Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Ferrocene/ferrocenium, cobaltocene/cobaltocenium and nickelocene/nickelocenium: From gas phase ionization energy to one-electron reduction potential in solvated medium

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Supplementary Information

Gas-phase IE predictions of ferrocene and cobaltocene by the complete basis set extrapolation technique

The individual energy corrections of extrapolated $\Delta E_{CCSD(T)/CBS}$ with corrections of ΔE_{CV}, ΔE_{SR}, ΔE_{SO}, and ΔE_{ZPVE}, for the IE[$Cp_2Fe(^1A_1') \rightarrow Cp_2Fe^+(^2B_1)$] and IE[$Cp_2Co(^2B_2) \rightarrow Cp_2Co^+(^1A_1')$] predictions using the CCSD(T)/CBS method are summarized in Table S1. By proceeding from CCSD(T)/cc-pVDZ to CCSD(T)/cc-pVQZ level, the valence electronic contribution at CCSD(T) level to IE(Cp_2Fe) increases from 6.372 (cc-pVDZ) to 6.714 (cc-pVQZ) eV. Augmenting the basis sets with diffuse functions yields 6.531 (aVDZ) and 6.700 (aVTZ) eV, respectively. Extrapolated from the valence electronic energies with the aug-cc-pVTZ and aug-cc-pVQZ basis sets using two-point extrapolation scheme ($E(X) = E_{\text{extrapolated CBS}} + \frac{B}{X^3}$) enables us to obtain effective CCSD(T)/CBS IE(Cp_2Fe) value of 6.788 eV, included with the CV (+0.035 eV), SR (–0.014 eV), SO (–0.017 eV) and ZPVE (+0.013 eV) corrections. Similarly, the CCSD(T)/CBS IE(Cp_2Co) value is 5.290 eV.

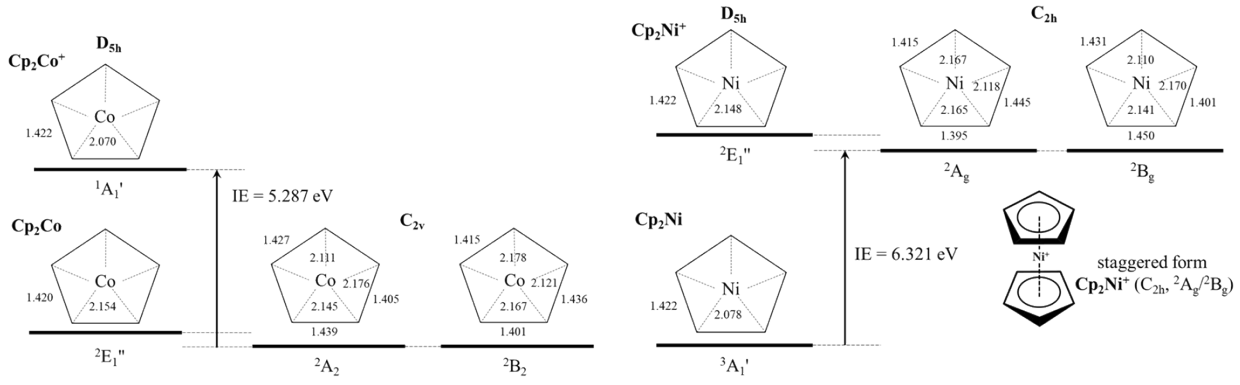

Figure S1. The relative energies of $Cp_2Co(^2E_1"$, $^2A_2$ and $^2B_2$ states)/$Cp_2Co^+(^1A_1')$ and Cp_2Ni ($^3A_1'$)/Cp_2Ni^+ ($^2E_1"$, ^2A_g and ^2B_g states) at the CCSD(T)-F12(b)/aug-cc-pVQZ level with the CV, SR, ZPVE and SO corrections. All optimized bond lengths (Å) are at the B3LYP/cc-pVQZ level.

Table S1. Individual energy corrections[a] to the IE(Cp_2Fe) and IE(Cp_2Co) predictions using the CCSD(T)/CBS methods (All values in eV).

		IE[$Cp_2Fe(^1A_1') \rightarrow Cp_2Fe^+(^2B_1)$] [b]	IE[$Cp_2Co(^2B_2) \rightarrow Cp_2Co^+(^1A_1')$] [b]
$\Delta E_{CCSD(T)}$	cc-pVDZ	6.372	4.991
	cc-pVTZ	6.612	5.150
	cc-pVQZ	6.714	5.194
	CBS_{DT} [c]	6.713	5.217
	CBS_{TQ} [c]	6.789	5.225
	aVDZ	6.531	5.115
	aVTZ	6.700	5.194
	CBS_{aDT} [c]	6.771	5.228
ΔE_{CV}		0.035	0.006
ΔE_{SR}		–0.014	–0.091
ΔE_{SO}		–0.017	0.007
ΔE_{ZPVE}		0.013	0.140
CCSD(T)/CBS IE [d]		6.788	5.290
CCSD(T)-F12/aVQZ IE [e]		**6.810 (F12a)** **6.790 (F12b)**	**5.295 (F12a)** **5.287 (F12b)**
G4MP2 (this work)		6.74	5.54
Other theoretical value		7.046 [f] 6.810 [g] 6.773 [h] 7.17 [i]	4.77 [n] 5.223 [g] 5.308 [h]
Exptl. value		6.747 ± 0.009 [j] 6.87 ± 0.07 [k] 6.72 ± 0.07 [l] 6.72 [m]	5.3275 ± 0.0006 [o] 5.25 ± 0.07 [p]

[a] See definition of E_{CV}, E_{SR}, E_{SO} and E_{ZPVE} from Table 1.

[b] For each pair of isoelectronic species, $Cp_2Fe^+(^2A_1$ and $^2B_1)$, $Cp_2Co(^2A_2$ and $^2B_2)$, the ionization process is arbitrarily referred to the species with a "B" symmetry.

[c] Extrapolated from the valence electronic energies with the cc-pV[D-T]Z, cc-pV[T-Q]Z and aug-cc-pV[D-T]Z basis sets using two-point extrapolation scheme, see ref. 40–43 for details.

[d] $IE = \Delta E_{CCSD(T)/CBS(aDT)} + \Delta E_{CV} + \Delta E_{SR} + \Delta E_{SO} + \Delta E_{ZPVE.}$

[e] see main text, $IE = \Delta E_{CCSD(T)\text{-}F12/agu\text{-}cc\text{-}pVQZ} + \Delta E_{CV} + \Delta E_{SR} + \Delta E_{SO} + \Delta E_{ZPVE.}$

[f] From ref. 7. G3(MP2)-RAD(-Full-TZ) value.

[g] From ref. 27. Correlation consistent composite approach (ccCA) values.

[h] From ref. 28. localized coupled cluster method (DLPNO-CCSD(T_0)) value.

[i] From ref. 29. The 0K IE=7.17 eV is obtained by correcting the 7.11 eV (685.633 kJ/mol, ωB97X-D value at 298 K) with the free energy contribution and temperature effect.

[j] From ref. 8. Obtained by photoionization efficiency measurement.

[k] From ref. 9. The 0K IE=6.87 ± 0.07 eV is obtained by correcting the 6.81 ± 0.07 eV (at 298 K) with the free energy contribution and temperature effect.

[l] From ref. 10. The 0K IE=6.72 ± 0.07 eV is obtained by correcting the 6.64 ± 0.07 eV (at 350 K) with the free energy contribution and temperature effect.

[m] From ref. 32. Obtained by photoelectron spectra.

[n] From ref. 26. PBE value.

[o] From ref. 24. Obtained by mass-analyzed threshold ionization.

[p] From ref. 11. The 0K IE=5.25 ± 0.07 eV is obtained by correcting the 5.36 ± 0.07 eV (at 350 K) with the free energy contribution and temperature effect.

Table S2. Free energies of solvation of Cp_2Fe/Cp_2Fe^+, Cp_2C_O/Cp_2Co^+ and Cp_2Ni/Cp_2Ni^+ in aqueous solution and nonaqueous solvents of acetonitrile, methanol, and acetone.

		ΔG_{solv}(in eV) [a]							
Model (SMD)		water		acetonitrile		methanol		Acetone	
Functionals	Basis set	Cp_2Fe	Cp_2Fe^+	Cp_2Fe	Cp_2Fe^+	Cp_2Fe	Cp_2Fe^+	Cp_2Fe	Cp_2Fe^+
M05-2X	6-31G(d)	–0.049	–2.212	–0.332	–2.464	–0.270	–2.394	–0.331	–2.417
	6-31G(d)/SDD	–0.055	–2.129	–0.337	–2.385	–0.275	–2.315	–0.336	–2.342
	def2-TZVP	–0.056	–2.166	–0.338	–2.420	–0.276	–2.350	–0.337	–2.376
Model (PCM)									
M05-2X	def2-TZVP	–0.054	–1.849	–0.050	–1.818	–0.049	–1.812	–0.044	–1.775
Model (uESE) [b]									
B3LYP	def2-TZVP	–0.022	–2.432	–0.340	–2.842	–0.270	–2.512	/	/
Experimental [c]		–0.123		–0.332		–0.316		–0.349	
Model (SMD)		water		acetonitrile		methanol		acetone	
Functionals	Basis set	Cp_2Co	Cp_2Co^+	Cp_2Co	Cp_2Co^+	Cp_2Co	Cp_2Co^+	Cp_2Co	Cp_2Co^+
M05-2X	6-31G(d)	–0.067	–2.106	–0.355	–2.375	–0.290	–2.315	–0.354	–2.216
	6-31G(d)/SDD	–0.054	–2.068	–0.343	–2.333	–0.278	–2.271	–0.343	–2.215
	def2-TZVP	–0.069	–2.092	–0.357	–2.358	–0.292	–2.298	–0.355	–2.229
Model (PCM)									
M05-2X	def2-TZVP	–0.055	–1.853	–0.051	–1.822	–0.050	–1.817	–0.046	–1.780
Model (uESE) [b]									
B3LYP	def2-TZVP	–0.004	–2.481	–0.324	–2.808	–0.254	–2.487	/	/
Model (SMD)		water		acetonitrile		methanol		acetone	
Functionals	Basis set	Cp_2Ni	Cp_2Ni^+	Cp_2Ni	Cp_2Ni^+	Cp_2Ni	Cp_2Ni^+	Cp_2Ni	Cp_2Ni^+
M05-2X	6-31G(d)	–0.058	–2.100	–0.350	–2.359	–0.283	–2.289	–0.349	–2.319
	6-31G(d)/SDD	–0.036	–2.059	–0.328	–2.319	–0.261	–2.250	–0.328	–2.281
	def2-TZVP	–0.059	–2.092	–0.350	–2.352	–0.283	–2.281	–0.349	–2.310
Model (PCM)									
M05-2X	def2-TZVP	–0.054	–1.842	–0.050	–1.811	–0.049	–1.805	–0.045	–1.769

Model (uESE) [b]									
B3LYP	def2-TZVP	–0.011	–2.362	–0.317	–2.765	–0.259	–2.448	/	/

[a] Calculated from the single point energies difference between at gas-phase and in solvent (eqn. (4)). The free energy change associated with moving from a gas-phase pressure of 1 atm to a liquid-phase concentration of 1 M ($\Delta G^{1atm \rightarrow 1M}$ = 1.89 kcal/mol, or 0.082 eV) has already been included in the present data.[90]

[b] The solvation energy calculation of acetone is unavailable in uESE.

[c] From ref. 15.

Table S3. Optimized geometry at B3LYP/cc-pVQZ level.

Cp_2Fe ($^1A_1'$), D_{5h}

Fe	0.00000000	0.00000000	0.00000000
C	0.00000000	1.20989200	1.69001500
H	0.00000000	2.28641000	1.67477000
C	1.15067500	0.37387700	1.69001500
H	2.17450500	0.70653900	1.67477000
C	0.71115700	-0.97882300	1.69001500
H	1.34391800	-1.84974400	1.67477000
C	-0.71115700	-0.97882300	1.69001500
H	-1.34391800	-1.84974400	1.67477000
C	-1.15067500	0.37387700	1.69001500
H	-2.17450500	0.70653900	1.67477000
C	0.00000000	1.20989200	-1.69001500
H	0.00000000	2.28641000	-1.67477000
C	1.15067500	0.37387700	-1.69001500
H	2.17450500	0.70653900	-1.67477000
C	0.71115700	-0.97882300	-1.69001500
H	1.34391800	-1.84974400	-1.67477000
C	-0.71115700	-0.97882300	-1.69001500
H	-1.34391800	-1.84974400	-1.67477000
C	-1.15067500	0.37387700	-1.69001500
H	-2.17450500	0.70653900	-1.67477000

Cp_2Fe^+ ($^2E_2'$), D_{5h}

Fe	0.00000000	0.00000000	0.00000000
C	0.00000000	1.20809700	1.75349000
C	-1.14896900	0.37332300	1.75349000
C	-0.71010200	-0.97737100	1.75349000
C	0.71010200	-0.97737100	1.75349000
C	1.14896900	0.37332300	1.75349000
H	0.00000000	2.28510300	1.74089700
H	-2.17326200	0.70613600	1.74089700
H	-1.34315000	-1.84868700	1.74089700
H	1.34315000	-1.84868700	1.74089700
H	2.17326200	0.70613600	1.74089700
C	0.00000000	1.20809700	-1.75349000
C	-1.14896900	0.37332300	-1.75349000

C	-0.71010200	-0.97737100	-1.75349000
C	0.71010200	-0.97737100	-1.75349000
C	1.14896900	0.37332300	-1.75349000
H	0.00000000	2.28510300	-1.74089700
H	-2.17326200	0.70613600	-1.74089700
H	-1.34315000	-1.84868700	-1.74089700
H	1.34315000	-1.84868700	-1.74089700
H	2.17326200	0.70613600	-1.74089700

Cp_2Fe^+ ($^2A_1$), C_{2v}

Fe	0.00000000	0.00000000	0.00129100
C	0.00000000	1.80187900	-1.20477200
C	-1.14747500	1.76603500	-0.37543900
C	-0.71292600	1.71087200	0.97773900
C	0.71292600	1.71087200	0.97773900
C	1.14747500	1.76603500	-0.37543900
H	0.00000000	1.81376900	-2.28214400
H	-2.17027300	1.76148100	-0.71333000
H	-1.34844400	1.68342100	1.84652900
H	1.34844400	1.68342100	1.84652900
H	2.17027300	1.76148100	-0.71333000
C	0.00000000	-1.80187900	-1.20477200
C	-1.14747500	-1.76603500	-0.37543900
C	-0.71292600	-1.71087200	0.97773900
C	0.71292600	-1.71087200	0.97773900
C	1.14747500	-1.76603500	-0.37543900
H	0.00000000	-1.81376900	-2.28214400
H	-2.17027300	-1.76148100	-0.71333000
H	-1.34844400	-1.68342100	1.84652900
H	1.34844400	-1.68342100	1.84652900
H	2.17027300	-1.76148100	-0.71333000

Cp_2Fe^+ ($^2B_1$), C_{2v}

Fe	0.00000000	0.00000000	0.00118800
C	0.00000000	1.70172900	1.21038100
C	1.15077900	1.73505100	0.37082400
C	0.70759600	1.79192900	-0.97601400
C	-0.70759600	1.79192900	-0.97601400
C	-1.15077900	1.73505100	0.37082400
H	0.00000000	1.67071700	2.28664500
H	2.17654200	1.71731400	0.69841400
H	1.33827000	1.79921000	-1.84946300
H	-1.33827000	1.79921000	-1.84946300
H	-2.17654200	1.71731400	0.69841400
C	0.00000000	-1.70172900	1.21038100
C	1.15077900	-1.73505100	0.37082400
C	0.70759600	-1.79192900	-0.97601400
C	-0.70759600	-1.79192900	-0.97601400
C	-1.15077900	-1.73505100	0.37082400
H	0.00000000	-1.67071700	2.28664500
H	2.17654200	-1.71731400	0.69841400

H	1.33827000	-1.79921000	-1.84946300
H	-1.33827000	-1.79921000	-1.84946300
H	-2.17654200	-1.71731400	0.69841400

$Cp_2Co(^2E_1")$, D_{5h}

Co	0.00000000	0.00000000	0.00000000
C	0.00000000	1.20779000	1.78368900
C	-1.14867600	0.37322800	1.78368900
C	-0.70992100	-0.97712200	1.78368900
C	0.70992100	-0.97712200	1.78368900
C	1.14867600	0.37322800	1.78368900
H	0.00000000	2.28444000	1.77374600
H	-2.17263100	0.70593100	1.77374600
H	-1.34276000	-1.84815100	1.77374600
H	1.34276000	-1.84815100	1.77374600
H	2.17263100	0.70593100	1.77374600
C	0.00000000	1.20779000	-1.78368900
C	-1.14867600	0.37322800	-1.78368900
C	-0.70992100	-0.97712200	-1.78368900
C	0.70992100	-0.97712200	-1.78368900
C	1.14867600	0.37322800	-1.78368900
H	0.00000000	2.28444000	-1.77374600
H	-2.17263100	0.70593100	-1.77374600
H	-1.34276000	-1.84815100	-1.77374600
H	1.34276000	-1.84815100	-1.77374600
H	2.17263100	0.70593100	-1.77374600

$Cp_2Co(^2A_2)$, C_{2v}

Co	0.00000000	0.00000000	0.00243600
C	0.00000000	1.74159400	1.19587300
C	1.15974300	1.80533800	0.36674400
C	0.71958300	1.77315100	-0.96691200
C	-0.71958300	1.77315100	-0.96691200
C	-1.15974300	1.80533800	0.36674400
H	0.00000000	1.72415300	2.27310800
H	2.18155100	1.79760000	0.70452900
H	1.34421900	1.76288100	-1.84413800
H	-1.34421900	1.76288100	-1.84413800
H	-2.18155100	1.79760000	0.70452900
C	0.00000000	-1.74159400	1.19587300
C	1.15974300	-1.80533800	0.36674400
C	0.71958300	-1.77315100	-0.96691200
C	-0.71958300	-1.77315100	-0.96691200
C	-1.15974300	-1.80533800	0.36674400
H	0.00000000	-1.72415300	2.27310800
H	2.18155100	-1.79760000	0.70452900
H	1.34421900	-1.76288100	-1.84413800
H	-1.34421900	-1.76288100	-1.84413800
H	-2.18155100	-1.79760000	0.70452900

$Cp_2Co(^2B_2)$, C_{2v}

Co	0.00000000	0.00000000	0.00658300
C	0.00000000	1.81072900	1.21611500
C	1.13754100	1.75179700	0.37648600
C	0.70032200	1.79207400	-0.99078900
C	-0.70032200	1.79207400	-0.99078900
C	-1.13754100	1.75179700	0.37648600
H	0.00000000	1.80445900	2.29218400
H	2.16400100	1.73754400	0.70305800
H	1.34070100	1.78272700	-1.85611100
H	-1.34070100	1.78272700	-1.85611100
H	-2.16400100	1.73754400	0.70305800
C	0.00000000	-1.81072900	1.21611500
C	1.13754100	-1.75179700	0.37648600
C	0.70032200	-1.79207400	-0.99078900
C	-0.70032200	-1.79207400	-0.99078900
C	-1.13754100	-1.75179700	0.37648600
H	0.00000000	-1.80445900	2.29218400
H	2.16400100	-1.73754400	0.70305800
H	1.34070100	-1.78272700	-1.85611100
H	-1.34070100	-1.78272700	-1.85611100
H	-2.16400100	-1.73754400	0.70305800

Cp_2Co^+ ($^1A_1'$), D_{5h}

Co	0.00000000	0.00000000	0.00000000
C	0.00000000	1.20969200	1.67931000
H	0.00000000	2.28620400	1.65869000
C	1.15048600	0.37381600	1.67931000
H	2.17430900	0.70647600	1.65869000
C	0.71103900	-0.97866200	1.67931000
H	1.34379700	-1.84957800	1.65869000
C	-0.71103900	-0.97866200	1.67931000
H	-1.34379700	-1.84957800	1.65869000
C	-1.15048600	0.37381600	1.67931000
H	-2.17430900	0.70647600	1.65869000
C	0.00000000	1.20969200	-1.67931000
H	0.00000000	2.28620400	-1.65869000
C	1.15048600	0.37381600	-1.67931000
H	2.17430900	0.70647600	-1.65869000
C	0.71103900	-0.97866200	-1.67931000
H	1.34379700	-1.84957800	-1.65869000
C	-0.71103900	-0.97866200	-1.67931000
H	-1.34379700	-1.84957800	-1.65869000
C	-1.15048600	0.37381600	-1.67931000
H	-2.17430900	0.70647600	-1.65869000

Cp_2Ni ($^3A_1'$), D_{5h}

Ni	-0.00005600	0.00007900	0.00047000
C	1.87756400	-1.18767400	-0.21532300
C	1.87685600	-0.16373700	-1.19699500
C	1.87701100	1.08635400	-0.52661000
C	1.87798000	0.83506700	0.86950400

C	1.87830900	-0.57036300	1.06183400
H	1.87346200	-2.24756900	-0.40605200
H	1.87211900	-0.30978000	-2.26395800
H	1.87251200	2.05595600	-0.99522700
H	1.87442000	1.58036900	1.64684400
H	1.87493000	-1.07938400	2.01086200
C	-1.87797200	-1.18726000	-0.21445300
C	-1.87824200	-0.16180900	-1.19461200
C	-1.87747000	1.08725300	-0.52231100
C	-1.87672800	0.83379500	0.87342000
C	-1.87709900	-0.57192300	1.06365700
H	-1.87417300	-2.24685900	-0.40682500
H	-1.87481500	-0.30623700	-2.26180100
H	-1.87336300	2.05757100	-0.98944500
H	-1.87208800	1.57791700	1.65188600
H	-1.87269300	-1.08240100	2.01189800

Cp_2Ni^+ ($^2E_1''$), D_{5h}

Ni	0.00000000	0.00000000	0.00000000
C	0.00000000	1.20974700	1.77452300
C	-1.15053800	0.37383200	1.77452300
C	-0.71107100	-0.97870600	1.77452300
C	0.71107100	-0.97870600	1.77452300
C	1.15053800	0.37383200	1.77452300
H	0.00000000	2.28660500	1.76976100
H	-2.17469000	0.70660000	1.76976100
H	-1.34403300	-1.84990200	1.76976100
H	1.34403300	-1.84990200	1.76976100
H	2.17469000	0.70660000	1.76976100
C	0.00000000	1.20974700	-1.77452300
C	-1.15053800	0.37383200	-1.77452300
C	-0.71107100	-0.97870600	-1.77452300
C	0.71107100	-0.97870600	-1.77452300
C	1.15053800	0.37383200	-1.77452300
H	0.00000000	2.28660500	-1.76976100
H	-2.17469000	0.70660000	-1.76976100
H	-1.34403300	-1.84990200	-1.76976100
H	1.34403300	-1.84990200	-1.76976100
H	2.17469000	0.70660000	-1.76976100

Cp_2Ni^+ (^2A_g), C_{2h}

Ni	0.00000000	0.00000000	0.00000000
C	0.00000000	1.78600600	1.13824300
C	0.80960100	2.00956100	0.00000000
C	0.00000000	1.78600600	-1.13824300
C	-1.35392600	1.53847700	-0.69752500
C	-1.35392600	1.53847700	0.69752500
H	0.32123800	1.84073000	2.16524200
H	1.86320400	2.22938600	0.00000000
H	0.32123800	1.84073000	-2.16524200

H	-2.19833700	1.35696000	-1.34047000
H	-2.19833700	1.35696000	1.34047000
C	0.00000000	-1.78600600	1.13824300
C	1.35392600	-1.53847700	0.69752500
C	1.35392600	-1.53847700	-0.69752500
C	0.00000000	-1.78600600	-1.13824300
C	-0.80960100	-2.00956100	0.00000000
H	-0.32123800	-1.84073000	2.16524200
H	2.19833700	-1.35696000	1.34047000
H	2.19833700	-1.35696000	-1.34047000
H	-0.32123800	-1.84073000	-2.16524200
H	-1.86320400	-2.22938600	0.00000000

Cp_2Ni^+ (^2B_g), C_{2h}

Ni	0.00000000	0.00000000	0.00000000
C	0.82746300	1.94096100	0.00000000
H	1.88710600	2.13686800	0.00000000
C	0.00000000	1.83165600	1.16286600
H	0.33376300	1.89618800	2.18419000
C	-1.29829800	1.54042300	0.72518300
H	-2.15843200	1.36083100	1.34817400
C	-1.29829800	1.54042300	-0.72518300
H	-2.15843200	1.36083100	-1.34817400
C	0.00000000	1.83165600	-1.16286600
H	0.33376300	1.89618800	-2.18419000
C	-0.82746300	-1.94096100	0.00000000
H	-1.88710600	-2.13686800	0.00000000
C	0.00000000	-1.83165600	-1.16286600
H	-0.33376300	-1.89618800	-2.18419000
C	1.29829800	-1.54042300	-0.72518300
H	2.15843200	-1.36083100	-1.34817400
C	1.29829800	-1.54042300	0.72518300
H	2.15843200	-1.36083100	1.34817400
C	0.00000000	-1.83165600	1.16286600
H	-0.33376300	-1.89618800	2.18419000