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Coupling of Geminal Dihalides with Disodium Tetracarbonyl Ferrate: a Novel Reactivity Pattern for Collman's Reagent†

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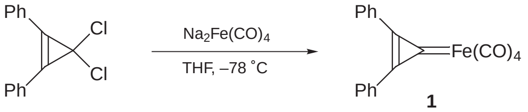
The reaction of *gem*-dihalides with $Na_2Fe(CO)_4$ results in the formation of alkenes instead of the iron(0) carbene complexes.

As part of our continuing efforts to determine the reactivity pattern of iron(O) carbene complexes we undertook the attempted synthesis of such complexes devoid of heteroatom stabilization at the carbene carbon.[1] Although the tungsten analogues were first prepared *via* a protocol involving modification of heteroatom stabilized complex with aryllithium[2] reagents or potassium triisopropoxyborohydride[3] followed by treatment with acid; we know of no account of similar procedures working with iron(O) carbene complexes. It has been our experience that simple modification of the iron(O) carbene complexes through nucleophilic substitution does not follow the same straightforward course as their chromium, molybdenum and tungsten analogues. The chemistry of disodium tetracarbonylferrate has been actively studied for over twenty years[4,5] but the synthesis of iron carbene complexes by double displacement reactions is unprecedented. 1,2-Diphenylcyclopropene and $Na_2Fe(CO)_4$ yield the novel 2,3-diphenylcyclopropene tetracarbonyliron(O) species **1** in 15% yield [eqn. (1)].



1

(1)

Presumably, the strained 3,3-dichloro-1,2-diphenylcyclopropene binds strongly to iron because the rehybridization on binding leads to the relief of strain and generation of aromaticity which accounts for the stability of the carbene complex **1** formed. The scope of this reaction was explored using symmetrical diaryl *gem*-dichloromethanes;[6] however, the desired carbene complex was not isolated and low temperature NMR provided no evidence of carbene formation. Instead, coupling products were isolated (Table 1), and this route has proven to be quite general for symmetrical diaryl *gem*-dichloromethanes. This reaction is relatively insensitive to the presence of strong electron donors or acceptors. For example, 3,3′-bis(trifluoromethylphenyl) and 4,4′-bis(methoxyphenyl) substitution gave the alkene in 34 and 37% yield, respectively. To date the best yield was obtained with the 4,4′-bis(methylphenyl) substituted derivative, which gave a 96% yield of the alkene. Although much remains to be established with respect to the scope of the reaction, it is our hypothesis that this reaction proceeds *via* an S_N2 mechanism. Further study of this reaction pattern, which to the best of our knowledge, has not been reported for $Na_2Fe(CO)_4$ will involve unsymmetrical starting materials including dihalides derived from enolizable ketones as well as the possibility of preparing inorganic derivatives and polymers.

Experimental

Disodium tetracarbonylferrate (1.2 g, 5.62 mmol) was transferred in an argon filled drybox to a 25 mL Schlenk flask. 15 mL of THF was added and the suspension was stirred at 25 °C for 10 min then cooled in a dry ice–ethanol bath. 2,3-Diphenyldichlorocyclopropene (1.33 g; 5.11 mmol) was added at –78 °C and gave **1**. δ_c (75 MHz, $CDCl_3$) 213.4, 193.78, 192.10 (s, Fe–CO), 132.25, 129.58, 129.77, 128.78. IR (ν/cm^{-1}) 2071, 2042, 2001vs [$Fe(CO)_4$], 2880s (C=C).

General Preparation of Alkenes.—Disodium tetracarbonylferrate (2.00 g, 9.35 mmol) was transferred in an argon filled drybox to a 100 mL Schlenk flask. 50 mL of THF was added and the suspension was stirred at 25 °C for 10 min then cooled in a dry ice–ethanol bath. 8.5 mmol of the *gem*-dihalide was added at –78 °C and the reaction mixture was allowed to warm slowly to 25 °C. The mixture was poured into benzene–hexanes (100 mL) and washed with water (100 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated on a rotary evaporator. The crude product was purified by column chromatography and eluted on silica gel in hexanes and characterized by NMR and MS.

2a δ_H(300 MHz, $CDCl_3$) 7.04–7.26 (5H, m). δ_C (75 MHz, $CDCl_3$) 126.47, 127.65, 131.38, 143.8. *m/z* 332 (100) [M^+], 253(40), 255(20), 178(6).

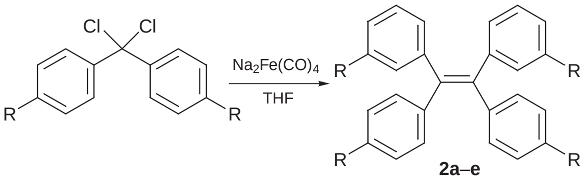
2b δ_H(300 MHz, $CDCl_3$) 7.5 (2H, d, *J* 8.1 Hz), 7.7 (2H, d, *J* 8.1 Hz). δ_C (75 MHz, $CDCl_3$) 128.74, 131.4. *m/z* 460(0.8) [M^+], 332(7), 250(38), 139(100), 111(50).

2c δ_H(300 MHz, $CDCl_3$) 3.9 (3H, s), 7.7 (2H, d, *J* 8.1 Hz), 7.8 (2H, d, *J* 8.1 Hz). δ_C (75 MHz, $CDCl_3$) 55.51, 113.73, 128.51, 131.10, 132.38. *m/z* 604(1.5), 372(1.5), 246(42), 135(100).

2d δ_H(300 MHz, $CDCl_3$) 7.1–7.3 (3H, m), 7.43 (1H, d, *J* 7.5 Hz). δ_C (75 MHz, $CDCl_3$) 124.33, 124.81, 127.87, 128.84, 131.30, 134.06, 142.28. *m/z* 604(100) [M^+], 585(10), 302(16), 233(18), 145(2).

2e δ_H(300 MHz, $CDCl_3$) 2.43 (3H, s), 7.24 (2H, d, *J* 8.1 Hz), 7.72 (2H, d, *J* 8.1 Hz). δ_C (75 MHz, $CDCl_3$) 21.37, 128.73, 129.97, 135.23, 142.64. *m/z* 604(1.8), 402(100), 388(18) [M^+], 195(24), 119(100), 57(70).

Table 1 Preparation of alkenes from symmetrical diaryl *gem*-dichloromethanes with $Na_2Fe(CO)_4$



Entry	Alkene	R	Yield(%)
1	**2a**	H	63
2	**2b**	Cl	54
3	**2c**	OMe	37
4	**2d**	*m*-CF_3	34
5	**2e**	Me	96

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† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

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