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# Nucleophilic addition reactions of bridged triene η$^6$-chromiumtricarbonyl complexes

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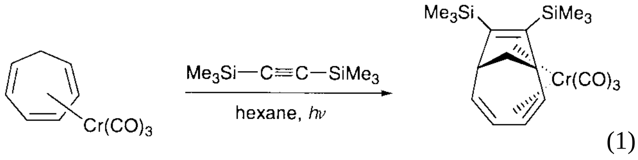
**Bridged triene η$^6$-chromiumtricarbonyl complexes have been shown to undergo regioselective addition reactions with a range of nucleophiles including organolithium reagents and enolates.**

Formation of the corresponding η$^6$-chromiumtricarbonyl complex provides a versatile method for enabling nucleophilic addition to aromatic compounds, and can result in the formation of substituted aromatic complexes or non-aromatic products.[1] Less well known are the corresponding seven-membered complexes derived from tropone, cycloheptatriene, and related heterocyclic systems.[2] These compounds have been demonstrated to undergo formal cycloaddition reactions with either alkynes or 1,3-dienes, *e.g.* eqn. (1)[2c,3]



(1)

1 2

Cycloheptatriene complex **1** undergoes efficient cycloaddition with bistrimethylsilylacetylene to give the bridged product complex **2** in good yield.† It seemed to us that the type of activation towards nucleophilic substitution seen in the arene complexes might also be operative in triene complexes such as **2**, although, as far as we are aware, this mode of reactivity has not been demonstrated.[4] Here we describe the first examples of additions to such complexes, which occur in a highly regioselective fashion with a range of nucleophiles.

The readily available bis-silylated complex **2** was used for the majority of our initial studies, and also because the vinyl silane functionality in the products could be synthetically useful. Addition of a number of nucleophiles to a solution of **2** in THF at −78 °C, followed by protic work-up, resulted in the formation of the metal-free adducts **3** and/or **4** as shown in Table 1.‡

The complex reacted with several varied alkyllithiums, dimethylcyanocuprate, the lithium enolates derived from ethyl acetate or *N*,*N*-dimethylacetamide, two examples of lithiated nitriles and a lithiated sulfone.§ In every case the initial addition reaction appears to be highly regioselective for the terminus of the complexed diene, whereas the position of subsequent protonation appears to be highly dependent upon the nature of the group being introduced. In most cases the presumed intermediate anionic dienyl complex undergoes protonation distal to the entering substituent, to give exclusively or mainly isomer **3**, whereas in a few cases the alternative isomer **4** predominates.

Although the proposed structures accorded with our expectations, and were supported by high field NMR data, we were concerned by the variable ratios of the two products formed and could not entirely rule out the possibility that the isomers formed were alternative regio- or stereoisomers. Fortunately we were able to obtain X-ray crystal structure determinations of certain derivatives, including the nitrile **3** (R = $CH_2CN$) and the sulfone **4** (R = $CH_2SO_2Ph$), which are illustrated in Fig. 1 and 2, respectively.¶

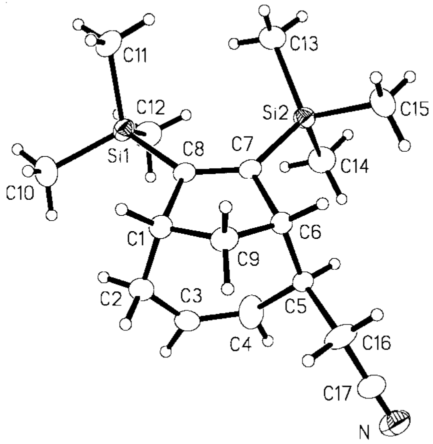
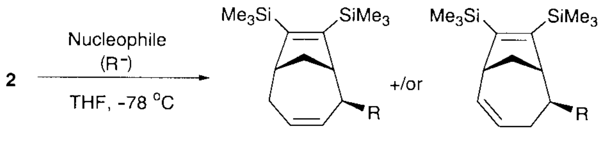


**Fig. 1** Crystal structure of nitrile adduct **3** (R = $CH_2CN$).

**Table 1** Nucleophilic addition to complex **2**



3 4

| Nucleophile (R−) | MeLi | $Me_2Cu$-(CN)$Li_2$ | $^nBuLi$ | PhLi | LiC-(OEt)=$CH_2$ | $CH_2$=C-(OLi)OEt | $CH_2$=C-(OLi)$NMe_2$ | $LiCH_2CN$ | LiC-$(CH_3)_2CN$ | $LiCH_2$-$SO_2Ph$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Yield (%) | 55 | 30 | 34 | 61 | 84 | 53 | 82 | 50 | 83 | 58 |
| **3**:**4** | 7:1 | 1.3:1 | **3**[a] | **3**[a] | **3**[a] | 1:2 | 5:1 | 5:1 | **3**[a] | 1:5 |

[a] Only isomer **3** detected by $^1H$ NMR of crude product.

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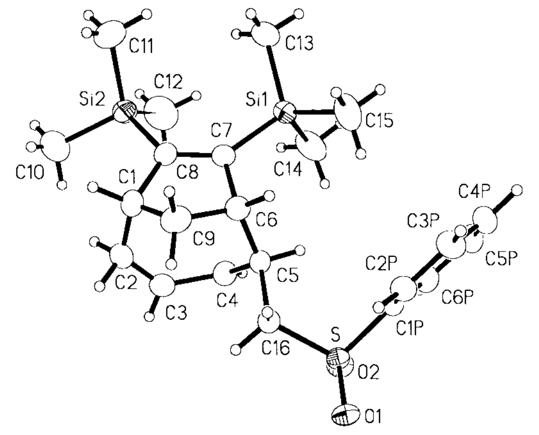
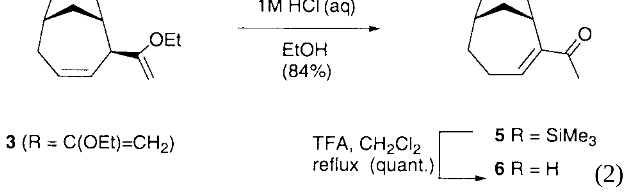


**Fig. 2** Crystal structure of sulfone adduct **4** (R = $CH_2SO_2Ph$).

These two structures confirm that the initial nucleophilic addition to **2** is indeed highly regioselective for the diene terminus, and also that the new substituent is *exo*-orientated in the bridged product. The structures also confirm the contrasting alkene regiochemistry assigned by NMR, but at present we have no convincing explanation for the isomer ratios seen with the different nucleophiles.

It was of interest to briefly examine the transformations possible with these types of product, for example the alkenyl ether product **3** could be converted into the α,β-unsaturated ketone **5** on treatment with dilute acid, eqn. (2).



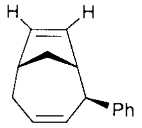
**3** (R = C(OEt)=$CH_2$)

**5** R = $SiMe_3$

**6** R = H

(2)

Treatment of this product under more vigorous acidic conditions (TFA, $CH_2Cl_2$, reflux) resulted in complete desilylation to give enone **6**. This type of desilylation was also shown to be possible on an alternative type of adduct, compound **3** (R = Ph), on reaction under the same conditions, to give product diene **7**.



**7**

In conclusion, we have demonstrated for the first time that efficient nucleophilic addition to bridged chromium complexes is possible. In the near future we hope to extend the chemistry to heterocyclic complexes, which could lead to a novel synthesis of the alkaloid anatoxin-a, and to provide further details of the scope and limitations of the chemistry.‖

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## Notes and references

† We obtained a yield of 69%, with even higher yields being possible (80%) according to ref. 3(*b*).

‡ *Typical experimental procedure*: A solution of the appropriate nucleophile in THF was added dropwise to a stirred solution of the bridged triene chromium complex (usually **2**) in THF at −78 °C. The resultant solution was stirred at this temperature until reaction appeared complete by TLC (typically 1 h), and then saturated $NH_4Cl(aq)$ solution was added and the mixture warmed to room temperature prior to extraction with $Et_2O$ (3 × 5 ml). The combined organic extracts were back washed with water, brine, dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography on silica gel afforded the addition adducts **3**/**4** as indicated in Table 1.

§ Nucleophiles which did not give clean reactions include the lithium enolate from acetophenone, PhMgCl, and the lithiated derivatives from benzylcyanide, 1,3-dithiane, methoxy methyl ether, *N*-boc-pyrrolidine and 2,3-dihydrofuran. It is unclear why some of these reactions failed, whereas closely related reactions indicated in Table 1 were successful. We have not so far been successful in quenching the intermediate anion with carbon electrophiles.

¶ For both **3** and **4** a crystal was encapsulated in a film of RS3000 perfluoropolyether oil and mounted on a glass fibre before transfer to the diffractometer.

*Crystal data* for **3**: $C_{17}H_{29}NSi_2$, $M$ = 303.59, monoclinic, $a$ = 11.370(2), $b$ = 16.982(4), $c$ = 19.115(4) Å, $\beta$ = 103.657(4), $U$ = 3587(2) Å$^3$, $T$ = 150(2) K, space group $P2_1/c$ (no 14), $Z$ = 8, $D_c$ = 1.125 g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 0.190 mm$^{-1}$, 8422 unique reflections measured and used in all calculations. Final $R_1$ [4937 $F \geqslant 4\sigma(F)$] = 0.0484 and $wR$ (all $F^2$) was 0.125. For **4**: $C_{22}H_{34}O_2SSi_2$, $M$ = 418.73, triclinic, $a$ = 6.8685(12), $b$ = 9.314(2), $c$ = 19.746(4) Å, $\alpha$ = 102.190(3), $\beta$ = 95.424(3), $\gamma$ = 98.875(3), $U$ = 1209.3(6) Å$^3$, $T$ = 150(2) K, space group $P\bar{1}$ (no. 2), $Z$ = 2, $D_c$ = 1.150 g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 0.247 mm$^{-1}$, 4685 unique reflections measured and used in all calculations. Final $R_1$ [$F \geqslant 4\sigma(F)$] = 0.0510 and $wR$ (all $F^2$) was 0.148. CCDC 182/1642. See http://www.rsc.org/suppdata/cc/b0/b002256j/ for crystallographic files in .cif format.

‖ One result employing the complex derived from diphenylacetylene indicated that the same type of nuclophilic addition process is possible.

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4 For related additions to iron complexes, see: W. A. Donaldson, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone, G. Wilkinson and L. S. Hegedus, Pergamon, Oxford, 1995, vol. 12, p. 623; for additions to cycloheptatriene complexes, see: M.-C. P. Yeh and C.-N. Chuang, *J. Chem. Soc., Chem. Commun.*, 1994, 703; W. Chen, J. B. Sheridan, M. L. Coté and R. A. Lalancette, *Organometallics*, 1996, **15**, 2700.