ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 590 (1999) 253–257

Journal of Organo metallic Chemistry

Conformational analysis of dicarbonyl(methylcyclopentadienyl)(2-(diethylamino)-2-oxoethyl) iron(II): a spectroscopic and molecular mechanics study

Douglas C. MacLaren, Stephen C. Mackie *

Department of Chemistry, University of Prince Edward Island, 550 University Avenue, Charlottetown, Prince Edward Island, Canada C1A 4P3

Received 4 June 1999; accepted 2 August 1999

Abstract

A combination of NMR and IR spectroscopic techniques was used to examine the conformational preferences of the previously unreported oxaallyliron compound dicarbonyl(methylcyclopentadienyl)(2-(diethylamino)-2-oxoethyl)iron(II) (**1**). IR studies revealed that **1** existed in *n*-pentane solutions as an equilibrium between two or more exchanging conformers through a rotation about the Fe–C_α bond. An additional contribution to the conformational dynamics of **1** was identified due to the resonance component of the amide group. The resonance contribution manifested in the observed restricted rotation about the C–N amide bond. Molecular mechanics calculations were used to model the conformational processes. The calculations predicted that the resonance stabilized conformation was the energetically preferred structure of **1**. This agrees with the experimental evidence that identified the influence of resonance on the conformation of **1**. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: NMR; IR; Dicarbonyl(methylcyclopentadienyl)(2-(diethylamino)-2-oxoethyl)iron(II); Oxaallyliron; Resonance stabilization; Molecular mechanics; Conformational dynamics

1. Introduction

Transition metal π-systems of various unsaturated organic ligands have been used to impart stereochemical control in the synthesis of substituted cyclic and acyclic hydrocarbons. In particular, the use of allylmetal systems in cycloaddition reactions with electrophilic π-systems has received a considerable amount of attention [1]. Such reactions provide alternative routes to substituted five-membered carboxcyclic and heterocyclic compounds. Many of these ring systems are useful synthetic building blocks for larger polycyclic compounds [2]. Our investigations are focused on analogous heteroallylmetal systems, namely oxaallyliron compounds, to determine if they exhibit similar reactivity towards the electron-deficient π-systems: specifically to determine how the reactivity and structure of the target compounds have been perturbed by replacing the allyl with the isoelectric and isostructural oxaallyl ligand (Fig. 1).

We have synthesized a series of piano-stool oxaallyliron systems of the general formula Fp‡–CH_2R, where Fp‡ = (η^5-C_5H_4R')$Fe(CO)_2$, R′ = H or CH_3, and R = $C(O)CH_3$, $C(O)N(C_2H_5)_2$, $C(O)C_6H_5$, C(O)-(OCH_3)(CH_3) (Ref. [3] and unpublished results). The IR spectra of *n*-pentane solutions of each of these compounds reveal two pairs of terminal carbonyl stretching (ν_{CO}) bands (Ref. [3] and unpublished results). This indicated that rotational isomerism is active in all of the oxaallyliron target compounds [4]. The

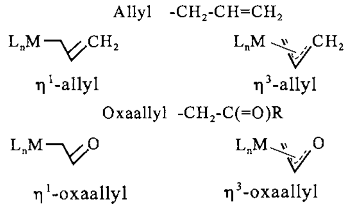


Fig. 1. The η^1- and η^3-coordination modes of the allyl and oxaallyl ligands to a generic metal fragment, L_nM.

---

* Corresponding author. Tel.: + 1-902-628-4328; fax: + 1-902-566-0632.
E-mail address: smackie@upei.ca (S.C. Mackie)

0022-328X/99/$ - see front matter © 1999 Elsevier Science S.A. All rights reserved.
PII: S0022-328X(99)00477-5

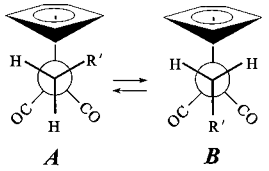


Fig. 2. The two rotamers resulting from rotation about the Fe–C$_\alpha$ bond of the piano-stool oxaallyliron systems of the general formula Fp‡–CH$_2$R.

observed isomerism is thought to be primarily due to the rotation about the Fe–C$_\alpha$ bond of the oxaallyliron compounds. Two possible rotational isomers (rotamers) of these compounds result from the rotation about this bond and are illustrated in Fig. 2 as Newman projections down the Fe–C$_\alpha$ bond (**A** and **B**). Similar conformational studies have been reported for dicarbonylcyclopentadienyl(2-oxopropyl)iron(II), (abbreviated Fp-2-oxopropyl, where Fp = (η^5-C_5H_5)-Fe(CO)$_2$) [3]. Our investigations are currently focused on determining the conformational preferences of the oxaallyliron compounds in solution, with the objective of correlating the structure of the compounds to their reactivity [5].

The conformational dynamics of the oxaallyliron compounds where R = C(O)N(C_2H_5)$_2$ are of particular interest due to the amide function. Here we will present the IR and NMR spectroscopic evidence pertaining to dicarbonyl(methylcyclopentadienyl)(2-(diethylamino)-2-oxoethyl)iron(II) (**1**), which supports the presence of rotational isomers of **1** in solution. IR spectroscopy is particularly useful for observing rotational isomerism in transition metal carbonyl compounds and its use is well documented in the literature [6]. Molecular mechanics calculations will be used to complement the spectroscopic evidence and to model the conformational processes of **1**.

2. Experimental

2.1. General comments

Iron pentacarbonyl (PCR), methylcyclopentadiene dimer (93%, Aldrich) and 2-chloro-*N*,*N*-diethylacetamide (97%, Aldrich) were used without further purification. Pentane, tetrahydrofuran and toluene were distilled over sodium benzophenone ketyl. Dichloromethane was distilled over calcium hydride. All distillations and collection of solvents took place under an atmosphere of nitrogen. All chemical manipulations were carried out using standard Schlenk line techniques under nitrogen [7]. IR spectra were collected using a Perkin–Elmer 1600 Series FTIR, operating at a resolution of 2.0 cm^{-1}. NMR spectra were obtained on either a Varian 300 MHz Gemini or a Bruker 300 MHz Avance™ spectrometer.

2.2. Preparation of compound **1**

Dicarbonyl(methylcyclopentadienyl)iron(II) dimer (Fp$'_2$) was prepared using established procedures [8]. The potassium salt of the Fp′ anion was prepared using the method described by Guerchais and co-workers [9]. A THF solution of 2-chloro-*N*,*N*-diethylacetamide (23 mmol) was added to a THF solution of KFp′ (13 mmol), both solutions being at −78°C. The reaction solution was stirred for 20 min at this temperature. The solution was allowed to warm to room temperature and then the solvent was removed under vacuum, leaving a brown oil. The product was purified using column chromatography (Silica (60–100 mesh); pentane–CH_2Cl_2–THF) and isolated as a golden-yellow oil (20% yield). IR (pentane, ν(CO), cm^{-1}): 2025.6 m, 2009.0 s, 1967.7 sh, 1957.1 s, 1614.0 m. ^{1}H-NMR (CD_2Cl_2, ppm): 0.95 (t, 3H (CH_3 of ethyl)), 1.1 (t, 3H (CH_3 of ethyl)), 1.54 (s, 2H(α-CH_2)), 1.85 (s, 3H(Cp′ CH_3)), 3.15 (q, 2H(CH_2 of ethyl)), 3.20 (q, 2H(CH_2 of ethyl)), 4.60 (m, 2H(Cp′ CH)), 4.70 (m, 2H(Cp′ CH)). ^{13}C{^{1}H}-NMR (CD_2Cl_2, ppm): −2.5 (s, 1C, α-CH_2), 12.9 (s, 1C, CH_3 of ethyl), 13.2 (s, 1C, CH_3 of ethyl), 14.6 (s, 1C, Cp′ CH_3), 39.7 (s, 1C, CH_2 of ethyl), 43.3 (s, 1C, CH_2 of ethyl), 85.0 (s, 1C, Cp′ CH), 85.8 (s, 1C, Cp′ CH), 102.7 (s, 1C, Cp′ *ipso*-C), 181.6 (s, 1C, oxo-CO), 216.8 (s, 2C, terminal CO). MS (CI nitrogen): *m*/*z* 306 (M + 1, 21%), 250 (100%); EI (70 eV): *m*/*z* 277 (M − 28, 12%), 249 (99%), 135 (100%), 79 (38%).

2.3. Molecular mechanics calculations

The molecular mechanics force field MMX in PCMODEL, version 6.0 for Windows 95, Serena Software, Box 3076, Bloomington, IN 47402-3076, USA, was used for the calculations. The rotational energy profiles were calculated using the dihedral driver option within PCMODEL. The details of the calculations are described elsewhere [3,10].

3. Results and discussion

Of the oxaallyliron compounds (Fp‡–CH$_2$R) studied, those where R = C(O)N(C_2H_5)$_2$ proved to be the most conformationally interesting. The presence of the diethylamino group increases the structural complexity of the compound, and therefore the number of possible conformers. The following discussion will highlight the conformational dynamics that were observed for **1**.

The IR spectrum of **1** clearly illustrates two pairs of ν_{CO} bands, indicating the presence of exchanging conformers in solution (Fig. 3) [3]. These ν_{CO} bands can be paired based on their relative intensities. The two strong peaks at 2009.0 and 1957.1 cm^{-1} are assigned to the more populated rotamer in solution. The other pair of peaks, at 2025.6 and 1967.7 cm^{-1}, is due to the less favored conformer in solution. In related Fp-alkyl systems the exchange has been attributed to rotation about the Fe–C_α bond [4,11].

The oxo-carbonyl ν_{CO} band of **1** is observed at 1614.0 cm^{-1}, approximately 50 cm^{-1} lower than that of the uncoordinated ligand precursor 2-chloro-*N*,*N*-diethylacetamide. Burkhardt et al. observed a similar shift of the oxo-carbonyl ν_{CO} band in the IR spectrum of a series of analogous η^1-oxaallyltungsten compounds relative to that of the uncoordinated ligand [12]. The shift is attributed to the interaction of the W–C_α bonding electrons with the oxo-carbonyl π orbital [12]. The addition of an alternative route for metal-to-ligand back bonding results in less metal-based electron density being channeled to the terminal carbonyls. Consequently the terminal ν_{CO} bands will be observed at higher wavenumbers in the IR spectrum relative to those of analogous compounds that do not have this additional pathway [3]. The net results of the iron-to-oxaallyl back bonding should be that the oxo-carbonyl ν_{CO} is observed at a lower wavenumber than that of the uncoordinated α-chloroketone and the terminal carbonyl ν_{CO} bands are observed at higher energy due to their accepting less electron density from the metal[1].

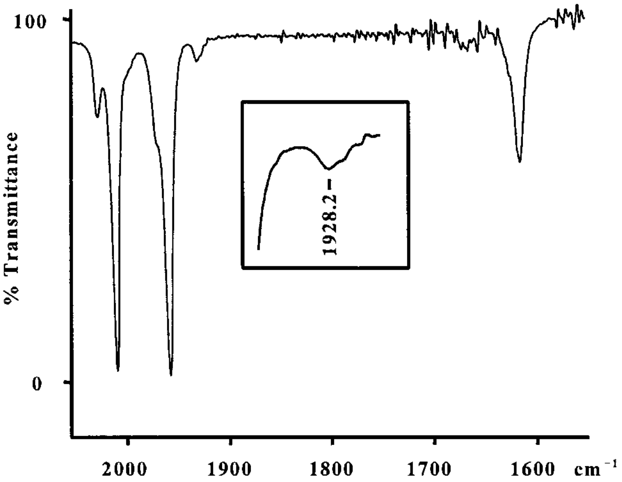
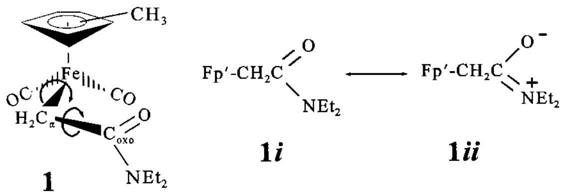


Fig. 3. IR spectrum of **1** in the ν_{CO} region (*n*-pentane solution).



Scheme 1. Illustrating compound **1** and the rotations about the Fe–C_α and C_α–C_{oxo} bonds. The amide resonance stabilization that results in the restricted rotation about the C_{oxo}–N bond is also illustrated (**1*i*** and **1*ii***).

This is not the case for **1**. The terminal carbonyl ν_{CO} bands are observed at ca. 2 cm^{-1} lower than those of Fp-allyl, yet the oxo-carbonyl ν_{CO} band is observed at the expected lower energy position (vide supra). The lower than expected terminal carbonyl ν_{CO} bands can not be solely attributed to the increased electron density on the Fe center due to the enhanced electron donating abilities of the methyl substituted Cp ring. Other contributing factors must be considered in order to properly interpret the IR data. One such factor is the possibility of resonance about the amide function of **1** (Scheme 1). The oxo-carbonyl ν_{CO} band of **1** is observed at approximately 40 cm^{-1} lower than that of the other oxaallyliron compounds that do not have available the resonance process. The shift to lower wavenumber of the oxo-carbonyl ν_{CO} band of **1** indicates a diminished bond order of the C_{oxo}–O_{oxo} bond and is consistent with **1*ii*** being an important contributor to the solution structure of **1**.

The rotation about the C_{oxo}–N bond is restricted due to the resonance process about the amide C–N bond (Scheme 1) [13]. This results in the two ethyl groups of the amino function being in different chemical environments; one is *cis* and the other is *trans* with respect to the oxo-oxygen. Separate signals are observed for each ethyl group of the amino function in the ^1H and $^{13}C\{^1H\}$-NMR spectra of **1**, illustrating that the ethyl groups are in magnetically different environments. A similar finding was reported for the related oxaallyltungsten compound $CpW(CO)_3(CH_2C(O)N(C_2H_5)_2)$, where ^1H and $^{13}C\{^1H\}$-NMR spectra of this compound revealed anisochronous ethyl groups [12]. The results of a NOESY experiment on **1** revealed an NOE between the hydrogens on the α-CH_2 and the methylene hydrogens at 3.15 ppm of one of the ethyl groups. This further supports the above assertion of the role of resonance in influencing the structure **1**, and confirms the magnetic inequivalent nature of the ethyl groups due to the restricted rotation about the C_{oxo}–N bond. The combined spectroscopic data suggest that the resonance contributor **1*ii*** significantly influences the solution structure of **1**.

A molecular mechanics analysis was initiated to enhance our understanding of the conformational dynam-

---

[1] This is illustrated by the IR spectra of Fp–$CH_2C(O)CH_3$ and Fp-allyl (both as *n*-pentane solutions), where the terminal carbonyl ν_{CO} bands of the former are observed at 2018.8 and 1968.8 cm^{-1} [3] and those of the latter compound at 2010.9 and 1959.2 cm^{-1}. The observation of the ν_{CO} bands of Fp–$CH_2C(O)CH_3$ at higher wavenumbers is due to the fact that less back bonding to the terminal carbonyls of the oxaallyliron compound is occurring than in the analogous Fp-allyl. This can be accounted for by the back bonding that is possible from the iron to the oxaallyl, that is, the electron density in the Fe–C_α bond interacts with the π orbital of the oxo-carbonyl. Therefore less metal-based electron density is transferred into the π* orbitals of the terminal carbonyls, thus the ν_{CO} bands of the Fp‡-oxaallyls should be observed in the IR spectrum at higher wavenumbers than those of the analogous allyliron compounds that do not have the alternative back bonding.

ics of **1**. Rotation about the Fe–C$_\alpha$ bond of the two resonance structures of **1** (Scheme 1) was examined using PCMODEL. Fig. 4(a) and (b) illustrates the resulting rotational energy profile about the Fe–C$_\alpha$ bond of **1*i*** and **1*ii***, respectively. The best conformer for **1*i*** corresponds to rotamer **A** of Fig. 2 and that of **1*ii*** to rotamer **B** of Fig. 2. Furthermore, the calculations suggest a low barrier to interconversion between rotamers **A** and **B** for **1*i*** (ca. 1.0 kcal mol^{-1}). A higher barrier to interconversion between **A** and **B** was calculated for the resonance structure **1*ii*** (ca. 2.2 kcal mol^{-1}). This suggests that the rotation about the Fe–C$_\alpha$ bond is restricted in **1*ii*** in comparison to that in **1*i***.

The rotation about the C$_\alpha$–C$_{oxo}$ bond was examined for **1*ii***. The calculations predicted limited rotation about this bond, such that it only rotates through ca. 100°. Not surprisingly, the limited rotation about the C$_\alpha$–C$_{oxo}$ bond of **1*ii*** orients the sterically demanding diethylamino group away from the metal fragment. Similar results were found for the rotation about the same bond in Fp-2-oxopropyl [3].

The calculated best conformer of **1** is dependent on how it is modeled; as **1*i*** the preferred rotamer is determined to be **A**, and as **1*ii*** it is **B**. The spectroscopic evidence indicates that the resonance contributor **1*ii*** influences the structure of **1**. Examination of the antisymmetric ^{13}C-ν_{CO} band at 1928.2 cm^{-1} in the IR spectrum of **1** (refer to insert in Fig. 3) revealed that it was composed of one peak of approximately 2% of the intensity of the main antisymmetric ν_{CO} band, and this peak had two low energy shoulders. The symmetry of the ^{13}C-ν_{CO} peak at 1928.2 cm^{-1} indicates that the major conformer in solution corresponds to rotamer **B** [6,14]. Close inspection of the ^{13}C-ν_{CO} band revealed that the two low energy shoulders are of approximately equal intensity and may be attributed to the minor rotamer in solution, corresponding to **A** [6]. This indicates that **1** is present in solution as an equilibrium between its two rotamers (**A** and **B**), and this equilibrium favors **B**.

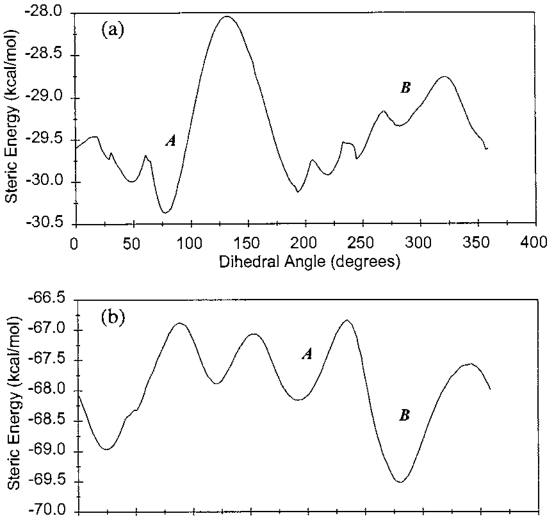
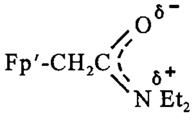


Fig. 4. Rotational energy profile about the Fe–C$_\alpha$ bond of (a) **1*i***, and (b) **1*ii*** (dihedral angle C$_{oxo}$–C$_\alpha$–Fe–C$_{CO}$). The labels refer to the Newman projections in Fig. 2.

4. Conclusions

The combined IR and NMR spectroscopic evidence conclusively identifies restricted rotation about both the Fe–C$_\alpha$ and C$_{oxo}$–N bonds in **1**; the latter is due to the inherent resonance of an amide group. Furthermore, the preferred conformer of **1** in a *n*-pentane solution is **B**. The static comparison of the resonance structures using molecular mechanics predicted a preference for **1*ii*** and agreed that rotamer **B** was the energetically favored conformer. Considering the influence of resonance on the structure of **1** it is best to consider **1** as the resonance hybrid **1*iii***.


$$\mathrm{Fp'\text{-}CH_2C}\overset{O^{\delta-}}{\underset{N^{\delta+}Et_2}{\vphantom{C}}}$$

1*iii*

It can be seen that **1*iii*** has a 1,3-dipole about the amide group. Analogous allylmetal compounds have been shown to participate in 1,3-dipolar cycloaddition reactions [1]. The 1,3-dipole in **1** is not a component of the oxaallyl backbone, suggesting that **1** would not exhibit similar reactivity in cycloaddition reactions as the analogous allylmetal compounds. This has been shown to be the case, whereby the reaction of **1** with tetracyanoethene produces a charge-transfer complex rather than the cycloaddition product [15]. Furthermore, the calculations suggest that the orientation of the ethyl groups will sterically block access of electrophiles to the oxaallyl backbone, supporting reactivity at another site within the molecule.

Acknowledgements

We gratefully acknowledge Chris Carrier and Diagnostic Chemicals, of Charlottetown, P.E.I., and Dr Henry Stronks, of Bruker, Canada, for the use of their respective NMR facilities, and Dr Stuart Grossert, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, for providing the mass spectral analyses. We acknowledge financial support of the University of Prince Edward Island through a Senate Committee on Research University Grant (to S.C.M.).

References

[1] (a) H.-W. Frühauf, Chem. Rev. 97 (1997) 523. (b) M.E. Welker, Chem. Rev. 92 (1992) 97.

[2] (a) A.G. Meyer, R. Aumann, Synlett (1995) 1011. (b) H. Kurosawa, A. Urabe, K. Miki, N. Kasai, Organometallics 5 (1986) 2002.

[3] S.A. DeGrace, S.W. Berry, S.C. Mackie, J. Organomet. Chem. 560 (1998) 63.

[4] K. Nakamoto, Infrared and Raman spectra of Inorganic and Coordination Compounds Part B, fifth ed., Wiley, New York, 1997, pp. 291–295.

[5] (a) P.L. Bogan, J.J. Irwin, B. Bosnich, Organometallics 8 (1989) 1450. (b) J.M. Brown, P.L. Evans, Tetrahedron 44 (1988) 4905.

[6] (a) W. Jetz, W.A.G. Graham, J. Am. Chem. Soc. 89 (1967) 2773. (b) J. Dalton, Inorg. Chem. 10 (1971) 1822. (c) F.A. Cotton, B.A. Frenz, A. Shaver, Inorg. Chim. Acta 7 (1973) 161. (d) C.L. Higgitt, A.H. Klann, M.H. Moore, B. Oelckers, M.G. Partridge, R.N. Perutz, J. Chem. Soc. Dalton Trans. (1997) 1269.

[7] D.F. Shriver, M.A. Drezdzon, The Manipulation of Air-Sensitive Compounds, second ed., Wiley, New York, 1986.

[8] J. Kleinberg (Ed.), Inorganic Synthesis, vol. 7, McGraw–Hill, New York, 1963, pp. 110–115.

[9] G. Poignant, S. Nlate, V. Guerchais, A.J. Edwards, P.R. Raithby, Organometallics 16 (1997) 124.

[10] (a) T.V. Timofeeva, J.-H. Lii, N.L. Allinger, J. Am. Chem. Soc. 117 (1995) 7452. (b) A. Beyer, P. Wolschann, A. Becker, G. Buchbauer, J. Mol. Struct. 196 (1989) 371.

[11] S.C. Mackie, M.C. Baird, Organometallics 11 (1992) 3712.

[12] E.R. Burkhardt, J.J. Dooney, R.G. Bergman, C.H. Heathcock, J. Am. Chem. Soc. 109 (1987) 2022.

[13] J. March, Advanced Organic Chemistry, fourth ed., Wiley, New York, 1992.

[14] I.S. Butler, A.E. Fenster, J. Organomet. Chem. 51 (1973) 307.

[15] M.J. Pushie, S.C. Mackie, manuscript in preparation.