

Synthesis and Characterization of an Arene Tricarbonyl Complex [C₈H₄N₂(CH₂)₂Fe(CO)₄Mo(CO)₃]

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Abstract

Reaction of 2,3-*bis* (σ -methylene) quinoxalinetetracarbonyliron [C₈H₄N₂(CH₂)₂Fe(CO)₄] (**1**) with *tris*(acetonitrile) molybdenumtricarbonyl [Mo(CO)₃(CH₃CN)₃] (**2**) results in the formation of an arenetricarbonyl complex [C₈H₄N₂(CH₂)₂Fe(CO)₄Mo(CO)₃] (**3**). The complex has been characterized by IR, ¹HNMR and mass spectral data.

Keywords: Quinoxaline, arene complex, ligand exchange, acetonitrile, milder condition, precursor.

Introduction

The synthesis of arenetricarbonyl complexes of group VIB metals by direct reaction of M(CO)₆ [M=Mo, Cr, W] with arene ligand is unsuitable for many aromatic molecules because high temperatures and long reaction times needed to effect substitution of carbonyl ligands [1]. This problem may be circumvented by prior formation of intermediate species of the type [M(CO)₃L₃; L=CH₃CN, THF, 4-methyl pyridine, NH₃] [2] which can undergo arene-L₃ exchange under milder conditions. In continuation along this line, we have investigated the reaction of 2,3-*bis*(σ -methylene) quinoxalinetetracarbonyl iron [C₈H₄N₂(CH₂)₂Fe(CO)₄] with *tris*(acetonitrile) molybdenumtricarbonyl [Mo(CO)₃(CH₃CN)₃]. The main objective was to see the possibility of the synthesis of arene tricarbonyl complex and the result is described in the present paper.

Experimental

All reactions and subsequent work-up were carried out in dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl prior to use. Acetonitrile was distilled under nitrogen over phosphorus pentoxide. Na₂[Fe(CO)₄] [3], [C₈H₄N₂(CH₂)₂Fe(CO)₄] [4] and [Mo(CO)₃(CH₃CN)₃] [5] were synthesized by the published method. Fe(CO)₅, Mo(CO)₆ were used as received. IR spectra were recorded on a Shimadzu 8010 spectrometer, ¹HNMR spectra on a Bruker 500 MHz spectrometer and mass spectra on a high resolution mass spectrometer.

Reaction of 2,3-*bis*(σ -methylene) quinoxalinetetracarbonyliron (**1**) with *tris*(acetonitrile) molybdenumtricarbonyl (**2**).

To a freshly prepared solution of [Mo(CO)₃(CH₃CN)₃] (0.1147g, 0.378 mmol) in acetonitrile (50 mL) was added dropwise a solution of 2,3-*bis*(σ -methylene)

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quinoxalinetetracarbonyliron (0.122g, 0.378 mmol) in the same solvent. (30 mL) under nitrogen at room temperature with vigorous stirring. After completion of addition, the mixture was allowed to stir for 30 hrs. The course of the reaction was monitored by analytical TLC. The solvent was then removed under reduced pressure and the residue was extracted with diethyl-ether and filtered on Kieselguhr. The filtrate was concentrated to dryness. The mixture was then chromatographed over a column of silica gel (230-400 mesh) and eluted with petroleum ether (40-60°C)-diethylether (1:2 v/v) which gave only one pale yellow band. The band on removal of solvent under vacuum yielded the arene complex, $[C_8H_4N_2(CH_2)_2Fe(CO)_4Mo(CO)_3]$ (**1**) as pale yellow crystals (0.074g, 36.4%).

IR (in cyclohexane): $\nu(CO)$ 2042, 1992, 1967 and 1942 cm^{-1} ; 1H NMR ($CDCl_3$): δ 2.72 (s, 4H), 7.67-7.63 (m, 2H), 7.98-7.94 (m, 2H); MS: m/z : 540 $[M^+]$, 324 $[M^+-Mo(CO)_3]$, 296 $[M^+-\{Mo(CO)_3 + CO\}]$, 268 $[M^+-\{Mo(CO)_3 + 2CO\}]$, 240 $[M^+-\{Mo(CO)_3 + 3CO\}]$, 212 $[M^+-\{Mo(CO)_3 + 4CO\}]$, 180 $[M^+-Mo(CO)_3]^+$, 156 $[M^+-\{Mo(CO)_3 + Fe(CO)_4\}]$, 152 $[M^+-\{Mo(CO)_3 + Fe(CO)_4 + CH_2\}]$, 128 $[M^+-\{Mo(CO)_3 + Fe(CO)_4 + 2CH_2\}]$, 121 $[M^+-Mo(CO)]^+$, 90 $[Mo]^+$ and 56 $[Fe]^+$.

Results and discussion

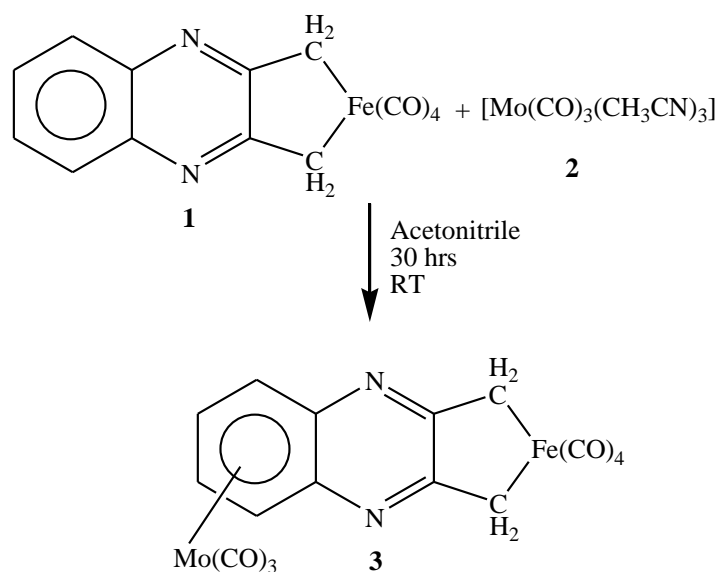
The reaction of 2,3-*bis*(σ -methylene)quinoxalinetetracarbonyliron (**1**) with *tris*(acetonitrile)-molybdenumtricarbonyl (**2**) in acetonitrile at room temperature under nitrogen atmosphere for 30 hrs resulted in the isolation of an arene complex **3** in 36.4% yield.

The IR spectrum of **3** in cyclohexane exhibited νCO bands at 2042, 1992, 1967 and 1942 cm^{-1} . These bands are regarded as terminal carbonyl stretching frequencies (1800-2140 cm^{-1}) [6]. The significant up-ward shifts in vibrational frequencies compared to those of starting σ -bonded complex $[C_8H_4N_2(CH_2)_2Fe(CO)_4]$ (νCO 1957 and 1934 cm^{-1}) [4], other similar and related compounds [7, 8, 9, 10] clearly indicates the formation of arene complex.

The 1H NMR spectrum of **3** in $CDCl_3$ exhibited signals at δ 2.72 (s, 4H), 7.67-7.63 (m, 2H) and 7.98-7.94 (m, 2H). The high field singlet at δ 2.72 is due to the methylene protons. The low field multiples at δ 7.67-7.63 and 7.98-7.94 are due to the four aromatic protons. The 1H NMR values of **3** are very similar to those of starting complex **1** [4, 10], which clearly indicates the formation of arene complex, where the $Mo(CO)_3$ moiety is attached to π -electrons of the aromatic ring.

The mass spectrum of **3** showed the molecular ion peak at m/z 540 corresponding to the proposed molecular formula $[C_8H_4N_2(CH_2)_2Fe(CO)_4]Mo(CO)_3$. Other important peaks at m/z, 324, 296, 268, 240, 212 and 156 indicates the successive loss $Mo(CO)_3$ moiety, four CO groups and Fe atom from M^+ .

Therefore on the basis of the above arguments and spectral evidences, structure **3** is assigned for this arene complex, which is shown in Scheme 1. The proposed structure of **3** also satisfies the 18-electron rule.



Scheme 1

Conclusion

Arene tricarbonyl complex, $[\text{C}_8\text{H}_4\text{N}_2(\text{CH}_2)_2\text{Fe}(\text{CO})_4\text{Mo}(\text{CO})_3]$ (**3**) has been prepared from the reaction of $[\text{C}_8\text{H}_4\text{N}_2(\text{CH}_2)_2\text{Fe}(\text{CO})_4]$ (**1**) with *tris*(acetonitrile) molybdenum tricarbonyl, $[\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3]$ (**2**). From our studies we can say that the synthesis of **3** can be possible from $[\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3]$ (**2**) by arene- $(\text{CH}_3\text{CN})_3$ exchange under milder conditions. Electron counts show the complex **3** conforms to the 18-electron rule. From this reaction it is expected that σ -bonded complex, $[\text{C}_8\text{H}_4\text{N}_2(\text{CH}_2)_2\text{Fe}(\text{CO})_4]$ (**1**) can serve as an important precursor for the synthesis of a series of arene tricarbonyl complexes, where $\text{M}(\text{CO})_3$ moiety [M Cr, Mo and W etc] is attached through π -electrons of the aromatic ring. Work in this respect is in progress and will be reported in future communications.

Acknowledgement

The authors are thankful to the Department of Chemistry, Jahangirnagar University for technical support.

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