 1.391 Å. In summary, the electrophilic $CpFe(CO)_2^+$ cation causes the vinyl amine to localize in resonance structure **3**.



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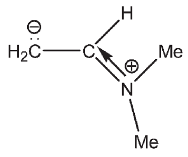

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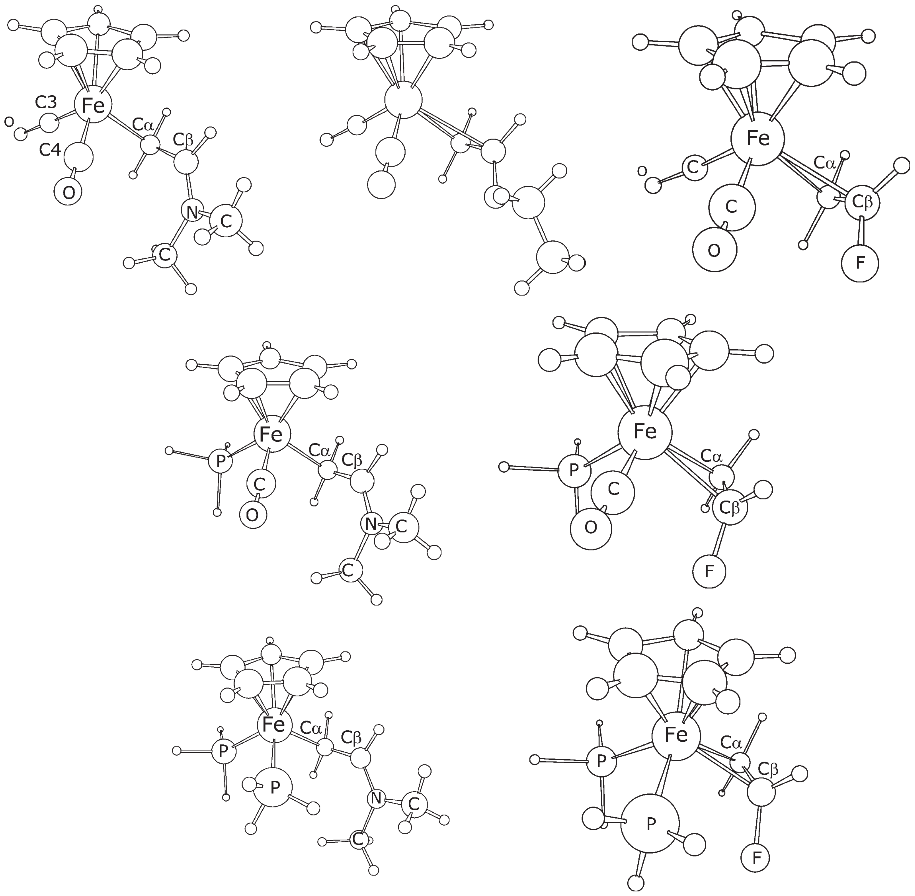


Fig. 3 DFT geometry-optimized structures (all are cations) of $[CpFe(CO)_n(PH_3)_{2-n}(H_2C{=}CHD_o)]^+$.

Table 3 Structural parameters (in Å and deg) from DFT geometry optimization

	$CpFe(CO)_2(H_2C{=}CHR)^+$			$CpFe(CO)(PH_3)(H_2C{=}CHR)^+$		$CpFe(PH_3)_2(H_2C{=}CHR)^+$	
R	F	OEt	NMe_2	F	NMe_2	F	NMe_2
LFe–C_α–C_β	76.1	90.99	102.9	74.2	99.5	71.6	98.5
Fe–C_α	2.188	2.156	2.113	2.158	2.127	2.130	2.167
Fe–C_β	2.286	2.585	2.799	2.222	2.745	2.142	2.752
C_α–C_β	1.371	1.391	1.423	1.375	1.418	1.381	1.405

$CpFe(CO)_2(H_2C{=}CHF)^+$. This olefin complex was calculated to evaluate the effects of a substituent that is a strong π-donor, but not as strong as OR or NR_2. The vinyl fluoride complex (Fig. 3 and Table 3) also shows unequal Fe–C (olefin) distances, the CHF carbon being more distant by 0.1 Å. The Fe–Cα–Cβ angle, 76.1°, also shows η^2-binding to be an appropriate description. The Fe–Cβ–Cα angle is 68.3°. The Cα–Cβ distance is shorter than those in the OEt and NMe_2 analogs.

NBO calculation

A natural bond orbital analysis (see Electronic supplementary information) of $CpFe(CO)_2(H_2C{=}CHD_0)^+$ is consistent with an increase in contribution of resonance form **B** and corresponding η^1-binding as D_0 varies from F to OEt to NMe_2. For D_0 = F, a localized double bond is observed between C_α and C_β and the natural charges on each atom have changed little from those of the free olefin. For D_0 = OEt, no localized double bond is observed either between C_α and C_β or between C_β and D_0; instead, some electron density is localized on C_β, consistent with a delocalized double bond (more equal contributions of the two resonance forms). For D_0 = NMe_2, resonance form **B** is observed with a localized double bond between C_β and D_0. The natural charge on D_0 is more positive and the charge on C_α more negative than in the corresponding free olefin, consistent with the η^1-binding observed in the geometry optimization.

Reduced electrophilicity of Fe

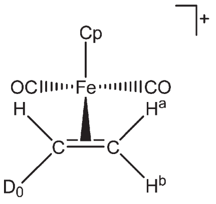
The electrophilicity of iron can be systematically reduced by formal replacement of CO groups by the less electron-withdrawing PH_3 ligands. Both $CpFe(CO)(PH_3)R^+$ and $CpFe(PH_3)_2R^+$ have been explored using the same DFT approach (Table 3). The analogs $(C_5H_5)Fe(CO)(PH_3)(C_2H_3F)^+$ and $(C_5H_5)Fe(PH_3)_2(C_2H_3F)^+$ show the results of progressively increasing back donation to vinyl fluoride: the Fe–C(olefin) asymmetry decreases (symmetric within 0.01 Å), the C=C bond lengthens (from 1.371 to 1.381 Å) and the C–F bond lengthens (from 1.329 to 1.358 Å), consistent with decreasing F-to-C π-donation.

At the other extreme, the vinyl dimethyl amine shows almost no reduction in the highly asymmetric interaction of Fe to Cα and Cβ as one, then two, PH_3 groups replace CO ligands in Fe. The Fe–Cβ distances, 2.799, 2.745 and 2.752 Å, respectively, are not even monotonic and thus confirm the *nonbonding* character of this interaction; the Fe–Cα, Cα–Cβ and Cβ–N distances lengthen, shorten and lengthen, respectively, as carbonyls are replaced by PH_3 (N is planar in all three species), but by less than 0.04 Å, consistent with only a minor decrease in the σ-electrophilicity of the $CpFeL_2^+$ fragment. That is, N-to-Cβ π-conjugation decreases, but only slightly.

The contrasting response of vinyl fluoride and vinyl dimethyl amine as ligands on $CpFeL_2^+$ can be summarized by saying that NMe_2 π-donation to Cβ is so strong that it prevents the amine from binding as an olefin, even to the π-basic $CpFe(PH_3)_2^+$, but the weaker π-donor F shows perceptible changes consistent with $CpFe(PH_3)_2^+$ competing with F for donation to the π system of the Cα–Cβ bond.

Spectroscopic evidence

The two $=CH_2$ protons provide an independent test of whether **A** correctly represents the only thermally accessible structure or whether **5** is the ground state or thermally accessible. In **4**, protons H^a and H^b are inequivalent, while in **5** they are equivalent. In fact (^1H NMR evidence), for D_o = OEt these protons are inequivalent at 20 °C and 400 MHz, while for D_o = NMe_2 they are equivalent. This is the best solution evidence that Cβ is bonded to iron when D_o = OEt, but not significantly bonded to Fe when D_o = NMe_2.



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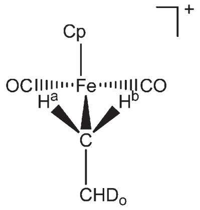

5

The CO infrared frequencies (Table 4) provide a good measure of the electron richness of the Fe center; a better π-acid ligand, L, in $CpFe(CO)_2L$ should result in less backbonding to the CO π* orbitals and so in higher ν(CO) values. If L is an olefin, it is a stronger π-acid than if it is an alkyl. Experimentally, the CO frequencies of the vinyl ether complex are significantly higher in energy than those of the vinyl amine, suggesting that the ether complex is more strongly interacting with the dπ orbitals of the metal. In contrast, the vinyl amine, with a significant contribution from the iminum resonance form **B**, is less π-acidic due to the delocalization of the lone pair on nitrogen into the π-system of the olefin. For comparison, simple σ-donors, such as alkyls, do not compete *via* backbonding for metal electron densit, and so result in complexes with significantly lower CO stretching frequencies (Table 4).

Conclusions

The presence and absence of disorder in these two solids is likewise a reflection of their very different structures. Because the vinyl ether is nearly η^2-bound to Fe, it is compact and disorders with one CO. Because the vinyl amine is best described as η^1-bond and thus pendant from Fe, it occupies much more

Table 4 Carbonyl absorption frequencies (cm^{-1}) for $CpFe(CO)_2R$

R	ν_1	ν_2
$C(CH_3)_3$[a]	2002	1946
$CH(CH_3)_2$[a]	2006	1952
CH_2CH_3[a]	2008	1954
CH_3[a]	2012	1959
$CH_2CH(NMe_2)$[b]	2034	1985
$CH_2CH(OEt)$[b]	2066	2026
C_2H_4[c]	2083	2049

[a] In *n*-hexane: W. Giering and M. Rosenblum, *J. Organomet. Chem.*, 1970, **25**, C71. [b] This work, in CD_2Cl_2. [c] E. O. Fischer and K. Fichtel, *Chem. Ber.*, 1961, **94**, 1200.

space than CO and shows no disorder with that compact ligand. This likewise explains why two so apparently similar PF_6 salts crystallize in different space groups.

Certain transition metal fragments, for example cationic $L_nCu^+ + L_3Pt^{II}$, have been established[8,9] to have quite low backbonding potential (π-basicity). A recent example of a dicationic Pt^{II} compound shows the ability to induce carbocationic behavior in coordinated ethylene.[10] The d^6 metal $CpFe(CO)_2{}^+$ studied here is quite π-electron poor at Fe [in contrast to the very nucleophilic and reducing $CpFe(CO)_2{}^-$] because of the two π-acid coligands on Fe^{II}; this seems to be responsible for the dramatic emergence of η^1-binding of the very nucleophilic enamine ligand. Thus, $CpFe(CO)_2(H_2C{=}CHNR_2)^+$ is an ideal case of a $CpFe(CO)_2{}^+$ fragment that is mainly a σ-Lewis acid and an enamine that has strong polarization to serve as a carbanionic σ-nucleophile rather than as a π-acid ligand (olefin).

The systematic reduction of the number of CO π-acid coligands is expected to increase the π-basicity of $CpFeL'L^+$ and this has been explored by a "computational experiment" *via* DFT calculations. This has not only confirmed expectations (for vinyl fluoride) but has shown an unexpected resistence of the enamine to bind in η^2 fashion to iron.

Thus, the NMe_2 group shows a remarkable ability to perturb the π bond of a vinyl group so strongly that it acts as a carbanion and thus nearly as a pure sigma ligand (a pseudo alkyl). Although the two carbonyl ligands and the 2+ oxidation state might be thought to leave $CpFe(CO)_2{}^+$ as a poor π-base [in contrast to the high σ-nucleophilicity of zerovalent iron in $CpFe(CO)_2{}^-$], not even the conversion to $CpFe(PH_3)_2{}^+$ causes $H_2C{=}CH(NMe_2)$ to bind in η^2 fashion to iron. Its nucleophilicity is concentrated on the unsubstituted carbon, as shown in **3**.

Finally, the inverse of this effect can also lead to marked asymmetry in the M–C distances of a bound olefin. Acrylonitrile bound to an electron-rich $L_2Ni(O)$ fragment shows the electron-*withdrawing* group to cause a 0.1 Å shortening in Ni–CH(CN) compared to $Ni{-}CH_2$.[11]

Experimental

Syntheses

The compounds were synthesized according to literature methods.[4,12]

[Fp(H₂C=CHNMe₂)][PF₆]. ^1H NMR (400 MHz, CD_2Cl_2, 20 °C): δ 8.0 (br s, 1H, $H_2C{=}C\mathit{H}NMe_2$), 5.16 (s, 5 H, Cp), 3.40 (s, 3H, $H_2C{=}CHN\mathit{Me}_2$), 2.97 (s, 3H, $H_2C{=}CHN\mathit{Me}_2$), 1.93 (br s, 2H, $\mathit{H}_2C{=}CHNMe_2$).

[Fp(H₂C=CHOEt)][PF₆]. ^1H NMR (400 MHz, CD_2Cl_2, 20 °C): δ 7.87 (br s, 1H, $H_2C{=}C\mathit{H}OEt$), 5.57 (s, 5H, Cp), 4.29 (br s, 2H, $H_2C{=}CHOC\mathit{H}_2CH_3$), 3.36 (br s, 1H, $\mathit{H}_2C{=}CHOEt$), 2.75 (br s, 1H, $\mathit{H}_2C{=}CHOEt$), 1.31 (br s, 3H, $H_2C{=}CHOCH_2C\mathit{H}_3$).

X-Ray structure determinations

General. A typical single crystal was selected from the bulk sample and affixed to the tip of a glass fiber with the use of silicone grease. The mounted sample was then transferred to the goniostat and cooled for characterization and data collection. The sample was handled under inert atmosphere to avoid any possibility of decomposition upon exposure to air. Data were collected on a Bruker platform goniometer equipped with a SMART 6000 CCD detector. A face-indexed absorption correction was applied by means of Bruker AXS' XPREP program. Data were corrected for instrumental effects, interframe scaling differences and other sources of systematic errors *via* the SADABS program. Equivalent reflections were averaged. The structures were solved by direct methods and completed by Fourier techniques. Selected data are given in Table 5.‡

[CpFe(CO)₂(H₂C=CHNMe₂)]PF₆. Frames were measured for 3 s each with a frame width of 0.3° in omega or phi. Three 180° omega frame runs and one 360° phi run were measured and the first 50 frames were remeasured at the end of the data collection. Frames were processed and integrated with the use of Bruker's SAINT software and reflections out to a maximum of 80° in 2θ were harvested. The data exhibited systematic absences uniquely characteristic of the centrosymmetric space group $P2_1/n$ and that assignment was confirmed by subsequent successful structure solution and refinement. Hydrogen atoms were located in a difference electron density map phased on the non-hydrogen atoms and freely refined as isotropic contributors in the final least-squares cycles. All non-hydrogen atoms were refined anisotropically. A final difference Fourier map had no unusual features. The largest peak resides between atoms N(13) and C(14), and has an intensity of 0.81 e $Å^{-3}$.

[CpFe(CO)₂(H₂C=CHOEt)]PF₆. Frames were measured for 20 s each with a frame width of 0.3° in omega. Five 180° frame runs were measured and the first 50 frames were remeasured at the end of the data collection. Frames were processed and integrated with the use of Bruker's SAINT software and reflections out to a maximum of 60° in 2θ were harvested. The data exhibit monoclinic symmetry and systematic absences indicative of the possible space groups centrosymmetric $C2/m$ and acentric $C2$ and Cm. Subsequent structure solution and refinement did not wholly distinguish between $C2/m$ and $C2$, but space group $C2/m$ was chosen because the structure could not be modelled any more satisfactorily in the less symmetric $C2$. Hydrogen atoms were placed in calculated positions and refined with a riding model in the final least-squares cycles. All non-hydrogen atoms were refined anisotropically. One of the two independent $PF_6{}^-$ positions exhibits a well-resolved disorder, with the two components being related by a rotation around one of the F–P–F axes. One carbonyl (C7–O8) and the entire vinyl ether of the cation are disordered about a mirror plane (one of the space group symmetry elements in the $C2/m$ model chosen, but a non-crystallographic mirror plane in the alternative $C2$ model). In addition, the Cp ring exhibits a 77:23 rotational disorder, but each disorder component conforms to the mirror symmetry.

Table 5 Crystallographic data for two CpFe complexes

Formula	$C_{11}H_{14}F_6FeNO_2P$	$C_{11}H_{13}F_6FeO_3P$
Formula weight	393.05	394.03
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/m$
T/K	113	133
a/Å	7.3364(17)	13.7979(18)
b/Å	25.006(6)	7.3558(9)
c/Å	8.1750(18)	15.251(2)
β/°	100.730(6)	108.775(3)
Z	4	4
U/$Å^3$	1473.5(6)	1465.5(3)
μ/mm^{-1}	12.012	12.111
Total reflections	49367	16064
Independent reflections	9138	2300
R_{int}	3.0%	6.6%
Obs. reflections [$I > 2\sigma(I)$]	7734	1916
$R(F)$ (obs. data)	0.0318	0.0609
$wR(F^2)$ (refinement data)	0.0872	0.1714

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† CCDC reference numbers 210226 and 210227. See http://www.rsc.org/suppdata/nj/b3/b305252d/ for crystallographic data in .cif or other electronic format.

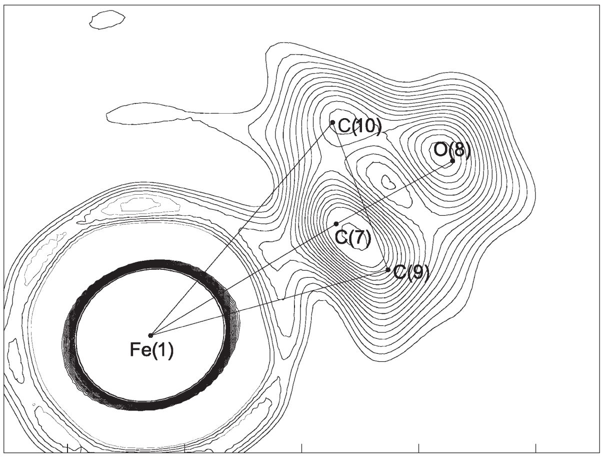

Fig. 4 A view of the electron density of one disordered carbonyl ligand with the two vinyl carbons of $H_2C{=}CHOEt$, showing the good resolution of vinyl carbon C10 from the carbonyl oxygen O8 but the overlap of the carbonyl C7 with the vinyl C9. Refined positions are shown as dots and bonds as straight lines. Electron density is contoured at 0.25 e Å^{-3} with the peak at Fe(1) not fully contoured.

The cation disorder has the most apparent effect where the vinyl ether ligand of one disorder component overlaps one of the carbonyl ligands of the other component, but the atomic positions of the relevant atoms are all well-resolved (Fig. 4). A referee has reduced the cell constants in the 1981 determination of the methoxy analog and finds it to be essentially isomorphous and thus to have similar packing.[4] That referee finds the Fe–C10 distance here [2.40(1) Å in this determination, longer than the 2.32(2) Å found earlier] and estimates that the present determination is "more reliable". The other carbonyl (C5–O6) is also disordered, albeit with the two components near each other on opposite sides of the mirror plane. The whole-moiety or near whole-moiety (excepting the Fe) disorder is apparent even in crystallographic models in the lower symmetry space groups *C*2 and *P*1. Models substituting centrosymmetric twinning in space group *C*2 for disorder in either *C*2 or *C*2/*m* did not agree as well with the data and did not provide more meaningful Fe positions. The largest peak in the final difference electron density map has an intensity of 1.36 e Å^{-3} and resides between atom Fe(1) and the centroid of the Cp ring.

Computational details

All calculations were performed with the Gaussian 98 package[13] at the B3PW91[14] level of theory. Basis sets used include LANL2DZ for Fe, 6-31G* for all carbon, oxygen, nitrogen, and fluorine atoms, and 6-31G** for all hydrogens.[15] The basis set LANL2DZ is the Los Alamos National Laboratory ECP plus a double zeta valence on Fe.[16] All optimizations were performed with C_1 symmetry and minima were confirmed by analytical calculation of frequencies, which were also used to compute zero point energy corrections without scaling. Each calculated complex was started from two separate initial geometries (η^1- and η^2-bound olefin); regardless of the initial geometry, they converged to the same reported structure.

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References

1 J. N. Coalter III, G. J. Spivak, H. Gerard, E. Clot, E. R. Davidson, O. Eisenstein and K. G. Caulton, *J. Am. Chem. Soc.*, 1998, **120**, 9388.
2 G. Ferrando, H. Gérard, G. J. Spivak, J. N. Coalter III, J. C. Huffman, O. Eisenstein and K. G. Caulton, *Inorg. Chem.*, 2001, **40**, 6610.
3 J. N. Coalter III, J. C. Bollinger, J. C. Huffman, U. Werner-Zwanziger, K. G. Caulton, E. R. Davidson, H. Gerard, E. Clot and O. Eisenstein, *New J. Chem.*, 2000, **24**, 9.
4 T. C. T. Chang, B. Foxman, M. Rosenblum and C. Stockman, *J. Am. Chem. Soc.*, 1981, **103**, 7361.
5 O. Eisenstein and R. Hoffmann, *J. Am. Chem. Soc.*, 1980, **102**, 6148.
6 The crystal of [CpFe(CO)2{H2C=CH(OMe)}]PF6 was disordered.
7 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.
8 A. J. Lupinetti, S. Strauss and G. Frenking, *Prog. Inorg. Chem.*, 2001, **49**, 1.
9 A. J. Lupinetti, V. Jonas, W. Thiel, S. H. Strauss and G. Frenking, *Eur.-J. Chem.*, 1999, **5**, 2573.
10 C. C. Hahn, M. Cucciolito and A. Vitagliano, *J. Am. Chem. Soc.*, 2002, **124**, 9038.
11 L. J. Guggenberger, *Inorg. Chem.*, 1973, **12**, 499.
12 A. Cutler, S. Raghu and M. Rosenblum, *J. Organomet. Chem.*, 1974, **77**, 381.
13 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, *GAUSSIAN 98 (Revision A.7)*, Gaussian, Inc., Pittsburgh, PA, 1998.
14 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098; A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372; A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; J. P. Perdue and Y. Wang, *Phys. Rev. B.*, 1991, **45**, 13 244.
15 P. C. P. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.
16 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270; W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284; P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.