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Novel coupling between tricarbonyl(7-azabenzonorbornadiene)iron complexes and cyclohexene to form stereospecifically a (C-5 substituted η^4-cyclohexadiene)Fe(CO)$_3$ moiety

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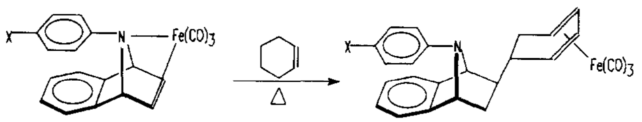
Abstract

Novel coupling between tricarbonyl(7-azabenzonorbornadiene)iron complexes **1** and cyclohexene occurs thermally and photochemically. Complexes **2** were formed stereospecifically with a yield of 21–34% via C–C bond formation from the exo-face of 7-ABND accompanied by the generation of ($^4\eta$-cyclohexadiene)Fe(CO)$_3$ moieties with Fe(CO)$_3$ *syn* to the new C–C bond. At the same time, C-5 of this moiety was functionalized with a bulky 7-ABND heterocycle.

Key words: Iron; Azobenzonorbornadiene; Carbonyl; Coupling; Cyclohexane; Stereospecific

Metal-mediated coupling reactions of norbornadienes or norbornene are rich and synthetically valuable [1]. However, to our knowledge similar reactions on the corresponding aza-analogues, *e.g.*, 7-azabenzonorbornadienes(ABND) have not been reported. We have been interested in the iron carbonyl-promoted reactions of 7-azabenzonorbornadienes(7-ABND), which have proved potentially useful for application in organic synthesis [2(a)]. During the reactions, two types of new complexes namely (ABND)Fe(CO)$_3$ and (ABND)Fe(CO)$_4$ were isolated and identified as the key intermediates [2]. Iron carbonyl is a cheaper and more versatile reagent and is known to be capable of isomerizing alkene through an (η^3-allyl)iron hydride intermediate which could be trapped by a suitable alkene such as 7-ABND containing a non-isomerable strained double bond. Cyclohexene was therefore chosen as the partner and allowed to react with (ABND)-Fe(CO)$_3$ in this study. Novel coupling was found to occur stereospecifically to produce complexes containing (C-5 substituted $^4\eta$-cyclohexadiene)Fe(CO)$_3$ moieties [3].

Reaction of **1** (**1a**, X = H; **1b**, X = F; **1c**, X = Cl) under thermal conditions (70–80°C) with cyclohexene in cyclohexane as solvent provided 7–11.4% yields of new complexes **2** (**2a**, X = H; **2b**, X = F; **2c**, X = Cl)



1 **2**

as the minor products as well as naphthalene as the major product (74–81%) which is expected as the result of nitrene-extrusion reaction. Complexes **2**, obtained as stable pale yellow crystals, show IR absorptions at ν_{CO} = 2038–2040 cm^{-1}, and 1953–1965 cm^{-1}. The structures of **2** agree with the above IR data, and also with the two non-equivalent bridgehead proton signals (δ 4.59, 4.97) and the high-field shifted signals of the coordinated vinylic protons H-1 and H-4 (δ 3.08, 3.31) as well as H-2 and H-3 (δ 5.23, 5.24) on the (C-5 substituted $^4\eta$-cyclohexadiene)Fe(CO)$_3$ moiety in the ^{1}H NMR spectra. The structures were further confirmed by ^{13}C NMR spectra [4*] and X-ray diffraction methods [5*]. An ORTEP diagram of the molecular structure of **2a** is shown in Fig. 1. The molecule consists of a (C-5 substituted $^4\eta$-cyclohexadiene)Fe(CO)$_3$ moiety. Three carbonyl groups coordinated to Fe atom

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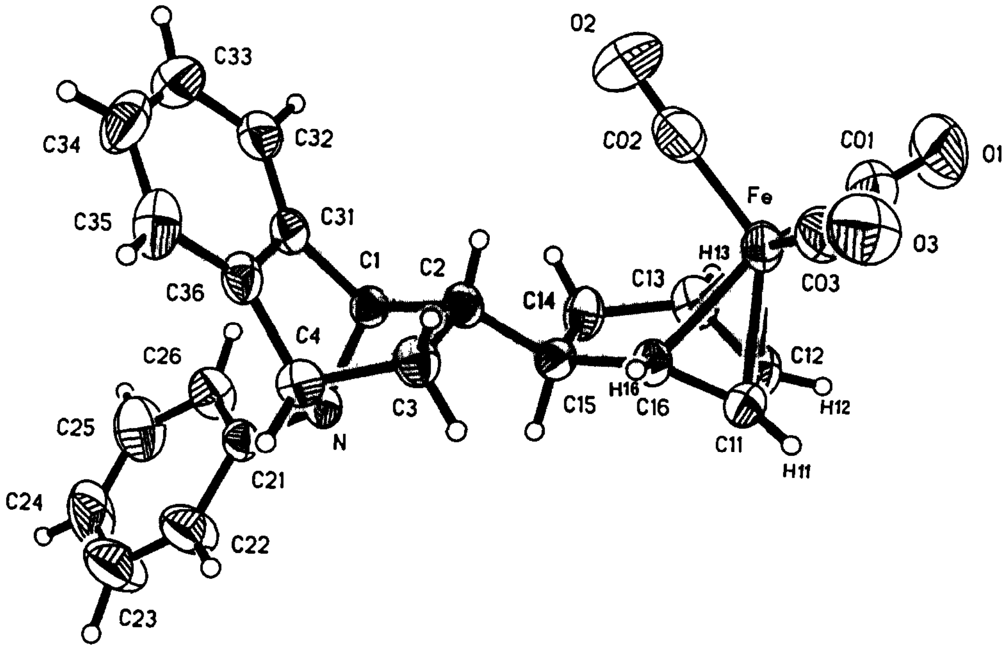

Fig. 1. ORTEP diagram of the molecular structure of **2a**.

are mutually *cis* to each other. The Fe–CO distances are 1.781(4), 1.782(4) and 1.791(6) Å, respectively. The conjugated double bonds on the cyclohexadiene ring interact in a π way with the Fe atom. The three C–C distances of the diene are C11C12 = 1.406(6), C12C13 = 1.399(6) and C11C16 = 1.427(5) Å. The nearly equivalent C–C distances indicate that the π electrons are delocalized on these four C atoms. The longer C–C distance compared with the C–C distance, 1.337(2) Å, of free ethylene [6] suggest that metal–olefin back bonding occurs. The two α angles [7] defined as the angle of H11C11C12 and H16C16C15, and the angle of H12C12C11 and H13C13C14 are 33.6° and 30.0°, respectively. The deviation of these two angles away from linearity also supports that there is a back bonding interaction. The bond angles and bond lengths are in the range of normal (diene)Fe(($CO)_3$ complexes [8].

Complexes **2** were also obtained by irradiation (at 300 nm, Rayleigh Photochemical Reactor) of a cyclohexane solution of **1** in the presence of excess cyclohexene. The yields of **2** were improved to double (14.2–21.8%) as compared with the case of thermal reaction (7–11.4%). Under photochemical condition the nitrene-extrusion reaction, leading to naphthalene, appear suppressed in such a way as to make the formation of complexes **2** appear enhance to slight but noticeable extent. Furthermore, this trend was clearly observed as neat cyclohexene was applied without cyclohexane as the solvent; the yields of **2** rose to 21–34% with further reduction in the production of naphthalene.

Under either thermal or photochemical conditions, the dissociation of the weakest Fe–N bond of **1** around the coordination sphere was presumably initiated to create a coordinatively unsaturated intermediate, from which further reaction pathways become available. Among them, as shown by our results, in the presence of cyclohexene the nitrene-extrusion reaction still prevailed while coupling reactions between **1** and cyclohexene were found to afford **2**. The formation of complexes **2** was accomplished via C–C bond formation accompanied by generation of ($^4\eta$-cyclohexadiene)Fe($CO)_3$ moieties. At the same time, C-5 of this moiety was functionalized with a bulky heterocycle.

The synthetic methods for ($^4\eta$-cyclohexadiene)Fe($CO)_3$ complexes, presented in Pettit and Emerson's review, where conjugated or nonconjugated dienes were allowed to react with $Fe(CO)_5$, $Fe_2(CO)_9$, or $Fe_3(CO)_{12}$ are already well known [9]. To the best of our knowledge, the formation of ($^4\eta$-cyclohexadiene)Fe($CO)_3$ from the reaction of ironcarbonyl complexes **1** and monoene such as cyclohexene may afford a new entry to the synthetic methodology.

We thus propose the intermediacy of (η^3-cyclohexenyl)iron hydride, which has been well-characterized and studied [10], is presumably formed upon coordination of cyclohexene on a coordinatively unsaturated complex species generated during the reactions and undergo metal hydride insertion into the ABND

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

double bond from *exo* side. No significant substituent effects were observed (X = H, F, Cl) However, the yields of **2** were apparently increased either as the reactions were carried out under neat cyclohexene as compared with cyclohexene/cyclohexane or under photochemical condition as compared with thermal conditions. This indicates that coordination of cyclohexene to the Fe atom leading to **1** with formation one C–C bond and Fe–mediated deamination where the cleavage of two C–N bonds is facilitated and favoured by higher temperature, are competitive pathways. Under photochemical and/or neat conditions at ambient temperature, the concentration of cyclohexene-coordinated complex species will increase further to result in better yields of **1** when compared to thermal conditions.

To conclude, a novel coupling reaction has occurred stereospecifically between complexes **1** and cyclohexene to produce (C-5 substituted $^4\eta$-cyclohexene)Fe-$(CO)_3$ complexes. This affords a new entry to a synthetic methodology for ($^4\eta$-cyclohexene)$Fe(CO)_3$ complexes. The mechanism for the formation of **2** is quite unusual and its elucidation requires further study. The coupling reactions of other types of (ABND)$Fe(CO)_3$ with a variety of olefins are now under investigation.

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4 Spectroscopic data for compound **2a**: IR (υ_{CO}, cm^{-1}, KBr): 2038, 1963; ^1H NMR spectrum (200 MHz, $CDCl_3$ standard $SiMe_4$): δ 7.4 (m, 6H), 6.71 (m, 2H), 5.26 (AB system, $\delta_A = 5.34$, $\delta_B = 5.23$, $J_{AB} = 5$ Hz, 2H), 4.97 (d, $^3J(H, H) = 4$ Hz, 1H), 4.59 (s, 1H), 3.08 (d, $J = 6.4$ Hz, 1H), 2.24 (m, 1H), 1.74 (m, 5H); $^{13}C\{^1H\}$ NMR (200 MHz, $CDCl_3$) δ 211.94, 128.50, 126.38, 126.1, 120.40, 120.20, 119.80, 117.55, 86.54, 83.56, 66.16, 65.13, 64.15, 62.63, 64.15, 62.63, 47.70, 37.33, 34.55, 33.91.

Compound **2b**: IR (υ_{CO}, cm^{-1}, KBr): 2040, 1953; ^1H NMR (80 MHz, $CDCl_3$): δ 7.27–6.68, 5.37–5.21 (t, 2H), 4.97 (d, 1H, $J = 4$ Hz), 4.59 (s, 1H), 3.31 (m, 1H), 3.08 (d, 1H, $J = 6.4$ Hz), 1.53–190 (m, 6H), 1.53–190 (m, 6H).

Compound **2c**: IR (υ_{CO}, cm^{-1}, KBr): 2038, 1965; ^1H NMR (200 MHz, $CDCl_3$): δ 7.11 (m, 2H), 5.29 (dt, 2H, AB system, $\delta_A = 5.35$, $\delta_B = 5.24$, $J_{AB} = 5.4$ Hz), 5.00 (d, 1H, $J = 4.2$ Hz), 4.53 (s, 1H), 3.31 (m, 1H), 3.06 (d, 1H, $J = 6.4$ Hz), 2.24 (m, 1H), 1.75 (m, 5H), $^{13}C\{^1H\}$ NMR (200 MHz, $CDCl_3$) δ 211.87, 150.15, 144.47, 128.44, 126.53, 126.25, 120.47, 120.23, 118.80, 86.57, 83.54, 66.44, 64.87, 64.44, 62.53, 47.68, 37.32, 34.54, 33.85.

5 Crystal data: **2a**, $(C_{22}H_{21}N)Fe(CO)_3$, monoclinic, $P2_1$, $a = 10.716(2)$, $b = 8.554(2)$, $c = 11.626(2)$ Å, $\beta = 94.06(2)°$, $V = 1063.0(2)$ Å^3, $Z = 2$, Dcalcd = 1.372 g/cm^3, $\mu = 0.735$ mm^{-1}. Data were collected on a Siemens P4 diffractometer. Structure solution and refinements were carried out with the SHELXTL PLUS crystallographic package. The structure was solved by heavy atom methods. All non-hydrogen atoms were refined anisotropically. Convergence to final R values of $R = 0.0341$ and $R_w = 0.0366$ and $S = 0.76$ by using 2774 reflections ($F > 4\sigma(F)$) and 295 parameters.

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