

SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF BROMO(*syn*- η^3 -2,4-PENTADIENYL)TRICARBONYLIRON

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(Received October 11th, 1985; in revised form January 11th, 1986)

Summary

The reaction between *trans*-1-bromopenta-2,4-diene and nonacarbonyldiiron in pentane yields (*syn*- η^3 -C₅H₇)Fe(CO)₃Br. The spectroscopic data and chemical reactivities of this compound are reported and discussed.

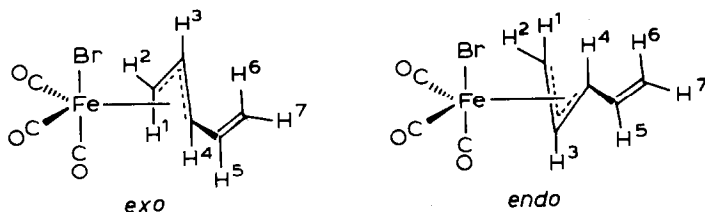
Introduction

The chemistry of pentadienyl-transition-metal complexes has recently attracted considerable attention [1,2]. The presence of appropriate reagents such as the pentadienyltin compound (C₅H₇)Sn(CH₃)₃ [3] and pentadienyl alkaline-metal salts C₅H₇M [4] (M = Li, Na, K) has largely contributed to the synthesis and prompted the rapid development in this area. The allyl halide is a convenient reagent for the preparation of many allyl-transition-metal compounds [5]. In principle, the 1-halo-penta-2,4-diene should be useful for the synthesis of the corresponding pentadienyl complexes; nevertheless, examples are rare in the literature [6]. In this paper, we report the synthesis of the title compound from the reaction of nonacarbonyldiiron with *trans*-1-bromopenta-2,4-diene and its chemical reactivities.

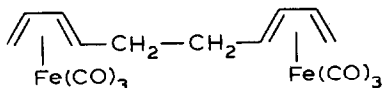
Results and discussion

When a pentane solution of *trans*-1-bromopenta-2,4-diene was stirred with Fe₂(CO)₉ at 30°C for 4 h, the red compound (*syn*- η^3 -C₅H₇)Fe(CO)₃Br (**1**) was obtained. The structure of **1** was assigned on the basis of the spectroscopic data. The formula of **1** was confirmed by both elemental analysis and the mass spectrum, which showed the highest mass ion of 286, 288 and fragment ions from the successive loss of CO. The resonances in the ¹H NMR spectrum (C₆D₆) 3.13 (d, H¹), 3.30 (d, H²), 3.95 (td, H³), 4.92 (dd, H⁷), 5.02 (dd, H⁴), 5.30 (dd, H⁶), 5.80 (dt, H⁵) ppm are characteristic of an η^3 -pentadienyl ligand. The *syn* configuration was assigned to compound **1** based on the magnitude of the coupling constant *J*(H³H⁴)

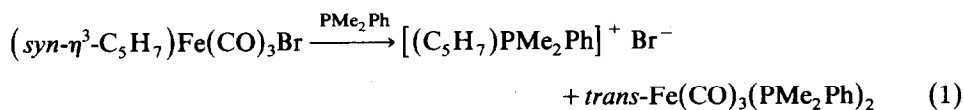
of 13 Hz, indicating that these two protons are in a *trans* arrangement. Moreover, the IR spectrum of **1** in pentane shows, in addition to the characteristic absorption band of $\nu(\text{C}=\text{C})$ (1620 cm^{-1}), bands of $\nu(\text{C}=\text{O})$ at 2087, 2044 and 2007 cm^{-1} . As inferred from the stereochemistry [7] of the related complex $(\eta^3\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_3\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCO}$), there might exist two isomers: the *endo* and *exo* forms. In general, the *endo* form is the major isomer in solution. In our case, none of the spectroscopic data showed the presence of the other isomer.



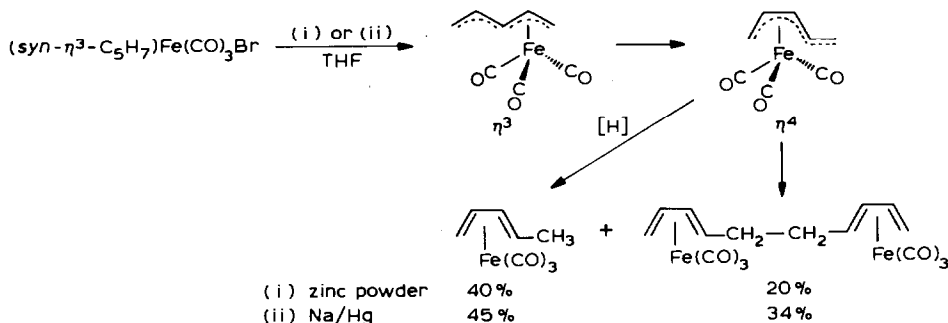
The reaction of 1-chloropenta-2,4-diene with excess $\text{Fe}_2(\text{CO})_9$ did not give the expected compound $(\text{syn-}\eta^3\text{-C}_5\text{H}_7)\text{Fe}(\text{CO})_3\text{Cl}$. 1,3,7,9-Decatetraene (50% yield) and bis(pentadienyl tricarbonyliron) (**2**, 20% yield) were isolated as products. The latter compounds have been obtained previously from the reaction of $\text{Fe}(\text{CO})_5$ with penta-1,4-diene-3-ol [8].



In order to explore further the chemical reactivities of the pentadienyl ligand in compound **1**, chemical reduction and ligand substitution reactions were performed. One of the carbonyl groups in the compound $(\eta^3\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_3\text{X}$ ($\text{X} = \text{Br}, \text{I}$) is prone to undergo substitution with trivalent phosphorus ligands [9]. However, the reaction of $\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)$ with compound **1** at 0°C gave the products shown in eq. 1:



The ionic compound $[(\text{C}_5\text{H}_7)\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)]^+ \text{Br}^-$ could also be obtained from the reaction of 1-bromopenta-2,4-diene with $\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)$ in pentane at 0°C . An example [10] of interest in the literature is the reaction of $(\eta^3\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_3\text{I}$ with tris(dimethylamino)phosphine, which results in the loss of both allyl and iodide to form *trans*- $\text{Fe}(\text{CO})_3[\text{P}(\text{Me}_2\text{N})_3]_2$. These results might lead us to believe that the reaction depicted in eq. 1 involves the attack of PMe_2Ph on iron which induces the elimination of pentadienyl bromide from the $\text{Fe}(\text{CO})_3$ moiety. Reduction of **1** with sodium amalgam or zinc powder in THF gave products consisting mainly of $(\eta^4\text{-trans-C}_5\text{H}_8)\text{Fe}(\text{CO})_3$ and bis(pentadienyl tricarbonyliron) (**2**). $(\eta^3\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_3\text{Br}$ can be converted into the radical $(\eta^3\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_3$ [11] by mild reduction, and into the anion $(\eta^3\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_3^-$ [12] by reduction with zinc powder or sodium amalgam. In our case, formation of the radical $(\text{C}_5\text{H}_7)\text{Fe}(\text{CO})_3$ as the reduction intermediate is more likely. As depicted in Scheme 1, the radical $(\eta^3\text{-C}_5\text{H}_7)\text{Fe}(\text{CO})_3$, in either η^3 - or η^4 -configuration, undergoes hydrogen abstrac-



SCHEME 1

tion or self-coupling to afford the observed products. Tetrahydrofuran is possibly the hydrogen source for the hydrogen abstraction reaction since the combined yields of the two products are rather high. The reluctance of the radical to undergo further reduction might arise from delocalization of the unpaired electron over the pentadienyl ligand which contributes to the stabilization.

Experimental

All reactions were carried out under dry nitrogen using Schlenk tube techniques. *trans*-1-Halopenta-2,4-dienes ($\text{CH}_2=\text{CHCH}=\text{CH}-\text{CH}_2\text{X}$, $\text{X} = \text{Cl}, \text{Br}$) were synthesized by treating penta-1,4-diene-3-ol [13] with the acid HX ($\text{X} = \text{Cl}, \text{Br}$) at 0°C . NMR spectra were recorded on either a Jeol FX-100 or a Varian EM-390 spectrometer. Microanalyses were performed at the Microanalytic Laboratory, National Taiwan University.

Preparation of $(\text{syn-}\eta^3\text{-C}_5\text{H}_7)\text{Fe}(\text{CO})_3\text{Br}$

trans-1-Bromopenta-2,4-diene (1.2 g, 8.2 mmol) in pentane (20 ml) was stirred with nonacarbonyldiiron (4.0 g, 11 mmol) at 30°C for 4 h. After the insoluble solids were filtered off, the solvent was evaporated in vacuo to leave a red oil. Recrystallization from pentane solution at -25°C afforded red crystals (1.5 g, 5.2 mmol), m.p. $5\text{--}6^\circ\text{C}$. Anal. Found: C, 33.20; H, 2.59. $\text{C}_8\text{H}_7\text{O}_3\text{BrFe}$ calcd.: C, 33.44; H, 2.46%; Mass spectrum, m/e : 286, 288 (M^+); 258, 260 ($M^+ - \text{CO}$); 230, 232 ($M^+ - 2\text{CO}$), 202, 204 ($M^+ - 3\text{CO}$). IR spectrum (in pentane) $\nu(\text{CO})$: 2087(vs), 2044(vs) and 2007(vs) cm^{-1} ; $\nu(\text{C}=\text{C})$ 1620 (w) cm^{-1} . ^1H NMR (100 MHz, C_6D_6): δ 3.13 (1H,d, H^1), 3.30 (1H,d, H^2), 3.95 (1H, td, H^3), 4.92 (1H,dd, H^7), 5.02 (1H,dd, H^4) 5.30 (1H,dd, H^6), 5.80 (1H, dt, H^5); $J(\text{H}^1\text{H}^3)$ 13 Hz, $J(\text{H}^2\text{H}^3)$ 8 Hz, $J(\text{H}^3\text{H}^4)$ 13 Hz, $J(\text{H}^4\text{H}^5)$ 9 Hz, $J(\text{H}^5\text{H}^7)$ 9 Hz, $J(\text{H}^6\text{H}^7)$ 1 Hz.

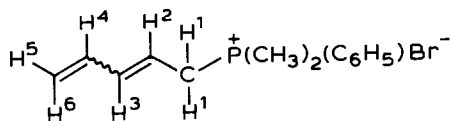
Reduction of $(\text{syn-}\eta^3\text{-C}_5\text{H}_7)\text{Fe}(\text{CO})_3\text{Br}$ with zinc powder

$(\eta^3\text{-C}_5\text{H}_7)\text{Fe}(\text{CO})_3\text{Br}$ (4.5 g, 15.6 mmol) was stirred with zinc powder (3.2 g, 50 mmol) in THF (20 ml) at 30°C for 3 h. After filtration, the solvent was evaporated in vacuo (2 torr) at 0°C . Distillation of the remaining oil in vacuo (10^{-3} torr) at 30°C afforded crude $(\eta^4\text{-trans-C}_5\text{H}_8)\text{Fe}(\text{CO})_3$ (1.28 g, 6.2 mmol), which was identified spectroscopically. The residue was extracted with pentane, and crystallization from this solvent gave yellow crystals (0.69 g, 1.6 mmol) of compound 2. The ^1H

NMR, IR and mass spectra of the latter were identical to those of an authentic sample reported in the literature [8]. Reduction of **1** with sodium amalgam was conducted in a similar manner, giving (η^4 -*trans*-C₅H₈)Fe(CO)₃ and **2** in 45 and 20% yields, respectively.

Reaction of (syn- η^3 -C₅H₇)Fe(CO)₃Br with P(CH₃)₂(C₆H₅)

P(CH₃)₂(C₆H₅) (2 g, 14 mmol) was added dropwise to a rapidly stirred solution of **1** (1.0 g, 3.5 mmol) in pentane (20 ml) at 0°C over 1 h. The insoluble precipitates characterized as *trans*-Fe(CO)₃[P(CH₃)₂(C₆H₅)₂] (1.1 g, 2.6 mmol) were filtered off. The solvent was evaporated to dryness to yield dark brown residues. The compound [(C₅H₇)P(CH₃)₂(C₆H₅)]⁺ Br⁻ was extracted with chloroform, and recrystallization from chloroform/pentane at -20°C gave colourless crystals (0.64 g, 2.2 mmol). Anal. Found: C, 54.14; H, 6.51. C₁₃H₁₈PBr calcd.: C, 54.54; H, 6.31%. ¹H NMR spectrum (90 MHz, CDCl₃): δ 2.50 (6H, d, P-CH₃, *J*(PH) 14 Hz), 4.05 (2H, dd, H¹, *J*(H¹P) 16 Hz, *J*(H¹H²) 7 Hz) 5.05–5.50 (3H, m, H⁶, H⁵ and H³), 6.00–6.40 (2H, m, H² and H⁴), 7.60–8.20 (5H, m, P-C₆H₅).



Acknowledgement

We wish to thank the National Science Foundation, R.O.C. (NSF-M007C-05) for financial support of this work.

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