Journal of Organometallic Chemistry, 216 (1981) 79—85
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

REACTION OF BIS(DIETHYL MUCONATE)CARBONYLIRON WITH MONODENTATE HETEROCYCLIC ORGANONITROGEN LIGANDS *

MARCO-A. DE PAOLI * and MINA MAKITA
Instituto de Química, Universidade Estadual de Campinas, 13.100 - Campinas, S.P. (Brasil)

(Received December 2nd, 1980)

Summary

The reaction of the title compound with monodentate nitrogen-containing heterocycles (pyridine, pyrazine and quinoline) yielded products in which one bidentate diene has been substituted by an heterocycle and a CO ligand, producing (diene)(heterocycle)$(CO)_2Fe$ compounds: (diethyl muconate)(pyridine)dicarbonyliron, (diethyl muconate)(pyrazine)dicarbonyliron and (diethyl muconate)(quinoline)dicarbonyliron.

Introduction

Bis(diethyl muconate)carbonyliron (muconic acid = hexa-2,4-dien-1,6-dioic acid), prepared by photolysis of pentacarbonyliron in presence of an excess of diene [1] was shown by X-ray diffraction to have a square pyramidal configuration with the two dienes occupying the basal/basal coordination sites [2]. This compound exchanges one of its muconate ligands for a variety of other ligands [3]. It is known to exchange one diethyl muconate for Schiff-type bases such as 2,2'-bipyridine, 2-benzoylpyridine anil and 2-benzoylpyridine *p*-methoxyanil, producing compounds of the type (1,4-diaza-1,3-diene)(diethyl muconate)carbonyliron [5]. These compounds retain the square pyramidal configuration, but the entering bidentate nitrogen-containing ligand occupies an apical/basal position in substitution of the basal/basal bidentate diene ligand. Products with the same configurations were obtained by the photolysis of the (diethyl muconate)tricarbonyliron complex in the presence of the diazadienes [4]. On the other hand, a different configuration for these compounds was achieved by the photolysis of (diazadiene)tricarbonyliron complexes in the presence of dienes. In this reaction the authors presented evidence that not

---

* Presented in part at the III^a Reunião Anual da Sociedade Brasileira de Química, Rio de Janeiro. 1980.

only the entering diene ligand, but also the diazadiene, have the basal/basal configuration [5].

We treated bis(diethyl muconate)carbonyliron with pyridine in an attempt to exchange one diene for two pyridine molecules to obtain a compound similar to that observed from reactions with 2,2′-bipyridine. However, when this reaction was carried out in toluene solution at room temperature we isolated a crystalline product which showed two very strong absorptions in the IR spectrum in the ν(CO) region and whose elemental analysis agreed with the formula (diethyl muconate)(pyridine)dicarbonyliron. A similar result was obtained with pyrazine and quinoline. The same compounds are obtained by photolysis of (diethyl muconate)tricarbonyliron in the presence of the heterocycles.

Experimental

Bis(diethyl muconate)carbonyliron and (diethyl muconate)tricarbonyliron were prepared as previously described [2]. Pyridine (Baker), pyrazine (Ega-Chemie) and quinoline (Eastman) were used as furnished. Toluene (Carlo Erba RPE) and petroleum ether 30—60 (Ecibra p.a.) were refluxed with potassium, distilled and degased prior to use. The reactions and purifications were carried out under argon. Elemental analysis were performed by the Analytical Laboratory of Rhodia, Paulinia. Spectra were recorded using the following spectrometers: IR, Perkin-Elmer 399B; ^{1}H NMR, Varian XL-100; mass spectra, Finnigan 1015-SL.

Synthesis

(Diethyl muconate)(pyridine)dicarbonyliron, [(muco)py(CO)$_2$Fe]. 6.3 mmol of pyridine were added to a solution of 0.44 mmol of bis(diethyl muconate)-carbonyliron in 15 ml of toluene with stirring at room temperature. After 24 hours, the solvent was evaporated and the residue extracted with petroleum ether. The product was recrystallized twice from a mixture of toluene and petroleum ether, yielding 80 mg of yellow crystals of m.p. 94—96°C (dec.). (IR data and elemental analysis in Table 1).

TABLE 1

IR ABSORPTION IN THE ν(CO) FREQUENCY REGION [a] AND ELEMENTAL ANALYSIS

	ν(CO) (cm^{-1}) (±2 cm^{-1})	Analysis Found (Calcd.) (%)		
		C	H	N
(muco)$_2$Fe(CO)	2038, 1700			
(muco)Fe(CO)$_3$ [b]	2070, 2010, 1720			
(muco)pyFe(CO)$_2$	1995, 1926, 1700	52.30	4.89	3.20
		(52.45)	(4.90)	(3.60)
(muco)pzFe(CO)$_2$	1995, 1929, 1690	48.74	4.45	6.98
		(49.26)	(4.60)	(7.18)
(muco)quinFe(CO)$_2$	2006, 1950, 1702	56.94	4.58	3.45
		(57.27)	(4.77)	(3.18)

[a] Measured in KBr pellets. [b] Measured in hexane solution.

(Diethyl muconate)(pyrazine)dicarbonyliron, [(muco)pz(CO)$_2$Fe]. 0.54 mmol of pyrazine was added to a solution of 0.27 mmol of bis(diethyl muconate)carbonyliron in 10 ml of toluene. The mixture was stirred at room temperature for 24 hours, filtered and evaporated to dryness. The residue was extracted with petroleum ether and recrystallized from a mixture of toluene and petroleum ether, yielding 40 mg of brownish-yellow crystals of m.p. 125—132°C (dec.) (IR data and elemental analysis in Table 1).

(Diethyl muconate)(quinoline)dicarbonyliron, [(muco)quin(CO)$_2$Fe]. 1.25 mmol of quinoline were added to a solution of 0.25 mmol of bis(diethyl muconate)carbonyliron dissolved in 10 ml of toluene. The mixture was stirred at room temperature for 25 hours, filtered and evaporated to dryness. The product was purified by column chromatography using alumina (neutral, Carlo Erba) and a mixture of toluene and ethyl acetate as eluent. After evaporation of solvent, the product was recrystallized from petroleum ether, yielding 33 mg of brownish-red crystals of m.p. 116°C (dec) (IR data and elemental analysis in Table 1).

The reactions were repeated under a strong argon stream, in order to try to remove the free CO, but the yields obtained were the same as before. By performing the reactions under CO atmosphere the yields increased to 75%.

Photochemical preparation of (muco)(heterocycle)(CO)$_2$Fe. 3.0 mmol of (diethyl muconate) tricarbonyliron and 9.0 mmol of the heterocycle were dissolved in 170 ml of toluene and irradiated for 24 hours with a Philips HPK 124 W lamp, in a Pyrex immersion-well apparatus, under a stream of argon. After this time, the volume of solvent was reduced by evaporation and petroleum ether was added to precipitate the product. The precipitate was recrystallized from a mixture of toluene and petroleum ether. In all three cases the yield was ca. 50% based on (diethyl muconate)tricarbonyliron.

Results and discussion

The reaction of bis(diethyl muconate)carbonyliron with pyridine, pyrazine and quinoline yields products which show two very strong absorptions in the IR spectrum in the ν(CO) region and whose elemental analysis agrees with the formula (diethyl muconate)(heterocycle)dicarbonyliron (Table 1). A shift of ca. 10 cm^{-1} towards lower frequency is also observed in the CO absorptions of the ester ligand due to electron donation by the heterocyclic nitrogen-containing ligands. As expected, the ν(C=C) absorption is not observed.

The mass spectra of these compounds show the molecular ion and the fragment ions, corresponding to the loss of the first CO, the second CO, the diethyl muconate ligand and the heterocycle (Table 2). The free ligand peaks are also observed. The low intensities of the peaks are due to the low decomposition temperature of the compounds in comparison to the required vaporization temperature of 100—110°C.

The ethyl group signals in the ^{1}H NMR spectrum of the (muco)pyFe(CO)$_2$ compound in deuterobenzene resemble the equivalent signals in the ^{1}H NMR spectrum of the (muco)(2,2'-bipyridine)carbonyliron compound [4]. We observed one pair of signals (δ = 1.15 ppm, triplet, and 1.03 ppm multiplet) corresponding to the methyl groups and another pair (δ = 4.18 ppm, quartet.

TABLE 2

70 eV MASS SPECTRA PEAKS (m/z) AND INTENSITIES (IN PARENTHESES) OF THE THREE COMPOUNDS DESCRIBED IN THIS WORK [a]

	M	M − CO	M − 2 CO	M − 2 CO − h	M − 2 CO − muco	muco	h
(muco)pyFe$(CO)_2$	389(0.09)	361(0.46)	333(1.03)	254(2.67)	135(1.30)	198(1.19)	79(100)
(muco)pzFe$(CO)_2$	390(0.02)	362(0.02)	334(0.02)	254(1.81)	136(0.60)	198(0.75)	80(100)
(muco)quinFe$(CO)_2$	439(0.03)	411(0.30)	383(1.47)	254(0.19)	185(4.56)		129(100)

[a] muco = diethyl muconate, h = heterocycle.

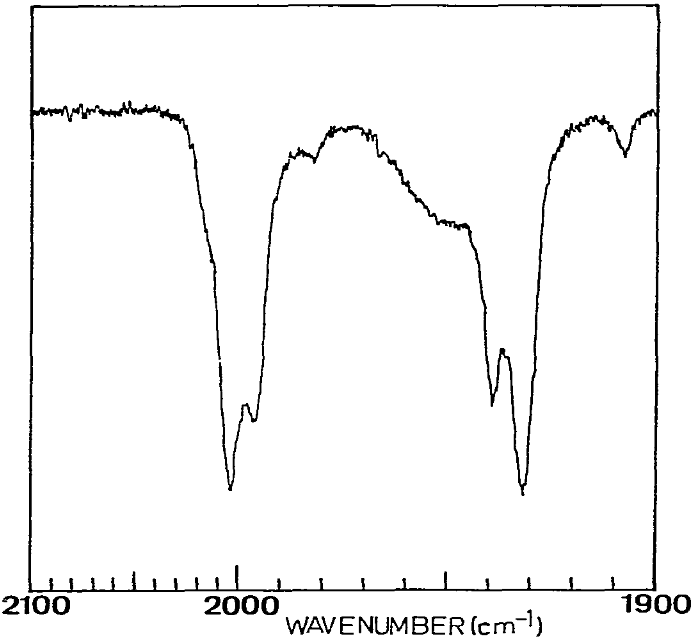
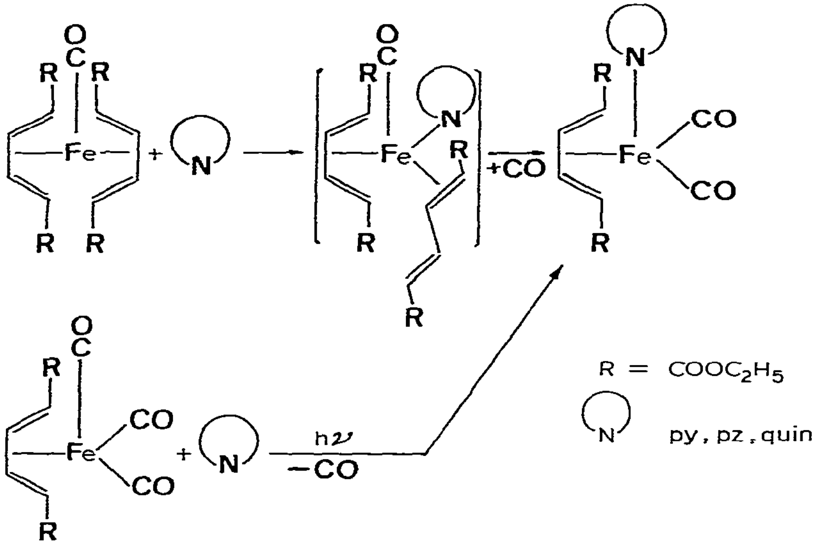


Fig. 1. IR spectrum of (muco)(py)(CO)$_2$Fe in KBr pellet in the region 2100—1900 cm^{-1}.

and 3.98 ppm, multiplet) corresponding to the methylene groups. These shifts indicate clearly an asymmetric interaction of the ethyl groups of the ester with the pyridine ligand. The spectra of the other two compounds show similar features.

It is known that electron-donating ligands occupy preferentially axial positions in iron compounds [6], Also, the reaction of nonacarbonyldiiron with pyridine and pyrazine yields compounds with the heterocycle in the axial position of a trigonal bipyramid [7]. On the other hand, the iron carbonyl compounds containing a diene and a diazadiene ligand have the apical position of a square pyramid occupied by a nitrogen of the diazadiene ligand [4]. Based on this and on our ^{1}H NMR spectral results, we have assigned to the new compounds a structure with the diene and the two carbonyls on the base of a square pyramid whose apical position is occupied by the nitrogen of the heterocycle. This structure should predominate in the solid state as demonstrated by the IR spectra. However, in these spectra we observe two less intense bands in the region of the ν(C=O) frequency (Fig. 1), suggesting the formation of a second species with different structure. All our attempts to isolate this species failed, and we tentatively assign this to an isomer where the heterocycle occupies a basal position. This would explain the different shift of the ν(C=O) bands: one is shifted to lower and the other to higher wavenumber.

No change in the yield is observed when the reaction is carried out in a large excess of pyridine or by passing a strong stream of inert gas through the reaction mixture. However, when we performed the reaction under CO atmosphere the yield increased from 30% to 75%. This confirms that the second CO ligand originated from a second molecule of the starting iron carbonyl complex. By irradiating (diethyl muconate)tricarbonyliron in the presence of the heterocycles, we substituted only one carbonyl, isolating the same products, even using longer photolysis times under an argon stream. A similar behavior was reported for the reaction of $[(\eta^4\text{-}C_6H_5CH{=}CHCH{=}NC_6H_5)(CO)_3Fe]$ with $AsPh_3$ and $SbPh_3$ [8].



SCHEME 1

The thermal reaction probably occurs in two steps (Scheme 1); in the first, one iron—diene bond opens with the subsequent coordination of the heterocycle and, in the second, the other bond opens simultaneously with coordination of CO. Although no η^4/η^2-bis(diene)dicarbonyliron compound has been isolated, the first step seems reasonable since the complete loss of a diene should favor the coordination of two heterocycles, specially in the presence of a large reagent excess. The second step seems more complicated, since there is no apparent reason why, when working under a stream of inert gas, we were not able to produce a compound with two heterocyclic ligands. A possible explanation could involve a carbonyl-bridged intermediate (which, however, we were unable to detect). All efforts to synthesize an iron carbonyl complex containing more than one heterocyclic ligand failed. This confirms the assumption that there is a strong steric hindrance in placing two heterocyclic rings together, bonded to an iron center. By dissolving nonacarbonyldiiron in pyridine or by irradiating a solution of pentacarbonyliron in a large excess of pyridine with UV light we isolated only the known (pyridine)tetracarbonyliron, confirming in part the suggested mechanism.

Acknowledgments

M.M. acknowledges financial support from FAPESP (grant No. 78/1454) and M.A.P. from CNPq (grant No. 30.0516/79QU). The authors also thank

BASF do Brasil for donation of pentacarbonyliron and the Alexander-von-Humboldt Foundation (F.R.G.) for the donation of reagents. We also thank Dr. F.Y. Fujiwara for performing the NMR measurements.

References

1 J. Buchkremer, Ph.D. Dissertation, Ruhr Universität, Bochum, 1973.
2 C. Krüger and Y.-H. Tsay, Angew. Chem., 83 (1971) 250.
3 F.W. Grevels, U. Feldhoff and K. Schneider, VIIth Int. Conf. Organometal. Chem., Venice, 1975, Abstr. No. 192.
4 M.A. De Paoli, H.-W. Fruehauf, F.-W. Grevels, E.A. Koerner von Gustorf, W. Riemer and C. Krüger, J. Organometal. Chem., 136 (1977) 219.
5 H.-W. Fruehauf, F.-W. Grevels and A. Landers, J. Organometal. Chem., 178 (1979) 349.
6 C.B. Ungermann and K.G. Caulton, J. Organometal. Chem., 94 (1975) C9.
7 F.A. Cotton and J.M. Troup, J. Amer. Chem. Soc., 96 (1974) 3438.
8 G. Bellachioma, G. Reichenbach and G. Cardaci, J. Chem. Soc. Dalton (1980) 634.