Addition reactions of lithiodimethylphenylsilane to ($\eta^4$-1,3-diene)-Fe(CO)$_3$ and ($\eta^6$-arene)Cr(CO)$_3$ complexes

Ming-Chang P. Yeh *, Peng-Yu Sheu, Jin-Xuan Ho, Yi-Lin Chiang, Dai-Yu Chiu, U. Narasimha Rao

Department of Chemistry, National Taiwan Normal University, 88, Ding-Jou Road, Sec. 4, Taipei 117, Taiwan

Received 9 September 2002; received in revised form 22 January 2003; accepted 17 March 2003

Abstract

Treatments of ($\eta^4$-cyclohexa-1,3-diene)Fe(CO)$_3$ complex with 1.2 equivalents of PhMe$_2$SiLi, followed by quenching the reactive intermediate with CF$_3$COOH generated 1-dimethyl(phenyl)silylcyclohex-1-ene and with 2-(phenylsulfonyl)-3-phenyloxaziridine produced [($\eta^4$-2-dimethyl(phenyl)silylcyclohexa-1,3-diene)Fe(CO)$_3$ complex as the major product. Additions of the silyl anion to ($\eta^6$-arene)Cr(CO)$_3$ and ($\eta^6$-cyclohepta-1,3,5-triene)Cr(CO)$_3$ complexes produce dienylsilanes after acid quenching.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Iron; Cyclohexadiene; Silane; Chromium; Arene

1. Introduction

Nucleophilic additions to conjugated dienes and arenes coordinated to a transition metal have attracted considerable interest in organic synthesis. Transition metals, such as molybdenum, palladium or iron, have been used to activate dienes toward nucleophilic addition reactions [1], and chromium, manganese, iron, or ruthenium have been utilized to activate arenes toward nucleophilic substitution and addition reactions [2]. Among them, nucleophilic additions to ($\eta^4$-1,3-diene)Fe(CO)$_3$ [3] and ($\eta^6$-arene)Cr(CO)$_3$ [4] complexes have been studied intensively and used in the synthesis of a number of complex molecules. The disadvantage of the additions, however, is the relatively narrow range of stabilized carbon nucleophiles. For example, organomagnesium or -lithium reagents suffer competitive addition to the carbon monoxide ligand of diene-Fe(CO)$_3$ complexes [5], and treatments of n-BuLi with ($\eta^6$-arene)Cr(CO)$_3$ complexes result in deprotonation at the arene ligand [6]. Carbon nucleophiles, such as ketone enolates, organocopper or -zinc reagents, fail to react with both complexes. Moreover, reports on the addition of silyl anions to ($\eta^4$-1,4-diene)Fe(CO)$_3$ and ($\eta^6$-arene)Cr(CO)$_3$ complexes are not found. Although the addition reactions of silicon–magnesium [(PhMe$_2$Si)$_3$MnMgMe] [7] and silicon–copper [PhMe$_2$Si-Cu(CN)Li] [8] reagents to 1,3-dienes were reported to give homoallyl- and allylsilanes after electrophilic quenching, both silylations were limited to acyclic 1,3-dienes bearing nonsubstituted terminal double bonds. It will be of great interest to extend the silylation reaction to cyclic 1,3-dienes. Here, we report, for the first time, on the addition of PhMe$_2$SiLi to both cyclic and acyclic dienes activated by Fe(CO)$_3$. The intermediates obtained from the addition can be directly treated with CF$_3$COOH to produce vinyl- and allylsilanes or with 2-(phenylsulfonyl)-3-phenyloxaziridine (also known as Davis reagent) to afford nucleophilic substituted iron–diene complexes. Moreover, nucleophilic addition reactions of ($\eta^6$-arene)Cr(CO)$_3$ and ($\eta^6$-cyclohepta-
1,3,5-triene)-Cr(CO)$_3$ complexes with PhMe$_2$SiLi to give dienyilsilanes after acid quenching will also be described.

2. Results and discussion

2.1. Addition of lithiodimethylphenylsilane to cyclic diene-irontricarbonyl complexes followed by electrophilic quenching

Lithiodimethylphenylsilane (PhMe$_2$SiLi) was prepared in tetrahydrofuran (THF) under argon according to a literature procedure [9]. Addition of a THF solution of PhMe$_2$SiLi (1.2 equivalents) to ($h_4$-cyclohexa-1,3-diene)Fe(CO)$_3$ complex (1a) in THF for 20 h at 25$^\circ$C under argon followed by quenching the reaction mixture with CF$_3$COOH produced 1-dimethyl(phenyl)silylcyclohex-1-ene (2a) in 55% after purification by flash column chromatography on silica gel and short-path distillation under reduced pressure. Under the same reaction conditions, quenching the reacti

Scheme 1.

None of the decrease in integration on the vinyl or homoallyl protons was found (compared to the integral of phenyl and dimethyl groups at the silicon). Trapping of 5 with Davis reagent afforded the C-2 silyl-substituted complex 3a as the major product and a trace of the C-1 silyl-substituted complex 3b (Eq. (1)). Reaction of the allyl anion 5 with Davis reagent gave 3a and 3b together with isolation of PhSO$_2$NH$_2$ and PhCHO. Migration of β-hydrides from 5 occurred at both C-4 and C-6 position to Davis reagent afforded PhSO$_2$NH$_2$ and PhCHO after aqueous process. Moreover, quenching 5 with benzoyl chloride followed by aqueous process produced vinylsilane 2a as the major product in 37% yield together with the C-1 substituted silyl diene 6 as the minor product in 15% yield (Eq. (2)). It was reasonable to view that quenching of 5 with benzoyl chloride was inefficient and vinylsilane 2a was generated during aqueous work up. Reaction of 5 with benzoyl chloride may produce the postulate intermediate 7a (Scheme 2). The intermediate 7a may undergo β-hydride elimination at C-4 to give 7b. Reductive elimination of 7b (to release benzaldehyde) followed by detachment of the double bond from the iron center furnished silyl diene 6. The reaction mechanism was proposed based upon isolation of benzaldehyde after flash column chromatography of the reaction mixture. It is important to mention that unlike stabilized carbanions attack at the internal position of the diene ligand of 1a at $-78^\circ$C (kinetically controlled reaction conditions) to give homoallyl anion intermediates and at the terminal position of the diene ligand at 25$^\circ$C (thermodynamically controlled reaction conditions) to afford allyl anion intermediates [3], the silyllithium reagent (PhMe$_2$SiLi) does not add to 1a at $-78^\circ$C and the addition occurs at internal positions of the cyclohexa-1,3-diene ligand at 25$^\circ$C to give 5. Attempts to trap 5 with other electrophiles such as benzyl bromide and CO failed.

\[ \text{PhMe}_2\text{SiLi} + \text{1a} \rightarrow \text{5} \] 

\[ \text{CF}_3\text{COOH} + \text{5} \rightarrow \text{2a} \]

\[ \text{1a} \rightarrow \text{5} \rightarrow \text{2a} \]
Vinylsilane 2a was isolated as the major product in each case in 20–40% yield after aqueous work up and column chromatography of the crude mixture.

Surprisingly, addition of PhMe₂SiLi to (η⁴-1-methoxycyclohexa-1,3-diene)Fe(CO)₃ complex (1b) also produced 3a in 60% yield after acid quenching. The formation of 3a is difficult to understand since it formally involves a kind of cine-substitution for methoxide. A possible reaction path involving α-methoxy elimination of the homoallyl anion intermediate 8 to generate the carbene intermediate 9 is proposed (Scheme 3). The postulate carbene intermediate 9 may undergo β-
hydride elimination (to give 10) followed by reductive elimination to provide 11. Recoordination of the pendant double bond to the iron center of 11 produced complex 3a. An additional methyl group at the C-5 position of the ring, for example, with complex 12 [10], the silylation occurred only at the less hindered C-2 position of the diene ligand to produce vinylsilane 13 in 41% yield after acid quenching. None of vinyllsilane derived from silyl anion addition at hindered terminal C-1 or C-4 positions was found.

2.2. Addition of lithiodimethylphenylsilane to acyclic diene-irontricarbonyl complexes followed by electrophilic quenching

Acyclic iron–diene complexes 14a and 14b also underwent silylation, however, at the less hindered terminal position (C-4) of the diene ligand to produce allylsilanes 15a [8] (37%) and 15b [8] (32%), respectively, as a single olefinic regioisomer in each case. None of the addition at the other terminus (C-1) and the internal position (C-3) of the diene ligand was found. Although the yields of the silyl addition to acyclic iron–diene complexes are low, the addition provides only a single allylsilane [8]. Thus, the steric hindrance imposed by an adjacent alkyl group at the C-2 position of acyclic diene ligands may impede the silyl anion attack at C-1 and C-3 positions of the diene ligands. Addition of the silyl anion at the less hindered terminal position (C-4) of the diene ligand generated allyl anions 16a and 16b. Protonation of 16a and 16b with CF3COOH gave allylsilanes 15a and 15b. To further prove the proposed allyl anion intermediate 16a, the anion intermediate 16a was quenched with CF3COOD. Allylsilane 17 was isolated in 40% yield. 1H-NMR of 17 shows that only two protons appear at the allylic carbon cis to the dimethyl(phenyl)silyl group. Moreover, the silylation failed to cyclic iron–diene complexes bearing an additional substituent at the C-2 position of the diene ligand. For example, addition of PhMe2SiLi to [η⁴-2-methyclohexa-1,3-diene]Fe(CO)₃ complex (18a) and [η⁴-2-methoxy cyclohexa-1,3-diene]Fe(CO)₃ complex (18b) failed to give any additional product. The starting complexes 18a and 18b were recovered quantitatively in both cases. This result further indicated that the silylation was limited to the diene ligand containing a substituent at the C-2 position, especially for C-2 substituted cyclic 1,3-diene iron complexes.

2.3. Addition of lithiodimethylphenylsilane to arene-chromiumtricarbonyl complexes followed by electrophilic quenching

The above reaction patterns were also observed for (η⁵-arene)Cr(CO)₃ complexes. For example, addition of PhMe₂SiLi to (η⁶-benzene)Cr(CO)₃ (19a) at 25 °C followed by acid quenching afforded dienylsilanes 6 and 20 (6:20 = 4:1) in 62% yield (Eq. (3)). The initial nucleophilic addition generated the (η⁵-cyclohexadienyl)Cr(CO)₃ anion intermediate 21. Protonation of 21 followed by hydride transfer (via supra) afforded 6 and 20. Quenching 21 with Davis reagent also resulted in hydride abstraction to generate [η⁵-dimethyl(phenyl)silylbenzene]Cr(CO)₃ complex (19e) in 30% yield together with the isolation of PhSO₂NH₂ and PhCHO. Moreover, addition of PhMe₂SiLi to arene–chromium complex containing a fluorine (19b), a chlorine (19c) or a methoxy (19d) group proceeded in an addition/elimina-
tion process to afford complex 19e in fair to good yields (19b, 70%; 19c, 36%; 19d, 56%). Changing to the seven-membered ring with (η⁶-cyclohepta-1,3,5-triene)-Cr(CO)₃ complex (22) also allowed the silyl anion addition to give silylated cyclohepta-1,3-diene derivatives 23a and 23b (23a:23b = 3:1) in 68% yield after acid quenching.

4. Experimental

4.1. General

All reactions were run under an argon atmosphere in oven-dried glassware unless otherwise indicated. Anhydrous solvents or reaction mixtures were transferred via an oven-dried syringe or cannula. THF was distilled under nitrogen from a deep blue sodium benzophenone ketyl solution. Complexes 1a and 1b and 14a and 14b were prepared by heating Fe₂(CO)₉ and the corresponding dienes in n-butyl ether. Complexes 19a–19d were obtained by refluxing the corresponding arenes with Cr(CO)₆ in n-butyl ether. Complex 22 was synthesized by refluxing cyclohepta-1,3,5-triene with Cr(CH₃CN)₃(CO)₃ in THF [11]. Flash column chromatography, following the method of Still, was carried out with E. Merck silica gel (Kieselgel 60, 230–400 mesh) using the indicated

3. Conclusion

The reaction outlined herein demonstrates that the addition of PhMe₂SiLi to diene-Fe(CO)₃ complexes produces vinyl- or allylsilanes after acid quenching. Treatments of the same reaction intermediate with Davis reagent proceeded in hydride abstraction to afford silyl-substituted diene-Fe(CO)₃ complexes. Nucleophilic addition reactions of (η⁶-arene)Cr(CO)₃ and (η⁶-cyclohepta-1,3,5-triene)Cr(CO)₃ complexes with PhMe₂SiLi generate dienylsilanes after acid quenching.
solvents [12]. 1H-NMR spectra were obtained with JEOL-EX 400 (400 MHz) and Varian G-200 (200 MHz) spectrometers. The chemical shifts are reported in parts per million with either tetramethylsilane (0.00 ppm) or CHCl3 (7.26 ppm) as internal standard. 13C-NMR spectra were recorded with a JEOL JMS-D100 spectrometer at an ionization potential of 70 eV and are reported as mass/charge (m/e) with percent relative abundance. High-resolution mass spectra were obtained with an AEI MS-9 double-focusing mass spectrometer and a JEOL JMS-HX 110 spectrometer.

4.1.1. General procedure for addition of PhMe2SiLi to (η4-1,3-diene)Fe(CO)3, (η5-arene)Cr(CO)3 and (η5-cyclohepta-1,3,5-triene)Cr(CO)3 complexes

In a typical procedure, to a solution of complex 1a (0.22 g, 5.0 mmol) in 9 ml of THF under argon at 0 °C was added rapidly, neat, via cannula, a solution of PhMe2SiLi [9] (0.06 g, 2.05 mmol, 41%) as a colorless liquid. A reaction mixture with trifluoroacetic acid (0.5 ml) produced 2 (0.15 g, 0.69 mmol, 37%) and 6 (0.06 g, 0.28 mmol, 15%) both as colorless liquid. Compound 6: IR (CH2Cl2) 3369, 2986, 1617, 1429, 1078 cm⁻¹; 1H-NMR (400 MHz, CDCl3) δ 7.54 (m, 2H), 7.36 (m, 3H), 6.24 (m, 1H), 5.98 (m, 1H), 5.91 (m, 1H), 2.10 (m, 4H), 0.36 (s, 6H); 13C-NMR (50 MHz, CDCl3) δ 138.36, 137.02, 134.06, 133.76, 128.97, 128.24, 127.78, 124.76, 24.14, 22.05. −3.72; MS (20 eV) m/e 214 [M⁺, 22], 197 (20), 135 (100), 121 (26); HRMS (EI) m/e Calc. for C14H18FeO3Si: 214.1178; Found, 214.1179.

4.1.2. 1-Dimethyl(phenyl)silylcyclohex-1-ene (2a)

The crude mixture from the addition of PhMe2SiLi to complex 1a (1.10 g, 5.0 mmol) followed by quenching the reaction mixture with benzoyl chloride (0.54 g, 3.75 mmol) afforded 2 (1.17 g, 0.69 mmol, 37%) and 6 (0.06 g, 0.28 mmol, 15%) both as colorless liquid. IR (CH2Cl2) 3369, 2986, 1617, 1429, 1078 cm⁻¹; 1H-NMR (400 MHz, CDCl3) δ 7.52 (m, 2H), 7.36 (m, 3H), 6.06 (m, 1H), 6.06 (m, 1H), 6.18 (m, 1H), 1.14 (m, 1H), 0.94 (d, J = 6.0 Hz, 3H) and 0.32 (s, 6H); 13C-NMR (100.4 MHz, CDCl3) δ 138.39, 137.6, 136.3, 134.0, 128.3, 127.8, 127.78, 124.76, 24.14, 22.05. −3.72; MS (20 eV) m/e 230 [M⁺, 49], 229 (100), 216 (27), 215 (28), 202 (64), 201 (34), 187 (31), 168 (51), 167 (43), 153 (28); HRMS (EI) m/e Calc. for C14H20Si: 230.1491; Found, 230.1473.

4.1.3. [η⁴-2-Dimethyl(phenyl)silylcyclohexa-1,3-diene]Fe(CO)₃ complex (3a)

Addition of PhMe2SiLi (6.0 mmol) to complex 1a (1.10 g, 5.0 mmol) followed by quenching the reaction mixture with 2-(phenylsulfonyl)-3-phenyloxaziridine (1.57 g) gave 3a (0.71 g, 2.0 mmol, 40%) as a colorless liquid and a trace of 3b (less than 20 mg). Only complex 3a can be isolated as a pure compound. IR (CH2Cl2) 3688, 3100, 2900, 1968, 1607, 1091 cm⁻¹; 1H-NMR (400 MHz, CDCl3) δ 7.64 (m, 2H), 7.41 (m, 3H), 5.11 (d, J = 8.0 Hz, 1H), 3.44 (m, 1H), 3.30 (m, 1H), 1.70 (m, 4H), 0.50 (s, 3H) and 0.49 (s, 3H); 13C-NMR (100.4 MHz, CDCl3) δ 212.5, 137.9, 133.9, 129.4, 127.9, 90.6, 89.8, 67.4, 65.9, 24.2, 23.9, −3.3, −4.0; MS (20 eV) m/e 354 [M⁺, 1], 326 (4), 298 (12), 270 (100), 271 (18), 268 (30); HRMS (EI) m/e Calc. for C17H18FeO3Si: 354.0375; Found, 354.0360.
(t, J = 8.6 Hz, 1H), 1.68 (s, 3H), 1.63 (d, J = 8.6 Hz, 2H), 1.50 (s, 3H), 0.26 (s, 6H); $^{13}$C-NMR (100.4 MHz, CDCl$_3$) δ 133.6, 128.8, 127.7, 119.3, 25.8, 17.7, 17.6, −3.2.

4.1.7. 2,6-Dimethyl-8-dimethyl(phenyl)silylocta-2,6-diene (15b) [8]

Addition of PhMe$_3$SiLi (6.0 mmol) to complex 14b (1.38 g, 5.0 mmol) followed by quenching the reaction mixture with trifluoroacetic acid (0.5 ml) gave 15b (0.44 g, 1.62 mmol, 32%) as a colorless liquid. $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.52 (m, 2H), 7.31 (m, 3H), 5.11 (m, 2H), 2.00 (m, 4H), 1.68 (s, 3H), 1.60 (s, 3H), 1.62 (m, 5H), 0.30 (s, 6H); $^{13}$C-NMR (100.4 MHz, CDCl$_3$) δ 133.6, 128.9, 127.7, 119.6, 39.9, 27.3, 26.8, 25.6, 17.6, 15.7, −3.4.

4.1.8. 1-Deutero-2-methyl-4-dimethyl(phenyl)silylbut-1-ene (17)

Addition of PhMe$_3$SiLi (3.75 mmol) to complex 14a (0.39 g, 1.88 mmol) followed by quenching the reaction mixture with CF$_3$COOD (0.29 ml) produced 17 (0.15 g, 0.75 mmol, 40%) as a colorless liquid. $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.53 (m, 2H), 7.36 (m, 3H), 5.17 (t, J = 8.6 Hz, 1H), 1.68 (s, 3H), 1.63 (d, J = 8.6 Hz, 2H), 1.50 (s, 2H), 0.26 (s, 6H).

4.1.9. Addition of PhMe$_3$SiLi to complex 19a followed by acid quenching generated dienyllsilanes 6 and 20

Addition of PhMe$_3$SiLi (6.0 mmol) to complex 19a (1.07 g, 5.0 mmol) followed by quenching the reaction mixture with trifluoroacetic acid (0.5 ml) gave 6 (0.54 g, 2.5 mmol, 50%) and 20 (0.13 g, 0.60 mmol, 12%) both as colorless liquid. The analytical data of 6 obtained from this addition is identical to that of the previous result obtained from quenching the anion intermediate 4b with benzoyl chloride. Attempts to obtain pure compound 20 were not successful. Complexation of the impure material with Fe$_2$(CO)$_9$ in refluxing ether produced complex 3a (0.04 g) after flash column chromatography of the crude mixture. The analytical data are consistent with that of complex 3a obtained from addition/quenching process as mentioned in Eq. (1).

4.1.10. ($^5$-$\text{Dimethyl(phenyl)silylbenzene}$)tricarbonylchromium complex (19e)

Addition of PhMe$_3$SiLi (6.0 mmol) to complex 16a (1.16 g, 5.0 mmol) followed by quenching the reaction mixture with 2-(phenylsulfonfyl)-3-phenyloxaziridine (1.57 g) or trifluoroacetic acid (0.5 ml) gave 19e (0.52 g, 1.5 mmol, 30%) as a yellow liquid. IR (CH$_2$Cl$_2$) 3688, 3367, 1968, 1890, 1606, 1427, 1083 cm$^{-1}$; $^1$H-NMR (200 MHz, CDCl$_3$) δ 7.52 (m, 2H), 7.40 (m, 3H), 5.50 (t, J = 6.4 Hz, 1H), 5.41 (d, J = 6.6 Hz, 2H), 5.13 (dd, J = 6.6, 6.4 Hz, 2H), 0.60 (s, 6H); $^{13}$C-NMR (50 MHz, CDCl$_3$) δ 135.90, 134.06, 129.89, 128.15, 99.97, 97.92, 95.65, 90.26, −2.96; MS (20 eV) m/e 348 [M$^+$, 24], 331 (33), 266 (28), 265 (89), 264 (80); HRMS (EI) m/e Calc. for C$_{17}$H$_{16}$CrO$_3$Si: 348.0274; Found, 348.0270.

4.1.11. 1-Dimethyl(phenyl)silylcyclohepta-1,3-diene (23a)

Addition of PhMe$_3$SiLi (6.0 mmol) to complex 22 (1.14 g, 5.0 mmol) followed by quenching the reaction mixture with trifluoroacetic acid (0.5 ml) produced 23a (0.58 g, 2.55 mmol, 51%) and 23b (0.19 g, 0.85 mmol, 17%) as a colorless liquid. Compound 23b rearranged to an unidentified mixture of silyl compounds upon standing at room temperature for ca. 20 h, and only $^1$H-NMR and $^{13}$C-NMR data could be obtained immediately after column separation. Only 23a could be isolated as a pure compound. Compound 23a: IR (CH$_2$Cl$_2$) 3676, 3376, 2989, 1607, 1427, 1083 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.51 (m, 2H), 7.33 (m, 3H), 6.14 (m, 1H), 5.88 (m, 2H), 2.35 (m, 4H), 1.79 (m, 2H), 0.35 (s, 6H); $^{13}$C-NMR (50 MHz, CDCl$_3$) δ 145.68, 138.55, 135.53, 134.78, 134.11, 128.90, 127.74, 126.04, 32.93, 32.58, 27.27, −3.43; MS (20 eV) m/e 228 [M$^+$, 60], 213 (96), 185 (31), 168 (50), 145 (34), 137 (97), 135 (49); HRMS (EI) m/e Calc. for C$_{15}$H$_{20}$Si: 228.1334; Found, 228.1323.

4.1.12. 1-Dimethyl(phenyl)silylcyclohepta-1,3-diene (23b)

$^1$H-NMR (400 MHz, CDCl$_3$) δ 7.44 (m, 5H), 5.76 (m, 4H), 2.33 (m, 3H), 1.94 (m, 1H), 1.83 (m, 1H), 0.30 (s, 6H); $^{13}$C-NMR (100.4 MHz, CDCl$_3$) δ 138.06, 135.22, 133.87, 133.05, 128.99, 127.73, 125.62, 123.25, 35.19, 31.86, 27.88, −3.78, −4.54.

Acknowledgements

This work was supported by grants from National Taiwan Normal University (ORD91-1) and the National Science Council (NSC 90-2113-M-003-008).

References


(c) M.F. Semmelhack, H. Rhee, Tetrahedron Lett. 34 (1993) 1399;

The silyl-cupration of PhMe2SiCu(CN)Li to isoprene or myrecene gave olefinic regioisomers. See: