

Reactions of (η^3 -Allyl)tetracarbonyliron Cations with the Highly Functionalized Copper Reagents $RCu(CN)ZnI$

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The addition of the highly functionalized copper reagents $RCu(CN)ZnI$ to (η^3 -allyl) $Fe(CO)_4$ cations occurs mainly at the unsubstituted allyl terminus to yield the functionalized isoprenyl derivatives; with substituents on both ends of the allyl, the regular isoprenyl adducts are isolated together with ketone products which are derived from nucleophilic additions to the carbon monoxide ligands.

Activation of conjugated dienes towards nucleophilic addition can be accomplished by complexation of dienes with tricarbonyliron. However, the utility of simple (η^4 -1,3-diene) $Fe(CO)_3$ complexes has been limited by the relatively narrow range of usable nucleophiles.¹ Ketone enolates react with complexes to give only poor yields and organolithium or Grignard reagents suffer competitive addition to the carbon monoxide ligands.² Nucleophiles such as 1-lithio-1,1-diphenylmethane, 2-lithio-2-methylpropionitrile, and 2-lithio-2-phenyl-1,3-dithiane add smoothly to the complexes. Moreover, organocupper or zinc reagents fail to react with the complexes. Alternatively, (η^4 -1,3-diene) $Fe(CO)_3$ complexes can be further activated towards nucleophilic addition by treatment with fluoroboric acid under an atmosphere of CO.³ The resulting (η^3 -allyl) $Fe(CO)_4$ cationic salts are known to undergo nucleophilic addition with a variety of soft nucleophiles. For example, triphenylphosphine, pyridine, malonates, secondary amines, electron-rich aromatic compounds, and organocadmium reagents are all capable of this addition.⁴ The cations undergo preferential nucleophilic attack at the less substituted allyl terminus completely stereospecifically,

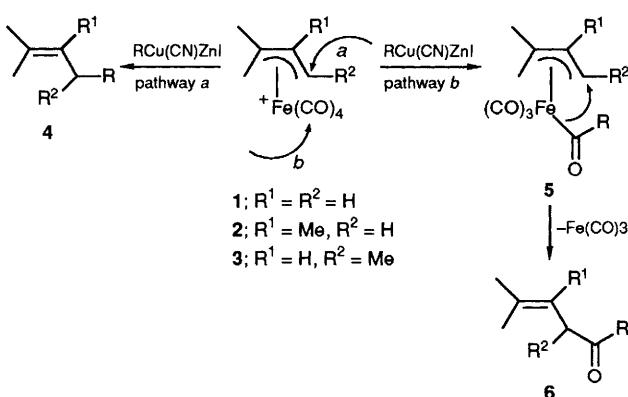
retaining the allyl fragment's geometry. These features make it useful from a synthetic standpoint since the additions offer an easy access to allyl and isoprenyl natural compounds. Nicholas recently has reported that allyl-metals [metal: $-SiMe_3$, $-SnMe_3$, $-Fe(C_5H_5)CO_2$] reacted with the cationic salts to give 1,5-dienes.⁵ However, treatment of cation **1** with allyl silane derivatives gave the (η^4 -isoprene) $Fe(CO)_3$ complex as the major product. This deprotonation was also found when cation **1** was treated with either organolithium or organocuprate reagents. Furthermore, organozinc reagents failed to couple with the cationic salts.[†] Herein we report that the highly functionalized copper reagents, generated by transmetallation of the corresponding functionalized zinc compounds with $CuCN \cdot 2LiCl$ in tetrahydrofuran (THF),⁶ react effectively with (η^3 -allyl) $Fe(CO)_4$ cationic salts to give a variety of polyfunctionalized isoprenyl derivatives.

[†] In our preliminary experiments, the addition of phenyllithium or phenylcuprate reagents (Ph_2CuLi) to cation **1** gave (η^4 -isoprene)tricarbonyliron(0) complex as the major product in both cases.

Table 1 Reactions of cations **1–3** with the highly functionalized $\text{RCu}(\text{CN})\text{ZnI}$ reagents **7a–e**

| Entry | $\text{RCu}(\text{CN})\text{ZnI}$ | Cation | Products ^a | Yield (%) | | |
|-------|---|----------|-----------------------|-----------------|--|-----------------|
| 1 | 7a ; R = $\text{EtO}_2\text{C}(\text{CH}_2)_3$ | 1 | | 57 ^b | | |
| 2 | 7b ; R = $\text{AcO}(\text{CH}_2)_4$ | 1 | | 68 ^b | | |
| 3 | 7c ; R = $\text{NC}(\text{CH}_2)_3$ | 1 | | 65 ^b | | |
| 4 | 7d ; R = $\text{NC}(\text{CH}_2)_2$ | 1 | | 45 ^b | | |
| 5 | 7e ; R = PhCH_2 | 1 | | 60 ^b | | |
| 6 | 7a | 2 | | 53 ^b | | |
| 7 | 7b | 2 | | 41 ^b | | |
| 8 | 7a | 3 | | 28 | | 9 23 |
| 9 | 7b | 3 | | 20 | | 20 |
| 10 | 7b | 3 | | 15 ^c | | 43 ^c |
| 11 | 7d | 3 | | 25 | | 28 |
| 12 | 7d | 3 | | 20 ^c | | 36 ^c |
| 13 | 7e | 3 | | 58 | | |
| 14 | 7e | 3 | | 62 ^c | | |

^a All products were purified by flash column chromatography on silica gel, followed by distillation under reduced pressure. All new compounds have been fully characterized by ¹H and ¹³C NMR, IR, mass and high resolution mass spectra. ^b A trace (<5%) of ketone **6** was also isolated. ^c The reaction mixture was stirred at –10 °C instead of the regular temperature (0 °C).

**Scheme 1** Proposed reaction pathways for the formation of isoprenyl compounds **4** and β,γ -unsaturated ketones **6**

Slow addition of a THF solution of the highly functionalized copper reagents $\text{RCu}(\text{CN})\text{ZnI}$ (1.2 mol equiv.) to a stirred suspension of cations in THF at 0 °C for 3 h under nitrogen, followed by work-up with saturated ammonium chloride solution, ether extraction, flash column chromatography on silica, and short-path distillation under reduced pressure yielded mainly alkene adducts with a trace of ketone products (<5%). Results of the additions are summarized in Table 1.[‡] The crude NMR spectra of the nucleophilic additions to cations **1** and **2** (entries 1–7, Table 1) showed that attack mainly occurred at the unsubstituted allyl terminus to produce polyfunctionalized isoprenyl compounds as the major products (pathway *a*, Scheme 1). A trace of ketone **6** was also isolated in each case. The formation of ketones can be accommodated by initial addition to a coordinated carbon monoxide ligand producing a metal–acyl intermediate **5**. Migration of the acyl to the less substituted terminus of the allyl, followed by detachment of the ironcarbonyl moiety from the alkene ligand produced the functionalized β,γ -unsaturated ketones (pathway *b*, Scheme 1). However, under the same reaction conditions, the addition of the copper reagents to cation **3** (entries 8, 9 and 11) gave the usual alkene adducts together with approximately an equal amount of ketone products. The steric congestion at the terminus of the allyl cation **3** may play an important role for the formation of the ketones. It was presumed that nucleophilic additions at the substituted C-1 position of cation **3** were slow. The copper reagents could then attack at a coordinated CO to form the acyl intermediate **5**. We have further examined the possibility of increasing the yields of ketones by addition of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ or carbon monoxide. The results did not appear to have any significant change. However, the yields of the ketone adducts increased when reactions were performed at –10 °C (entries 10 and 12, Table 1). Nevertheless, the reaction of the benzylic

[‡] Spectroscopic data: alkene **8**: ¹H NMR (CDCl_3) δ 4.86 (1H, d, *J* 9.3 Hz), 4.11 (2H, q, *J* 7.1 Hz), 2.32–2.18 (3H, m), 1.68–1.54 (6H, m), 1.33–1.19 (6H, m) and 0.98–0.83 (4H, m); ¹³C NMR (CDCl_3) δ 173.8, 131.0, 130.1, 60.1, 337.2, 34.5, 32.2, 25.7, 23.0, 21.2, 17.9 and 14.2; IR (CH_2Cl_2 , solution) ν/cm^{−1} 3056m, 2964s, 1726s, 1448m, 1375m, 1188m and 1031mm; mass (EI) *m/z* 198 (M^+ , 5%), 109 (10), 83 (100), 69 (86), 55 (42), 41 (32) and 32 (48); high resolution, calc. for $\text{C}_{12}\text{H}_{22}\text{O}_2$ 198.1619; found *m/z* 198.1610.

Ketone **9**: ¹H NMR (CDCl_3) δ 4.99 (1H, dd, *J* 9.6, 1.4 Hz), 4.1 (2H, 1, *J* 7.2 Hz), 3.38–3.30 (1H, m), 2.54–2.46 (2H, m), 2.33–2.26 (2H, m), 1.93–1.83 (2H, m), 1.71 (6H, dd, *J* 4.9, 1.3 Hz), 1.25 (3H, t, *J* 7 Hz) and 1.10 (3H, d, *J* 6.8 Hz); ¹³C NMR (CDCl_3) δ 211.4, 173.2, 134.6, 124.0, 60.2, 46.5, 39.2, 33.3, 25.7, 18.9, 18.1, 16.4 and 14.2; IR (CH_2Cl_2 , solution) ν/cm^{−1} 3064w, 2974s, 2932s, 1726s, 1448m, 1425m, 1376m, 1252w, 1099s and 1064s cm^{−1}; mass (EI) *m/z* 226 (M^+ , 1%), 180 (25), 162 (9), 142 (100), 114 (99), 87 (99), 83 (99), 66 (26), 58 (28), 55 (99), 43 (99), 41 (94), 29 (72) and 17 (95); high resolution, calc. for $\text{C}_{13}\text{H}_{22}\text{O}_3$ 226.1568; found *m/z* 226.1571.

copper reagent **7c** (entries 13, 14) with cation **3**, either at 0 or at $-10\text{ }^{\circ}\text{C}$, did not produce ketone adducts.

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