Journal of Organometallic Chemistry, 464 (1994) C23–C24

JOM 24157PC

Preliminary Communication

Synthesis and characterization of the novel complex μ-(η^2,η^2-dibenzylideneacetone)$Fe_2(CO)_8$ **

Andrés C. Cano C., Noé Zúñiga-Villarreal,
Cecilio Alvarez T., Rubén A. Toscano,
Marisol Cervantes and Aída Daz

Instituto de Química, UNAM, Cto. Exterior, Cd. Universitaria, 04510 México, D.F. (Mexico)

Henri Rudler

Laboratoire de Chimie Organique, URA 408, T45, 4 Place Jussieu, 75252 Paris 05 (France)

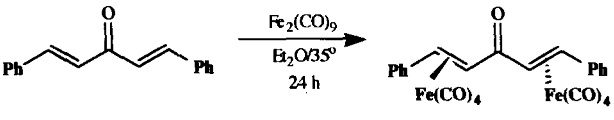
(Received April 5, 1993; in revised form September 2, 1993)

Abstract

The thermal reaction of $Fe_2(CO)_9$ with dibenzylideneacetone in boiling diethyl ether gives the dinuclear yellow-orange air-stable μ-(η^2,η^2-dibenzylideneacetone)$Fe_2(CO)_8$ (I). The structure of the complex was determined by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy, and X-ray crystallography.

Key words: Iron; Carbonyl; Vinyl; Ketene; Ketone

As part of our interest in the reactivity of ketene complexes of transition metals towards nucleophiles and especially tertiary amines [1], we carried out the synthesis of a large variety of $Fe(CO)_3$ complexes of α,β-unsaturated ketones, the starting material for such ketene complexes. It is well known that α,β-unsaturated ketones and aldehydes react thermally with $Fe_2(CO)_9$ to afford tri- and tetracarbonyl complexes [2]. Some tricarbonyl complexes can be obtained by heating their less stable tetracarbonyl precursors [3,4c]. Reaction of the ketones $PhC(CH_3)CHCOPh$ and 2,6-dibenzylidenecyclohexanone with the iron carbonyl leads directly to the tricarbonyl complex in both cases; the tetracarbonyl complexes were not observed during these reactions [3]. In an attempt to synthesize the tricarbonyl complex of benzylideneacetone, we discovered that the dinuclear complex I was formed from the thermal reaction of dibenzylideneacetone and diiron nonacarbonyl (eqn. (1)).



I

The dinuclear nature of this kind of complex makes it unique since, to our knowledge, there are no reports in the literature of dinuclear complexes with two $-Fe(CO)_4$ fragments bridged by an α,β-unsaturated ketone.

Dibenzylideneacetone (1 equiv.) reacts with diiron nonacarbonyl (1.2 equiv.) under mild conditions (refluxing diethyl ether, 24 h) to give an air-stable crystalline solid of composition $C_{25}H_{14}O_9Fe_2$. [m.p. 130°C (dec.), yield, 40.2% with respect to $Fe_2(CO)_9$]. The IR spectrum shows four ν(MC=O) bands at 2094s, 2068vs, 2012vs, 1991vs cm^{-1} (in $CHCl_3$), typical of (olefin)$Fe(CO)_4$ systems with a local carbonyl C_{2v} symmetry [2–4]; the ketone ν(CO) appears as a band of medium intensity at 1630 cm^{-1}. The ^{1}H NMR spectrum (200 MHz, $CDCl_3$) exhibits signals besides those for the two phenyl groups at 7.1–7.4 ppm (m, 10H) for four vinylic protons at 5.29 ppm (d, 2H) and at 4.78 ppm (d, 2H) with $J = 11.3$ Hz; thus these protons experience an upfield shift with respect to those of the free ligand which give signals at respectively 7.72 and 7.05 ppm, $J = 17.4$ Hz [5], this upfield shift is also observed in the ^{13}C NMR spectrum (200 MHz, $CDCl_3$) where the complexed ligand shows resonances besides those for the metal carbonyls at 207.3 ppm, for the ketone carbonyl at 186.0 ppm, and for the aromatic carbons at 141.8–126.2 ppm, for the vinyl carbons at 57.6 and 52.8 ppm. In the free ligand these latter signals appear respectively at 142.9 and 125.5 ppm [5].

The structure of complex I, determined by X-ray diffraction [7*], possesses a nearly perfect C_2 symmetry with the $-Fe(CO)_4$ moieties and phenyl rings lying on opposite faces of the fairly planar divinyl ketone.

Correspondence to: Dr. C. Alvarez.

** Contribution no. 1189 of the Instituto de Química, UNAM.

* Reference number with asterisk indicates a note in the list of references.

0022-328X/94/$7.00
SSDI 0022-328X(93)24157-Z

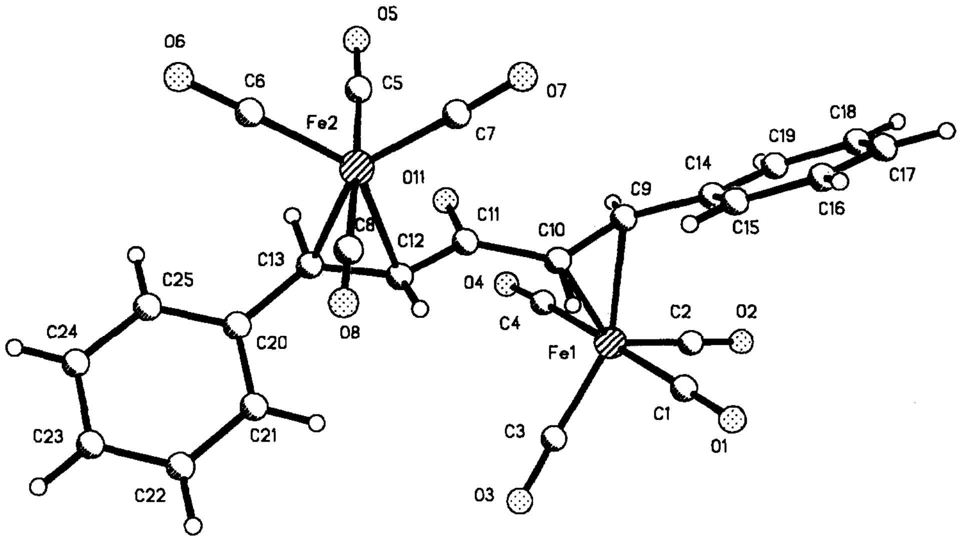


Fig. 1. Molecular structure and atom numbering scheme for complex 1. Selected bond distances and angles are as follows: C(9)–C(10), 1.392(8) Å; C(12)–C(13), 1.394(7) Å; Fe(1)–C(9), 2.141(6) Å; Fe(1)–C(10), 2.116(6) Å; Fe(2)–C(12), 2.118(6) Å; Fe(2)–C(13), 2.159(6) Å. C(10)–C(11)–C(12), 115.7(4)°; C(11)–C(12)–C(13), 123.4(4)°; C(10)–C(11)–O(121), 121.4(6)°; C(12)–C(11)–O(11), 122.9(5)°.

The geometry around each iron atom can be described as a slightly distorted trigonal bipyramid with the apical planes tilted by 69° and 47° with respect to the plane of the divinyl ketone. The C–C axis of the double bond lies in the equatorial plane; this geometry agrees well with that of the mono-(olefin)$Fe(CO)_4$ and related dinuclear complexes, the structures of which have been reported [8]. The molecular structure and the atom numbering scheme are shown in Fig. 1. The C–C distances of the bound olefinic moieties [1.392(8) and 1.39(7) Å] are basically the same and suggest that the dibenzylideneacetone ligand behaves as a π-acid. The distances of the vinylic carbon atoms attached to the metal are essentially the same, the bond angles around C(9), C(10), C(12) and C(13) atoms show that they present an sp^2 hybridization. The solid state conformation of the dibenzylideneacetone ligand is *s-cis*. The relative lengths of axial and equatorial Fe–CO bonds in complex **I** are similar within experimental error boundaries.

It is interesting to point out the great stability of complex **I**, since it has been reported that the dihydrofuranone tetracarbonyl iron complex undergoes loss of a CO when refluxed in diethyl ether for 16 hours to give the tricarbonyliron complex [4d]. Similar reaction conditions led to tricarbonyl iron complexes of several vinyl ketones [6]. In our hands, further heating of complex **I** or heating at higher temperature (80°C in benzene) only caused decomposition. We are testing the reactivity of this new complex towards various nucleophiles and trying to synthesize complexes containing the same structural features.

Acknowledgements

CONACyT (México) and the European Community for supporting this project.

References and notes

1 C. Alvarez-Toledano, A.C. Cano, R.A. Toscano, A. Parlier and H. Rudler, *Bull. Soc. Chim. Fr.*, in press.

2 E. Weiss, K. Stark, J.E. Lancaster and H.D. Murdoch, *Helv. Chim. Acta, 46* (1963) 288.

3 (a) A.M. Bradie, B.F.G. Johnson, P.L. Josty and J. Lewis, J. Chem. Soc., Dalton Trans., (1972) 2031; (b) J.A.S. Howell, B.F.G. Johnson, P.L. Josty and J. Lewis, *J. Organomet. Chem., 39* (1972) 329.

4 (a) F.A. Cotton and P. Lahuerta, *Inorg. Chem., 14* (1975) 116; (b) C. Krüger, *J. Organomet. Chem., 22* (1970) 697; (c) B.M. Chisnall, M. Green, R.P. Hughes and A.J. Welch, *J. Chem. Soc., Dalton Trans.*, (1976) 1899; (d) M. Green and R.P. Hughes, *J. Chem. Soc., Dalton Trans.*, (1976) 1907.

5 *The Sadtler Standard Spectra*, ^{1}H NMR spectrum No. 6858M and ^{13}C NMR spectrum No. 1058C.

6 N.M. Alcock, C.J. Richards and S.E. Thomas, *Organometallics, 10* (1991) 231.

7 Crystal data for I: $C_{25}H_{14}O_9Fe_2$, $M = 570.12$; triclinic, space group $P\bar{1}$; $a = 9.677(5)$, $b = 10.635(5)$, $c = 13.471(6)$ Å, $\alpha = 104.24(3)°$, $\beta = 105.46(4)°$, $\gamma = 104.75(4)°$, $V = 1216.7$ Å^3, $Z = 2$, $D_x = 1.56$ g cm^{-3}, $F(000) = 576$; μ(Cu Kα) = 100.6 cm^{-1}. Data collected on a Nicolet P3F diffractometer at room temperature: $R = 0.051$, $R_w = 0.057$ for 2341 observed reflections ($F > 3\sigma(F)$).

8 (a) J.A. Deeming, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 4, Pergamon, Oxford, 1982, p. 387 and references therein; (b) L.K. Liu, C.H. Sun, C.-Z. Yang, Y.-S. Wen, C.-F. Wu, S.-Y. Shih and K.-S. Lin, *Organometallics, 11* (1992) 972; (c) Y. Hsiou, Y. Wang and L.-K. Liu, *Acta Crystallogr., C45* (1989) 721; (d) P.-S. Lei and P. Vogel, *Organometallics, 5* (1986) 2500 and references therein.