Conformation of a MnCp(CO)_2 -thienothiophene carbene complex: A spectroscopic and computational study

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The carbene complex $[\text{MnCp(CO)}_2\text{C(OEt)(TT)}]$, (TT = 3,6-dimethylthieno[3,2-*b*]thiophene) **1**, was synthesized according to the classical Fischer method. The novel complex was fully characterized using various spectroscopic techniques. The infrared spectrum of the complex, recorded as a solution in dichloromethane, revealed a four-band spectrum in the carbonyl region instead of the expected two-band spectrum. A density functional theory (DFT) study was undertaken to explain the presence of more than one conformer in solution. The crystal structure of **1** is reported.

Keywords: Manganese, carbene complex, thienothiophene, DFT, spectroscopy

Introduction

The current interest in thiophenes as molecules with potential electro-optical properties for use as molecular devices¹ was recently extended to include thieno[3,2-*b*]thiophenes.² Research in this area has, unfortunately been limited by the lack of convenient synthetic methods until Choi and co-workers³ reported a one-pot synthesis of 3,6-dimethylthieno[3,2-*b*]thiophene, which promoted investigation of the properties of these molecules in coordination chemistry. Even though the traditional Fischer carbene complexes contained group VI transition metals (W and Cr),⁴ complexes containing group VII transition metals (Mn and Re) have grown in numbers in the literature.⁵ In particular, complexes of the type $\text{Cp(CO)}_2\text{MnC(X)R}$ are common and have been investigated extensively.⁶ From X-ray structures determined as part of these investigations, it had been concluded⁷ that: (i) the electronic nature of the groups bonded to the carbene carbon atom influences the bond order of the formal metal-carbon double bond, which may vary from close to 1 to greater than 2; (ii) there is competition for π -bonding between the three moieties bonded to the carbene carbon atom and thus

bond length variations depend on the π -donating ability of each of these moieties; and (iii) the steric bulk of the moieties around the carbene carbon atom has an effect on the bond angles. From these conclusions it is expected that different conformations of these complexes are therefore possible.

In alkoxycarbene complexes it was spectroscopically observed that the different positions of the alkoxy substituent itself, relative to the other substituents of the carbene carbon atom, can lead to *syn-anti* isomerism⁸ (Scheme 1). In a density functional theory (DFT) study of Cr- and W-containing alkoxycarbene complexes a clear preference for the *anti* isomer was found.⁹ Experimentally, the crystal structures observed for a large number of these complexes revealed that the great majority favored the *anti* configuration.¹⁰ However, the two isomers could be distinguished spectroscopically from each other only by NMR spectroscopy. The infrared spectra of the two isomers were identical. Beck *et al.*⁸ suggested that the orientation of the R-group of the OR-carbene carbon substituent has little effect on the metal-carbon bond and thus results in identical IR spectra for both isomers. It is concluded that considering the OR carbene ligand only is not sufficient but that the orientations of both carbene ligands OR and R' mutually and relative to the metal moiety need to be evaluated.

Scheme 1: *Syn-anti* isomerism in $\text{M}(\text{CO})_5$ carbene complexes

By changing the metal ligand system from $\text{M}(\text{CO})_5$ to $\text{ML}(\text{CO})_2$ ($\text{L} = \text{Cp}$, MeCp , $\pi\text{-C}_6\text{H}_6$, $\pi\text{-MeC}_6\text{H}_5$), a second type of isomerisation was observed.⁸ The NMR data for these complexes denote the presence of only one conformer, while in the IR spectra two different sets of bands, indicating two different species, were present. The relative intensities of these bands were solvent independent. This is in stark contrast to *syn-anti* isomerisation where, experimentally, the solvent has a strong effect on the isomer ratio.¹¹ Beck *et al.*⁸ ascribed the presence of these species to steric reasons. Although this type of isomerisation has been reported for both Cr- and Mn-containing complexes, we limited this study to Mn-containing complexes with the

general formula $[(\text{CO})_2\text{LMnC}(\text{OR})\text{R}']$, with $\text{R}' = \text{arene}$ and $\text{L} = \text{Cp}$, MeCp , $\pi\text{-C}_6\text{H}_6$, $\pi\text{-MeC}_6\text{H}_5$.

Possible conformations of these carbene complex species are shown in Figure 1.

Figure 1: Possible conformations of a $(\text{CO})_2\text{LMnC}(\text{OR})(\text{aryl})$ complex

From MO calculation studies¹² it was found that the energies of the conformations **I**, **II** and **III** differ due to a barrier of rotation of the carbene ligand around the metal- $\text{C}_{\text{carbene}}$ bond. MO calculations favor conformations **I** and **II**, where the carbene plane coincides with the pseudo-mirror plane of the $[\text{MnC}(\text{CO})_2]$ moiety. It is suggested that the major factor determining the orientation is the interaction of the carbene empty p orbital with the a' (horizontal) metal fragment orbital, which has a better overlap than with the a'' (vertical) metal fragment orbital. Experimental data¹³ confirm the theoretical predictions, with all known structures of $[\text{MeCp- or CpMn}(\text{CO})_2(\text{carbene})]$ complexes exhibiting conformations **I** or **II**. Only two structures, both containing bulky carbene substituents, could be found for conformation **III**, where the carbene plane lies perpendicular to the pseudo-mirror plane of the $[\text{MnC}(\text{CO})_2]$ moiety.

In a recent article by Valyaev *et al.*¹⁴, three different conformations were identified for a series of complexes $[\text{Cp}(\text{CO})_2\text{Mn}=\text{C}(\text{Ph})\text{OC}_6\text{H}_2\text{X}_3-2,4,6]$ with $\text{X}=\text{F}$, Cl , Br , I , H , Me . On the solution IR spectrum, three different pairs of bands were observed in the carbonyl region. It was demonstrated that two of the conformations

exhibited weak interactions between the O-aryl ring and the CO ligands, affecting the carbonyl stretching frequencies.

Results and discussion

Complex **1** was isolated as a byproduct in the biscarbene formation reaction, based on the typical Fischer method for synthesis of carbene complexes.¹⁵ The biscarbene complex was obtained almost exclusively in the reaction; no ester decomposition product¹⁶ was formed and the monocarbene complex **1** could only be isolated in a low yield for the reaction with $[\text{MnCp}(\text{CO})_3]$. The red-brown monocarbene complex **1** was crystallized from 1:1 hexane:dichloromethane (DCM) solution and its structure was determined by single-crystal X-ray diffraction. The structure has the conformation type **IIIb**, the least likely conformation according to experimental and theoretical predictions.^{5,12} This is ascribed to the bulkiness of the 3,6-dimethylthieno[3,2-*b*]thienyl substituent. The presence of the methyl group on the 3-position of the substituent implies that the existence of the *syn*-isomer is highly improbable in this case.

In the infrared spectra of the compound using dichloromethane as the solvent (Figure 2), the carbonyl stretching frequencies are observed as four strong bands, instead of the usual two bands expected for these complexes. Literature reports disclose the same occurrence on the IR spectra of $[\text{MnCp}(\text{CO})_2\{\text{C}(\text{OMe})\text{Ph}\}]$,¹⁷ $[\text{MnCp}(\text{CO})_2\{\text{C}(\text{OEt})\text{Ph}\}]$,¹⁸ $[\text{Cr}(\text{CO})_2(\pi\text{-Ar})\{\text{C}(\text{OMe})\text{Ph}\}]$ ⁸ and $[\text{MnCp}(\text{CO})_2\{\eta^2\text{-C}_2\text{H}_4\}]$.¹⁹

Figure 2: Carbonyl region on IR spectrum of **1**

The solid state IR spectrum of **1** contains only the expected two bands²⁰ (at 1908 and 1838 cm⁻¹). It is thus concluded that more than one conformer dominates in solution and therefore contributes to the IR spectrum. In an attempt to identify these two possible conformers, a DFT study of complex **1** was undertaken.

X-ray crystallography

Complex **1** crystallized as red-brown needles from a 1:1 hexane:dichloromethane solution. The molecular structure of **1** is shown in Figure 3 and the selected bond lengths and angles in Table 1.

Figure 3: Structure of **1** showing the atom numbering scheme

Table 1: Selected bond lengths and angles for **1**

<i>Bond lengths (Å)</i>		<i>Bond angles (°)</i>	
Mn-C(1)	1.944(6)	Mn-C(1)-O(1)	127.8(4)
Mn-C(12)	1.779(7)	Mn-C(1)-C(2)	126.0(4)
Mn-C(13)	1.786(7)	O(1)-C(1)-C(2)	106.2(5)
C(12)-O(2)	1.170(8)		

C(13)-O(3)	1.162(8)	<i>Torsion angles (°)</i>	
C(1)-O(1)	1.344(7)	Mn-C(1)-C(2)-S(1)	-8.3(7)
C(1)-C(2)	1.460(8)	Mn-C(1)-C(2)-C(3)	173.8(5)
O(1)-C(10)	1.454(8)	C(1)-C(2)-C(3)-C(4)	179.7(6)
S(1)-C(2)	1.765(6)	S(1)-C(5)-C(4)-S(2)	-178.1(3)
S(1)-C(5)	1.721(6)	C(3)-C(4)-C(5)-C(6)	178.1(5)
C(2)-C(3)	1.410(8)	C(12)-Mn-C(1)-C(2)	-42.0(6)
C(3)-C(4)	1.430(9)	C(13)-Mn-C(1)-C(2)	-130.7(6)

Molecular modeling

The calculations reported in this paper were obtained using the GAUSSIAN 03²¹ suite of programs and were restricted to the monocarbene complex, **1**. Two aspects had to be considered: firstly, the lowest energy conformation of the carbene plane vs. the pseudo-mirror plane of the [MnCp(CO)₂] moiety had to be found (scan I), and secondly, this minimum conformation had to be employed in evaluating the orientations of the OR and R' carbene ligands mutually and relative to the [MnCp(CO)₂] moiety (scan II). From these results the conformers responsible for the observed IR spectrum had to be identified.

Scan I:

To determine the theoretical minimum energy conformation for the complex between the two extreme options, namely a carbene plane coinciding with the metal fragment pseudo-mirror plane (conformations **I** and **II**) or a carbene plane perpendicular to the metal fragment pseudo-mirror plane (conformation **III**), the dihedral angle C(12)-Mn-C(1)-C(2) was scanned over 360° in 5° increments (Scheme 2). The set of coordinates obtained from the crystal structure was used as input.

Scheme 2: Dihedral angle C(12)-Mn-C(1)-C(2) used in scan I

Chart 1: Relative energy profile for scan I of dihedral angle C(12)-Mn-C(1)-C(2)

Two minimum energy conformations, with identical energy values, could be identified (Figure 4), namely conformer **1i** and conformer **1ii**, for which the chosen dihedral angle C(12)-Mn-C(1)-C(2) corresponded to 141° and 311°, respectively. These dihedral angles correlate with conformation **III**, particularly conformation **IIIb**, in Figure 1 and are thus similar to the crystal structure of complex **1** where the corresponding dihedral angle is 318°. Indeed, conformer **1ii** is almost identical to the crystal structure (RMS = 0.0315), whereas conformer **1i** represents its mirror image.

Figure 4: Lowest energy conformers for scan I as seen from Chart 1

Conformer **1iii**, with a dihedral angle of 236°, represents the conformation where the carbene plane coincides with the pseudo-mirror plane of the metal fragment (conformation **II**, Figure 1) but the arene ring has an

intermediate conformation between **IIa** and **IIb** and is rotated 26° out of the carbene plane. This conformation is highest in energy with a value of 26.87 kJ/mol. Conformer **1iv** (15.56 kJ/mol) represents conformation **I** in Figure 1 and since the arene ring is rotated only 13° out of the carbene plane, it represents conformation **Ia** in particular (Figure 5). Energy values are given relative to conformer **1ii**.

Figure 5: Structure of highest energy conformer of scan I, conformer **1iii**, and conformer **1iv**, representing conformation **Ia** of Figure 1

It is concluded that the theoretically predicted lowest energy conformation correlates with the crystal structure of complex **1**, i.e. conformation **III** and in particular **IIIb**. However, from this scan the phenomenon of the four bands in the infrared spectrum of **1** can still not be explained. Conformers **1i** and **1ii** have identical vibrational spectra since they are mirror images of each other.

Scan II:

An energy profile for complex **1** was obtained by turning two sets of dihedral angles through 360° in increments of 10° each. The sets of dihedral angles C(3)-C(2)-C(1)-O(1) and C(1)-O(1)-C(10)-C(11) were each set to a starting value of 1° and were scanned simultaneously (Scheme 3). Four definite areas, each containing a local energy minimum, were identified (Charts 2 and 3). These conformations were found to be conformers **1v**, **1vi**, **1vii** and **1viii**.

Scheme 3: Dihedral angles C(3)-C(2)-C(1)-O(1) and C(1)-O(1)-C(10)-C(11) used in scan II

Chart 2: Relative energy profile for scan II of dihedral angles C(3)-C(2)-C(1)-O(1) and C(1)-O(1)-C(10)-C(11)

Chart 3: Contour relative energy plot for scan II of dihedral angles C(3)-C(2)-C(1)-O(1) (ϕ_1) and C(1)-O(1)-C(10)-C(11) (ϕ_2)

The conformers **1v**, **1vi**, **1vii** and **1viii** were each optimized without any constraints in both vacuum and solvated media. Their respective vibration frequency spectra were calculated. No imaginary frequencies were observed. These optimized structures are shown in Figure 6. Conformers **1v** and **1vi** were found to be structurally identical with an RMS value of 0.0008, whereas conformers **1vii** (15.82 kJ/mol) and **1viii** (15.83 kJ/mol) were mirror images of each other. The energy values are reported relative to **1v**. Conformers **1v** and **1vi** resemble the crystal structure of complex **1** (RMS values of 0.0475 and 0.0476 respectively), whereas conformers **1vii** and **1viii** represent a conformation where the methyl substituent is “locked” symmetrically between the two carbonyl ligands. The distances between the hydrogen atom on this methyl group and the two carbon atoms of the two carbonyl ligands are 2.756 Å and 2.826 Å. This may be the reason why this conformation is also observed in the solution IR spectrum. However, a study of the second-order perturbation theory (SOPT) of the NBO method revealed no formal bonding interactions between these atoms.¹⁴

Figure 6: Minimum energy conformers for scan II as seen from Chart 2

Frequency calculations on the four conformers divided them into two sets: conformers **1v** and **1vi** gave identical frequency data, whereas conformers **1vii** and **1viii** also gave frequency data that were identical to each other, but which differed from the frequency data for conformers **1v** and **1vi**. Both the experimental and calculated carbonyl frequency data are summarized in Table 2. Theoretical vibrational data usually need to be scaled for numerical compatibility to the experimental data (Figure 7). The scaling factor was calculated as described in literature²² and found to be 1.040 in this case, similar to literature reports for this functional and basis set combination²³.

Figure 7: Comparison of experimental (solid line) and theoretical (dashed lines) absorption bands

Table 2: Calculated and experimental spectroscopic data of the four minimum energy conformers

Conformer	Experimental (DCM solution) [ν_{CO} , cm^{-1}]	Calculated (DCM solution) [ν_{CO} , cm^{-1}]
Conformer 1v	1933, 1871 <1902> ^a	1943, 1869 <1906>
Conformer 1vi	1933, 1871 <1902>	1943, 1869 <1906>
Conformer 1vii	1961, 1893 <1927>	1957, 1889 <1923>
Conformer 1viii	1961, 1893 <1927>	1957, 1889 <1923>

[a] Averaged frequencies of the two ν_{CO} bands

The geometric data for the four minimum conformations are summarized in Table 3.

Table 3: Summary of geometric data^a

Property	Crystal structure	Conformer 1v	Conformer 1vi	Conformer 1vii	Conformer 1viii
<i>Bond distance (Å)</i>					
Mn-C(carbene)	1.944	1.936 (1.948)	1.936 (1.948)	1.909 (1.912)	1.909 (1.913)
Mn-C(CO) av.	1.783	1.773 (1.763)	1.773 (1.763)	1.776 (1.769)	1.776 (1.769)
Mn-C(Cp) av.	2.160	2.246 (2.243)	2.246 (2.243)	2.251 (2.247)	2.251 (2.247)
<i>Bond angle (°)</i>					
Mn-C(carbene)-C(arene)	126.0	126.5 (126.5)	126.5 (126.4)	127.1 (126.4)	127.1 (126.3)
Mn-C(carbene)-OEt	127.8	126.8 (126.5)	126.8 (126.5)	126.2 (126.8)	126.2 (126.9)
OEt-C(carbene)-C(arene)	106.2	106.7 (106.9)	106.7 (107.0)	105.9 (106.1)	105.8 (106.1)
<i>Dihedral angle (°)</i>					
Carbene plane/arene plane	8.8	8.5 (8.9)	8.6 (8.9)	54.7 (56.4)	54.5 (56.5)
Carbene plane/Cp plane	31.1	31.6 (31.2)	31.6 (31.1)	40.9 (41.4)	41.1 (41.6)
Arene plane/Cp plane	38.0	39.4 (38.2)	39.5 (38.1)	52.1 (53.4)	52.2 (53.4)
Carbene plane/Pseudo-mirror plane of Mn	86.3	85.0 (85.7)	85.1 (86.0)	56.2 (55.9)	55.8 (55.7)
Arene plane/Pseudo-mirror plane of Mn	88.4	78.0 (79.0)	78.0 (79.2)	52.9 (52.9)	52.7 (53.1)
<i>Conformation</i> (according to Figure 1)	IIIb	IIIb	IIIb	Hybrid between I and III and a and b	Hybrid between I and III and a and b

^aThe values in brackets refer to the dichloromethane (DCM) solvated geometric data

Two different sets of conformers, each set with its unique infrared vibrations, were identified from DFT calculations (Figure 6). One of these conformer sets was identified as being effectively isostructural to the solid state crystal structure (conformation **IIIb**, Figure 1). The other set, a conformer and its mirror image, represents an intermediate conformation between **I** and **III**, and **a** and **b** (Figure 1), where the arene plane is twisted *ca.* 56° from the carbene plane and twisted *ca.* 53° from the pseudo-mirror plane of the metal moiety. On the structures of this second set of conformers, the structures exhibit a hydrogen atom on the C9 atom that is equidistant from the two oxygen atoms of the carbonyl ligands, 3.108 Å from the O2 atom and 3.096 Å from the O3 atom. This interaction may result in restricting rotation of the heteroaromatic substituent of the carbene, locking it between the two carbonyl ligands (Figure 8). This results in the observation of this conformer on the IR spectrum.

Figure 8: Space fill model of conformer **1vii**

The combined theoretical solvent infrared spectra of these conformations result in a pattern similar to the experimental four-band spectrum (Figure 7). The lower of the two sets of bands is assigned to the **IIIb** conformation and the higher set to the hybrid conformation. The two conformation sets are both present in significant amounts in solution.

Conclusion

Using DFT calculations, it was possible to identify two different sets of conformers for **1**. The theoretical infrared spectra of these two conformers show good agreement with the experimental spectrum of **1**. Steric

reasons have been proposed as a possible explanation for the observation of two different conformers in solution.

Experimental

General

Infrared spectra were recorded in dichloromethane (DCM) on a BOMEM Michelson – 100 FT spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Brüker AC-300 spectrometer, using deuterated chloroform. Fast atom bombardment (FAB) mass spectra were recorded on a VG 70 SEQ instrument. All the solvents were dried under an inert atmosphere of nitrogen gas, following conventional laboratory methods, prior to use. Chromatographic separations and purification were performed using nitrogen gas-saturated Kieselgel (0.063–0.200 mm). All compounds were synthesized and characterized under an inert atmosphere of argon or nitrogen gas, using standard Schlenk tube methods.²⁴ The following compounds were prepared according to known literature methods: triethyloxonium tetrafluoroborate²⁵ and 3,6-dimethylthieno[3,2-*b*]thiophene.²⁶

X-ray crystallography

The intensity data for **1** were collected at –90 °C on a Nonius Kappa CCD diffractometer using graphite-crystal monochromated Mo-K α radiation. Data were corrected for Lorentz and polarization effects but not for absorption.²⁷ The structures were solved by Direct Methods (SHELXS)²⁸ and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97).²⁹ In the structure refinements, all hydrogen atoms were included in calculated positions and treated as riding on the atom to which they are attached, with isotropic displacement parameters calculated as $X \times U_{eq}$ of the atom to which they are attached; $X = 1.5$ for the methyl hydrogens and 1.2 for all other hydrogens. All non-hydrogen atoms were refined with anisotropic displacement parameters. Ortep-3 for Windows³⁰ and POV-Ray for Windows³¹ were used for the structure representation. Table 4 lists the crystallographic data for complex **1**.

Table 4: Crystallographic data for complex **1**

	1
Chemical formula	C ₁₈ H ₁₇ MnO ₃ S ₂
MW (g mol ⁻¹)	400.38
Crystal system	Triclinic
Space group	P1
<i>a</i> (Å)	7.1469(8) Å
<i>b</i> (Å)	9.467(1) Å
<i>c</i> (Å)	13.241(2) Å
α (°)	75.563(7)°
β (°)	88.732(8)°
γ (°)	86.297(9)°
Volume (Å ³)	865.76(19)
<i>Z</i>	2
<i>d</i> _{calcd} (Mg m ⁻³)	1.536
μ (mm ⁻¹)	1.016
Crystal size (mm ³)	0.22 x 0.20 x 0.12
θ range (°)	3.18 to 27.57
Index range	-9 $\leq$ h $\leq$ 9, -12 $\leq$ k $\leq$ 12, -15 $\leq$ l $\leq$ 17
Number of reflections collected	6064
Number of independent reflections	3824 [<i>R</i> (int) = 0.0698]
Absorption corrections <i>T</i> _{max} , <i>T</i> _{min}	0.8878, 0.8073
Parameters	217
<i>R</i> ₁ , <i>wR</i> ₂ (<i>F</i> _o ² > 2σ <i>F</i> _o ²)	0.1003, 0.2024
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1555, 0.2272

Molecular modeling

The calculations reported in this paper were obtained using the GAUSSIAN 03²¹ suite of programs. Scans I and II were done using Hartree-Fock spin-restricted calculations with the effective core potentials basis set LANL2DZ. Each of the minimum energy conformations was optimized using spin-restricted DFT

wavefunctions (RB3LYP),^{32,33} a functional often used in transition metal calculation³⁴, with the effective core potentials basis set LANL2DZ³⁵. DFT-optimized calculations were carried out in the singlet spin state with $S = 1/2$ and the optimized structures were confirmed to be local minima by performing harmonic vibration frequency analyses (no imaginary frequency found). No symmetry constraints were applied and only the default convergence criteria were used during the geometric optimizations. Frequency calculations of the optimized structures were calculated using the IEF-PCM solvent model.

Synthesis of carbene complex 1

0.67 g (4.0 mmole) of TT was dissolved in 50 ml of hexane. 1.2 ml (8.0 mmole) of TMEDA and 5.5 ml (8.8 mmole) of n-butyl lithium were added at room temperature. The mixture was refluxed for 45 minutes and then cooled to 0°C. After the addition of 50 ml of THF, 1.63 g (8.0 mmole) of $\text{Mn}(\text{C}_5\text{H}_5)(\text{CO})_3$ was added and the suspension stirred for one hour. The color of the reaction changed to dark brown. After completion of the reaction, the solvent was removed *in vacuo*. 1.50 g (8.1 mmole) of triethyl oxonium tetrafluoroborate was dissolved in 20 ml of dichloromethane and this was added to the cooled reaction residue (-20°C). An immediate color change to a purple-brown solution was observed. Stirring was maintained for a further hour while the mixture was allowed to reach room temperature. The mixture was then filtered, the solvent removed and the components of the residue were separated on a silica gel column. Two products were isolated: the first was a reddish-brown monocarbene complex (**1**) (yield: 0.43 g; 27%) and the second was a purple-brown biscarbene complex¹⁵ (yield: 1.49 g; 59%).

1: ^1H NMR(δ (ppm), J(Hz)): H7 6.94 (s), 4.3; OCH_2CH_3 4.67 (q), 6.9; Cp 4.67 (s); Me3 2.34 (s); Me6 2.27 (s); OCH_2CH_3 1.52 (t), 6.9. ^{13}C NMR (δ_{ppm}): C(carbene) 321.2; C2 155.3; C5 141.5; C4 141.0; C3 130.3; C7 123.1; C6 122.0; OCH_2CH_3 72.3; OCH_2CH_3 15.4; Me3 15.2; Me6 14.7; $\text{Mn}(\text{CO})_2$ 231.3. IR (cm^{-1}): 1961 (s), 1933 (s), 1893 (s), 1871 (s). MS (m/z): M^+ 400.0.; $\text{M}^+ - \text{CO}$ 371.0; $\text{M}^+ - 2\text{CO}$ 344.0; $\text{M}^+ - 2\text{CO} - \text{CH}_2\text{CH}_3$ 315.0; $\text{M}^+ - 3\text{CO} - \text{CH}_2\text{CH}_3$ 286.9; $\text{M}^+ - 3\text{CO} - \text{CH}_2\text{CH}_3 - \text{Cp}$ 221.9.

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Supporting Information Available: Computational detail containing input files and a CIF file with crystallographic information. This material is available.

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