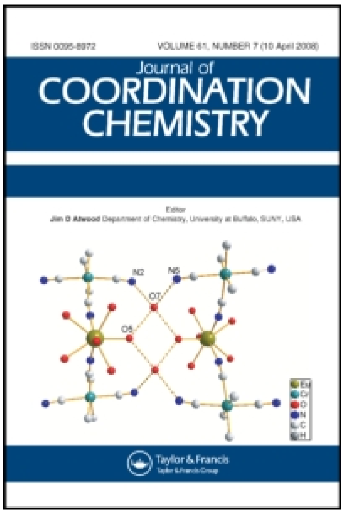

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SYNTHESIS OF NOVEL DINUCLEAR COMPLEXES OF Fe(O) DERIVED FROM 1,2-DICARBONYLIC MONOHYDRAZONES

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SYNTHESIS OF NOVEL DINUCLEAR COMPLEXES OF Fe(O) DERIVED FROM 1,2-DICARBONYLIC MONOHYDRAZONES

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Synthesis of three novel dinuclear complexes of Fe(O) are reported. **1a–c** were prepared by reaction of the corresponding monohydrazones with $Fe_2(CO)_9$. The structures of the complexes were determined by IR, ^1H and ^{13}C-NMR and HR-MS.

Keywords: Dinuclear Fe(O) complexes; monohydrazones; bimetallic; $Fe_2(CO)_9$

INTRODUCTION

The ever increasing interest in transition metal complexes has led to exploration of a wide range of functional groups in order to prepare novel compounds. For example, the role of Fe(O) η^4–vinylketene complexes in organometallic chemistry and organic synthesis has been recently demonstrated by Thomas *et al.*[1–5] Especially noteworthy is formation of

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vinylketene complexes from reaction of an alkyllithium with iron tricarbonyl complexes of vinylketones under a carbon monoxide atmosphere.[6] In our previous work related to the preparation of novel (η^2), (η^2, η^2)-dinuclear and (η^4)–Fe(O) complexes derived from dibenzylideneacetone, Thomas' method was applied to the subsequent transformation to Fe(O) ketene complexes.[7]

On the other hand, metal hydrazones have been extensively used in recent years as antitumor reagents,[8] antibacterial compounds,[9] in antianemic formulations,[10] etc, and also have widespread application in synthetic and analytical chemistry.[11] Our interest was focused on the coordination ability of Fe(O) towards monohydrazones of 1,2-dicarbonylic compounds as heteroatom analogues of α,β-unsaturated ketones. To the best of our knowledge, no reports of metalhydrazone complexes with free carbonyl groups coordinated to Fe(O) have appeared in the literature.

We herein present our preliminary findings concerning the novel dinuclear complexes of Fe(O) **1a–c** derived from monohydrazones of 1,2-dicarbonylic compounds (Figure 1).

RESULTS AND DISCUSSION

Formation of Di-μ-N-[(2-oxo-1,2-diphenylethaniminato)]-$Fe_2(CO)_4$, Complex 1a

When benzil-monodiphenylhydrazone was allowed to react with $Fe_2(CO)_9$ in anhydrous diethyl ether under reflux in a nitrogen atmosphere for 18 h, the

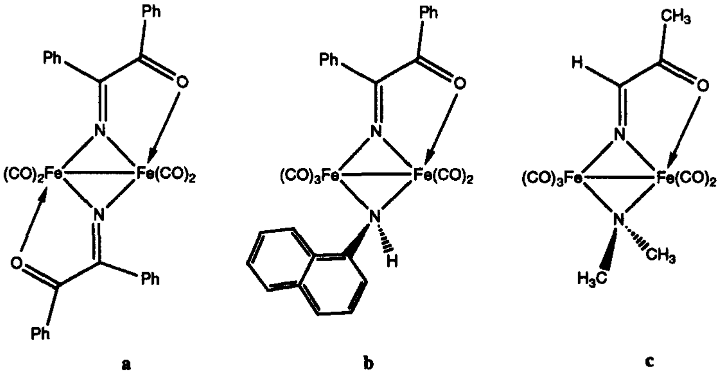

FIGURE 1 Complexes derived from 1,2-dicarbonylic monohydrazones.

formation of a new complex was observed by thin layer chromatography. After evaporation of the solvent, the reaction mixture was chromatographed on silica-gel to produce the new complex **1a** (20% yield), and an organic compound in 35% yield.

The new complex, isolated as a red solid, was assigned structure **1a** from spectral data. IR analysis revealed absorption bands $\nu(C{\equiv}O)$ at 2071(s), 2038(vs) and 1995(s) cm^{-1}; a band at 1670(m) cm^{-1}, assigned to a coordinated CO group, was also observed. The ^1H-NMR spectrum displayed only a multiple signal between δ 6.9–8.7 ppm for protons attached to phenyl groups. The ^{13}C-NMR spectrum showed signals in the range δ 121–143 ppm from aromatic carbons, while the signals at 180, 193 and 210 ppm were assigned to the carbon atoms of an imine, CO and coordinated $C{\equiv}O$ groups, respectively. Mass spectrometry of this complex showed a molecular ion with m/z 640, and successive loss of four CO groups, a fact which along with the simplicity of ^1H and ^{13}C-NMR spectra prompted us to assume the existence of a symmetric dinuclear complex. High resolution mass spectrometry with FAB ion mode technique enabled us to determine some aspects of the structural assignment. Isotopic contributions of peaks in 528, 556, 584, 612 and 640 m/z led to elemental composition for species $[(M-4CO)^+, C_{28}H_{20}O_2N_2Fe_2^+]$, $[(M-3CO)^+, C_{29}H_{20}O_3N_2Fe_2^+]$, $[(M-2CO)^+, C_{30}H_{20}O_4N_2Fe_2^+]$, $[(M^+-CO)^+, C_{31}H_{20}O_5N_2Fe_2^+]$ and $[(M)^{+\bullet}, C_{32}H_{20}O_6N_2Fe_2^+]$, respectively. The unsaturation number of species with m/z 528, 554 and 584 held for values of 21, 22 and 23 unsaturations respectively. For a m/z 612, three alternative possibilities of elemental composition can be assumed, but there is only one which agrees for 24 unsaturations and a logical increase in the C and O content, according to the fragmentation pattern in the normal mass spectrum: M^+-CO. Finally, with m/z 640, we again found several (four) possibilities of elemental composition and only one which agreed with the number of unsaturations (25): $M^{+\bullet}$, $C_{32}H_{20}O_6N_2Fe_2^+$. Taking into account all these observations and considering that a number of nitrogen-bridged dinuclear derivatives of iron carbonyl compounds of this type have been prepared *inter alia* by Bagga *et al.*[12] from an azine and $Fe_2(CO)_9$ and by Kilner and Midcalf[13] as well as by Albini and Kisch,[14] the complex was given structure **1a** (Figure 1).

The organic compound, obtained as a colorless solid in 35% yield, was spectroscopically characterized and found to be diphenylamine. The presence of this by-product allowed us to assume rupture of the N–N bond of the ligand to give **1a** and diphenylamine.

Formation of μ-N-[(amino-1-naphthyl)-μ-N-(2-oxo-1,2-diphenylethaniminato)]-$Fe_2(CO)_5$, Complex 1b

The mono-1-naphthylhydrazone of benzil reacted with $Fe_2(CO)_9$ in the same conditions and after 18 h formation of **1b** was observed. After separation by chromatographic methods, the complex was obtained in 11.6% yield as a red solid and, based on the results for reaction of benzil-monodiphenylhydrazone and $Fe_2(CO)_9$, we expected that any benzilmonohydrazone would lead to the dinuclear complex **1a**, but in this case the NMR spectra were totally different from that of **1a**: the 300 MHz spectra had signals in the ^{1}H-NMR solely at δ 7.1–8.2 ppm for aromatic protons; the ^{13}C-NMR spectrum featured signals at δ 120–136 ppm corresponding to carbons of the naphthyl group and at δ 193–210 ppm signals attributed to coordinated C≡O groups, at δ 181 ppm a signal for a noncoordinated CO group and at δ 151 ppm a signal for the imine carbon. Its IR (KBr) spectrum displayed a weak absorption at 3064 cm^{-1} (N–H) and a typical pattern in the ν(C≡O) region with very strong absorptions between 1979–2067 cm^{-1} and at 1661(s) cm^{-1} for an α,β-unsaturated CO group. The complex showed a molecular ion of *m*/*z* 602 in its mass spectrum (electronic input, EI) and successive loss of five CO groups. High-resolution mass spectra exhibited only peaks from the fragment (M^+–CO) that indicated structure **1b** with successive loss of five CO groups, elementary composition and unsaturation number (U.S.) for peaks with *m*/*z* 574, U.S. = 22 [$(M-CO)^+$, $C_{28}H_{18}O_5N_2Fe_2$]; *m*/*z* 546, U.S. = 21 [$(M-2CO)^{+\bullet}$, $C_{27}H_{18}O_4N_2Fe_2$]; *m*/*z* 518, U.S. = 20 [$(M-3CO)^{+\bullet}$, $C_{26}H_{18}O_3N_2Fe_2$]; *m*/*z* 490, U.S. = 19 [$(M-4CO)^{+\bullet}$, $C_{25}H_{18}O_2N_2Fe_2$]; *m*/*z* 462, U.S. = 18 [$(M-5CO)^{+\bullet}$, $C_{24}H_{18}ON_2Fe_2$].

High-resolution mass spectral peak analysis afforded only one elementary composition in each case and, in this reaction, no naphthylamine was isolated or detected as a by-product. Considering both mass spectrometric data for successive loss of five CO groups and the lack of the 'expected' by-product naphthylamine, we concluded that the naphthyl fragment resulting from the rupture in the N–N bond of the ligand was coordinated to the metal atoms and spectroscopic data were in agreement with structure **1b**.

As a result of the above evidence, an alternative approach was made for the direct reaction between $Fe_2(CO)_9$ and dibenzilazine and, surprisingly, no reaction occurred.

Formation of μ-N-[(aminodimethyl)-μ-N(2-oxo-2-methylethaniminato)]-$Fe_2(CO)_5$, Complex 1c

The monodimethylhydrazone of pyruvaldehyde reacted with an excess of $Fe_2(CO)_9$ in anhydrous diethyl ether at room temperature to yield **1c** after

18 h. Silica-gel chromatography of the reaction mixture obtained upon evaporation of the solvent afforded the complex in 40% yield. This new compound, a red solid, displayed a complex pattern in the $\nu(C \equiv O)$ region of its IR spectrum, with bands at 2070, 2061, 1979, 1995, 1939 cm^{-1} (all vs).

In the ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) for **1c**, the singlet (3H) for the methyl of the acyl group appeared at δ 1.85 ppm and at δ 2.25 ppm another singlet (6H) for the two methyl groups attached to the nitrogen atom was observed; the proton of the imine was found at δ 4.07 ppm (1H). In mass spectrometry, the molecular ion peak with *m/z* 366 ($M^{+\bullet}$, $C_{10}H_{10}O_6N_2Fe_2^{+\cdot}$) was observed with successive loss of five CO groups and HR-MS confirmed the data for (M^+) as well as for $(M–CO)^+$.

From the above evidence we assigned structure **1c** for the complex.

CONCLUSION

In summary we report the synthesis of three novel dinuclear complexes of Fe(O) derived from 1,2-dicarbonyl monohydrazones conceived as the α,β-unsaturated-ketone analogues with β-positioned heteroatoms.

EXPERIMENTAL SECTION

General Methods

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian 300S spectrometer. IR spectra were recorded on a Perkin-Elmer 283 B or 1420 spectrometer. The FAB spectra were obtained on a JEOL JMS SX 102A mass spectrometer operated at an accelerating voltage of 10 kV. Samples were desorbed from a nitrobenzyl alcohol matrix using 6 keV Xenon atoms. The EI ionization mass spectra were acquired on a JEOL JMS-AX505 HA mass spectrometer operated in the positive ion mode. The acquisition conditions were: ion source temperature 230°C, ionization energy 70 eV, emission current 0.14 μA and ionization current 100 μA. Mass measurements in FAB were performed at 10000 resolution using electrical field scans and the polyethylene glycol ions as reference material. Melting points were measured using a Mel-Temp II apparatus and are uncorrected. Column chromatography was performed with Merck silica-gel (70–230 mesh) using ethyl acetate : hexane in different ratios as eluent. The starting materials were obtained from commercial suppliers (Aldrich and Fluka) and used as received. Reactions were perfomed under a nitrogen atmosphere in carefully dried glassware. Diethyl ether was distilled from sodium-benzophenone under an argon atmosphere.

Synthesis of Bis[μ-N-(imino-2-oxo-1,2-diphenylethane)]–$Fe_2(CO)_4$, Complex 1a

A solution of benzil-monodiphenylhydrazone (0.5 g, 1.3 mmol) in anhydrous diethyl ether was treated with $Fe_2(CO)_9$ (0.84 g, 2.7 mmol) under reflux for 18 h. After the reaction was complete, the solvent was evaporated under vacuum and the reaction mixture chromatographed on silica-gel. Elution with hexane/ethyl acetate in diferent ratios gave diphenylamine (35% yield) as a white solid (m.p. 45°C). IR (KBr): ν 3399 cm^{-1} (N–H). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.9–7.3 (m, 10H, Ar). ^{13}C-NMR (300 MHz, $CDCl_3$): δ 143.1, 129.3, 121.0, 117.6 (Ar). EI-MS. (M^+) 179 and **1a** (20% yield) as a red solid (m.p. 117°C). IR (KBr): ν 2071(s), 2038(vs), 1995(s) cm^{-1} ($C\equiv O$) and 1670(m) cm^{-1} (CO). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.3–6.9 (m, 20H, Ar). ^{13}C-NMR (300 MHz, $CDCl_3$): δ 210 (M–CO), 193 (CO), 180 (C=N), 121–143 (Ar). HR-MS. (M^+), $C_{32}H_{20}O_6N_2Fe_2$, Found: 639.9961 Calc.: 640.0020; (M^+–CO) $C_{31}H_{20}O_5N_2Fe_2$, Found: 612.0049, Calc.: 612.0071; $(M-2CO)^+$ $C_{30}H_{20}O_4N_2Fe_2$, Found: 584.0145, Calc.: 584.0122; $(M-3CO)^+$ $C_{29}H_{20}O_3N_2Fe_2$, Found: 556.0181, Calc.: 556.0173; $(M-4CO)^+$ $C_{28}H_{20}O_2N_2Fe_2$, Found: 528.0258, Calc.: 528.0224.

Synthesis of μ-N-[(amino-1-naphthyl)-μ-N-(imino-2-oxo-1,2-diphenylethane)]–$Fe_2(CO)_5$, Complex 1b

A solution of mono-1-naphthylhydrazone (1 g, 2.9 mmol) reacted with $Fe_2(CO)_9$ (3 g, 8.3 mmol) in anhydrous diethyl ether at room temperature for 18 h. After chromatography as above, we obtained **1b** (11.6% yield) as a red solid (m.p. 45°C). IR (KBr): ν 3064(w) cm^{-1}(NH), 2067(vs), 2034(vs), 2005(vs), 1979(vs) cm^{-1} ($C\equiv O$) and 1661(s) cm^{-1} (CO). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.2–7.1 (m, 17H, Ar). ^{13}C-NMR (300 MHz, $CDCl_3$): δ 210–193 (M–CO), 181 (CO), 151 (C=N), 136–120 (Ar). EI-MS. (M^+) 602. HR-MS. $(M-CO)^+$ $C_{28}H_{18}O_5N_2Fe_2$, Found: 573.9909, Calc.: 573.9915; $(M-2CO)^+$ $C_{27}H_{18}O_4N_2Fe_2$, Found: 545.9965, Calc.: 545.9965; $(M-3CO)^+$ $C_{26}H_{18}O_3N_2Fe_2$, Found: 518.0016, Calc.: 518.0016; $(M-4CO)^+$ $C_{25}H_{18}O_2N_2Fe_2$, Found: 490.0072, Calc.: 490.0067. $(M-5CO)^+$ $C_{24}H_{18}O_1N_2Fe_2$, Found: 462.0127, Calc.: 462.0118.

Synthesis of μ-N-[(aminodimethyl)-μ-N(imino-2-oxo-2-methylethane)]-$Fe_2(CO)_5$, Complex 1c

A solution of pyruval-monodimethylhydrazone (3 g, 26.3 mmol) reacted with $Fe_2(CO)_9$ (16 g, 52.5 mmol) in anhydrous diethyl ether at room temperature for 18 h. After chromatography as above, the complex **1c** (40% yield) was obtained as a red solid (m.p. 63°C). IR (KBr): ν 2070(vs), 2061(vs), 1979(vs), 1955(vs), 1939(vs) cm^{-1} (C≡O). ^1H-NMR (300 MHz, $CDCl_3$): δ 4.07 (s, 1H, H-C=N), 2.25 (s, 6H, Me_2N), 1.85 (s, 3H, CH_3C). ^{13}C-NMR (300 MHz, $CDCl_3$): δ 208, 212 (M-CO), 51, 73 ($(CH_3)_2N$), 22 (CH_3CO). EM (*m*/*z*): 366 (M^+, $C_{10}H_{10}O_6N_2Fe_2$), 338 $(M-CO)^+$, 310 $(M-2CO)^+$, 282 $(M-3CO)^+$, 254 $(M-4CO)^+$, 226 $(M-5CO)^+$. HR-MS. $(M)^+$ $C_{10}H_{10}O_6N_2Fe_2$, Found: 365.9235, Calc.: 365.9238; $(M-CO)^+$ $C_9H_{10}O_5N_2Fe_2$, Found: 337.9288, Calc.: 337.9289.

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