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Reactive MALDI mass spectrometry of saturated hydrocarbons: A theoretical study

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ABSTRACT

Recently it has been shown that the cobaltocenium cation, prepared by the laser ablation of a $CoCp(CO)_2$/fullerene matrix, may react with alkanes and polyethylenes in the gas phase via a dehydrogenation reaction to produce $[Co(Cp)_2(\text{alkadiene})]^+$ ions without chain scission (W.E. Wallace, Chem. Commun. 2007, 4525–4527). To better understand these experimental observations, density functional calculations were used to obtain the gas phase binding energies and molecular structures of cobaltocenium, $Co(Cp)_2{}^+$, with 1,3-butadiene, 2,4-hexadiene, and 2,3-hexadiene. Calculations were conducted for both *cis* and *trans* molecular configurations, in both singlet and triplet electronic states, and with a variety of cyclopentadienyl hapticities. For 1,3-butadiene the 18-electron rule would predict a $[Co(\eta^3\text{-Cp})_2(\eta^4\text{-1,3-butadiene})]^+$, however, the lowest energy structure, $[Co(\eta^5\text{-Cp})_2(\text{1,3-butadiene})]^+$, has a higher than expected cyclopentadienyl hapticity. In this structure a distance of nearly 0.5 nm between the metal core and the butadiene ligand leads to very little electron sharing. Thus the detected ions are better described as non-covalent ion–molecule complexes. In turn, the lack of orbital overlap leads to a low enthalpy giving the *cis*-butadiene complex a −13.0 kJ/mol binding energy and the *trans*-butadiene binding a −3.8 kJ/mol binding energy. These low binding energies lead to low levels of charged alkanes in the reactive ion formation process in agreement with experimental observations.

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1. Introduction

The development of novel polyolefins with increased versatility continues so rapidly that it has outpaced the creation of new analytical methods necessary to understand these deceptively complex materials [1]. At the same time mass spectrometry, particularly the matrix-assisted laser desorption/ionization (MALDI) method, has grown to be an indispensible tool for the polymer chemist [2]. However, mass spectrometry of polyolefins (as well as high-mass saturated hydrocarbon molecules typical of the petroleum industry) is not practiced routinely due to the great difficulty in putting these analytes into the gas phase as intact (unfragmented) ions. This is particularly true when the analyte molecular mass is greater than several hundred g/mol. The creation of pseudomolecular ions through the attachment of protons or alkali metal cations, for example Na^+ [3], results in complexes that are too unstable to survive at typical laser ablation plume energies. Transition metals can have substantially higher binding energies, for example Cu^+, Co^+, or Zn^{2+} [4]; however, these ions tend to insert into C—C bonds and fragment the analyte under typical mass spectrometry conditions [5–7]. Fragmentation prevents the measurement of molecular mass distribution, and leads to uncontrolled complexity that confounds the determination of molecular structure.

In light of these difficulties several new ionization methods have recently been created. Covalent cationization is a method whereby a reactive end group (in the specific cases where one is available) is chemically converted into an easily ionizable phosphonium [8–10] or sulfonate group [11]. Upon laser ablation during a matrix-assisted laser desorption/ionization (MALDI) experiment, the end group, typically a salt, is dissociated resulting in intact saturated hydrocarbon cations with masses up to 15000 u [9]. Another approach using atmospheric-pressure photoionization leading to chlorine anion attachment has been demonstrated on polyethylene waxes with masses up to 1500 u [12]. In other work, the gas phase reaction of the cobalt cyclopentadienyl cation, $CoCp^+$, has been shown to ionize saturated hydrocarbons via a gas phase dehydrogenation reaction without backbone fragmentation when the reactive $CoCp^+$ ion is prepared separately in the gas phase before hydrocarbon introduction [13–19]. In a similar way $ClMn(H_2O)^+$ introduced to hydrocarbons in the gas phase was shown to create pseudomolecular alkane ions with masses up to 600 u by the attachment of a $ClMn^+$ cation without any analyte fragmentation [20].

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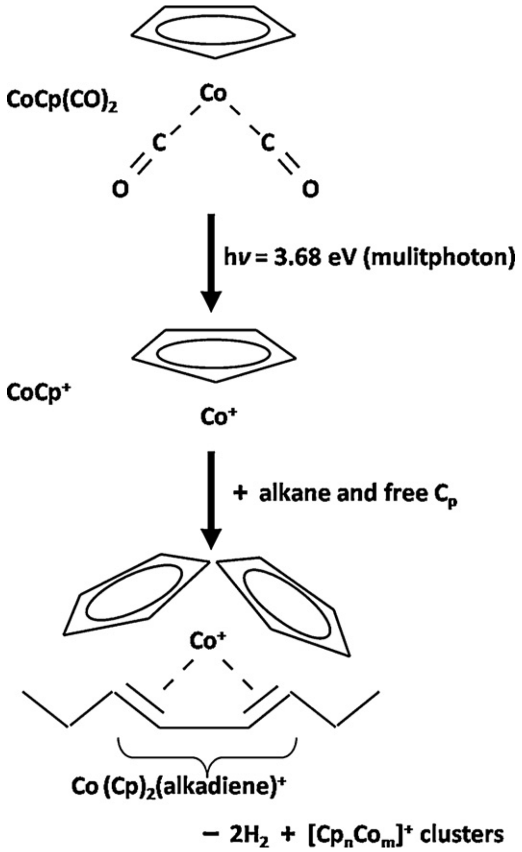

Fig. 1. Simplified schematic of the laser plume chemistry that produces the CoCp$_2$-alkadiene ion complex. For the calculated structure of the Co(Cp$_2$)(alkadiene)$^+$ complex see Fig. 2.

More recently, methods have been explored for polyolefin and high-mass saturated hydrocarbon mass spectrometry that can be employed without the use of preparative chemical reactions and on common MALDI time-of-flight mass spectrometers typically used by polymer chemists. Their interests are typically in masses well in excess of 10,000 u making MALDI time-of-flight mass mass spectrometry the method of choice. In 2007 Wallace demonstrated [21] the creation of intact alkanes and polyethylenes in the gas phase through the use of a matrix-assisted laser desoprtion/ionization matrix made by the intercalation of cobalt cyclopentadienyl dicarbonyl, CoCp(CO)$_2$, into the C$_{60}$ fullerene molecular crystal lattice. This produced ions of the form [Co(Cp)$_2$(alkane - 2H$_2$)]$^+$ where -2H$_2$ indicates the loss of two hydrogen molecules from the saturated hydrocarbon as shown schematically in Fig. 1. It is this loss of hydrogen that suggests the name "reactive" MALDI. Under ultraviolet laser ablation CoCp(CO)$_2$ loses its two loosely bound carbonyl groups and ionizes to become CoCp$^+$. In the laser ablation plume the CoCp$^+$ ion gains another cyclopentadienyl ligand and reacts with the gas phase alkane creating a locally unsaturated region through the loss of two H$_2$ molecules. (However, the order of these two steps has not been confirmed.) The two Cp ligands block insertion of the cobalt atom into the C–C bonds preventing alkane fragmentation. While this reaction was shown to produce intact polyethylene without fragmentation up to approximately 2800 g/mol the ion yield was very low. This limits its use on even moderately polydisperse polymer samples where the amount of any specific oligomer present may well be below the sensitivity of common MALDI time-of-flight mass spectrometers. Thus, a theoretical study was undertaken to understand the energetics and structure of the reactive MALDI process as a first step toward suggesting future research directions for reactive MALDI of saturated hydrocarbons.

2. Computational methods

It has been reported previously that quite modest level calculations provide binding energies for the type of complexes investigated in this paper that are in good agreement with experiment [4]. Quantum chemical calculations were performed initially using the Spartan computer code [22,23]. The BP86 density functional was used in conjunction with the DN** numerical basis set as the calculations using this code are comparatively fast. Additionally, our experience has shown they are normally not far off other density functional theory (DFT) results (using the same functional). Further calculations were performed using the Gaussian03 computer code (revision B.03) [24] running on an IBM Power6 575 computer cluster. Finally, additional calculations were performed using the Turbomole computer code (version 6.0) [25] to evaluate singlet-triplet splitting for Co-complexes, involving the B3LYP hybrid functional and the SV(P) basis set, implemented on the same IBM computer cluster.

3. Results

To explore the structure and energetics of pseudomolecular ions that are likely to be formed, and are in agreement with the observed experimental masses, quantum mechanical calculations on the stability of a series of cobalt dicyclopentadienyl complexes involving 1,3-butadiene, 2,4-hexadiene and 2,3-hexadiene adducts were performed. All complexes were initially assumed to be in the electronic singlet state. The results of energy optimizations for all structures with the 1,3-butadiene ligand in either the *cis* or the *trans* are collected in Table 1. The first column in the table gives the value in hartree, the units in which the calculations were made. Energy differences are given in SI units of kJ/mol where 1 hartree = 2625.49929 kJ/mol. Optimized geometries for the entries in Table 1 where the butadiene is in the *cis* configuration are shown in Fig. 2. Somewhat surprisingly, the most stable structure for the [Co(Cp)$_2$(1,3-butadiene)]$^+$ ion complex, both with the butadiene in *cis* conformation as well as in the *trans* conformation, is a geometry where the 1,3-butadiene is 'outside' the CoCp$_2$$^+$ complex, while the CoCp$_2$$^+$ remains almost a perfect cobaltocene sandwich-type structure: Co(η^5-Cp)$_2$-1,3-butadiene. Furthermore, these two structures are the only stable structures with respect to dissociation into the components 1,3-butadiene and CoCp$_2$$^+$, with the complex with the butadiene in the *cis* conformation (value of −13.0 kJ/mol in Table 1) being more stable than the complex with the butadiene in the *trans* conformation (−3.8 kJ/mol). Additionally the structures of several [Co(Cp)$_2$(2,4-hexadiene)]$^+$ ion complexes were optimized in order to check whether the butadiene moiety is of sufficient length to be characteristic of longer analytes used in the experiments. The results (binding energies, geometry) were only marginally different from those obtained on the corresponding butadiene complexes, viz. the corresponding data in Table 1, and thus butadiene seems sufficiently large to model our complexes of interest. Furthermore, we considered the possibility that consecutive double bonds such as in 2,3-hexadiene would form a more stable complex; however, the results are very similar to those for 1,3-butadiene and 2,4-hexadiene as shown by the relative stabilities collected in Table 1.

Thus, at this stage, it seems that only the Co(η^5-Cp)$_2$-butadiene could be associated with the MALDI observations [21]. To further substantiate this, we first need to demonstrate that it is indeed the singlet state of the Co$^+$-complex is actually the more stable compared to the triplet state. In the calculations collected in Table 1 we had assumed the singlet state to be the more stable electronic configuration. It is known that, depending on the chemical composition of the Co$^+$-complex, either the singlet or the triplet state is the minimum energy electronic state. We have therefore performed

Table 1
BP86 density functional results obtained using the DN** numerical basis and the Spartan program. The relative energy with respect to (w.r.t.) dissociation refers to dissociation into the butadiene and the $\mathrm{CoCp_2}$ complex. Recall that 1 hartree = 2625.49929 kJ/mol.

Molecular structure	Total energy (hartree)	Relative energy (kJ/mol)	Relative energy w.r.t dissociation (kJ/mol)
1,3-Butadiene complexes			
[Co(η^5-Cp)$_2$ - *cis*-1,3-butadiene]$^+$	−1926.14525	0	−13.0
[Co(η^2-Cp)(η^5-Cp)$^+$ - *cis*-1,3-butadiene]$^+$	−1926.08513	+159	+146
[Co(η^1-Cp)(η^5-Cp)$^+$ - *cis*-1,3-butadiene]$^+$	−1926.07952	+172	+159
[Co(η^1-Cp)(η^1-Cp)$^+$ - *cis*-1,3-butadiene]$^+$	−1926.08436	+159	+146
[Co(η^5-Cp)$_2$ - *trans*-1,3-butadiene]$^+$	−1926.14846	0	−3.8
[Co(η^2-Cp)(η^5-Cp)$^+$ - *trans*-1,3-butadiene]$^+$	−1926.08792	+159	+155
[Co(η^1-Cp)(η^5-Cp)$^+$ - *trans*-1,3-butadiene]$^+$	−1926.08547	+163	+163
[Co(η^1-Cp)(η^1-Cp)$^+$ - *trans*-1,3-butadiene]$^+$	−1926.09026	+151	+151
2,4-Hexadiene complexes			
[Co(η^5-Cp)$_2$ - *cis*-2,4-hexadiene]$^+$	−2004.80902	0	−16.3
[Co(η^2-Cp)(η^5-Cp)$^+$ - *cis*-2,4-hexadiene]$^+$	−2004.74848	+159	+142
[Co(η^1-Cp)(η^5-Cp)$^+$ - cis-2,4-hexadiene]$^+$	−2004.74283	+176	+159
[Co(η^1-Cp)(η^1-Cp)$^+$ - *cis*-2,4-hexadiene]$^+$	−2004.74815	+159	+142
[Co(η^1-Cp)(η^1-Cp)$^+$ - *trans*-2,4-hexadiene]$^+$	−2004.80956		−4.2
2,3-Hexadiene complexes			
[Co(η^5-Cp)$_2$ - 2,3-hexadiene]$^+$	−2004.78893	0	−3.0
[Co(η^2-Cp)(η^5-Cp)$^+$ - 2,3-hexadiene]$^+$	−2004.72995	+155	+142
[Co(η^1-Cp)(η^5-Cp)$^+$ - 2,3-hexadiene]$^+$	−2004.71108	+205	+192
[Co(η^1-Cp)(η^1-Cp)$^+$ - 2,3-hexadiene]$^+$	Did not converge		
Isolated species			
cis-1,3-Butadiene	−156.03930		
trans-1,3-Butadiene	−156.04610		
cis-2,4-Hexadiene	−234.70170		
trans-2,4-Hexadiene	−234.70701		
2,3-Hexadiene	−234.68307		
Co(η^5-Cp)$_2{}^+$	−1770.10103		

calculations using the Turbomole program, which is very well suited to study higher spin-states without having to bother about convergence in the evaluation of the electronic wavefunction. The energy difference between the singlet and the triplet states of the $\mathrm{Co^+}$ ion has been reported as 52.8 kcal/mol (220.9 kJ/mol) experimentally and 61.1 kcal/mol (255.6 kJ/mol) according to B3LYP calculations in favour of the triplet state [26]. We recalculated this value using the B3LYP method and the SV(P) basis set, yielding 201 kJ/mol. As this is very close to the experimental value, our level of calculations are sufficiently reliable to find out whether the sin-

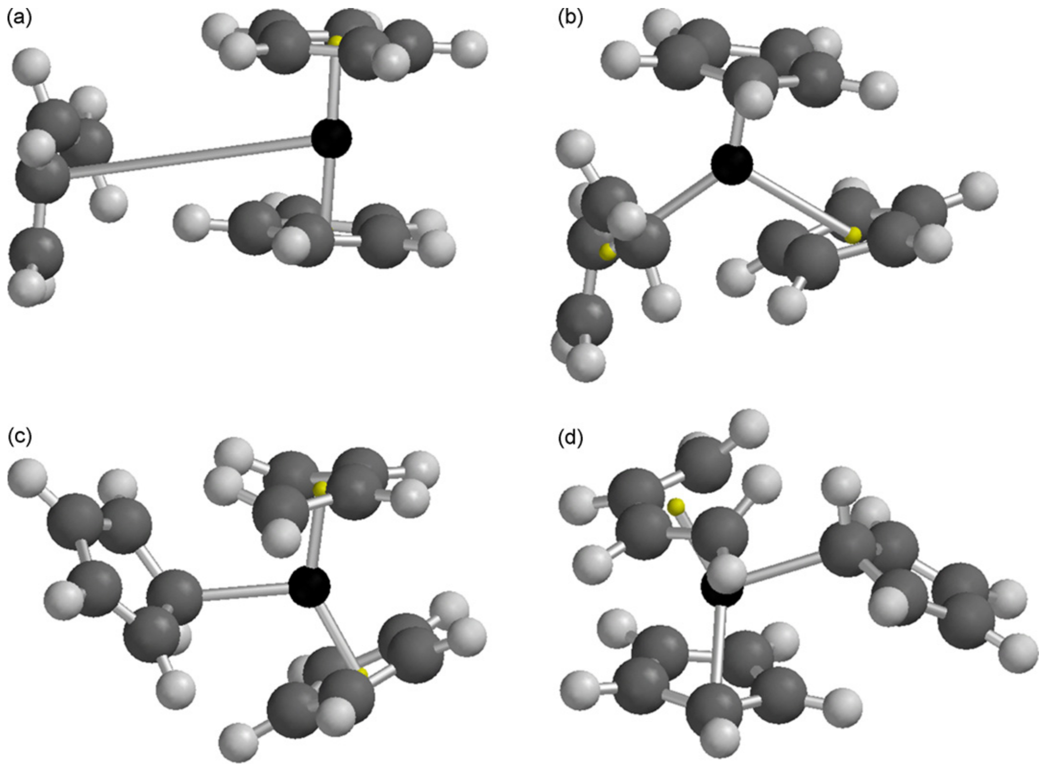

Fig. 2. (a–d) Spartan BP86/DN** calculated structures for the [$\mathrm{CoCp_2}$ -*cis*-1,3-butadiene]$^+$ complexes. Order as in first three rows of Table 1: (a) Co(η^5-Cp)$_2$ (*cis*-1,3-butadiene)$^+$, (b) Co(η^2-Cp)(η^5-Cp)(*cis*-1,3-butadiene)$^+$, (c) Co(η^1-Cp)(η^5-Cp)(*cis*-1,3-butadiene)$^+$, and (d) Co(η^1-Cp)(η^5-Cp)(*cis*-1,3-butadiene)$^+$ from a different angle. Key: black spheres (cobalt), dark gray spheres (carbon), and light gray spheres (hydrogen). Smallest spheres (yellow online) give the center of the ligand bonding.

Table 2
Calculations on selected complexes to determine the singlet–triplet energy difference using the B3LYP hybrid density functional method while using the SV(P) basis set and, for a single case, the larger TZVP basis set, using the Turbomole program. The relative energy with respect to (w.r.t.) dissociation refers to dissociation into the butadiene and the $\mathrm{CoCp_2}$ complex. (1 hartree = 2625.49929 kJ/mol).

Molecular structure	Total energy (B3LYP/SV(P)) (hartree)	Relative energy w.r.t. dissociation (kJ/mol)
[Co (η^5-Cp)$_2$ - *cis*-1,3-butadiene]$^+$		
Singlet:	−1924.60491	0
Triplet:	−1924.55925	+121
[Co (η^2-Cp)(η^5-Cp) - *trans*-1,3-butadiene]$^+$		
Singlet:	−1924.54241	0
Triplet:	−1924.54109	+3.3
[Co (η^1-Cp) (η^5-Cp) - *cis*-1,3-butadiene]$^+$		
Singlet:	−1924.52679	+205
Triplet:	−1924.53500	+184
	Total energy (B3LYP/TZVP) (hartree)	Relative energy w.r.t. disscoation (kJ/mol)
[Co (η^5-Cp)$_2$ - *cis*-1,3-butadiene]$^+$		
Singlet:	−1925.39749	0
Triplet:	−1925.35390	+113

glet or the triplet state is more stable for our $[\mathrm{Co(Cp)_2(alkadiene)}]^+$ complexes.

The next step is obviously the evaluation of triplet–singlet energy differences for selected $[\mathrm{Co(Cp)_2(alkadiene)}]^+$ complexes in order to validate that the singlet-complexes of Table 1 are the appropriate ones. In Table 2 we have collected the total energies for the singlet and triplet states of the $[\mathrm{Co(Cp)_2(1,3\text{-}butadiene)}]^+$ complexes. In addition, we have used a larger basis set (TZVP) to confirm the result for the energetically most stable complex: $[\mathrm{Co(\eta^5\text{-}Cp)_2}(\textit{cis}\text{-}1,3\text{-butadiene})]^+$. These results confirm that what we reported in Table 1 is indeed the correct: the singlet state is the more stable electronic state for these species.

The next series of calculations was performed using B3LYP and the 6-31++(d,p) basis set using Gaussian03. These calculations were performed on the various complexes previously described with the Spartan program in order to show the results collected in Table 1 are not strongly depending on the method of calculation type (e.g., BP86, B3LYP, and basis set). The results of these B3LYP calculations are comprised in Table 3. These results confirm, similar to the conclusions for the data in Table 1, that the $[\mathrm{Co(\eta^5\text{-}Cp)_2(1,3\text{-}butadiene)}]^+$ complexes, both *cis* and *trans*, are weakly stable with respect to dissociation.

Finally, we checked the trends in relative energies by evaluating total energies for $[\mathrm{Co(\eta^5\text{-}Cp)_2}$ - *cis*-1,3-butadiene$]^+$ and $[\mathrm{Co(\eta^5\text{-}Cp)_2}$ - *trans*-1,3-butadiene$]^+$ using various quantum mechanical methods and basis sets: HF, BLYP, BP86 and B3LYP, each with the 6-31G(d,p) and 6-31G++(d,p) basis set. The results have been collected in Table 4. The conclusion is, in brief, that the results presented in Table 1 are once more sustained: the *cis*- and *trans*-butadiene $\mathrm{Co(\eta^5\text{-}Cp)_2}$ complexes are stable with respect to dissociation, with a dissociation energy that is in the range of 13–21 kJ/mol.

4. Discussion

With respect to reactive MALDI of high-mass saturated hydrocarbons the most important observation is that the butadiene in the two stable configurations discovered is held very weakly to, and at a great distance from, the cobalt core. This result holds true for a variety of computational approaches, including Hartree-Fock, density functional theory, and the hybrid B3LYP method, as well as several different basis sets. In such a case electrostatic forces, specifically image forces induced in the π-electrons of the diene by the charged cobalt core, are the primary source of bonding. Thus, $[\mathrm{Co(Cp)_2(1,3\text{-}butadiene)}]^+$ can still be viewed naively as an 18-electron structure with the butadiene providing no valence electrons to the complex. Additionally, since this is a site-specific interaction, there is no chain-length effect as observed with bare metal cations interacting with alkanes [4]. Further dehydrogenation of the analyte could hypothetically lead to enhanced electrostatic interaction, however this was never observed experimentally.

When compared to earlier work where reactive CoCp^+ ion is prepared separately in the gas phase before hydrocarbon introduction [13–18], we have calculated (B3LYP with a 6-31++G(d,p) basis set) that the energy for the gas reaction of CoCp^+ with *trans*-1,3-butadiene is −239.3 kJ/mol. This suggests that the butadiene moiety is fully ligated to the cobalt core and forms a 17-electron structure. Further recall that in these experiments the ion complex does not have to survive the laser ablation process but must only survive at room temperature in the mass spectrometer. This insures abundant $[\mathrm{CoCp(alkadiene)}]^+$ ion complexes in the mass spectrum.

So how does the weak $[\mathrm{Co(Cp)_2(alkadiene)}]^+$ complex survive the MALDI process? We believe the answer is found in the details of how the MALDI experiments were conducted [21]. Specifically, in the sample preparation were the saturated hydrocarbon analyte

Table 3
B3LYP hybrid density functional theory results using the 6-31++G(d,p) basis set and the Gaussian03 program. The relative energy with respect to (w.r.t.) dissociation refers to dissociation into the butadiene and the $\mathrm{CoCp_2}$ complex. Structures for the four *cis* compounds are shown in Fig. 2. (1 hartree = 2625.49929 kJ/mol).

Molecular structure	Total energy (B3LYP/6-31++G(d,p))	Relative energy w.r.t dissociation	
	(hartree)	(hartree)	(kJ/mol)
cis-Butadiene	−156.00501		
trans-Butadiene	−156.01071		
$\mathrm{CoCp_2}^+$	−1769.56736		
[Co (η^1-Cp)(η^5-Cp) - *cis*-1,3-butadiene]$^+$	−1925.50251	0.06986	+183.3
[Co (η^1-Cp)(η^5-Cp) - *cis*-1,3-butadiene]$^+$	−1925.49860	0.07377	+193.7
[Co (η^2-Cp)(η^5-Cp) - *cis*-1,3-butadiene]$^+$	−1925.51013	0.06224	+163.6
[Co (η^5-Cp)(η^5-Cp) - *cis*-1,3-butadiene]$^+$	−1925.57771	−0.00534	−14.0
[Co (η^2-Cp)(η^5-Cp) - *trans*-1,3-butadiene]$^+$	−1925.51381	0.06427	+168.6
[Co (η^5-Cp)(η^5-Cp) - *trans*-1,3-butadiene]$^+$	−1925.58488	−0.00680	−17.9

Table 4

Total complex energies (in hartree) given in the top five rows and dissociation energies (in kJ/mol) given in the last two rows for the [Co(η^5-Cp)$_2$ - 1,3-butadiene]$^+$ complexes for various computational approaches. (1 hartree = 2625.49929 kJ/mol).

Molecular structure	HF		BLYP	
	6-31G(d,p)	6-31++G(d,p)	6-31G(d,p)	6-31++G(d,p)
cis-1,3-butadiene	−154.92553	−154.93228	−155.90766	−155.91841
trans-1,3-butadiene	−154.930323	−154.93720	−155.91364	−155.92447
CoCp$_2$$^+$	−1765.394523	−1765.41228	−1769.428567	−1769.45327
[Co(η^5-Cp)$_2$ - *cis*-1,3-butadiene]$^+$	−1920.32721	−1920.34965	−1925.344401	−1925.37771
[Co(η^5-Cp)$_2$ - *trans*-1,3-butadiene]$^+$	−1920.33237	−1920.35487	−1925.35050	−1925.38397
[Co(η^5-Cp)$_2$ - *cis* -1,3-butadiene]$^+$ – [(CoCp$_2$$^+$ +*cis*-1,3-butadiene]	−18.8	−13.4	−21.3	−15.9
[Co(η^5-Cp)$_2$ - *trans*-1,3-butadiene]$^+$ – [(CoCp$_2$$^+$ +*trans*-1,3-butadiene]	−19.7	−14.2	−21.8	−16.3
	BP86		B3LYP	
	6-31G(d,p)	6-31++G(d,p)	6-31G(d,p)	6-31++G(d,p)
cis-1,3-butadiene	−155.98422	−155.99216	−155.99605	−156.00501
trans-1,3-butadiene	−155.99010	−155.99807	−156.00166	−156.01070
CoCp$_2$$^+$	−1769.76834	−1769.79206	−1769.54540	−1769.56734
[Co(η^5-Cp)$_2$ - *cis*-1,3-butadiene]$^+$	−1925.76055	−1925.79091	−1925.54997	−1925.57888
[Co(η^5-Cp)$_2$ - *trans*-1,3-butadiene]$^+$	−1925.76660	−1925.79714	−1925.55582	−1925.58488
[Co(η^5-Cp)$_2$ - *cis*-1,3-butadiene]$^+$ –[(CoCp$_2$$^+$ +*cis*-1,3-butadiene]	−20.9	−17.6	−22.2	−17.2
[Co(η^5-Cp)$_2$ - *trans*-1,3-butadiene]$^+$ – [(CoCp$_2$$^+$ +*trans*-1,3-butadiene]	−21.3	−18.4	−22.2	−18.0

is deposited on top of the CoCp(CO)$_2$/fullerene bimolecular matrix with the reliance of mixing in the laser ablation plume. This preparation was required because the matrix cannot be deposited from solution without disturbing its unique bimolecular crystal structure. Thus, the typical hand spotting of a matrix + analyte solution was not feasible. Ions formed on the leading edge of the ablation plume where the analyte resides will not be at thermodynamic equilibrium. Adding to this is the fact that the MALDI target was heated to 125 °C to melt the alkane or polyethylene samples. Heating allowed a lower laser threshold to be used since the laser energy is not required to overcome the heat of crystallization of the analyte [10]. Heating of the MALDI sample has been shown to produce non-equilibrium ions during the laser ablation event [27]. Thus, rapid plume expansion and layering method in MALDI allows *non-equilibrium* ions to form. These ions can then have energies below the previously suggested 90 kcal/mol (377 kJ/mol) limit necessary for MALDI [3,4].

At this time the exact plume chemistry is not known. Intercalation of Co(Cp)$_2$ (cobaltocene) rather than CoCp(CO)$_2$ into the C$_{60}$ matrix does not produce [Co(Cp)$_2$(alkadiene)]$^+$ ions or [Co(Cp)$_2$C$_{60}$]$^+$ ions but does produce Co$_n$Cp$_m$$^+$ cluster ions in abundance. This suggests that there is a requirement to have CoCp$^+$ ions in the gas phase at some point in the laser ablation process. It is likely that these ions are required to dehydrogenate the alkane. However, the great stability of the Co(Cp)$_2$$^+$ ion ($\mathrm{CoCp^+ + Cp \rightarrow Co(Cp)_2{}^+}$, −469 kJ/mol) means that much of the free CoCp$^+$ is used up in the formation of Co(Cp)$_2$$^+$ and related Co$_n$Cp$_m$$^+$ cluster ions. This would imply the release of cobalt into the plume either as Co^0 or as Co$^+$, however, Co$^+$ was never observed in the mass spectra. This suggests that it was rapidly neutralized by free electrons in the ablation plume. In contrast, when the bimolecular CoCp(CO)$_2$/C$_{60}$ was used with *polystyrene* analytes [Co(polystyrene)]$^+$ ions were produced indicating the likely presence of free Co$^+$ in the plume. Curiously, no [Co(Cp)$_n$(polystyrene)]$^+$ ions were observed. It was our hypothesis that the CoCp$^+$ half-sandwich would combine with a six-membered phenyl ring on the polystyrene to form a stable pseudomolecular ion due to the great stability of the [CoCp(benzene)]$^+$ complex previously reported [28]. This hypothesis was not borne out experimentally.

Finally, the role of Co$_n$Cp$_m$$^+$ cluster ions in the laser ablation plume is also unknown. Little has been published on their gas phase reactivity. Müller and Fenderl have shown through 50 eV electron-impact ionization of pure CoCp(CO)$_2$ at high gas densities that many dinuclear cluster ions form with a variety of CO and hydrocarbon ligands [29]. This includes [Co$_2$Cp(C$_3$H$_3$)]$^+$, a dicobalt cyclopentadienyl core attached to an unsaturated hydrocarbon. The assumption was that the C$_3$H$_3$ moiety comes from the fragmentation of the cyclopentadienyl ring under electron bombardment. More recently it has been shown that partially ligated ruthenium carbonyl anion clusters react with pentane to produce ion complexes with high levels of pentane dehydrogenation and no C—C bond cleavage [30]. This points to the possible future use of organometallic cluster ions as cationizing agents for high-mass saturated hydrocarbons in reactive MALDI.

5. Conclusions

The binding energies for several equilibrated configurations of the [Co(Cp)$_2$(1,3-butadiene)]$^+$ ion were calculated where the Cp rings were individually given different hapticities (η^5, η^3, η^2, η^1). The configuration with η^5,η^5 was the only stable configuration found. Singlet and triplet states were calculated with the singlet state found as the most stable. *Cis* and *trans* configurations showed preference for η^5,η^5 with the *cis* configuration being slightly more stable. The low binding energies of the stable structures suggest that Co(Cp)$_2$(1,3-butadiene)]$^+$ is best described as an ion–molecule complex with the butadiene loosely associated with the cobaltocenium core.

The calculations reported here qualitatively describe what was observed experimentally in regard to reactive MALDI of saturated hydrocarbons. Specifically, the low abundance of ionized analytes can be attributed to the low binding energy of the organometallic–alkadiene complex and to the specific layering of the MALDI sample during preparation. Looking forward, DFT calculations may be used in the future to predict more stable adducts if they exist. This would expedite the development of reactive MALDI by preventing the exploration of thermodynamically infeasible organometallic cations.

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