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PREPARATION OF PENTAMETHYLCYCLOPENTADIENYLDIALKYLNITROSYLIRON COMPLEXES *

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Summary

The dimer $[(CH_3)_5C_5Fe(NO)]_2$ has been prepared by octane reflux of $[(CH_3)_5C_5Fe(CO)_2]_2$ under a NO atmosphere. Oxidative cleavage of the dimer with iodine yields $(CH_3)_5C_5Fe(NO)I_2$. Alkylation with two equivalents of RLi or RMgX ($R = CH_3$, $CH_2C_6H_5$, or $CH_2SC_6H_5$) leads to the dialkyl derivatives in good yields. All compounds are new and have been characterized by elemental analyses, IR, mass, ^1H and ^{13}C NMR spectra.

Introduction

The use of organoiron complexes as reagents in organic synthesis has reached a high level of efficiency and utility in the last ten years [1,2]. The vast majority of η^1-organoiron complexes which have been described thus far contain a single η^1-organic ligand and at least two stabilizing π-acid ligands such as CO and/or η^5-C_5H_5 [3]. In sharp contrast, relatively few organoiron complexes containing the nitrosyl (NO) ligand have been reported and the synthetic potential of such systems remains relatively unexplored [4]. We report herein the preparation of a series of new organoiron nitrosyl complexes, and preliminary studies of their chemistry are discussed.

Results and discussion

Recent studies in our laboratories have centered on the preparation and chemistry of cyclopentadienyldialkylnitrosyliron complexes, $(C_5H_5)Fe(NO)R_2$. We have found these complexes to be useful in the study of: (i) NO-insertion into metal–alkyl bonds

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[5], and (ii) reductive-elimination processes [6]. However, these studies have been hampered somewhat by low yields and/or poor thermal stability of the parent dialkyls.

Peralkylcyclopentadienyl ligands are well known for their ability to enhance certain physical and chemical properties in metal complexes relative to their unsubstituted C_5H_5 counterparts. For the compounds described herein, the use of the pentamethylcyclopentadienyl ligand has allowed for the synthesis of desired dialkylnitrosyliron complexes in greatly improved yields and with markedly enhanced thermal stabilities.

Synthesis of $[(CH_3)_5C_5Fe(NO)]_2$ and $(CH_3)_5C_5Fe(NO)I_2$ follows the methods of preparation for the C_5H_5 analogues [7,4a] with minor modifications. The metal–nitrosyl stretching frequencies ($\nu(N{\equiv}O)$) for $[(CH_3)_5C_5Fe(NO)]_2$ and $(CH_3)_5C_5Fe(NO)I_2$, as expected, were lower by 37 and 50 cm^{-1}, respectively, than for the corresponding C_5H_5 complexes.

Alkylation (eq. 1) of the diiodide complex is accomplished conveniently in diethyl ether at $-78°C$ using either a lithium alkyl or Grignard reagent for introduction of

$$\underset{(I)}{(CH_3)_5C_5Fe(NO)I_2} \xrightarrow[-78°C,\ Et_2O]{RLi\ \text{or}\ RMgX} (CH_3)_5C_5Fe(NO)R_2 \qquad (1)$$

$$(IIa: R = CH_3;\quad IIb: R = CH_2C_6H_5;\quad IIc: R = CH_2SC_6H_5)$$

the alkyl ligand. The major by-product observed is the dimer $[(CH_3)_5C_5Fe(NO)]_2$ (III), which is easily recovered on work-up of the desired dialkyl. In the preparation of IIa, CH_3MgCl is the reagent of choice as alkylation with $CH_3Li \cdot LiBr$ results in decreased yield of IIa and concomitant increased yield of III via reduction of I. This is not a problem in the case of $LiCH_2C_6H_5 \cdot 2C_4H_8O$ and $LiCH_2SC_6H_5 \cdot 2C_4H_8O$ and, in addition, the ability to employ these reagents as weighable crystalline solids, thereby obviating the additional procedure of titration, makes them very convenient reagents. The product dialkyls IIa, b, c are obtained as green crystalline solids, moderately air stable in the solid state at room temperature, but decomposing rapidly in O_2-containing solutions to as yet uncharacterized products. They are best stored as solids under inert atmosphere at temperatures below 0°C. The dibenzyl derivative IIb serves to illustrate the enhanced thermal stabilities of the C_5Me_5 complexes relative to their C_5H_5 counterparts (eq. 2) [6].

$$(C_5R_5)Fe(NO)(CH_2C_6H_5)_2 \xrightarrow{\Delta} [(C_5R_5)Fe(NO)]_2 + C_6H_5CH_2CH_2C_6H_5$$

$$(R = H,\ t_{1/2} \approx 30\ \text{min}\ T\ 0°C; \qquad (2)$$

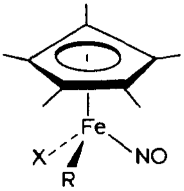
$$R = CH_3,\ t_{1/2} \approx 7\ \text{h}\ T\ 30°C)$$

The di(thiophenyl)methyl complex (IIc) undergoes an analogous reductive-coupling reaction (eq. 3).

$$\underset{(IIc)}{C_5Me_5Fe(NO)(CH_2SC_6H_5)_2} \xrightarrow[\substack{20°C \\ t_{1/2} \approx 5\ d}]{} \underset{(III)}{[(C_5Me_5)Fe(NO)]_2} + C_6H_5SCH_2CH_2SC_6H_5$$

$$(3)$$

This facile decomposition pathway has precluded the mass spectral observation of molecular ions for IIb and c. In each case, (i) the highest mass ion (EI or CI mode) corresponds to the dimer (III), and (ii) the base peak can be assigned to $[R]^+$, i.e., $[C_6H_5CH_2]^+$, *m/e* 91 (from IIb); and $[C_6H_5SCH_2]^+$, *m/e* 123 (from IIc). We defer discussion of kinetic and mechanistic details for the reductive-elimination reactions alluded to above until later contributions [6]. So as to avoid parasitic reductive-elimination processes and provide additional avenues of reactivity, we have initiated parallel studies of mono-alkylated iron complexes of the type shown (IV) [9].



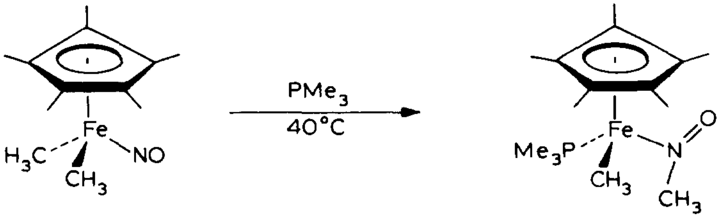
$(R = CH_3, C_6H_5, CH_2C_6H_5;$
$X = I, N(SiMe_3)_2, SCN)$

(IV)

The preparation and reactivity of such systems will be the subject of future papers.

In the ^1H NMR spectra of $(CH_3)_5C_5Fe(NO)R_2$, where $R = CH_2C_6H_5$ (IIb) and $CH_2SC_6H_5$ (IIc), the diastereotopic non-equivalence of the metal-bound methylene protons is indicated by the observance of AB quartets centered at δ 2.77 ppm (J(AB) 7.45 Hz, $\Delta\delta$ 0.49 ppm) and δ 2.85 ppm (J(AB) 5.86 Hz, $\Delta\delta$ 0.83 ppm), respectively. The observed values for J(AB) in these complexes are well within the range expected [8] for geminal H–C–H coupling constants, and the assignments have been confirmed by homonuclear decoupling experiments.

One of the most important modes of reactivity observed thus far for the dialkylnitrosyliron complexes involves migratory insertion of NO into the metal–carbon bond. For example, IIa undergoes such an insertion readily under mild conditions (eq. 4) [5,10].



(4)

(IIa) (V)

An identical insertion reaction has been reported [4b] for $(C_5H_5)Fe(NO)(CH_3)_2$, the $(C_5H_5)Fe(NO)(CH_3)_2$ having been obtained by a novel, albeit low yield (7%) alkyl transfer reaction. The generality of NO-insertion reactions in organoiron systems such as those described herein is under current study and will be reported subsequently.

Experimental

All procedures were performed in Schlenk-type glassware using normal bench-top Schlenk techniques [11], in Schlenk-type glassware interfaced to a high vacuum (10^{-4}–10^{-5} Torr) line, or in an argon filled glove-box. Argon (Linde, prepurified) was purified further by passage through a supported MnO oxygen removal column [12] and a Linde 4-Å molecular sieve column. Nitric oxide was purified by passage through a −78°C trap containing silica gel [13]. Toluene, octane, diethyl ether and pentane (previously refluxed over and distilled from Na/benzophenone) were transferred via cannula immediately prior to use. Dichloromethane was refluxed over and distilled from CaH_2 immediately prior to use and transferred via cannula. The lithium reagent $LiCH_2C_6H_5 \cdot 2C_4H_8O$ was obtained by metalation of toluene with s-butyllithium (Aldrich) in the presence of tetrahydrofuran [14]. Yellow needles of the complex were isolated from cold (−78°C) toluene/THF solutions. The lithium reagent $LiCH_2SC_6H_5 \cdot 2C_4H_8O$ was obtained by metalation of thioanisole with s-butyllithium in the presence of tetrahydrofuran. Colorless prisms of the complex were isolated from cold (−20°C) THF/pentane solutions.

All infrared spectra were recorded on a Perkin-Elmer 599B spectrometer and were calibrated with polystyrene film. Mass spectra were recorded on a VG 7070 mass spectrometer operating in the CI or EI mode. Both ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer. Multiplicities of ^{13}C resonances were determined with off-resonance decoupling methods. Chemical shifts are reported relative to internal $Si(CH_3)_4$. Elemental analyses were performed in-house by Mr. J. Papillon.

Preparation of $[(CH_3)_5C_5Fe(NO)]_2$ *(III)*

In the glove box, a 300 ml three-neck flask fitted with a three-way stopcock (Ar/NO inlet) was charged with 10 g (20.2 mmol) $[(CH_3)_5C_5Fe(CO)_2]_2$ [15], a septum and a stopper. Freshly distilled octane (ca. 200 ml) was added via cannula and a reflux condensor attached. The reaction was then refluxed for 18 h under a NO atmosphere. The reaction was allowed to cool under an argon flush and the solvent removed in vacuo. The solid was loaded into an inert-atmosphere continuous extraction apparatus and extracted with 100 ml CH_2Cl_2 through a plug (2.5 × 2.5 cm) of silica. The solution was then cooled to −78°C and the crystalline solid separated by filtration to yield 6.74 g (85% based on recovered starting material) of $[(CH_3)_5C_5Fe(NO)]_2$. Anal.: Found: C, 54.57; H, 6.93; N; 6.22. $C_{20}H_{30}N_2O_2Fe_2$ calcd.: C, 54.32; H, 6.85; N, 6.33%. ^1H NMR (CD_2Cl_2): δ 1.43 ppm, s; ^{13}C NMR (CD_2Cl_2): δ 8.30 ppm, q ($C_5\mathit{Me}_5$), δ 96.46 ppm, s (C_5Me_5). IR (cm^{-1} in C_6H_6): $\nu(N{\equiv}O)$ 1472s. Mass spectrum, EI (15 eV); *m/e* 442, rel. int. 100.

Preparation of $(CH_3)_5Fe(NO)I_2$ *(I)*

A 200 ml side-arm Schlenk flask was charged with 5.0 g (11.3 mmol) of $[(CH_3)_5C_5Fe(NO)]_2$ and 5.74 g (22.6 mmol) I_2 and a magnetic stir-bar. Freshly distilled CH_2Cl_2 (ca. 150 ml) was added via cannula and the solution stirred at room temperature for 8 h. The solvent was removed in vacuo, and the solid was loaded into the continuous extraction apparatus described above. Extraction with CH_2Cl_2 (ca. 125 ml) yielded a deep violet solution. Upon completion of extraction, the solution was concentrated to ca. 75 ml and cooled to −78°C. Filtration of the cold solution yielded 8.91 g (18.8 mmol, 83%) of black crystalline $(CH_3)_5C_5Fe(NO)I_2$. Anal.: Found: C, 25.23; H, 3.11; N, 2.90. $C_{10}H_{15}I_2NOFe$ calcd.: C, 25.29; H, 3.18; N, 2.95%. ^1H NMR (CD_2Cl_2): δ 2.15 ppm, s; ^{13}C NMR (CD_2Cl_2): δ 12.67 ppm, q ($C_5\mathit{Me}_5$), δ 110.69 ppm, s (C_5Me_5). IR (cm^{-1} in C_6H_6): $\nu(N{\equiv}O)$ 1785s. Mass spectrum EI (15 eV): *m/e* 475, rel. int. 1.37; *m/e* 444, rel. int. 15.6; *m/e* 347, rel. int. 65.2; *m/e* 317, rel. int. 100.

Preparation of $(CH_3)_5C_5Fe(NO)(CH_3)_2$ (IIa)

A 50 ml Schlenk flask was charged with 0.48 g (1.0 mmol) of I in the glove-box and a septum was attached. Diethyl ether (25 ml) was added via cannula, and the solution was cooled to −78°C. By syringe, 0.70 ml of CH_3MgCl (2.9 *M* in THF, 2.03 mmol) was added dropwise to the stirred solution. The reaction mixture was stirred at −78°C for 2 h and then allowed to warm slowly to 0°C. Stirring was continued at 0°C for an additional 2 h. The ether was removed in vacuo, and pentane (30 ml) was added via cannula. After stirring at room temperature the solution was filtered through a fine-porosity Schlenk frit. The solids were washed repeatedly by Soxhlet extraction by condensing 5–10 ml portions of pentane from the filtrate into the upper portion of the filtration apparatus. The pentane was removed in vacuo. The crude, dark green solid was then taken into the glove-box, dissolved in CH_2Cl_2 and chromatographed on SiO_2 (1 cm × 25 cm column) with CH_2Cl_2. The emerald-green band was collected and concentrated down, in vacuo, to ca. 10 ml. An aliquot (ca. 5 ml) of pentane was added and the green solution cooled to −78°C. The bright crystalline solid was isolated by cold filtration and dried in vacuo; yield: 80–85%. Anal.: Found: C, 57.24; H, 8.31; N, 547. $C_{12}H_{21}NOFe$ calcd.: C, 57.38; H, 8.43; N, 5.58%. ^1H NMR (tol-d_8): δ 0.94 ppm, s, 6H; δ 1.50 ppm, s, 15 H; ^{13}C NMR (tol-d_8): δ 5.98, q (Fe–CH_3); δ 8.66, q (C_5Me_5); δ 101.15 ppm, s (C_5Me_5). IR (cm^{-1} in C_6H_6): $\nu(N{\equiv}O)$ 1753 vs. Mass spectrum, CI: *m/e* 251 (M^+), 236 (base).

Preparation of $(CH_3)_5C_5Fe(NO)(CH_2C_6H_5)_2$

A 30 ml round-bottom flask with a side arm addition tube was charged with 0.47 g (1.0 mmol) $(CH_3)_5C_5Fe(NO)I_2$ and the addition tube charged with 0.48 g (2.0 mmol) of $LiCH_2C_6H_5 \cdot 2C_4H_8O$. Diethyl ether (20 ml) was condensed into the flask in vacuo at −78°C and the lithium reagent added. The reaction mixture was stirred at −78°C for 4 h, and at −20°C for an additional 4 h. The diethyl ether was then removed in vacuo. Toluene (25 ml) was condensed into the flask and the residue was extracted and filtered as described above for the dimethyl derivative. The filtrate was cooled to −78°C overnight. A yellow-green precipitate was then isolated by filtration. Yield: 40–45%. This complex may be recrystallized from cold toluene/pentane solutions. Anal.: Found: C, 71.23; H, 7.08; N, 3.62. $C_{24}H_{29}NOFe$ calcd.: C, 71.46; H, 7.25; N, 3.47%. ^1H NMR (CD_2Cl_2): δ 1.16, s, 15 H; δ 2.77 ppm, AB quartet (J(AB) 7.45 Hz, $\Delta\delta$ 0.489 ppm), 4H; δ 6.9–7.2, m, 10 H; ^{13}C NMR (CD_2Cl_2): δ 8.76, q (C_5Me_5); δ 22.07, t (Fe–CH_2); δ 102.3, s (C_5Me_5); δ 123.8, δ 127.5, δ 128.6, δ 139.6 ($CH_2C_6H_5$). IR (cm^{-1} in Nujol and fluorolube mulls): $\nu(N{\equiv}O)$ 1752vs. Mass spectrum, EI (15 eV): *m/e* 442, rel. int. 11.2; *m/e* 91, rel. int. 100.

Preparation of $(CH_3)_5C_5Fe(NO)(CH_2SC_6H_5)_2$

A 30 ml round-bottom flask with a side arm addition tube was charged with 0.47 g (1.0 mmol) of $(CH_3)_5C_5Fe(NO)I_2$ and the addition tube charged with 0.55 g (2.0 mmol) of $LiCH_2SC_6H_5 \cdot 2C_4H_8O$. The reaction was conducted exactly the same as for the dibenzyl derivative above. The yellow-green precipitate obtained was recrystallized from cold (−78°C) toluene/pentane solution. Yield: 63%. Anal.: Found: C, 61.83; H, 6.27; N, 2.91. $C_{24}H_{29}NOS_2Fe$ calcd.: C, 61.66; H, 6.25; N, 3.00%. ^1H NMR (CD_2Cl_2): δ 1.70, s, 15 H; δ 2.85 ppm, AB quartet (J(AB) 5.86 Hz, $\Delta\delta$ 0.829 ppm), 4H; δ 7.0–7.4, m, 10 H; ^{13}C NMR (CD_2Cl_2); δ 8.97 ppm, q (C_5Me_5); δ

26.37 ppm, t (Fe–CH_2); δ 104.61 ppm, s (C_5Me_5); δ 124.1, δ 126.1, δ 128.5, δ 145.3 ppm ($-CH_2SC_6H_5$). IR (cm^{-1} in Nujol mull) ν(N≡O) 1758vs. Mass spectrum, EI (15 eV): *m/e* 442, rel. int. 12.3; *m/e* 123, rel. int. 100.

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