Tetrathioorthocarbonate as a C^{4+} Synthon. Nickel-catalysed Alkylative Alkenation of Tetrathioorthocarbonate with Grignard Reagents

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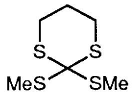
The nickel-catalysed cross-coupling reactions of tetrathioorthocarbonate **1** with Grignard reagents give the corresponding substituted alkenes in moderate to good yields; this reaction demonstrates the first example of using tetrathioorthocarbonate as a C^{4+} synthon.

Direct replacement of the C–X bonds in CX_4 by nucleophiles is rare and there seems to be little doubt that a decrease in S_N2 (on carbon) reactivity should parallel an increase in the number of halogen atoms attached to the same carbon atom.[1] To the best of our knowledge, replacement of all four C–X bonds by C–C bonds in one pot, whilst considering CX_4 as a C^{4+} synthon, is not known. The substitution of halogens of CX_4 (X = Cl or Br) by silyl groups is reportedly promoted by lithium metal.[2] There has been increasing interest in the transition-metal catalysed cross-coupling reactions of aliphatic C–X bonds with Grignard reagents.[3,4] The key to the success of these reactions relies, *inter alia*, on the ability to facilitate the facile oxidative addition of the C–X bond by the use of a metal catalyst and a rapid follow-up coupling process. Since the C–X bond energy decreases with increasing number of these bonds attached to this carbon atom, we felt that the cross-coupling reaction of CX_4 could take place leading to the formation of the C–C bond. Tetrathioorthocarbonate **1** has

Table 1 Nickel-catalysed reactions of **1** with Grignard reagents

Grignard reagent	Product	Yield (%)
MeMgI	**2a**	66[a]
Bu^nMgBr	**2b**	75
c-$C_6H_{11}MgBr$	**2c**	56
Me_3CCH_2MgBr	**2d**	69
Me_3SiCH_2MgCl	**2e**	54
$Ph(Me)_2SiCH_2MgCl$	**2f**	43
PhMgBr	**4**	60
Bu^tMgCl	**5**	42

[a] Isolated as 1,2-dibromo-2-methylpropane.



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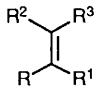

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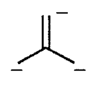

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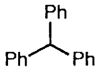
	R	R^1	R^2	R^3
a	Me	Me	H	H
b	Bu^n	Bu^n	H	H
c	c-C_6H_{11}	c-C_6H_{11}	–$(CH_2)_5$–	
d	Bu^tCH_2	Bu^tCH_2	Bu^t	H
e	Me_3SiCH_2	Me_3SiCH_2	Me_3Si	H
f	$Ph(Me)_2SiCH_2$	$Ph(Me)_2SiCH_2$	$Ph(Me)_2Si$	H
g	Ph	H	Me	Me
h	$PhCH_2$	Me	H	H



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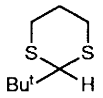

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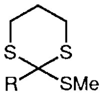

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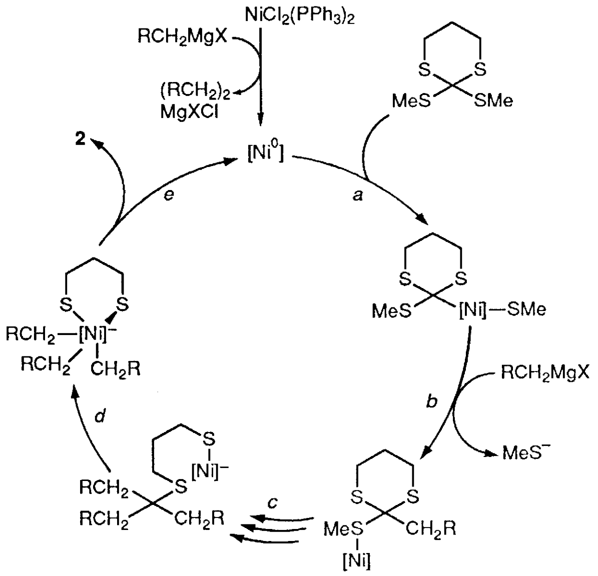
been known for two decades, but its chemistry has not been explored.[5] In a continuation of our interest in the nickel catalysed cross-coupling reactions of dithioacetals,[6] we report an unprecedented approach using **1** as a C^{4+} synthon.

In a typical procedure, the sulfur compound **1** was treated with 6 equiv. of the Grignard reagent in the presence of 5 mol% of $[NiCl_2(PPh_3)_2]$ in refluxing benzene–diethyl ether for 16 to 36 h to give, after the usual work-up, the alkene **2**.† Representative examples are shown in Table 1. To illustrate, the reaction of cyclohexyl Grignard reagent with **1** under these conditions afforded alkene **2c**. The sterically hindered neopentyl Grignard reagent behaved similarly, alkene **2d** being obtained in a satisfactory yield. This reaction is particularly useful in synthesizing silyl-substituted isobutenes **2e** and **2f**.† Whereas 1,3-bis(trimethylsilyl)propene can serve as a 1,3- or 3,3-propene dianion synthon,[7] tris-silanes **2e** and **2f** could be considered as a possible isobutene trianion synthon **3**.

The overall reaction appears to involve the replacement of three C–S bonds by three C–C bonds and the remaining C–S bond undergoes a formal elimination process to give the alkene **2**. Accordingly, the mechanism (Scheme 1) should essentially be similar to those proposed for the nickel-catalysed alkenation of benzylic or allylic dithioacetals.[6] However, treatment of **1** with PhMgBr under the same conditions gave triphenylmethane **4** in 60% yield. When the same reaction mixture was quenched with D_2O, no deuterium incorporation was observed in **4**. Presumably, the successive introduction of the three phenyl groups may occur, and the cleavage of the fourth C–S bond leads to the formation of an intermediate which abstracts hydrogen from the solvent molecule to give **4**. The reaction of **1** with Bu^tMgCl under similar conditions afforded **5** in 42% yield. These results indicated that the cross-coupling reaction occurs sequentially, and the corresponding orthothioester **6** and dithioacetal **7** should be intermediates for these reactions. Although orthothioester **6** ($R = PhCH_2$) reacted with MeMgI under similar reaction conditions to give a 1:2 mixture of **2g** and **2h** in 79% yield, simple aliphatic dithioacetals **7** are inert under these conditions.[6,8] The high reactivity of **1** and **6** in these coupling reactions is somewhat striking. It is noteworthy that an intramolecular chelation by a heteroatom may enhance the reactivity of the C–S bond in the nickel-catalysed cross-coupling reaction.[9] Such a kind of coordination may also take place during the course of the reaction of **1** and of **6** with Grignard reagents.



Scheme 1 Steps *c* proceed *via* similar steps as in steps *a* and *b* to replace the two carbon–sulfur bonds by two carbon–carbon bonds. [Ni] denotes the nickel species which may contain other ligands such as phosphine.

In summary, we have demonstrated the first example of using tetrathioorthocarbonate as the C^{4+} synthon to synthesise various substituted alkenes. Our results indicated that certain aliphatic C–S bonds can be activated by the presence of the heteroatom(s) at the same carbon atom such that the nickel-catalysed cross-coupling reaction can proceed smoothly.

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† All compounds gave satisfactory spectroscopic properties (^1H and ^{13}C NMR and/or accurate mass). ^1H NMR data ($CDCl_3$, 300 MHz) for **2e**: δ 0.01 (s, 9 H), 0.51 (s, 18 H), 1.57 (s, 2 H), 1.66 (s, 2 H) and 4.72 (s, 1 H). For **2f**: δ 0.15 (s, 6 H), 0.22 (s, 6 H), 0.26 (s, 6 H), 1.68 (s, 2 H), 1.72 (s, 2 H), 4.90 (s, 1 H) and 7.27–7.32 (m, 15 H). ^{13}C NMR data ($CDCl_3$, 75 MHz) for **2e**: δ −1.2, −0.5, 0.7, 29.3, 33.4, 117.5 and 127.2. For **2f**: −3.0, −2.5, −0.6, 28.8, 32.6, 117.0, 127.6, 127.7, 128.5, 128.9, 133.6, 133.9, 138.8, 139.5 and 140.7. Accurate mass: **2e**: 272.1835 (calc. for $C_{13}H_{32}Si_3$ 272.1812). **2f**: 458.2275 (calc. for $C_{28}H_{38}Si_3$: 458.2281).

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