Cyclopropanation of Tricarbonyl(styrene)chromium(0)

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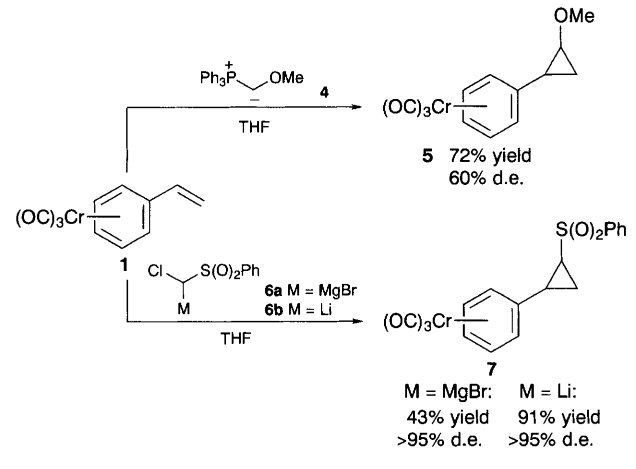
Tricarbonyl(styrene)chromium(0) **1** reacts with sulfur and phosphorus ylides, and α-chloro organometallics to give tricarbonylchromium(0) complexes of mono-, di- and tri-substituted cyclopropanes.

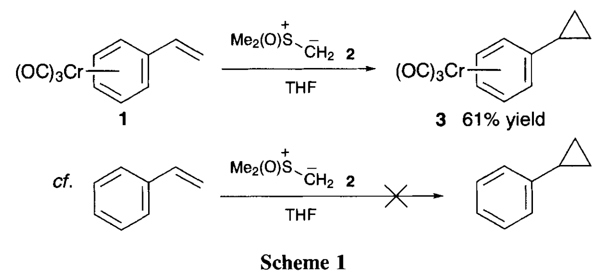
As a result of our recent discovery of a novel route to optically pure tricarbonylchromium(0) complexes of 2-substituted styrenes,[1,2] we are currently interested in the reactivity of alkenes bearing an (arene)tricarbonylchromium(0) substituent. Considering the rich and diverse chemistry normally associated with alkenes, the carbon-carbon double bond of tricarbonyl(styrene)chromium(0) **1** has received scant attention to date, and reported reactivity studies on this complex have revealed only that it undergoes Pauson–Khand chemistry,[3] rhodium-catalysed hydroformylation,[4] cycloadditions with cyclopentadiene[5] and nitrile oxides,[6] and attack by nucleophiles.[5,7,8] We report herein reactions which transform the carbon–carbon double bond of tricarbonyl(styrene)chromium(0) **1** into various cyclopropanes. These reactions not only represent a previously unreported mode of reactivity of tricarbonylchromium(0) complexes of styrenes, but they also generate an essentially new[†] and potentially interesting class of (arene)tricarbonylchromium(0) complex.

Addition of nucleophiles to tricarbonylchromium(0) complexes of styrenes occurs at their β-carbons to give α-carbanions which are stabilised by the adjacent (arene)tricarbonylchromium(0) unit and which may subsequently be reacted with electrophiles.[5,7,8] Although yields for this two-step process may be good,[7,8] and stereochemical control has recently been reported to be excellent,[8] the generality of the sequence with respect to the nucleophiles and electrophiles is somewhat limited. The low yields obtained with anything other than a narrow range of reagents has been attributed to an apparent ready reversibility of the nucleophilic addition step[7] and/or the formation of dimeric products arising from attack of the α-carbanions on a second molecule of the styrene complex.[5,7,11] We reasoned that incorporation of an intramolecular electrophilic quench may limit the severity of these problems. To test our hypothesis, tricarbonyl(styrene)chromium(0) **1**[‡] was added to sulfur ylide **2** [derived from $(Me_3SO)^+I^-$/NaH]. After the reaction between **1** and **2** had proceeded for 5 days at room temp. in THF, we were pleased to find that tricarbonyl(cyclopropylbenzene)chromium(0) **3** had indeed been formed and that it could be isolated from the product mixture in 61% yield. In contrast, rection of styrene itself with ylide **2** at room temp. for 1 day did not generate any cyclopropylbenzene whatsoever (Scheme 1).

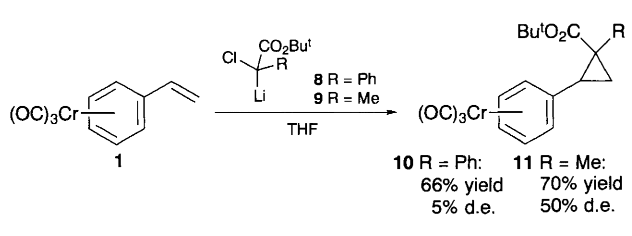
In order to probe this new mode of reactivity further, and to test not only whether or not more highly substituted cyclopropanes may be synthesised by this method but also how effective different types of nucleophiles and electrophiles would be, the sulfur ylide **2** was replaced with several other reagents which, it was proposed, would react in a similar manner. Thus the phosphorus ylide **4** [derived from $(MeOCH_2PPh_3)^+Cl^-$/Bu^{t}OK] was reacted with complex **1**: this reaction gave a 72% isolated yield of the novel[§] disubstituted cyclopropyl complex **5** (Scheme 2). ^{1}H NMR spectroscopy of the crude product mixture revealed that complex **5** has been formed in 60% diastereoisomeric excess. In contrast, reaction of complex **1** with $ClC(H)(MgBr)S(O)_2Ph$ **6a** [$ClCH_2S(O)_2Ph$/EtMgBr] proceeded to produce only one diastereoisomer of the novel complex **7**. The yield for this reaction was relatively low (43%) but it was found that this improved to 91% with the use of the lithium derivative **6b** [$ClCH_2S(O)_2Ph$/LDA]. As the reactions of **6a** and **6b** with tricarbonyl(styrene)chromium(0) **1** may proceed by a different reaction pathway to ylides **2** and **4**, it was considered prudent to execute a second control experiment involving uncomplexed styrene. Generation and reaction of **6b** with styrene under identical conditions to those used to form the cyclopropylbenzene complex **7** from the styrene complex **1**, however, did not generate any cyclopropane. Finally, trisubstituted cyclopropanes were synthesised using reagents **8** and **9** [derived from $ClC(H)(CO_2Bu^t)Ph$/LDA and $ClC(H)(CO_2Bu^t)Me$/LDA respectively]. Addition of **8** and **9** to complex **1** gave good yields of the novel complexes **10** and **11** respectively (Scheme 3)[¶].



Scheme 2



Scheme 1



Scheme 3

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Footnotes

† Tricarbonyl(cyclopropylbenzene)chromium(0) **3** has been prepared in 20% yield from cyclopropylbenzene and $[Cr(CO)_3(NH_3)_3]$,[9] and it has been used in arene exchange studies (details of preparation unreported).[10] To the best of our knowledge, these are the only reports of tricarbonylchromium(0) complexes of cyclopropyl substituted arenes.

‡ Complex **1** was prepared in 51% yield [based on $Cr(CO)_6$] by heating at reflux under nitrogen a mixture of styrene and $Cr(CO)_6$ (3 : 1) in dioxane–THF (4 : 1) for 70 h.[3]

§ All novel complexes (**5**, **7**, **10** and **11**) and the previously uncharacterised complex **3** gave satisfactory spectroscopic (IR, ^{1}H NMR, ^{13}C NMR and low-resolution MS) and microanalytical or high resolution MS data.

¶ Although complex **11** was formed as a mixture of diastereoisomers, it was found that they could be easily separated by column chromatography. The relative stereochemistry of the isomers of **5**, **7**, **10** and **11** could not be determined conclusively by examination of their ^{1}H NMR spectra due to the considerable overlap of expected ranges of J values for geminal, *cis* and *trans* couplings in cyclopropanes.

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