

## SONOCHEMICAL SYNTHESIS OF SOME CHALCONETRICARBONYLIRON(0) COMPLEXES

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**ABSTRACT.** Sonication was applied to provide energy for the chemical reaction between diiron nonacarbonyl and 1,3-di-(hetero)aryl-propenone derivatives. New chalcone tricarbonyliron(0) complexes were obtained and characterized by IR spectroscopy. Advantages of this synthetic method are related to short reaction times and good yields.

**Keywords:** *chalconetricarbonyliron(0), heteroarylchalcone, sonochemistry, IR spectroscopy.*

### INTRODUCTION

Many applications of organometallic derivatives in synthetic chemistry were developed based on the capacity of steric and electronic properties of the ligands to modify the reactivity of metal complexes and thus to modulate their catalytic activity.

Several organic compounds were proved to form stable tricarbonyliron complexes and among these, a special attention was given to butadiene-tricarbonyliron [1-4] and heterodiene ( $-C=C-C=Y$  where  $Y=O, N$ ) tricarbonyliron complexes [5-8], due to tunable donor/acceptor interactions between these  $\pi$ -ligands and low-valent metal center.

Diaryl-substituted  $\alpha,\beta$ -unsaturated ketones (generic name chalcones) are such  $\pi$ -ligands which were proved to establish strong donor/acceptor interactions with iron(0). The first reported preparation of chalcone tricarbonyliron(0) compounds  $(Fe(ch)(CO)_3)$  where  $ch$  = benzylideneacetone, chalcone, 2'-hydroxychalcone, and 2,6-dibenzylidene-cyclohexanone), was a thermal procedure consisting of heating the enone with enneacarbonyldi-iron in toluene at 70-80 °C, which afforded the complexes in moderate yields ( $\approx 30\%$ ), as air-stable crystalline solids. [7]. Several other chalcones, obtained by Claisen Schmitt condensation of acetophenone with various substituted benzaldehydes, were also coordinated to iron(0) by heating at

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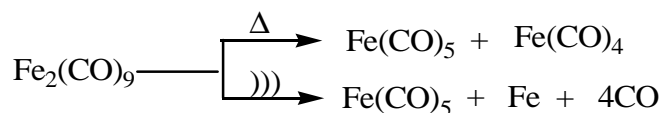
reflux with  $\text{Fe}_2(\text{CO})_9$  in ether solution for 16 h. The complexes were all obtained as orange-red air-stable solids in good to modest yields [9] and extensive structural studies were performed.

Applications of sonochemistry were reported in both homogeneous liquids and in heterogeneous liquid-solid systems. The chemical effect of ultrasound has proved to be extremely useful in the synthesis of a wide range of nanostructured materials [10], preparation of biomaterials (most notably protein microspheres) [11], etc. Even though the chemical effects of ultrasound do not come from a direct interaction with molecular species, the acoustic cavitation (consisting in the formation, growth and implosive collapse of bubbles in a liquid) serves as a mean of concentrating the diffuse energy of sound and thus, chemical reactions which require high energy can be performed in apparently mild conditions [12].

Thermal procedures affording  $\text{Fe}(\text{ch})(\text{CO})_3$  complexes encouraged us to perform the sonication of diironnonacarbonyl in the presence of some chalcones prepared by the Claisen Schmitt condensation of acetophenone derivatives with (hetero)aromatic carboxaldehydes. In this paper we describe the synthesis of new 1,3-di-(hetero)aryl-propenone-tricarbonyliron(0) complexes by sonication.

## RESULTS AND DISCUSSION

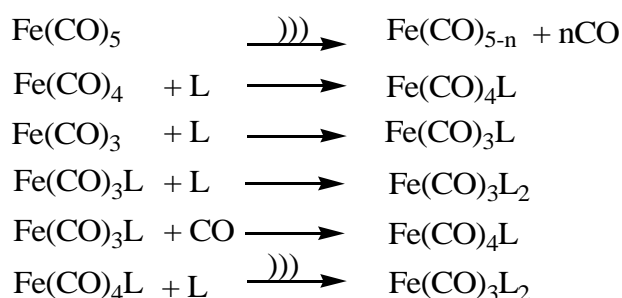
The sonochemistry of metal carbonyl compounds dissolved in organic liquids was first reported in 1981, by P. F. Schubert, J. W. Goodale and Suslick who performed the first sonochemistry study of discrete organometallic complexes and demonstrated the effects of ultrasound on metal carbonyls. Sonolysis of  $\text{Fe}(\text{CO})_5$  in alkane solvents causes the clusterification to  $\text{Fe}_3(\text{CO})_{12}$  but in the presence of added Lewis bases, sonochemical ligand substitution also occurs. Thermal decomposition of diiron nonacarbonyl appears at 100 °C according to scheme 1, but sonolysis of  $\text{Fe}_2(\text{CO})_9$  in decalin yields  $\text{Fe}(\text{CO})_5$  and finely divided iron at rates fast compared to  $\text{Fe}_3(\text{CO})_{12}$  formation [13].



Scheme 1

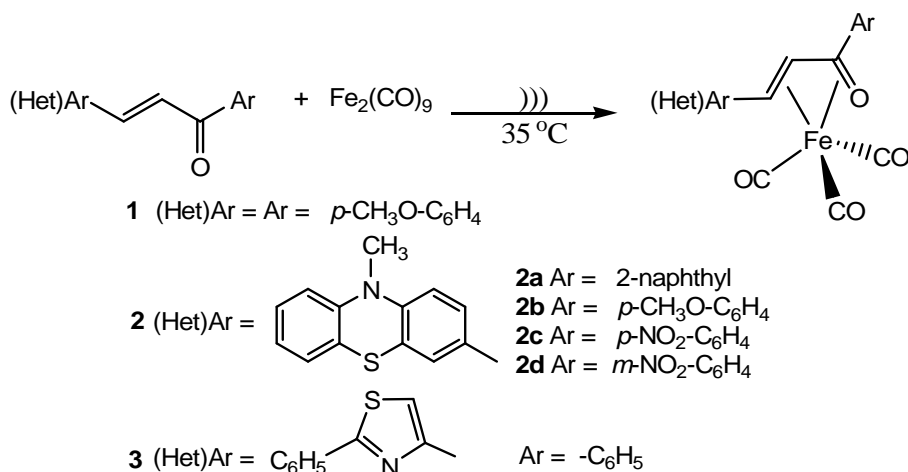
Sonication of  $\text{Fe}(\text{CO})_5$  in the presence of ligands (abbreviated L) produces iron carbonyl derivatives  $\text{Fe}(\text{CO})_{5-n}\text{L}_n$  ( $n=1,2$ ) according to the general mechanism shown in scheme 2 (L = phosphines or phosphates, [14]). The  $\text{Fe}(\text{CO})_4\text{L} : \text{Fe}(\text{CO})_3\text{L}_2$  ratio is dependent on ligand and its concentration.

1,3-Bis(*p*-methoxyphenyl)-propenone **1** and heteroaromatic chalcones containing phenothiazine units **2** [15] and thiazole units **3** [16] respectively, were subjected to sonication in an ultrasonic bath in the presence of diironnonacarbonyl; new Fe(ch)(CO)<sub>3</sub> complexes were thus obtained according to scheme 3.



Scheme 2

Short reaction times were required for the preparation of Fe(ch)(CO)<sub>3</sub> complexes containing chalcones **1**, **2a**, **2b**, **3**, in excellent to good yields. The sonication of heteroaromatic chalcones containing nitro-substituents in the aromatic rings (**2c**, **2d**) was not successful in terms of complex preparation and produced the decomposition of the starting material. Table 1 shows the reaction characteristics for the preparation of Fe(ch)(CO)<sub>3</sub> complexes.



Scheme 3

The major bonding interactions between the  $\alpha,\beta$ -unsaturated carbonyl unit in the chalcone and the iron(0)tricarbonyl fragment were rationalized in terms of the frontier molecular orbitals involved [9]. The theoretical calculations by Calhorda and Vichi [17] using the extended Huckel method illustrate that the bonding between the metal and the  $\alpha,\beta$ -unsaturated carbonyl ligand is dominated by donation from filled orbitals  $\pi_1$  and  $\pi_2$  to vacant metal-centered orbitals and donation from a filled metal orbital to the vacant  $\pi_3$ -orbital of the ligand, while donation to  $\pi_4$  is thought to be only a minor component. In solution, the complex is approximating  $C_{3v}$ -symmetry due to rapid rotation around the  $Fe(CO)_3$  chalcone axis, an effect that was observed in the IR and  $^{13}C\{^1H\}$  NMR reported spectra [9].

**Table 1.** The reaction characteristics for the preparation of  $Fe(ch)(CO)_3$  complexes by sonication of chalcones with  $Fe_2(CO)_9$

Chalcone	Sonication time [min]	Yields [%]
<b>1</b>	30	70
<b>2a</b>	45	55
<b>2b</b>	45	56
<b>3</b>	30	80
<b>2c</b>	60	0
<b>2d</b>	60	0

The IR spectra of **1-3** complexes were recorded. In agreement with the formulation as iron tricarbonyl derivatives their IR spectra show three strong  $\nu(CO)$  bands in the region  $2100-1900\text{ cm}^{-1}$ . Strong bands in the region  $1600-1700\text{ cm}^{-1}$  found in the spectra of the free chalcones disappeared on co-ordination. The recorded values for the stretching vibrations of CO units in the prepared  $Fe(ch)(CO)_3$  complexes **1-3** are listed in table 2.

The position of the infrared bands due to the CO stretching vibrations in the structure of the  $Fe(ch)(CO)_3$  was found to be finely tuned by the structure of the chalcone unit. The amount of electron density available at the metal center that may be donated into the antibonding orbitals of the carbon monoxide ligands may be approximated from the frequency of the infrared bands due to the CO stretching vibrations: thus, aromatic units containing substituents with net electron-withdrawing properties were proved to determine CO stretch bands situated at higher frequencies, whereas net electron-donating substituents result in bands at lower frequencies [9].

**Table 2.** IR spectroscopic data for the CO stretching bands in Fe(ch)(CO)<sub>3</sub> complexes **1-3**

Complex	$\nu_{\text{co}}$ (cm <sup>-1</sup> )
<b>1</b>	2085; 2022; 1987
<b>2a</b>	2050; 1993; 1964
<b>2b</b>	2049; 1983; 1957
<b>3</b>	2092; 2018; 1977

1-Aryl-3-phenothiazinyl-propenones **2** contain an extended  $\pi$  conjugated system which benefit from the electron-donor effect of the phenothiazine nucleus. As it can be seen from the values listed in table 2, the electron-donor properties of the phenothiazine moiety in complexes **2a**, **2b** determines the lowest values for the CO stretching bands, whereas according to this criterion the 2-phenyl-thiazole unit in **3** appears to be less electron-donor.

## CONCLUSIONS

An advantageous method for the synthesis of chalconetricarbonyliron(0) complexes appears to be the sonochemical  $\pi$ -ligand substitution which occurs when Fe<sub>2</sub>(CO)<sub>9</sub> is treated with chalcones in organic solvents. As compared to previously reported thermal procedures employed for the synthesis of Fe(ch)(CO)<sub>3</sub> complexes, ultrasonic irradiation increased the yields and dramatically reduced the reaction time.

IR spectroscopy can be employed for the structural assignment of chalconetricarbonyliron(0) complexes based on the three strong absorption bands due to carbonyl stretching vibrations which appear in the characteristic region 2100-1900 cm<sup>-1</sup>.

## EXPERIMENTAL SECTION

Ultrasonic bath: Elma S15H  
 FT-IR spectrometer Bruker Vector 22  
 Merck reagents were used.

### *General procedure for sonication of chalcone and Fe<sub>2</sub>(CO)<sub>9</sub>*

In a round-bottomed flask fitted with a condenser and a gas inlet, chalcone (1 mmol) was dissolved in dried dichloromethane and in the stirred solution nitrogen gas was bubbled for approx. 5 minutes (until saturation was reached). 2.5 mmol Fe<sub>2</sub>(CO)<sub>9</sub> were added carefully maintaining the nitrogen atmosphere. The reaction flask was placed in an ultrasonic bath and sonicated at 35 °C for several minutes (according to table 1). The product mixture was then filtered through celite using DCM as eluent and the solvent was removed *in vacuo*. The raw product was purified by column chromatography (silica gel; eluent ethyl-ether/petroleum-ether:1/4) and recrystallised from hexane, to give the complex as air relatively stable crystalline material.

**$\eta^4$ -((E)-1,3-di-(4-methoxyphenyl)-2-propen-1-one)-tricarbonyl-iron(0)**

0.28 g (yields 70%) orange-yellow crystals m.p.= 90-91 °C

IR (cm<sup>-1</sup>): 2085, 2022, 1987, 1628, 1601, 1572, 1512, 1475, 1280, 1230, 1160, 1034, 839.

**$\eta^4$ -((E)-3-(10methyl-phenothiazin-3yl)-1-(2-naphthyl)-2-propen-1-one)-tricarbonyliron(0)**

0.3 g (yields 55%) brown-red crystals, m.p. = 95-96 °C

IR (cm<sup>-1</sup>): 2050, 1993, 1964, 1597, 1573, 1469, 1337, 1258, 749.

**$\eta^4$ -((E)-3-(10methyl-phenothiazin-3yl)-1-(4-methoxyphenyl)-2-propen-1-one)-tricarbonyliron(0)**

0.28 g (yields 56%) brown-red crystals, m.p.=149-150 °C

IR (cm<sup>-1</sup>): 2049, 1983, 1957, 1600, 1588, 1498, 1454, 1332, 1259, 810, 757, 738.

**$\eta^4$ -((E)-3-(2-phenyl-thiazol-4yl)-1-(4-phenyl)-2-propen-1-one)-tricarbonyl-iron(0)**

0.34g (yields 80%) light yellow, m.p.86-88 °C

IR (cm<sup>-1</sup>): 2092, 2018, 1977, 1639, 1599, 1468, 1274, 1200, 763, 688.

## ACKNOWLEDGMENTS

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## REFERENCES

1. H. Rheilem, A. Grubl, G. Hessling, O. Pfrengle, *Justus Liebigs Ann. Chem.* **1930**, 482, 161.
2. B.F. Hallam, P.L. Pauson, *J. Chem. Soc.* **1958**, 642.
3. R. Pettit, G.F. Emerson, *Adv. Organomet. Chem.* **1964**, 1, 1.
4. M.R. Churchill, R. Mason, *Adv. Organomet. Chem.* **1967**, 5, 93.
5. S. Otsuka, T. Yoshida, A. Nakanima, *Inorg. Chem.* **1967**, 6, 20.
6. H. tom Dieck, H. Bock, *J. Chem. Soc., Chem. Commun.* **1968**, 678.
7. A.M. Brodie, B.F.G. Johnson, P.L. Josty, J. Lewis, *J. Chem. Soc., Dalton. Trans.* **1972**, 2031.
8. D. Liebfritz, H. tom Dieck, *J. Organomet. Chem.* **1976**, 105, 255.
9. B. E. Moulton, A. K. Duhme-Klair, I. J. S. Fairlamb, J. M. Lynam, and A. C. Whitwood, *Organometallics*, **2007**, 26 (25), 6354.

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10. K.S. Suslick in *Kirk-Othmer Encyclopedia of Chemical Technology*, 4<sup>th</sup> Ed. J. Wiley & Sons: New York, **1998**, vol. 26, 517.
11. K. S. Suslick, M. W. Grinstaff, *J. Am. Chem. Soc.*, **1990**, 112, 780.
12. K. S. Suslick, *Science*, **1990**, 247, 1439.
13. K. S. Suslick, P. F. Schubert and J. W. Goodale, *J. Am Chem. Soc.* **1981**, 103, 7342.
14. K. S. Suslick, J. W. Goodale, P. F. Schubert and H. H. Wang, *J. Am Chem. Soc.* **1983**, 105, 5781.
15. L. Găină, A. Csámpai, G. Túrós, T. Lovász, V. Zsoldos-Mády, I. A. Silberg and P. Sohár, *Org. & Biomol. Chem.* **2006**, 4, 4375.
16. I. Simiti, V. Zaharia, M. Coman, H. Demian, A. Muresan, *Pharmazie*, **1988**, 43(2), 82.
17. M. J. Calhorda, E. J. S. Vichi, *Organometallics* **1990**, 9, 1060.