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Preliminary communication

Synthesis of 5,1′-alkynyl- and 5,1′-alkenyl-1,3-cyclohexadienetricarbonyliron complexes using aluminum reagents

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Abstract

Dimethylaluminum acetylides react with (η^5-cyclohexadienyl)tricarbonyliron fluoroborate (**1**) to give the corresponding C(5) alkynyl substituted complexes in high yields without competing reduction products. Using this method, phenylethynyl and trimethylsilylethynyl groups have been added to the cationic complex at C(5). In the latter case, the yield can be improved substantially if tris(trimethylsilylethynyl)aluminum is used instead. Desilylation of this complex yields the 5-ethynyl complex. Hydrogenation with Lindlar's catalyst yields the corresponding alkenyl complex. Oxidative removal of the $Fe(CO)_3$ moiety yields the organic ligand in near quantitative yields. Use of aluminum reagents as alkynyl anion synthons in reactions with **1** is a far superior method compared to the use of either lithium acetylides which give complicated mixtures of products or 1-trimethylsilylalkynes which are unreactive.

The addition of nucleophiles to (η^5-cyclohexadienyl)tricarbonyliron salt **1** ($X^- = BF_4^-$, PF_6^-) has proved to be a valuable method for the synthesis of substituted 1,3-cyclohexadiene and cyclohexenones and a few natural products [1]. While a great many varieties of nucleophiles have been successfully added to **1**, attempts to add strongly basic nucleophiles often result in the formation of reduced dimeric products [2]. In order to circumvent this problem, in some cases trialkylsilyl derivatives of the anions have been used successfully as the anion synthons [3,4]. For example, allyltrimethylsilane [2c,3] and phenyltrimethylsilane [4] have been used to transfer allyl and phenyl groups to the ring of the complex **1**. However, (1-propenyl)trimethylsilane [5] and vinyltrimethylsilane [2c] have failed to transfer the corresponding alkenyl groups to **1**. Use of tetraorganoborate salts as alkenyl [6] and biphenylyl [7] anion synthons in reactions with **1** has also been reported. However, methods for the synthesis of the 5-alkynyl complexes have not been reported. In view of the reactivity of carbon–carbon triple bonds, development of a general method for the synthesis of 5,1′-alkynylcyclohexadiene tricarbonyliron complexes would greatly enhance the synthetic utility of these complexes.

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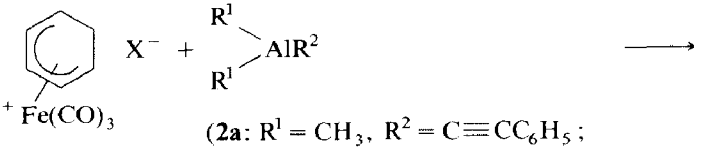
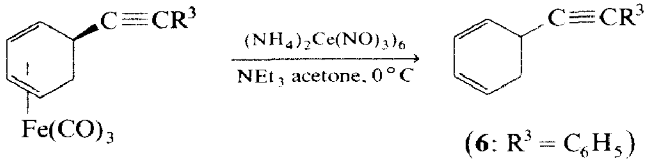
Three potential approaches to introduce an alkynyl moiety at C(5) of **1** include treating **1** with (a) lithium acetylides (b) trialkylalkynylsilanes in the presence of transition metal catalysts, or (c) dialkylalkynyl or tris(alkynyl)aluminum compounds. Trialkylalkynylsilanes have been used to transfer an alkynyl group to an electrophilic carbon in organic molecules, such as haloaromatic compounds, α,β-unsaturated acyl cyanides and acid halides in the presence of catalysts such as palladium(II) salts [8a] and $TiCl_4$ [8b]. The alkynylaluminum reagents have been used to transfer an alkynyl moiety to electrophilic carbons in epoxides, tertiary halides and α,β-unsaturated ketones [8c] and propargylium cobalt complexes [8d].

Reaction of **1** with lithium phenylacetylide gave complex mixture of products. Attempts to use 1-trimethylsilylpropyne as the propynyl anion synthon in reactions with **1** in a variety of solvents in the absence or presence of catalytic amounts of copper(I), silver(I), palladium(II) salts or $TiCl_4$, either failed or gave only traces of the desired product [5]. Reactions of **1** with 2.2-equivalents of dimethyl(2-phenylethynyl)aluminum, (**2a**), generated in situ in ether/hexane at 0 °C according to the reported procedure [9], yielded [5-(2′-phenylethynyl)cyclohexadiene]$Fe(CO)_3$ (**3a**) in 91% yield [10*]. No other products were detected by TLC. Reaction of dimethyl(2-



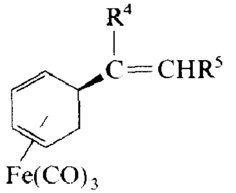
(**1**)

(**2a**: $R^1 = CH_3$, $R^2 = C{\equiv}CC_6H_5$;
2b: $R^1 = CH_3$; $R^2 = C{\equiv}CSiMe_3$;
2c: $R^1 = R^2 = C{\equiv}CSiMe_3$)



(**3a**: $R^3 = C_6H_5$;
3b: $R^3 = SiMe_3$;
3c: $R^3 = H$)

(**6**: $R^3 = C_6H_5$)



(**4a**: $R^4 = C{\equiv}CSiMe_3$, $R^5 = SiMe_3$;
4b: $R^4 = C{\equiv}CH$, $R^5 = SiMe_3$;
4c: $R^4 = H$; $R^5 = C_6H_5$)

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

trimethylsilylethynyl)aluminum (**2b**) with **1** under similar conditions led to the formation of two products, as observed by TLC. The reaction period was slightly longer (3 h) than that for the previous reaction (1 h 45 min). Separation of the components of the product mixture by chromatography yielded the desired complex **3b** as the major product (47% yield) and **4a** as the minor product (7.6% yield) [10*].

In an attempt to maximize the formation **3b** at the expense of formation of **4a**, several approaches were tested. Conducting the reaction at lower temperatures suggested that reaction did not occur in the temperature range −78 to −15 ° C. At temperatures above −15 ° C, formation of both the products was rapid. Decrease in the molar ratio of the aluminum reagent to **1** from 2.2/1.0 to 1.1/1.0 resulted in decreased yields of both the products (35 and 3.6% of **3b** and **4a**, respectively). Reaction of tris(trimethylsilylethynyl)aluminum (**2c**), generated in situ according to the reported procedure [12*], with **1** in the molar ratio 1.1/1.0 in 1.2-dichloroethane at 0 ° C, yielded **3b** in much higher yield (65%) and **4a** in only trace quantities (0.5%) [12*]. During the initial phase of the progress of the reaction, only the formation of the major product was detected. As the reaction progressed, the formation of the minor product was observed. Although this method is superior to the previous method for the synthesis of **3b**, it has the disadvantage that two moles of alkynyl moieties per mole of the aluminum reagent are not utilized. However, it has been shown [11] that if the reaction is worked up quickly, the unused alkyne can be recovered in good yields.

The mechanism of formation of the minor product **4a** is unclear. It could have formed either by the slow addition of excess of the aluminum reagent **2** (a) to the major product **3b**, or (b) first to itself generating a new aluminum reagent **5**, which then reacts with **1** to give **4a**. In an attempt to investigate the first possibility, when pure **3b** was treated with **2b** at 0 ° C in the same solvent system, no **4a** was detected. Attempts to desilylate **3b** with boric acid in aqueous methanol failed. However, anhydrous sodium bicarbonate in methanol [14*] at room temperature desilylated **3b** to give **3c** in 62% after purification. When the same method was used with **4a**, cleavage of only the alkynyl C–Si bond took place to give **4b** [15]. Attempt to methylate the terminal alkyne in **3c** by lithiation with methyllithium at 0 ° C followed by reaction with methyl iodide failed, due to the decomposition of the anionic intermediate complex. Use of alternative methods to alkylate **3c** are being investigated.

The feasibility of the use 5,1′-alkynyl substituted complexes (**3**) in the synthesis of 5,1′-alkenyl complexes was studied by catalytic hydrogenation of **3a** in the presence of Lindlar's catalyst in absolute ethanol at H_2 pressure of 1 atm. The *cis*-alkene complex **4c** was obtained in quantitative yield [16*].

Attempts to oxidatively remove the $Fe(CO)_3$ from **3a** with excess $(NH_4)_2Ce(NO_3)_6$ in aqueous acetone (2% H_2O) at room temperature gave exclusively diphenylacetylene. However, when the reaction was done at 0 ° C, in dry acetone with 2.0 equivalents dry triethylamine and 3.2 equivalents $(NH_4)_2Ce(NO_3)_6$, 5-(2-phenylethynyl)cyclohexa-1,3-diene (**6**) was obtained in 94% as a colorless oil after purification by chromatography [18*].

In conclusion, dialkynylaluminum derivatives can be successfully used as alkyne anion synthons in reactions with **1** to obtain the alkynyl-substituted complexes to the exclusion of any reduced dimeric products. The products can be hydrogenated to give *cis*-alkene or demetallated to give 5-substituted 1,3-cyclohexadienes.

References and Notes

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10 The typical procedure for the reaction is as follows. An ice-cold supernatant ether/hexane solution of dimethylalkynylaluminum was decanted into a stirred suspension of $[(C_6H_7)FeCO_3]BF_4$ in ether kept at 0 °C and stirred. The progress of the reaction was monitored by TLC on silica gel (10% ether in hexane). Upon completion of reaction, the reaction mixture was poured into a saturated solution of KH_2PO_4. To this mixture, few drops of 10% H_2SO_4 was added to dissolve any precipitated solids. The layers were separated and the organic layer was washed successively with saturated $NaHCO_3$ solution and saturated NaCl solution and dried. The brownish yellow oil obtained upon removal of the solvent was purified by either preparative or column chromatography on silica gel (eluent 10% ether in hexanes). For the dimethyl(trimethylsilylethynyl)aluminum reaction, complete separation of the major and minor products required two preparative chromatographic separations. The purified products were recrystallized from 95% ethanol. All products were characterized by NMR, IR and mass spectrometry. ^1H NMR spectra were run at 300 MHz. The mass spectra were run at 12 eV. The NMR data for all the compounds reported in this study is consistent with *exo*-substitution at C(5) [17].

Compound **3a**: m.p. 88–89.5 °C; IR (CH_2Cl_2): ν 2230, 2050, 1975 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.80 (d, 1H, $H(6)_{exo}$), 2.26(m, 1H, $H(6)_{endo}$), 3.15(m, 2H, H(1), H(4)), 3.28(m, 1H, H(5)), 5.40, 5.60(m,, 2H, H(2), H(4)), 7.20–7.40(m, 5H, C_6H_5); MS, 320(M^+).

Compound **3b**: m.p. 53–54.5 °C; IR (CH_2Cl_2): ν 2160, 2040 and 1970 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.11(s, 9H, $Si(CH_3)_3$), 1.69(d, 1H, $H(6)_{exo}$, $J_{6\text{-}exo,6\text{-}endo}$ 14.9 Hz), 2.17(m, 1H, $H(6)_{endo}$), 2.94(dt, 1H, H_5, J(H5), $H(6))_{endo}$ 11.07 Hz, J(H(5), H(4)) or J(H(5), $H(6)_{exo}$ 3.4 Hz), 3.10, 3.20(m, 2H, H(1), H(3)), 5.36, 5.47(m, 2H, H(2), H(3)); MS 316 (M^+).

Compound **4a**: m.p. 64–66.5 °C; IR (CH_2Cl_2); ν 2140, 2030, 1975 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.13(s, 9H, $C{=}CSi(CH_3)_3$), 0.22(s, 9H, $C{\equiv}CSiMe_3$), 1.39(dd, 1H, $H(6)_{exo}$), 2.10(m, 1H, $H(6)_{endo}$), 3.12(m, 2H, H(1), H(4)), 3.80(dt, 1H, H(5)), 5.40(t, 1H, H(2) or H(3)) 5.48(t, 1H, H(2) or H(3), 5.75(s, 1H, $C{=}C(H)Si\leq$).

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12 The experimental procedure used in ref. 11 was followed with minor changes. Thus, to a solution of lithium trimethylsilylacetylide generated in ether at 0 °C, was added small batches of anhydrous aluminum chloride and stirred for 30 min. Ether was removed under vacuum and solid $[(C_6H_7)Fe(CO)_3BF_4$ was added followed by anhydrous 1,2-dichloroethane. Upon completion of reaction, the solution was poured into 3 *N* HCl and the organic layer was successively washed with $NaHCO_3$ solution, water and saturated NaCl solution and dried.

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14 A suspension of 0.245 g complex, 0.500 g anhydrous $NaHCO_3$ in 5 ml anhydrous methanol were stirred at room temperature for 32 h. The reaction was followed by TLC (silica gel, 5% ethyl acetate in benzene). The reaction mixture was diluted with ether, filtered and washed with water followed by NaCl solution and finally dried. The crude product was purified by preparative chromatography on silica gel, to yield a yellow oil (62%) which solidified in freezer.

Compound **3c**: m.p. 33–34°C; IR (CH_2Cl_2): ν 3300, 2160, 2040 and 1980 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.72 (d, 1H, $H(6)_{exo}$), 2.03 (d, 1H, ≡C–H), 2.18 (m, 1H, $H(6)_{endo}$), 2.87 (m, 1H, $H(5)_{endo}$), 33.10–3.19 (m, 2H, H(1),H (4)), 5.33, 5.45 (m, 2H, H(2), H(4)); MS, 244 (M^+).

15 Compound **4b**: IR (CH_2Cl_2): ν 3300 (≡C–H), 2040, 1975 cm^{-1}; ^1H NMR ($CDCl_3$): d 0.15 (s, 9H, $(CH_3)_3Si$), 1.38 (dd, 1H, $H(6)_{exo}$, $J_{6\text{-}exo,6\text{-}endo)}$ 15 Hz), 2.10 (m, 1H, $H(6)_{endo}$), 3.06 (m, 1H, H(4)), 3.15 (m, 1H, H(1)), 3.30 (d, 1H, C≡CH), 3.75 (m, 1H, $H(5)_{endo}$), 5.32, 5.48 (m, 2H, H(2), H(3)), 5.70 (d, 1H, C=CHSi$\leqslant$). The assignments for H(4), $H(5)_{endo}$ were made from decoupling experiments.

16 Compound **4c**: m.p. 64–66.5°C; ^1H NMR ($CDCl_3$): δ 1.43(d, 1H, $H(6)_{exo}$, $J_{6\text{-}exo,6\text{-}endo}$ 14.9 Hz), 2.13(m, 1H, $H(6)_{endo}$), 3.06, 3.12(m, 2H, H(1), H(4), 3.25(tt, 1H, $H(5)_{endo}$, $J(H(5,6)_{endo}$, 10.6 Hz, $J(H5,6)_{exo})$ 3.6 Hz), 5.16(t, or dd with overlap, 1H, H(2), J(H(1),H(2)) 11.0 Hz), 5.34, 5.42(m, 2H, H(2), H(3)) 6.28(d, 1H, H(2), J(CH=CH) 11.3 Hz), 7.25(m, 5H, C_6H_5); MS, 322(M^+). The coupling constants in the NMR data were obtained by decoupling method.

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18 Compound **6**: IR ($CHCL_3$): ν 2880, 2840, 2240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.28–7.42(m, 5H, C_6H_5), 5.81–6.00(m, 4H, H(1), H(2), H(3), H(4)), 3.52 (m, 1H, H(5)), 2.47(m, 2H, H(6)); MS, 180 (M^+), 179, 178, 165, 102.