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

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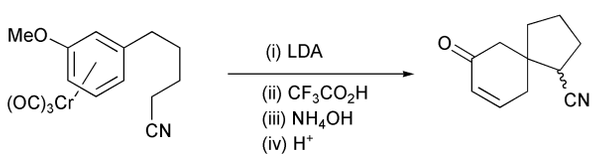
The metal-mediated addition of a range of nucleophiles to several bridged η^6-chromiumtricarbonyl complexes has been demonstrated for the first time. The reaction proceeds in regio- and stereoselective fashion and in fair to good yield. The new reaction was applied to the synthesis of an advanced intermediate towards anatoxin-a.

Introduction

Over 20 years ago, seminal work by the research group of Semmelhack established the viability of nucleophilic substitution reactions of η^6-chromiumtricarbonyl complexes.[1] Particularly interesting in the context of natural product synthesis were the classic examples of intramolecular addition reactions leading to various kinds of annulated products, *e.g.* Scheme 1.[2]



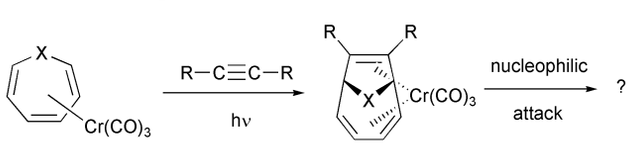
1 **2**

Scheme 1

Nucleophilic attack is facilitated by the metal, the reaction proceeding *via* an intermediate anionic η^5-cyclohexadienyl complex in which the negative charge resides largely at the chromium centre.

The scope and limitations of nucleophilic addition to chromium arenes are now firmly established, including: (i) the types of nucleophiles that undergo addition and those that do not. (ii) The regiochemical control possible in reactions of substituted complexes. (iii) The type of product formed, which may be a product complex, a metal free aromatic or a dearomatised (diene or diene-derived) product. More details of these possibilities can be found in a recent review.[3]

We became interested in exploring the nucleophilic addition chemistry of a much less common type of organometallic system, namely the bridged complexes generated by formal [6 + 2] cycloaddition of seven-membered η^6-chromium-tricarbonyl complexes **3**, Scheme 2.[4–7]



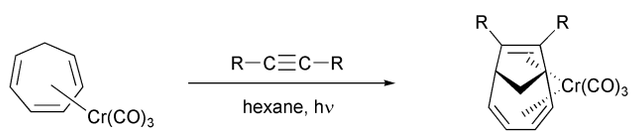
3 **4**

Scheme 2

We were aware of no chemistry of the unusual η^6-complexes **4**, other than de-metallation to provide bridged products that have applications in natural products synthesis.[5] It seemed reasonable that the activating effect of the chromium tricarbonyl unit present in the bridged complexes would enable nucleophilic addition to these compounds in a similar fashion to that seen with the arene complexes.[8] Here we describe our results, which demonstrate that this is indeed possible with a range of nucleophiles in regio- and stereoselective fashion.[9]

Results and discussion

We chose to commence our study by preparing bridged complexes **6** and **7** from cycloheptatriene complex **5**[10] using the photolytic conditions described by Sheridan and co-workers, Scheme 3.[7]



5

6 R = $SiMe_3$ 69%
7 R = Ph 21%

Scheme 3

Reaction of **5** in degassed hexane at room temperature using a 125 W medium pressure mercury lamp gave **6** in good yield, although we found the corresponding preparation of **7** more problematic (the reported yield is 85%). Analogous reactions involving bis-ethers or silyl ethers of 1,4-dihydroxybut-2-yne were not successful in our hands.

The addition of nucleophiles to a solution of **6** in THF at −78 °C, followed by protic work-up, resulted in the formation of the metal-free adducts **8** and/or **9** as shown in Table 1.†

The complex **6** reacted with several different 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 and no products arising from addition to the internal position or to the bis-silylalkene part were observed. This might be expected since the intermediate organometallic benefits from allylic stabilisation, although steric factors may also come into play. However, the position of subsequent protonation appears to be highly dependent upon

† We checked that the bridged triene corresponding to **6** did not undergo nucleophilic addition, thus establishing the crucial role of the chromiumtricarbonyl unit.

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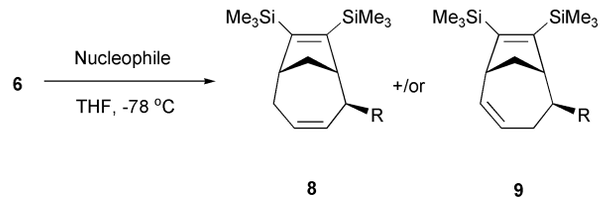
Table 1 Nucleophilic addition to complex **6**



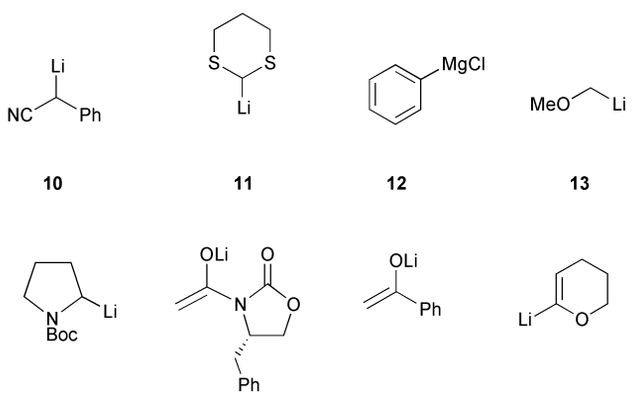
Nucleophile	MeLi	$Me_2Cu(CN)Li_2$	^nBuLi	PhLi	$LiC(OEt)=CH_2$	$CH_2=C(OLi)OEt$	$CH_2=C(OLi)NMe_2$	$LiCH_2CN$	$LiC(CH_3)_2CN$	$LiCH_2SO_2Ph$
Product (**8/9**)	a	a	b	c	d	e	f	g	h	i
Yield (%)	55	30	34	61	84	53	82	50	83	58
8 : 9	7 : 1	1.3 : 1	**8**[a]	**8**[a]	**8**[a]	1 : 2	5 : 1	5 : 1	**8**[a]	1 : 5

[a] Only isomer **8** detected by ^1H NMR of crude product. Compound **8d** was isolated as the corresponding methyl ketone – see text.

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 **8**, whereas in a few cases the alternative isomer **9** predominates.

Although the proposed structures accorded with our expectations, and were supported by high field NMR data, we were also able to obtain X-ray crystal structure determinations of the nitrile **8g** (R = CH_2CN) and the sulfone **9i** (R = CH_2SO_2Ph), which confirmed our assignments and were illustrated in our earlier communication.[9]

A number of analogous reactions were unsuccessful, including those involving the varied nucleophiles **10**–**17** shown below.

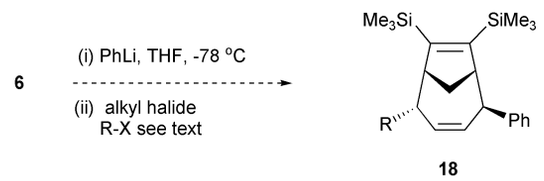


10 **11** **12** **13**

14 **15** **16** **17**

Many of these failures appear explicable in isolation, but are more difficult to explain when compared to the successful examples. For instance, some of the failed reactions involve quite bulky nucleophiles, but the successful reaction leading to nitrile **8h** appears more demanding than most. The failure of the dithiane anion **11** is surprising given the excellent results obtained with arene complexes and we were especially disappointed by the lack of reaction with **14** and **15**, given the possibilities for chiral nucleophile driven desymmetrisation. That lithiated dihydropyran **17** should fail to undergo addition is perhaps the most mysterious, given the smooth reaction observed with the acyclic variant, ethyl vinyl ether, leading to **8d** (this adduct was isolated as the corresponding methyl ketone, following mild acid treatment).

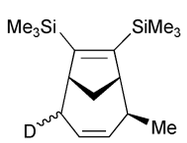
With the success of the nucleophilic addition reactions we were interested to see if this process could be followed *in situ* by a second carbon–carbon forming reaction by inclusion of an appropriate electrophile. This type of chemistry has been explored extensively in the arene series, most notably by Kundig and co-workers, and can provide a nicely stereocontrolled route to dialkylated cyclohexadienes, and also ketones *via* CO insertion.[3,11] With this in mind we tested the transformation shown in Scheme 4.



Scheme 4

Unfortunately, we were unable to detect the desired product **18** (or any alternative isomer) using MeI, allyl bromide or propargyl‡ bromide as the electrophile, even in the presence of additives such as DMPU, MeCN, CO or PPh_3, and only the usual product **8c** was obtained.

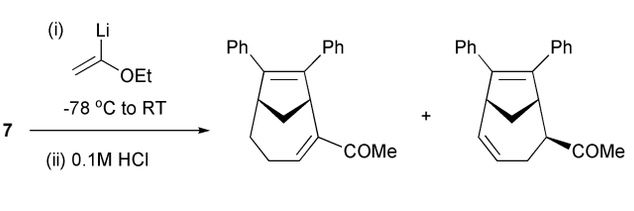
Attempts at deuterium quenching of the intermediate anions were successful only with d-trifluoroacetic acid (and not D_2O or MeOD), this giving complete incorporation, *e.g.* to give d-**8a**.



d-**8a**

Interestingly d-**8a** was obtained as a *single* regioisomer but as a 1 : 1 mixture of epimers. Thus, it appears that the ratio of regioisomers (**8** : **9**) is dependent upon the nature of the proton quench, and that the protonation does not involve initial delivery to the metal centre, since this would be expected to yield *endo*-deuterated product only. Unfortunately we were unable to pursue these aspects in more detail.

Nucleophilic addition to the diphenyl substituted cycloadduct complex **7** was also studied briefly. Reaction with lithiated ethyl vinyl ether proved sluggish compared with the corresponding reaction with **6**, and afforded the separable ketones **19** and **20** in modest yield following acidic work-up, Scheme 5.

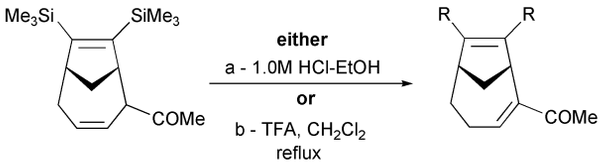


19 14% **20** 26%

Scheme 5

‡ The IUPAC name for propargyl is prop-2-ynyl.

At this point we were particularly interested in these types of ketone and enone products and so we examined the chemistry of methyl ketone **8d** as outlined in Scheme 6.

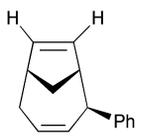


8d

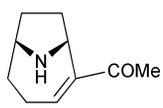
21 R = $SiMe_3$ 84% (via a)
22 R = H quant. (via b)

Scheme 6

Mild acid treatment effected alkene conjugation to give enone **21**, whereas the use of TFA resulted in additional double desilylation to give **22**. Surprisingly, desilylation of this type of fully substituted bis-silylalkene appeared unprecedented in the literature and so we also demonstrated the analogous conversion of **8c** into bicyclic alkene **23** under the same conditions.



23 84%



24

At this stage we recognised the structural analogy between the carbon bridged enones, such as **22**, and the well-known homotropane alkaloid anatoxin-a **24**.[12] Bearing in mind the transformations described above, the potential for this methodology to provide a new route to anatoxin seemed clear, providing that analogous chemistry of aza-bridged complexes could be accomplished. With this in mind we prepared the known complexes **25** and **26**,[13,7] and then established that addition of lithiated ethyl vinyl ether resulted in formation of methyl ketone **27** in reasonable yield, Scheme 7.

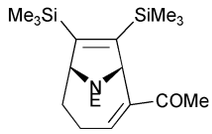
As in the previous reactions using this particular nucleophile, none of the alternative alkene regioisomer was observed.

With the complete skeleton of anatoxin-a in place completion of a formal total synthesis required only alkene isomerisation, selective hydrogenation and double desilylation (a number of *N*-protected derivatives are known), which had proved facile on the carbon-bridged systems.

Unfortunately, to date we have been unable to complete this synthesis. Treatment of compound **27** under a wide range of conditions, including TBAF, TFA, TsOH, HI and HF–pyridine, did not remove the silicon substituents, although most conditions did result in formation of the enone **28** (use of 2.0 M HCl gave this compound in quantitative yield).

The use of TBAT (tetrabutylammonium triphenyldifluorosilicate)[14] as fluoride source under forcing conditions, THF–HMPA at 80 °C, appeared to remove one of the silicon substituents, but further exposure to these vigorous conditions lead only to destruction of the material.

In conclusion, we have demonstrated for the first time that metal-mediated nucleophilic addition to bridged η^6-chromium-



28

tricarbonyl complexes, such as **6**, **7** and **26**, is possible. The process appears quite general, but successful reaction is rather nucleophile dependent for reasons that are not completely clear at present. The regio- and stereochemical control possible, make this a potentially useful access to certain types of bridged product, as demonstrated by our synthesis of an advanced intermediate towards anatoxin-a. A total synthesis of this alkaloid target remains tantalising and requires only a more effective method for removal of unwanted silicon substituents.

Experimental

General Details

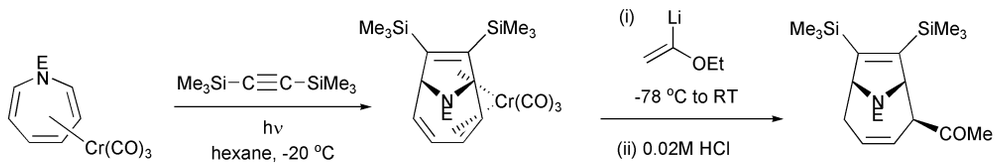
Melting points were recorded on a Stuart Scientific SMP3 apparatus and are uncorrected. Microanalytical data were obtained on a Perkin-Elmer 240B elemental analyser. Infrared spectra were recorded on a Perkin-Elmer 1600 or a Nicolet Protégé 460 FTIR machine and are reported in cm^{-1}.

NMR spectra were recorded on Bruker AM400, AV400, DRX500, Jeol FX 270, or Varian Unity Inova 300 machines, using $CDCl_3$ as solvent at 298 K. Chemical shifts are given in ppm downfield from tetramethylsilane, using either the TMS or residual protic solvent as an internal standard. *J* values are recorded in Hz and rounded to the nearest half integer value. The following abbreviations apply- (app.) apparent, (b) broad, (s) singlet, (d) doublet, (t) triplet, (q) quartet, (m) multiplet, (dd) double doublet, *etc*. Where necessary, proton and carbon assignments were assisted with ^{1}H COSY, HMQC, DEPT or NOE sequences. The chemical shifts of multiplets corresponding to a single proton are quoted as a point, representing the centre of the multiplet. Where the signals for two or more protons overlap, a range is quoted. Diagnostic signals only are given in some cases for minor components of isomer mixtures where signals are obscured by those from the major isomer.

Mass spectra were obtained using a VG Micron Autospec or VG Micromass 70E spectrometer, using electron impact (EI), or fast atom bombardment (FAB), using *m*-nitrobenzyl alcohol as the matrix.

Photolyses were conducted in Pyrex flasks (fitted with a cooling jacket if necessary) with a water-cooled Pyrex well containing a 125 W Hanovia medium pressure Hg lamp. A 0.7 M $CoSO_4$ solution was used in the coolant to absorb wavelengths above approximately 400 nm.

All reaction mixture temperatures refer to values recorded for an external cooling bath. Room temperature implies temperatures in the range 20–25 °C. Reaction progress was monitored by thin layer chromatography (TLC) performed on Merck Kieselgel 60 F_{254} aluminium backed plates, which were visualised by a combination of ultraviolet light and potassium permanganate. Flash column chromatography was performed



25 E = CO_2Et

26 87%

27 52%

Scheme 7

using Merck Kieselgel 60 (230–440 mesh), in the indicated solvent. Degassing of solvent was undertaken by bubbling argon through the solvent.

Organic solvents and reagents were dried by distillation from the following as required: THF, Et_2O (sodium–benzophenone ketyl); MeOH (magnesium); DMF ($MgSO_4$); Me_3SiCl (calcium hydride). Petrol refers to petroleum ether (bp 40–60 °C), which was distilled before use. All other solvents and reagents were used as received from commercial suppliers unless otherwise stated. Compounds prepared and used subsequently without further purification were judged to be of suitable purity by NMR analysis.

5-Methyl-7,8-bis(trimethylsilyl)bicyclo[4.2.1]nona-3,7-diene 8a and 5-methyl-7,8-bis(trimethylsilyl)bicyclo[4.2.1]nona-2,7-diene 9a by MeLi addition

MeLi (1.58 M in hexane, 0.16 ml, 0.25 mmol) was added dropwise to a stirred solution of complex **6** (100 mg, 0.25 mmol) in THF (4 ml) at −78 °C under an atmosphere of nitrogen. The resultant solution was warmed to 0 °C over 2 h, quenched by the addition of saturated aqueous NH_4Cl (1 ml) and warmed to room temperature prior to extraction with diethyl ether (3 × 5 ml). The combined organics were washed with water (10 ml), brine (10 ml), dried ($MgSO_4$) and concentrated *in vacuo* to give a yellow oil. Flash chromatography (petroleum ether) afforded an inseparable mixture of the *title compounds* **8a** and **9a** (39 mg, 55%, 7 : 1) as a colourless oil, ν_{max} ($CHCl_3$)/cm^{-1} 2954, 2900, 1655 and 1603 (C=C), 876; δ_H(400 MHz; $CDCl_3$) major isomer **8a**: 0.16 (9H, s, $Si(CH_3)_3$), 0.17 (9H, s, $Si(CH_3)_3$), 1.03 (3H, d, *J* 7.0, CH_3), 1.63 (1H, d, *J* 12.0, 9′-H), 1.80 (1H, app. dt, *J* 12.0, 8.0, 9-H), 2.22 (1H, dm, *J* 18.5, *exo* 2-H), 2.30 (1H, dm, *J* 18.5, *endo* 2-H), 2.39 (1H, br s, 5-H), 2.85 (1H, br d, *J* 8.0, 6-H), 3.06 (1H, ddd, *J* 8.0, 5.0, 3.0, 1-H), 5.13–5.19 (2H, m, 3-H and 4-H), minor isomer **9a**: 0.14 (9H, s, $Si(CH_3)_3$), 0.21 (9H, s, $Si(CH_3)_3$), 0.97 (3H, d, *J* 7.0, CH_3), 1.50 (1H, app. dt, *J* 11.5, 7.5, 9-H), 1.74 (1H, d, *J* 11.5, 9′-H), 2.00–2.19 (3H, m, 4-H and 5-H), 2.96 (1H, dd, *J* 7.5, 5.0, 6-H), 3.27 (1H, app. t, *J* 7.5, 1-H), 5.47 (1H, ddd, *J* 11.5, 7.5, 3.5, 3-H), 5.78 (1H, ddd, *J* 11.5, 7.5, 3.5, 2-H); δ_C(68 MHz; $CDCl_3$) major isomer **8a**: 1.2 ($Si(CH_3)_3$), 1.3 ($Si(CH_3)_3$), 21.4 (CH_3), 33.7 (CH_2), 37.0 (CH_2), 40.5 (CH), 50.3 (CH), 57.4 (CH), 122.8 (olefinic CH), 131.3 (olefinic CH), 155.8 (*C*-$Si(CH_3)_3$), 157.5 (*C*-$Si(CH_3)_3$), minor isomer **9a**: 1.0 ($Si(CH_3)_3$), 1.5 ($Si(CH_3)_3$), 18.8 (CH_3), 32.3 (CH_2), 34.2 (CH_2), 36.4 (CH), 52.4 (CH), 58.7 (CH), 128.6 (olefinic CH), 133.4 (olefinic CH), 151.5 (*C*-$Si(CH_3)_3$), 156.1 (*C*-$Si(CH_3)_3$); *m/z* (EI) 278 (M^+, 9%), 263 (6), 210 (41), 195 (13), 122 (63), 73 (100) (Found M^+, 278.1892. $C_{16}H_{30}Si_2$ requires 278.1886).

Bridged products 8a and 9a by cuprate addition

MeLi (1.31 M in hexane, 0.38 ml, 0.50 mmol) was added dropwise to a stirred solution of cuprous cyanide (23 mg, 0.25 mmol) in THF (1 ml) at −78 °C under an atmosphere of argon. The mixture was warmed to −40 °C prior to dropwise cannula addition of complex **6** (100 mg, 0.25 mmol) in THF (4 ml). The resultant solution was stirred at this temperature for 3 h and then quenched by the addition of saturated aqueous NH_4Cl (1 ml) and warmed to room temperature prior to extraction with diethyl ether (2 × 5 ml). The combined organics were washed with water (10 ml), brine (10 ml), dried ($MgSO_4$) and the solvent removed *in vacuo* to give an orange oil. Flash chromatography (^{n}pentane) afforded an inseparable mixture of the *title compounds* **8a** and **9a** (21 mg, 30%, 1.3 : 1) as a colourless oil with spectroscopic data as described above.

2-(^{2}H)-5-Methyl-7,8-bis(trimethylsilyl)bicyclo[4.2.1]nona-3,7-diene d-8a

MeLi (1.5M in hexane, 0.50 ml, 0.75 mmol) was added dropwise to a stirred solution of complex **6** (100 mg, 0.25 mmol) in THF (5 ml) at −78 °C under an atmosphere of nitrogen. The resultant solution was stirred for 4 h at this temperature, quenched by the addition of d-TFA (0.19 ml, 2.51 mmol) and allowed to warm to 0 °C before being poured into NH_4OH (10 ml). Following extraction with diethyl ether (3 × 5 ml), the combined organics were washed with water (10 ml), brine (10 ml), dried ($MgSO_4$) and concentrated *in vacuo* to give a yellow oil. Flash chromatography (petroleum ether) afforded the *title compound* d-**8a** (64 mg, 98%) as a colourless oil, ν_{max} ($CHCl_3$)/cm^{-1} 2955, 2980, 1936 (C–D), 1654 and 1602 (C=C), 1249, 832; δ_H(400 MHz; $CDCl_3$) 0.16 (9H, s, $Si(CH_3)_3$), 0.17 (9H, s, $Si(CH_3)_3$), 1.03 (3H, d, *J* 7.0, CH_3), 1.63 (1H, d, *J* 12.0, 9′-H), 1.80 (1H, app. dt, *J* 12.0, 8.0, 9-H), 2.22 (0.6H, m, *exo* 2-H), 2.30 (0.4H, m, *endo* 2-H), 2.39 (1H, br s, 5-H), 2.85 (1H, br d, *J* 8.0, 6-H), 3.06 (1H, ddd, *J* 8.0, 5.0, 3.0, 1-H), 5.13–5.19 (2H, m, 3-H and 4-H); δ_C(100 MHz; $CDCl_3$) 1.3 ($Si(CH_3)_3$), 21.5 (CH_3), 33.7 (CH_2), 36.7 (t, *J* 19.0, CHD), 40.6 (CH), 50.3 (CH), 57.5 (CH), 122.9 (olefinic CH), 131.4 (olefinic CH), 156.0 (*C*-$Si(CH_3)_3$), 157.6 (*C*-$Si(CH_3)_3$); *m/z* (EI) 279 (M^+, 8%), 264 (8), 210 (60), 195 (18), 122 (80), 73 (100) (Found M^+, 279.1937. $C_{16}H_{29}DSi_2$ requires 279.1949).

5-^{n}Butyl-7,8-bis(trimethylsilyl)bicyclo[4.2.1]nona-3,7-diene 8b

^{n}BuLi (1.49 M in hexane, 0.17 ml, 0.25 mmol) was added dropwise to a stirred solution of complex **6** (100 mg, 0.25 mmol) in THF (5 ml) at −78 °C under an atmosphere of nitrogen. The resultant yellow solution was stirred at this temperature for 4 h, quenched by the addition of saturated aqueous NH_4Cl (1 ml) and warmed to room temperature prior to extraction with diethyl ether (3 × 5 ml). The combined organics were washed with water (5 ml), brine (5 ml), dried ($MgSO_4$) and concentrated *in vacuo* to give a yellow wax. Flash chromatography (petroleum ether) afforded the *title compound* **8b** (27 mg, 34%) as a colourless oil, (Found: C, 72.56; H, 11.44. $C_{19}H_{36}Si_2$ requires C, 72.17; H, 11.32%); ν_{max} ($CHCl_3$)/cm^{-1} 2898, 2859, 1654 (C=C), 877; δ_H(400 MHz; $CDCl_3$) 0.16 (9H, s, $Si(CH_3)_3$), 0.17 (9H, s, $Si(CH_3)_3$), 0.92 (3H, t, *J* 7.0, CH_3), 1.20–1.48 (6H, m, 3 × CH_2), 1.60 (1H, d, *J* 12.0, 9′-H), 1.80 (1H, app. dt, *J* 12.0, 8.0, 9-H), 2.18–2.34 (3H, m, 2-H and 5-H), 2.97 (1H, br d, *J* 8.0, 6-H), 3.06 (1H, m, 1-H), 5.18 (1H, m, 4-H), 5.28 (1H, m, 3-H); δ_C(100 MHz; $CDCl_3$) 1.2 ($Si(CH_3)_3$), 1.4 ($Si(CH_3)_3$), 14.1 (CH_3), 23.1 (CH_2), 30.2 (CH_2), 34.2 (CH_2), 35.8 (CH_2), 36.8 (CH_2), 45.5 (CH), 50.4 (CH), 55.0 (CH), 123.2 (olefinic CH), 130.5 (olefinic CH), 155.9 (*C*-$Si(CH_3)_3$), 157.9 (*C*-$Si(CH_3)_3$); *m/z* (EI) 320 (M^+, 5%), 210 (53), 195 (12), 122 (81), 73 (100) (Found M^+, 320.2365. $C_{19}H_{36}Si_2$ requires 320.2356).

5-Phenyl-7,8-bis(trimethylsilyl)bicyclo[4.2.1]nona-3,7-diene 8c

PhLi (1.19 M in cyclohexane–diethyl ether, 1.51 ml, 1.80 mmol) was added dropwise to a stirred solution of complex **6** (200 mg, 0.50 mmol) in THF (5 ml) at −78 °C under an atmosphere of nitrogen. The resultant dark orange solution was stirred at this temperature for 3 h, quenched by the addition of saturated aqueous NH_4Cl (1 ml) and warmed to room temperature prior to extraction with diethyl ether (3 × 5 ml). The combined organics were washed with water (10 ml), brine (10 ml), dried ($MgSO_4$) and concentrated *in vacuo* to give an orange oil. Flash chromatography (^{n}hexane) afforded the *title compound* **8c** as a white crystalline solid (104 mg, 61%), mp 64 °C (from ethanol–water) (Found: C, 73.81; H, 9.78. $C_{21}H_{32}Si_2$ requires C, 74.04; H, 9.47%); ν_{max} ($CHCl_3$)/cm^{-1} 3080, 3061, 3025, 3004, 2945, 2889, 2842, 1658, 1599, 1533, 1256, 827; δ_H(400 MHz; $CDCl_3$) 0.18 (9H, s, $Si(CH_3)_3$), 0.29 (9H, s, $Si(CH_3)_3$), 1.56 (1H, d, *J* 12.0, 9′-H), 1.66 (1H, app. dt, *J* 12.0, 7.5, 9-H), 2.39 (1H, dm, *J* 16.0, 2-H*H*), 2.44 (1H, app. dtd, *J* 16.0, 4.5, 2.5, 2-*H*H), 3.06 (1H, app. dt, *J* 7.5, 4.5, 1-H), 3.14 (1H, dd, *J* 7.5, 2.0, 6-H), 3.74 (1H, br s, 5-H), 5.39 (1H, dm, *J* 12.0, 4-H), 5.54 (1H, dm, 12.0, 3-H), 7.19–7.36 (5H, m, 5 × ArCH); δ_C(100 MHz; $CDCl_3$) 1.2 ($Si(CH_3)_3$), 1.6 ($Si(CH_3)_3$), 34.1 (CH_2), 37.1 (CH_2), 50.1 (CH),

51.8 (CH), 58.9 (CH), 126.0 (olefinic CH), 126.8 (olefinic CH), 127.7 (ArCH), 128.2 (ArCH), 128.4 (ArCH), 144.6 (ArC), 157.1 (*C*-Si(CH$_3$)$_3$), 157.5 (*C*-Si(CH$_3$)$_3$); *m*/*z* (EI) 340 (M$^+$, 8%), 210 (28), 185 (11), 122 (43), 73 (100) (Found M$^+$, 340.2032. $C_{21}H_{32}Si_2$ requires 340.2043). Also isolated was metal-free starting material (20 mg, 15%, data were in accordance with the previously reported literature).[7]

5-Acetyl-7,8-bis(trimethylsilyl)bicyclo[4.2.1]nona-3,7-diene 8d

^{t}BuLi (1.43 M in hexane, 5.24 ml, 7.46 mmol) was added dropwise to a stirred solution of ethyl vinyl ether (0.85 ml, 8.93 mmol) in THF (10 ml) at −78 °C under an atmosphere of nitrogen. The yellow reaction mixture was warmed to 0 °C and the resultant colourless solution was recooled to −78 °C before dropwise cannula addition of complex **6** (500 mg, 1.25 mmol) in THF (10 ml). After 1 h at this temperature, HCl (0.02 M in ethanol, 5 ml) was added and the mixture allowed to warm to room temperature before being poured into HCl (0.02 M in ethanol, 60 ml) and stirred for 30 min. The resultant pale orange solution was diluted with diethyl ether (50 ml), washed with saturated aqueous $NaHCO_3$ and extracted with diethyl ether (3 × 20 ml). The combined organics were washed with water (20 ml), brine (20 ml), dried ($MgSO_4$) and concentrated *in vacuo* to give an orange oil. Flash chromatography (petroleum ether–CH_2Cl_2, 7 : 3) afforded the *title compound* **8d** (321 mg, 84%) as a colourless oil, ν_{max} ($CHCl_3$)/cm^{-1} 2901, 2825, 1698 (C=O), 1660 (C=C), 1355, 877; δ_H(500 MHz; $CDCl_3$) 0.16 (9H, s, Si(CH$_3$)$_3$), 0.20 (9H, s, Si(CH$_3$)$_3$), 1.50 (1H, d, *J* 12.0, 9′-H), 1.89 (1H, app. dt, *J* 12.0, 8.0, 9-H), 2.22 (3H, s, CH$_3$), 2.28 (1H, dm, *J* 18.5, 2-H*H*), 2.36 (1H, app. dtd, *J* 18.5, 4.5, 2.5, 2-*H*H), 3.08 (1H, app. dt, *J* 8.0, 4.5, 1-H), 3.29 (1H, br s, 5-H), 3.41 (1H, ddd, *J* 8.0, 2.5, 1.5, 6-H), 5.37 (1H, dddd, *J* 12.5, 6.0, 3.0, 1.5, 4-H), 5.51 (1H, dddd, *J* 12.5, 6.0, 2.5, 1.5, 3-H); δ_C(125 MHz; $CDCl_3$) 1.2 (Si(CH$_3$)$_3$), 1.4 (Si(CH$_3$)$_3$), 29.5 (CH$_3$), 35.6 (CH$_2$), 36.8 (CH$_2$), 50.6 (CH), 52.0 (CH), 60.2 (CH), 123.0 (olefinic CH), 128.7 (olefinic CH), 155.5 (*C*-Si(CH$_3$)$_3$), 158.4 (*C*-Si(CH$_3$)$_3$), 209.0 (C=O); *m*/*z* (FAB) 307 (MH$^+$, 21%), 211 (31), 154 (21), 136 (23), 73 (100) (Found MH$^+$, 307.1892. $C_{17}H_{30}OSi_2$ requires 307.1913).

5-Ethoxycarbonylmethyl-7,8-bis(trimethylsilyl)bicyclo[4.2.1]-nona-3,7-diene 8e and 5-ethoxycarbonylmethyl-7,8-bis-(trimethylsilyl)bicyclo[4.2.1]nona-2,7- diene 9e

^{n}BuLi (2.01 M in hexane, 4.97 ml, 10.0 mmol) was added dropwise to a stirred solution of diisopropylamine (1.40 ml, 10.0 mmol) in THF (10 ml) at −78 °C under an atmosphere of nitrogen. The resultant solution was warmed to 0 °C for 15 min then recooled to −78 °C before addition of ethyl acetate (0.98 ml, 10.0 mmol). The reaction mixture was stirred for 1 h at this temperature after which time an aliquot (0.44 ml, 0.25 mmol was removed) and added dropwise to a stirred solution of complex **6** (100 mg, 0.25 mmol) in THF (4 ml) at −78 °C. The mixture was stirred at this tempearature for 6 h, quenched by the addition of saturated aqueous NH_4Cl (1 ml) and extracted with diethyl ether (3 × 5 ml). The combined organics were washed with water (5 ml), brine (5 ml), dried ($MgSO_4$) and concentrated *in vacuo* to give a yellow oil. Flash chromatography (ethyl acetate–petrol, 1 : 20) afforded an inseparable mixture of the *title compounds* **8e** and **9e** (47 mg, 53%, 1 : 2) as a colourless oil; ν_{max} ($CHCl_3$)/cm^{-1} 2902, 1725 (C=O), 1372, 871 (Si-CH$_3$); δ_H(500 MHz; $CDCl_3$) major isomer **9e**: 0.14 (9H, s, Si(CH$_3$)$_3$), 0.23 (9H, s, Si(CH$_3$)$_3$), 1.26 (3H, t, *J* 6.5, CH$_3$), 1.55 (1H, app. dt, *J* 12.0, 7.5, 9-H), 1.63 (1H, d, *J* 12.0, 9′-H), 2.14–2.42 (4H, m, 4-H and C*H*$_2$CO$_2$CH$_2$CH$_3$), 3.02–3.09 (2H, m, 5-H and 6-H), 3.29 (1H, app. t, *J* 7.5, 1-H), 4.09–4.22 (2H, m, CH$_2$CO$_2$C*H*$_2$CH$_3$), 5.46 (1H, ddd, *J* 11.0, 8.5, 2.5, 3-H), 5.81 (1H, ddd, *J* 11.0, 8.0, 3.5, 2-H), minor isomer **8e**: 0.16 (9H, s, Si(CH$_3$)$_3$), 0.28 (9H, s, Si(CH$_3$)$_3$), 1.28 (3H, t, *J* 7.0, CH$_3$), 1.58, (1H, d, *J* 12.0, 9′-H), 1.85 (1H, m, 9-H), 2.14–2.42 (4H, m, 2-H and C*H*$_2$CO$_2$CH$_2$CH$_3$), 2.82 (1H, br s, 5-H), 2.91 (1H, dd, *J* 8.0, 2.5, 6-H), 3.05 (1H, m, 1-H), 4.09–4.22 (2H, m, -CH$_2$CO$_2$C*H*$_2$CH$_3$), 5.18–5.27 (2H, m, 3-H and 4-H); δ_C(68 MHz; $CDCl_3$) both isomers: 1.2 (Si(CH$_3$)$_3$), 1.4 (Si(CH$_3$)$_3$), 14.2 (CH$_3$), 30.1 (CH$_2$), 34.1 (CH$_2$), 37.9 (CH$_2$), 40.5 (CH$_2$), 42.3 (CH), 50.2 (CH), 54.7 (CH), 60.3 (CO$_2$*C*H$_2$CH$_3$), 125.1 (olefinic CH), 128.3 (olefinic CH), 156.6 (*C*-Si(CH$_3$)$_3$), 173.0 (C=O); *m*/*z* (FAB) 350 (M$^+$, 15%), 335 (11), 263 (3), 154 (36), 136 (32), 122 (16), 73 (100) (Found MH$^+$, 351.2145. $C_{19}H_{34}O_2Si_2$ requires 351.2176).

5-*N*,*N*-Dimethylamidomethyl-7,8-bis(trimethylsilyl)bicyclo-[4.2.1]nona-3,7-diene 8f and 5-*N*,*N*-dimethylamidomethyl-7,8-bis(trimethylsilyl)bicyclo[4.2.1]nona-2,7-diene 9f

^{n}BuLi (1.52 M in hexane, 6.58 ml, 10.0 mmol) was added dropwise to a stirred solution of diisopropylamine (1.40 ml, 10.0 mmol) in THF (10 ml) at −78 °C under an atmosphere of nitrogen. The resultant solution was warmed to 0 °C for 15 min then recooled to −78 °C before addition of *N*,*N*-dimethylacetamide (0.93 ml, 10.0 mmol). The reaction mixture was stirred for 2 h at this temperature after which time an aliquot (0.47 ml, 0.25 mmol) was removed and added dropwise to a stirred solution of complex **6** (100 mg, 0.25 mmol) in THF (3 ml) at −78 °C. The resultant light orange solution was stirred for 30 min and then quenched by the addition of saturated aqueous NH_4Cl (1 ml) and warmed to room temperature prior to extraction with diethyl ether (3 × 5 ml). The combined organics were washed with water (10 ml), brine (10 ml), dried ($MgSO_4$) and the concentrated *in vacuo* to give a yellow oil. Flash chromatography (diethyl ether–petroleum ether, 1 : 1) afforded an inseparable mixture of the *title compounds* **8f** and **9f** (72 mg, 82%, 5 : 1) as a colourless crystalline solid, mp 77–78 °C (from ethanol–water); (Found: C, 65.05; H, 10.40; N, 3.89. $C_{19}H_{35}NOSi_2$ requires C, 65.27; H, 10.09; N, 4.01%); ν_{max} ($CHCl_3$)/cm^{-1} 3005, 2942, 2883, 2842, 2234, 1652, 1621, 1591, 1254, 828; δ_H(500 MHz; $CDCl_3$) major isomer **8f**: 0.14 (9H, s, Si(CH$_3$)$_3$), 0.17 (9H, s, Si(CH$_3$)$_3$), 1.58 (1H, d, *J* 12.0, 9′-H), 1.86 (1H, app. dt, *J* 12.0, 8.0, 9-H), 2.22 (1H, dm, *J* 18.5, 2-H*H*), 2.28 (1H, app. dtd, *J* 18.5, 4.5, 2.5, 2-*H*H), 2.34 (1H, dd, *J* 14.5, 8.0, CH*H*CONMe$_2$), 2.41 (1H, dd, *J* 14.5, 8.0, C*H*HCONMe$_2$), 2.85 (1H, br s, 5-H), 2.95 (4H, br s, N(CH$_3$) and 6-H), 3.02 (3H, s, N(CH$_3$)), 3.06 (1H, m, 1-H), 5.22 (1H, ddm, *J* 12.5, 5.5, 4-H), 5.27 (1H, ddm, *J* 12.5, 5.0, 3-H), minor isomer **9f**: (diagnostic signals) 0.13 (9H, s, Si(CH$_3$)$_3$), 0.23 (9H, s, Si(CH$_3$)$_3$), 2.95 (3H, s, N(CH$_3$)), 3.01 (3H, s, N(CH$_3$)), 5.46 (1H, ddd *J* 11.0, 8.5, 3.0, 3-H), 5.80 (1H, ddd, *J* 11.0, 8.0, 3.5, 2-H); δ_C(68 MHz; $CDCl_3$) major isomer **8f**: 1.2 (Si(CH$_3$)$_3$), 34.5 (CH$_2$), 35.5 (CH$_3$), 36.8 (CH$_2$), 37.7 (CH$_3$), 38.9 (CH$_2$), 42.3 (CH), 50.2 (CH), 54.9 (CH), 124.6 (olefinic CH), 129.0 (olefinic CH), 156.2 (*C*-Si(CH$_3$)$_3$), 157.0 (*C*-Si(CH$_3$)$_3$), 172.0 (C=O), minor isomer **9f**: 1.4 (Si(CH$_3$)$_3$), 35.4 (CH$_2$), 35.5 (CH$_3$), 36.2 (CH$_2$), 37.4 (CH$_3$), 38.5 (CH$_2$), 42.3 (CH), 51.9 (CH), 57.1 (CH), 128.3 (olefinic CH), 134.0 (olefinic CH), 152.0 (*C*-Si(CH$_3$)$_3$), 156.2 (*C*-Si(CH$_3$)$_3$), 172.7 (C=O); *m*/*z* (EI) 349 (M$^+$, 35), 334 (33), 276 (11), 159 (28), 140(63), 73 (100) (Found M$^+$, 349.2245. $C_{19}H_{35}NOSi_2$ requires 349.2257).

5-Cyanomethyl-7,8-bis(trimethylsilyl)bicyclo[4.2.1]nona-3,7-diene 8g and 5-cyanomethyl-7,8-bis(trimethylsilyl)bicyclo[4.2.1]-nona-2,7-diene 9g

^{n}BuLi (1.57 M in hexane, 6.37 ml, 10.0 mmol) was added dropwise to a stirred solution of diisopropylamine (1.40 ml, 10.0 mmol) in THF (10 ml) at −78 °C under an atmosphere of nitrogen. The resultant solution was warmed to 0 °C for 15 min then recooled to −78 °C before addition of acetonitrile (0.52 ml, 10.0 mmol). The reaction mixture was stirred for 1.5 h at this temperature after which time an aliquot (0.30 ml, 0.17 mmol) was removed and added dropwise to a stirred solution of

complex **6** (66 mg, 0.17 mmol) in THF (4 ml) at −78 °C. The resultant brown solution was quenched immediately by the addition of saturated aqueous NH_4Cl (1 ml) and warmed to room temperature prior to extraction with diethyl ether (3 × 5 ml). The combined organics were washed with water (10 ml), brine (10 ml), dried ($MgSO_4$) and concentrated *in vacuo* to give a yellow oil. Flash chromatography (dichloromethane–petrol, 2 : 7) afforded an inseparable mixture of the *title compounds* **8g** and **9g** (25 mg, 50%, 5 : 1) as a white crystalline solid, mp 106–108 °C (from ethanol–water); (Found: C, 66.96; H, 9.96; N, 4.75. $C_{17}H_{29}NSi_2$ requires C, 67.26; H, 9.62; N, 4.61%); δ_H(500 MHz; $CDCl_3$) major isomer **8g**: 0.17 (9H, s, $Si(CH_3)_3$), 0.20 (9H, s, $Si(CH_3)_3$), 1.55 (1H, d, *J* 12.5, 9′-H), 1.90 (1H, app. dt, *J* 12.5, 8.0, 9-H), 2.22–2.38 (3H, m, 2-H and CH*H*CN), 2.42 (1H, dd, *J* 16.5, 6.5, C*H*HCN), 2.67 (1H, br s, 5-H), 3.08–3.14 (2H, m, 1-H and 6-H), 5.30 (1H, dm, *J* 12.5, 4-H), 5.37 (1H, dm, *J* 12.5, 3-H), minor isomer **9g**: 0.15 (9H, s, $Si(CH_3)_3$), 0.24 (9H, s, $Si(CH_3)_3$), 1.52 (1H, d, *J* 12.0, 9′-H), 1.62 (1H, app. dt, *J* 12.0, 7.5, 9-H), 1.98 (1H, ddd, *J* 13.5, 8.5, 3.5, 4-H*H*), 2.22–2.38 (3H, m, 4-*H*H, 5-H and CH*H*CN), 2.44 (1H, dd, *J* 16.5, 6.5, C*H*HCN), 3.19 (1H, dd, *J* 7.5, 5.0, 6-H), 3.34 (1H, app. t, *J* 7.5, 1-H), 5.45 (1H, ddd, *J* 11.0, 8.5, 2.5, 3-H), 5.86 (1H, ddd, *J* 11.0, 7.5, 3.0, 2-H); δ_C(100 MHz; $CDCl_3$) major isomer **8g**: 1.2 ($Si(CH_3)_3$), 23.3 (CH_2), 33.7 (CH_2), 36.8 (CH_2), 42.2 (CH), 50.1 (CH), 54.4 (CH), 119.0 (C≡N), 126.1 (olefinic CH), 127.2 (olefinic CH), 156.0 (*C*-$Si(CH_3)_3$), 158.0 (*C*-$Si(CH_3)_3$), minor isomer **9g**: 1.1 ($Si(CH_3)_3$), 20.7 (CH_2), 29.5 (CH_2), 34.2 (CH_2), 39.0 (CH), 51.9 (CH), 55.9 (CH), 119.5 (C≡N), 126.6 (olefinic CH), 135.0 (olefinic CH), 156.0 (*C*-$Si(CH_3)_3$), 158.0 (*C*-$Si(CH_3)_3$); *m*/*z* (EI) 303 (M^+, 15%), 288 (33), 210 (63), 122 (64), 73 (100) (Found M^+, 303.1829. $C_{17}H_{29}NSi_2$ requires 303.1839).

5-Dimethylcyanomethyl-7,8-bis(trimethylsilyl)bicyclo[4.2.1]-nona-3,7-diene 8h

^{n}BuLi (1.49 M in hexane, 6.70 ml, 10.0 mmol) was added dropwise to a stirred solution of diisopropylamine (1.40 ml, 10.0 mmol) in THF (10 ml) at −78 °C under an atmosphere of nitrogen. The resultant solution was warmed to 0 °C for 15 min then recooled to −78 °C before addition of isobutyronitrile (0.91 ml, 10.0 mmol). The reaction mixture was stirred for 1 h at this temperature after which time an aliquot (0.48 ml, 0.25 mmol was removed) and added dropwise to a stirred solution of complex **6** (100 mg, 0.25 mmol) in THF (5 ml) at −78 °C. The mixture was stirred at this temperature for 20 min, quenched by the addition of saturated aqueous NH_4Cl (1 ml) and warmed to room temperature. The product was extracted with diethyl ether (3 × 5 ml) and the combined organics were washed with water (10 ml), brine (10 ml), dried ($MgSO_4$) and concentrated *in vacuo* to give an orange oil. Flash chromatography (diethyl ether–petrol, 1 : 20) afforded the *title compound* **8h** (69 mg, 83%) as a yellow solid, mp 80–81 °C (from ethanol–water); (Found: C, 68.69; H, 10.01; N, 4.08. $C_{19}H_{33}NSi_2$ requires C, 68.81; H, 10.03; N, 4.22%); ν_{max} ($CHCl_3$)/cm^{-1} 2949, 2901, 2825, 2233, 1657 (C=C), 872; δ_H(500 MHz; $CDCl_3$) 0.16 (9H, s, $Si(CH_3)_3$), 0.18 (9H, s, $Si(CH_3)_3$), 1.46 (3H, s, CH_3), 1.47 (3H, s, CH_3), 1.84 (1H, app. dt, *J* 12.0, 8.0, 9-H), 2.08 (1H, d, *J* 12.0, 9′-H), 2.24–2.32 (2H, m, 2-H*H* and 5-H), 2.44 (1H, app. dtd, *J* 18.5, 4.0, 2.5, 2-*H*H), 3.10 (1H, app. dt, *J* 8.0, 4.0, 1-H), 3.31 (1H, br d, *J* 8.0, 6-H), 5.41 (1H, ddm, *J* 12.5, 4.5, 4-H), 5.54 (1H, ddm, *J* 12.5, 6.5, 3-H); δ_C(68 MHz; $CDCl_3$) 1.2 ($Si(CH_3)_3$), 1.5 ($Si(CH_3)_3$), 26.4 (CH_3), 27.2 (CH_3), 34.2 (CH_2), 36.5 (CH_2), 36.9 (*C*-CN), 50.6 (CH), 51.6 (CH), 52.3 (CH), 124.0 (olefinic CH), 125.6 (C≡N), 129.3 (olefinic CH), 156.8 (*C*-$Si(CH_3)_3$), 157.9 (*C*-$(CH_3)_3$); *m*/*z* (FAB) 332 (MH^+, 7%), 136 (11), 95 (11), 73 (100) (Found MH^+, 332.2222. $C_{19}H_{34}Si_2$ requires 332.2298). Also recovered was metal-free starting material (11 mg, 17%, data were in accordance with the previously reported literature).[7]

5-Phenylsulfonylmethyl-7,8-bis(trimethylsilyl)bicyclo[4.2.1]-nona-3,7-diene 8i and 5-phenylsulfonylmethyl-7,8-bis(trimethylsilyl)bicyclo[4.2.1]nona-2,7-diene 9i

^{n}BuLi (1.36 M in hexane, 0.18 ml, 0.25 mmol) was added dropwise to a stirred solution of methylphenylsulfone (39 mg, 0.25 mmol) in THF (4 ml) at −78 °C under an atmosphere of nitrogen. The resultant orange solution was stirred for 1 h before dropwise cannula addition to a stirred solution of complex **6** (100 mg, 0.25 mmol) in THF (2 ml) at −78 °C. The mixture was stirred at this temperature for 20 min, quenched by the addition of saturated aqueous NH_4Cl (1 ml) and warmed to room temperature. The product was extracted with ethyl acetate (3 × 5 ml) and the combined organics were washed with water (10 ml), brine (10 ml), dried ($MgSO_4$) and concentrated *in vacuo* to give a yellow oil. Flash chromatography (ethyl acetate–petrol, 1 : 20) afforded an inseparable mixture of the *title compounds* **8i** and **9i** (61 mg, 58%, 1 : 5) as a colourless crystalline solid, mp 84 °C (from ethanol–water); ν_{max} ($CHCl_3$)/cm^{-1} 2951, 2927, 1650, 1306 and 1134 (SO_2), 867; δ_H(500 MHz; $CDCl_3$) major isomer **9i**: 0.12 (9H, s, $Si(CH_3)_3$), 0.13 (9H, s, $Si(CH_3)_3$), 1.43 (1H, d, *J* 12.0, 9′-H), 1.55 (1H, app. dt, *J* 12.0, 7.5, 9-H), 2.13 (1H, ddd, *J* 16.0, 7.0, 3.0, 4-H*H*), 2.21 (1H, ddd, *J* 16.0, 8.5, 3.0, 4-*H*H), 2.42 (1H, m, 5-H), 2.99 (1H, dd, *J* 7.5, 5.0, 6-H), 3.06 (1H, dd, *J* 14.5, 3.5, CH*H*SO_2Ph), 3.21 (1H, dd, *J* 14.5, 8.0, C*H*HSO_2Ph), 3.28 (1H, app. t, *J* 7.5, 1-H), 5.44 (1H, ddd, *J* 11.0, 8.5, 3.0, 3-H), 5.84 (1H, ddd, *J* 11.0, 8.0, 3.0, 2-H), 7.55–7.61 (2H, m, 2 × H *meta*), 7.66 (1H, app. tt, *J* 7.0, 1.0, H *para*), 7.91–7.96 (2H, dm, *J* 8.0, H *ortho*), minor isomer **8i**: (diagnostic signals) 0.12 (9H, s, $Si(CH_3)_3$), 0.13 (9H, s, $Si(CH_3)_3$), 1.46 (1H, d, *J* 12.0, 9′-H), 1.85 (1H, app. dt, *J* 12.0, 7.5, 9-H), 2.21–2.29 (2H, m, 2-H), 2.42 (1H, m, 5-H), 3.29 (1H, dd, *J* 14.5, 6.5, CH*H*SO_2Ph), 5.30 (1H, ddm, *J* 13.5, 6.0, 4-H), 5.36 (1H, dm, *J* 13.0, 3-H); δ_C(100 MHz; $CDCl_3$) major isomer **9i**: 0.8 ($Si(CH_3)_3$), 1.2 ($Si(CH_3)_3$), 28.9 (CH_2), 35.2 (CH_2), 36.6 (CH), 51.8 (CH), 57.2 (CH), 59.0 (*C*H_2SO_2Ph), 127.2 (olefinic CH), 127.9 (olefinic CH), 129.2 (ArCH), 133.5 (ArCH), 135.0 (ArCH), 140.0 (ArC), 153.0 (*C*-$Si(CH_3)_3$), 154.8 (*C*-$Si(CH_3)_3$), minor isomer **8i**: 0.8 ($Si(CH_3)_3$), 1.1 ($Si(CH_3)_3$), 30.0 (CH_2), 34.6 (CH_2), 39.6 (CH), 49.8 (CH), 55.5 (CH), 61.2 (*C*H_2SO_2Ph), 126.0 (olefinic CH), 127.0 (olefinic CH), 127.9 (ArCH), 129.2 (ArCH), 133.5 (ArCH), 140.0 (ArC), 153.0 (*C*-$Si(CH_3)_3$), 154.8 (*C*-$Si(CH_3)_3$); *m*/*z* (EI) 418 (M^+, 10%), 210 (15), 137 (16), 122 (19), 73 (100) (Found M^+, 418.1816. $C_{22}H_{34}O_2SSi_2$ requires 418.1818).

5-Acetyl-7,8-diphenylbicyclo[4.2.1]nona-4,7-diene 19 and 5-acetyl-7,8-diphenylbicyclo[4.2.1]nona-2,7-diene 20

^{t}BuLi (1.6 M in hexane, 1.30 ml, 2.07 mmol) was added dropwise to a stirred solution of ethyl vinyl ether (0.21 ml, 2.17 mmol) in THF (10 ml) at −78 °C under an atmosphere of nitrogen. The yellow reaction mixture was warmed to 0 °C and the resultant colourless solution was recooled to −78 °C before dropwise cannula addition of complex **7** (210 mg, 0.52 mmol) in THF (4 ml). The reaction mixture was slowly warmed to 0 °C over 6 h, HCl (0.1 M in ethanol, 5 ml) was added and the mixture allowed to warm to room temperature before being poured into HCl (0.1 M in ethanol, 60 ml) and stirred for 30 min. The resultant pale yellow solution was diluted with diethyl ether (50 ml), washed with saturated aqueous $NaHCO_3$ and extracted with diethyl ether (3 × 10 ml). The combined organics were washed with water (10 ml), brine (10 ml), dried ($MgSO_4$) and concentrated *in vacuo* to give a yellow oil. Flash chromatography (dichloromethane–petrol, 3 : 7) afforded *title ketone* **20** (31 mg, 26%) as a colourless oil, ν_{max} ($CHCl_3$)/cm^{-1} 2937, 1703 (C=O); δ_H(500 MHz; $CDCl_3$) 1.47 (1H, d, *J* 11.5, 9′-H), 2.20 (3H, s, CH_3), 2.52 (1H, app. dt, *J* 11.5, 8.0, 9-H), 2.58–2.73 (2H, m, 4-H), 3.37 (1H, app. t, *J* 8.0, 6-H), 3.97 (1H, app. dt, *J* 8.0, 4.5, 5-H), 4.52 (1H, d, *J* 8.0, 1-H), 5.90 (1H, ddd, *J* 11.0, 8.0, 3.0, 3-H), 6.17 (1H, ddd, *J* 11.0, 8.0, 3.0, 2-H),

6.99–7.37 (10H, m, 10 × ArH); *m/z* (EI) 314 (M^+, 100%), 271 (31), 231 (21), 218 (24), 205 (32) (Found M^+, 314.1661. $C_{23}H_{22}O$ requires 314.1671). Further elution afforded *title enone* **19** (22 mg, 14%) as a colourless oil, ν_{max} ($CHCl_3$)/cm^{-1} 2936, 1665 (C=O), 1454, 1073; δ_H(500 MHz; $CDCl_3$) 1.88 (1H, d, *J* 12.0, 9′-H), 2.14 (1H, app. dt, *J* 12.0, 7.0, 9-H), 2.41 (3H, s, CH_3), 2.68 (1H, dd, *J* 15.5, 7.0, 2-H*H*), 2.81 (1H, m, 2-*H*H), 3.24 (1H, m, 3-H), 3.34 (1H, app. dt, *J* 14.0, 7.0, 3-H*H*), 4.34 (1H, d, *J* 7.0, 6-H), 4.78 (1H, app. t, *J* 7.0, 1-H), 6.79–6.84 (2H, m, 4-H and ArH), 7.05–7.19 (4H, m, 4 × ArH), 7.28–7.35 (3H, m, 3 × ArH), 7.69 (2H, d, *J* 6.9, 2 × ArH); δ_C(100 MHz; $CDCl_3$) 26.0 (CH_3), 39.0 (CH_2), 39.6 (CH_2), 41.0 (CH), 55.3 (CH), 57.9 (CH_2), 92.8 (*C*-Ph), 98.8 (*C*-Ph), 126.6 (ArCH), 127.2 (ArCH), 127.3 (ArCH), 128.8 (ArCH), 129.1 (ArCH), 139.2 (ArC), 140.5 (ArC), 146.5 (C-4), 148.5 (C-5), 199.0 (C=O); *m/z* (EI) 314 (M^+, 30%), 271 (10), 223 (32), 105 (100), 77 (27) (Found M^+, 314.1660. $C_{23}H_{22}O$ requires 314.1671).

5-Acetyl-7,8-bis(trimethylsilyl)bicyclo[4.2.1]nona-4,7-diene 21

Ketone **8d** (40 mg, 0.13 mmol) was treated with HCl (1.0 M in ethanol, 8 ml) and stirred at room temperature for 3 d. The mixture was diluted with diethyl ether (5 ml), neutralised with aqueous $NaHCO_3$ (20 ml) and extracted with diethyl ether (3 × 5 ml). The combined organic extracts were washed with water (10 ml), dried ($MgSO_4$) and concentrated *in vacuo* to give a pale yellow oil. Flash chromatography (dichloromethane–petrol, 3 : 7) afforded the *title enone* **21** (33 mg, 84%) as a colourless oil; ν_{max} ($CHCl_3$)/cm^{-1} 2928, 2858, 1660 (C=O), 1623 (C=C), 877 (Si-CH_3); δ_H(500 MHz; $CDCl_3$) 0.07 (9H, s, $Si(CH_3)_3$), 0.22 (9H, s, $Si(CH_3)_3$), 1.21 (1H, d, *J* 11.5, 9′-H), 1.62 (1H, dddd, *J* 14.0, 12.5, 3.5, 2.0, 2-H*H*), 1.81 (1H, dm, *J* 14.0, 2-*H*H), 1.90 (1H, app. dtd, *J* 11.5, 7.5, 1.5, 9-H), 2.17 (1H, app. ddt, *J* 16.5, 9.0, 3.5, 3-H*H*), 2.26 (1H, m, 3-*H*H), 2.29 (3H, s, CH_3), 3.18 (1H, ddd, *J* 7.5, 5.5, 1.5, 1-H), 4.24 (1H, dd, *J* 7.5, 1.5, 6-H), 6.87 (1H, ddd, *J* 9.0, 3.5, 1.0, 4-H); δ_C(100 MHz; $CDCl_3$) 0.9 ($Si(CH_3)_3$), 1.3 ($Si(CH_3)_3$), 25.4 (CH_2), 25.6 (CH_3), 33.6 (CH_2), 42.2 (CH_2), 48.3 (CH), 52.2 (CH), 144.1 (C-4), 148.3 (C-5), 152.6 (*C*-$Si(CH_3)_3$), 156.8 (*C*-$Si(CH_3)_3$), 198.5 (C=O); *m/z* (EI) 306 (M^+, 20%), 291 (30), 233 (11), 147 (13), 109 (16), 73 (100) (Found M^+, 306.1850. $C_{17}H_{30}OSi_2$ requires 306.1835).

5-Acetylbicyclo[4.2.1]nona-4,7-diene 22

Trifluoroacetic acid (0.50 ml, 6.54 mmol) was added dropwise to ketone **8d** (200 mg, 0.65 mmol) in dichloromethane (12 ml) at room temperature and the solution was heated at reflux for 14 h. The reaction mixture was cooled to room temperature before addition of saturated aqueous $NaHCO_3$ (5 ml) and extraction with dichloromethane (3 × 5 ml). The combined organics were washed with water (10 ml), brine (10 ml), dried ($MgSO_4$) and concentrated *in vacuo* to give a yellow oil. Flash chromatography (dichloromethane–petroleum ether, 2 : 3) afforded the *title compound* **22** (106 mg, 100%) as a colourless oil; ν_{max} ($CHCl_3$)/cm^{-1} 3688, 2931, 1712 (C=O), 1601 (C=C); δ_H(500 MHz; $CDCl_3$) 1.27 (1H, d, *J* 11.5, 9′-H), 1.73 (1H, m, 2-H*H*), 1.86 (1H, m, 2-*H*H), 2.12 (1H, app. dt, *J* 11.5, 8.0, 9-H), 2.25–2.42 (2H, m, 3-H), 2.29 (3H, s, CH_3), 2.86 (1H, app. dt, *J* 8.0, 2.5, 1-H), 4.05 (1H, dd, *J* 8.0, 2.5, 6-H), 5.54 (1H, dd, *J* 5.5, 2.5, 7-H), 5.94 (1H, dd, *J* 5.5, 2.5, 8-H), 6.88 (1H, dd, *J* 8.0, 3.0, 4-H); δ_C(100 MHz; $CDCl_3$) 25.6 (CH_3), 26.2 (CH_2), 34.5 (CH_2), 40.2 (CH), 41.9 (CH_2), 43.1 (CH), 129.4 (olefinic CH), 133.0 (olefinic CH), 144.2 (olefinic CH), 147.3 (olefinic C), 198.9 (C=O); *m/z* (EI) 162 (M^+, 64%), 147 (25), 119 (43), 96 (98), 87 (100) (Found M^+, 162.1051. $C_{11}H_{14}O$ requires 162.1045).

5-Phenylbicyclo[4.2.1]nona-3,7-diene 23

Trifluoroacetic acid (0.04 ml, 0.44 mmol) was added dropwise to **8c** (10 mg, 0.03 mmol) in dichloromethane (5 ml) at room temperature and the solution was heated at reflux for 2 h. The reaction mixture was cooled to room temperature before addition of saturated aqueous $NaHCO_3$(aq.) (1 ml) and extraction with dichloromethane (3 × 5 ml). The combined organics were washed with water (5 ml), brine (5 ml), dried ($MgSO_4$) and concentrated *in vacuo* to give a yellow oil. Flash chromatography (petroleum ether) afforded the *title compound* **23** (5 mg, 84%) as a colourless oil; ν_{max} ($CHCl_3$)/cm^{-1} 2950, 2899, 1633, 868; δ_H(500 MHz; $CDCl_3$) 1.69 (1H, d, *J* 12.5, 9′-H), 1.80 (1H, app. dt, *J* 12.5, 8.0, 9-H), 2.34 (1H, dm, *J* 18.5, 2-H*H*), 2.49 (1H, app. dtd, *J* 18.5, 5.0, 2.5, 2-*H*H), 2.84 (1H, br s, 1-H), 2.91 (1H, br d, *J* 8.0, 6-H), 3.66 (1H, br s, 5-H), 5.43 (1H, dm, *J* 12.5, 4-H), 5.56 (1H, dm, *J* 12.5, 3-H), 5.78 (1H, dd, *J* 5.5, 2.5, 7-H), 5.94 (1H, dd, *J* 5.5, 2.5, 8-H), 7.21 (1H, app. t, *J* 7.0, H *para*), 7.26 (2H, d, *J* 7.0, 2 × H *ortho*), 7.31 (2H, app. t, *J* 7.0, 2 × H *para*); δ_C(100 MHz; $CDCl_3$) 32.7 (CH_2), 37.4 (CH_2), 41.4 (CH), 50.2 (CH), 52.7 (CH), 126.1 (olefinic CH), 126.6 (olefinic CH), 127.7 (ArCH), 128.3 (ArCH), 128.4 (ArCH), 134.5 (olefinic CH), 134.7 (olefinic CH), 144.4 (ArC); *m/z* (EI) 169 (M^+, 1%), 130 (100), 115 (14), 77 (2) (Found M^+, 196.1253. $C_{15}H_{16}$ requires 196.1252).

5-Acetyl-7,8-bis(trimethylsilyl)-9-ethoxycarbonyl-9-azabicyclo-[4.2.1]nona-3,7-diene 27

^{t}BuLi (1.5 M in hexane, 4.02 ml, 6.03 mmol) was added dropwise to a stirred solution of ethyl vinyl ether (0.69 ml, 7.25 mmol) in THF (10 ml) at −78 °C under an atmosphere of nitrogen. The yellow reaction mixture was warmed to 0 °C and the resultant colourless solution recooled to −78 °C before dropwise cannula addition of complex **26** (481 mg, 1.02 mmol) in THF (12 ml). The brown reaction mixture was stirred for 1 h at this temperature prior to addition of HCl (0.02 M in ethanol, 5 ml) and the resultant red solution was allowed to warm to room temperature before being poured into HCl (0.02 M in ethanol, 60 ml) and stirred for 30 min. The resultant yellow solution was diluted with diethyl ether (50 ml), poured into saturated aqueous $NaHCO_3$ (5 ml) and extracted with diethyl ether (3 × 20 ml). The combined organics were washed with water (20 ml), brine (20 ml), dried ($MgSO_4$) and concentrated *in vacuo* to give an orange oil. Flash chromatography (dichloromethane–petrol, 3 : 7) afforded the *title compound* **27** (250 mg, 52%) as a colourless oil, (Found: C, 59.81; H, 8.71; N, 3.69. $C_{19}H_{33}NOSi_2$ requires C, 60.11; H, 8.76; N, 3.69%); ν_{max} ($CHCl_3$)/cm^{-1} 3428, 2958, 1704, 1357; δ_H(400 MHz; $CDCl_3$, 333 K) 0.21 (9H, s, $Si(CH_3)_3$), 0.27 (9H, s, $Si(CH_3)_3$), 1.24 (3H, t, *J* 7.0, OCH_2CH_3), 2.23 (3H, br s, CH_3), 2.35 (1H, dd, *J* 18.5, 6.5, 2-H*H*), 2.85 (1H, br d, *J* 18.5, 2-*H*H), 3.29 (1H, br s, 5-H), 4.03–4.18 (2H, m, OCH_2CH_3), 4.99 (1H, br s, 1-H), 5.25 (1H, br s, 6-H), 5.28 (1H, dddt, *J* 12.5, 6.0, 3.0, 1.0, 4-H), 5.56 (1H, app. ddt, *J* 12.5, 6.5, 1.0, 3-H); δ_C(100 MHz; $CDCl_3$, 2 rotamers) major rotamer: 0.8 $Si(CH_3)_3$), 14.4 (OCH_2CH_3), 29.6 (CH_3), 36.1 (C-2), 61.1 (OCH_2CH_3), 61.7 (C-5), 67.9 (C-1), 69.2 (C-6), 122.7 (C-4), 128.0 (C-3), 152.4 ($NCO_2CH_2CH_3$), 152.7 (*C*-$Si(CH_3)_3$) 154.7 (*C*-$Si(CH_3)_3$), 207.5 (C=O), minor rotamer: 1.0 $Si(CH_3)_3$), 14.8 (OCH_2CH_3), 28.9 (CH_3), 36.3 (C-2), 61.1 (OCH_2CH_3), 61.7 (C-5), 67.4 (C-1), 69.2 (C-6), 123.1 (C-4), 128.3 (C-3), 152.6 ($NCO_2CH_2CH_3$), 153.2 (*C*-$Si(CH_3)_3$) 154.2 (*C*-$Si(CH_3)_3$), 206.9 (C=O); *m/z* (FAB) 380 (MH^+, 35%), 307 (13), 284 (55), 268 (24), 154 (57), 136 (50), 73 (100) (Found MH^+, 380.2068. $C_{19}H_{34}NO_3Si_2$ requires 380.2077).

5-Acetyl-7,8-bis(trimethylsilyl)-9-ethoxycarbonyl-9-azabicyclo-[4.2.1]nona-4,7-diene 28

Ketone **27** (7 mg, 0.02 mmol) was treated with HCl (2.0 M in ethanol, 5 ml) and stirred at room temperature for 3 d. The mixture was diluted with ethyl acetate (10 ml), neutralised with aqueous 2 M NaOH (5 ml) and extracted with ethyl acetate (3 × 5 ml). The combined organic extracts were washed with water (5 ml), brine (5 ml), dried ($MgSO_4$) and concentrated

in vacuo to give a yellow oil. Purification by passing through a plug of silica (diethyl ether–petrol, 3 : 7) afforded the *title compound* **28** (7 mg, 100%) as a colourless oil, ν_{max} ($CHCl_3$)/cm^{-1} 2954, 1685, 1669; δ_H(400 MHz; $CDCl_3$, 2 rotamers, 333 K) 0.15 (9H, s, $Si(CH_3)_3$), 0.29 (9H, s, $Si(CH_3)_3$), 1.10–1.40 (3H, m, OCH_2CH3), 1.82–1.93 (1H, dm, *J* 14.5, 2-H*H*), 2.21–2.50 (3H, m, 2-*H*H and 3-H), 2.32 (3H, s, CH_3), 3.97–4.23 (2H, m, OCH_2CH_3), 4.95 (1H, br s, 1-H), 5.92 (1H, d, *J* 1.5, 6-H), 6.88 (1H, br d, *J* 8.5, 4-H); δ_C(100 MHz; $CDCl_3$) 0.8 $Si(CH_3)_3$), 1.3 $Si(CH_3)_3$), 14.7 (OCH_2CH_3), 24.6 (CH_2), 25.6 (CH_3), 32.3 (CH_2), 60.7 (OCH_2CH_3), 63.3 (CH), 68.8 (CH), 145.2 (C-4), 146.6 (C-5), 149.9 (*C*-$Si(CH_3)_3$), 152.2 (*C*-$Si(CH_3)_3$), 152.4 ($NCO_2CH_2CH_3$), 196.2 (C=O), *m*/*z* (EI) 379 (M^+, 32%), 364 (16), 306 (42), 73 (100) (Found M^+, 379.2015. $C_{19}H_{33}NO_3Si_2$ requires 379.1999).

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