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SOME DIELS—ALDER REACTIONS OF η^1-BONDED CYCLOPENTADIENYLMETAL COMPOUNDS

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Summary

Bis(cyclopentadienyl)mercury readily undergoes Diels—Alder reactions with $RC\equiv CR$ ($R = CO_2Me$ or CF_3), $CF_3CF{=}CFCF_3$, $CF_3CF{=}CF_2$, $(CF_3)_2C{=}C(CN)_2$, $C_2(CN)_4$ and $Ph\overline{N{-}CO{-}N{=}N{-}CO}$ to give stable adducts characterised by ^1H, ^{19}F and ^{13}C NMR spectroscopy. Similar reactions of $CF_3C\equiv CCF_3$ and $CF_3CF{=}CFCF_3$ with the cyclopentadiene derivatives $Me_3MC_5H_5$ and $(Me_3M)_2C_5H_4$ (M = Si, Sn) are also described.

In this paper we describe reactions of bis(cyclopentadienyl)mercury, 5-trimethylsilylcyclopentadiene, 5-trimethylstannylcyclopentadiene, 5,5-bis(trimethylsilyl)cyclopentadiene and 5,5-bis(trimethylstannyl)-cyclopentadiene with hexafluoro-but-2-yne and some fluoro-olefins. Reactions of bis(cyclopentadienyl)mercury with some other dienophiles are also reported.

Following the discovery of $Hg(C_5H_5)_2$, Wilkinson and Piper [1] observed that the compound formed an adduct with maleic anhydride. Recently others [2] have reported a reaction between the mercury compound and *p*-benzoquinone. Although Diels—Alder reactions of bis(cyclopentadienyl)mercury have not been studied extensively, numerous papers have described such reactions of the cyclopentadiene derivatives $C_5H_5MMe_3$ (M = Si, Ge, Sn) [3—11].

The reactions of bis(cyclopentadienyl)mercury studied by us are outlined in Scheme 1. The fluoro-organic compounds employed are known [12] to be highly reactive dienophiles in 1,4-addition reactions, as are tetracyanoethylene and 4-phenyl-1,2,4-triazoline-3,5-dione. Reactions occurred readily to afford in high yield bicyclo [2.2.1.]hepta-2,5-diene (I, II), bicyclo[2.2.1]hept-5-ene (III—VI), and 5,8-dihydro-5,8-methano-1*H*-[1.2.4]triazolo[1.2a]pyridazine-2-phenyl-1,3-dione (VII) derivatives of mercury.

In other studies involving the cyclopentadiene-silyl and -stannyl derivatives $C_5H_5MMe_3$ and $C_5H_4(MMe_3)_2$ (M = Si, Sn), reactions readily occurred with hexa-

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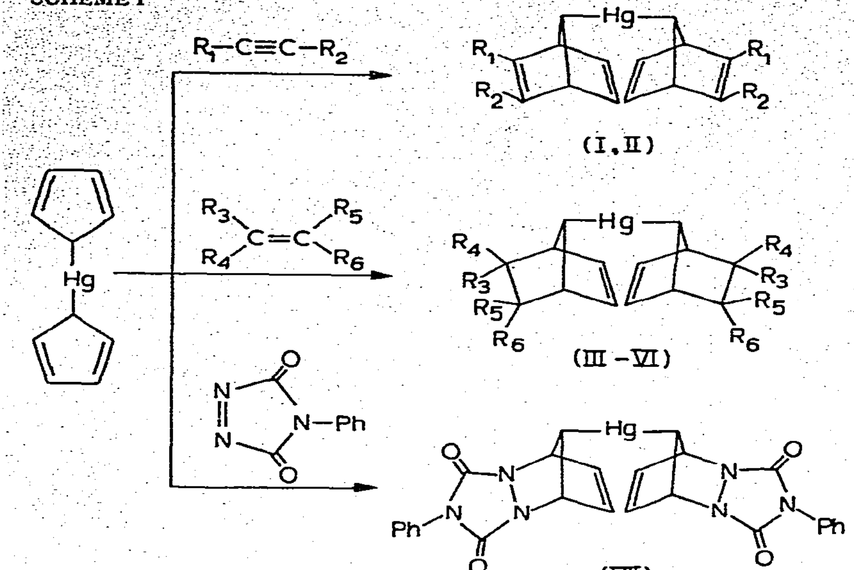
SCHEME I



(I, II)

(III – VI)

(VII)

(I) $R_1 = R_2 = COOCH_3$

(II) $R_1 = R_2 = CF_3$

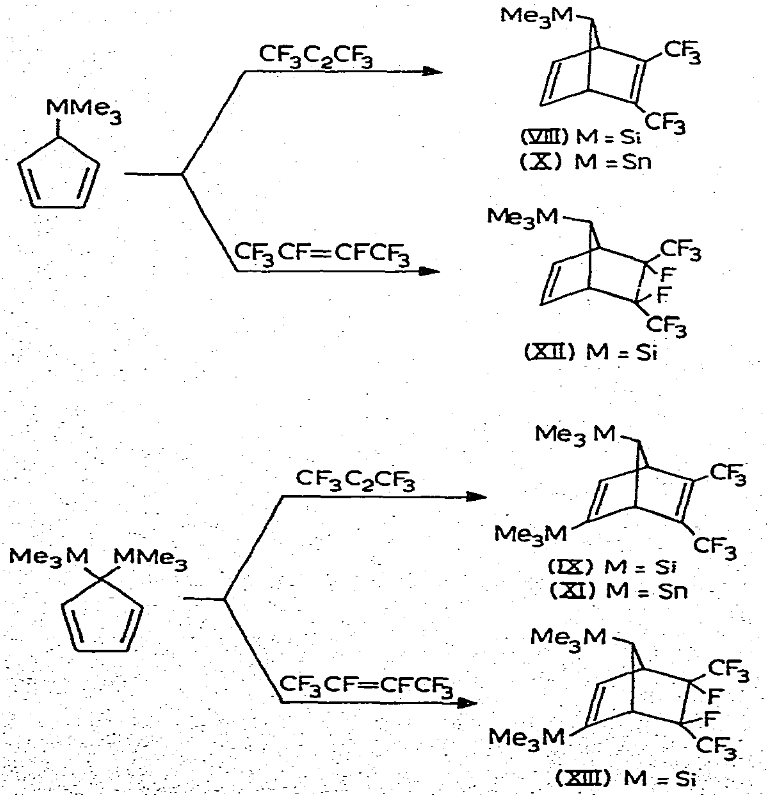
(III) $R_3 = R_5 = F;\ R_4 = R_6 = CF_3$

(IV) $R_3 = R_5 = R_6 = F;\ R_4 = CF_3$

(V) $R_3 = R_4 = CF_3;\ R_5 = R_6 = CN$

(VI) $R_3 = R_4 = R_5 = R_6 = CN$

SCHEME II

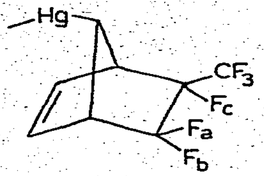


(VIII) M = Si
(X) M = Sn

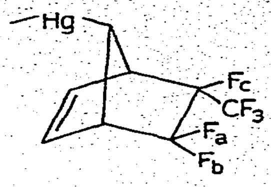
(XII) M = Si

(IX) M = Si
(XI) M = Sn

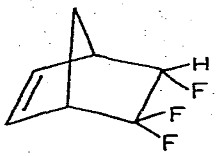
(XIII) M = Si



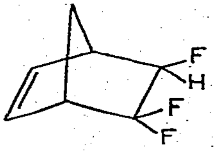
(IVa)



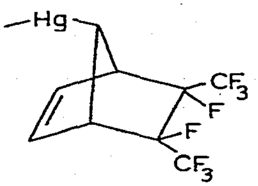
(IVb)



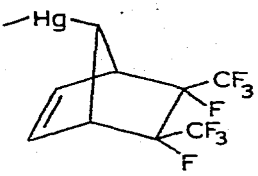
(XIV)



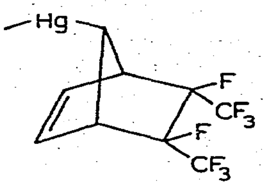
(XV)



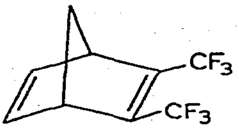
(IIIa)



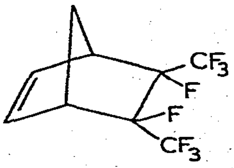
(IIIb)



(IIIc)



(XVI)



(XVII)

fluoro-but-2-yne and with octafluoro-but-2-ene to give the products shown in Scheme 2.

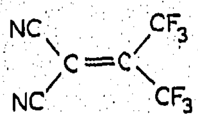
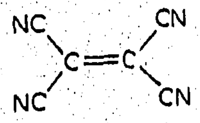
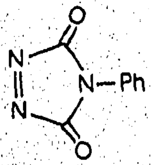
The new compounds were characterised by elemental analysis and mass spectra, and by ^{1}H NMR spectroscopy (Tables 1 and 2). The ^{1}H spectra are in accord with the compounds being bicyclo[2.2.1]hepta-2,5-diene and bicyclo[2.2.1]-hept-5-ene derivatives substituted in the 7-position [4]. Additional structural information was obtained from their ^{19}F (see Experimental) and ^{13}C (Table 3) NMR spectra, and is discussed below.

The ^{19}F NMR spectrum of IV showed two sets of signals corresponding to two possible configurations (IVa and IVb) of the bicyclo[2.2.1]hept-5-ene ring system, although three isomers of IV are possible as the molecules contain two bicyclo[2.2.1]hept-5-ene systems. The CF$_3$ group with the lower field chemical shift was assigned the *exo*-structure (IVa), since one of the associated fluorine signals (F$_b$ in this case) showed no coupling other than to F$_a$, and *J*(F *endo*—F *endo*) is known [13] to be zero in XIV whereas *J*(F *exo*—F *exo*) is 12.5 Hz in

(continued on p. 37)

TABLE 1

ANALYTICAL AND ^1H NMR SPECTROSCOPIC DATA FOR ADDUCTS OF BIS(CYCLOPENTADIENYL)MERCURY

Dienophiles	Products	M.p.[a] (°C)	Analysis[b] (%)				Mol. wt.[b,c]	^1H NMR (τ, ppm)[d]			
			C	H	N	F		1,4	5,6	7	Other
$H_3COOCC{\equiv}CCOOCH_3$	I	147–148	43.2 (43.0)	3.8 (3.6)	— —	— —	615 (614.99)	5.86	2.98	7.82	6.24 (CH_3)
$F_3CC{\equiv}CCF_3$	II	127	33.0 (33.0)	1.5 (1.5)	— —	34.7 (34.8)	655 (654.85)	5.88	2.92	7.80	—
$F_3CCF{=}CFCF_3$	III[e]	176	30.1 (29.6)	1.5 (1.4)	— —	41.8 (41.6)	735 (730.85)	6.60	3.59	7.97	—
$F_3CCF{=}CF_2$	IV[e]	154 (dec.)	29.8 (30.4)	1.7 (1.6)	— —	35.8 (36.1)	632 (630.83)	{6.59 6.78}	{3.40 3.69}	8.23	—
	V	190 (dec.)	35.4 (34.8)	1.2 (1.3)	7.2 (7.3)	30.4 (30.0)	[f] (758.91)	{5.86 5.96}	{2.95 3.45}	8.05	—
	VI	100 (dec.)	45.4 (45.0)	1.9 (1.7)	18.8 (19.0)	— —	[f] (586.93)	6.44	3.10	8.12	—
	VII	201	45.6 (45.8)	3.1 (3.0)	12.0 (12.3)	— —	[f] (681.04)	6.32	3.72	8.38	2.20 2.55 2.70 (Ph)

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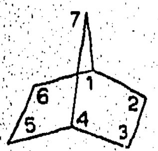
[a] Melting points are uncorrected. [b] Calculated in brackets. [c] Molecular weights from mass spectra. [d] For the position of protons in a bicyclo[2.2.1]heptene ring we used the following numbers:



[e] Mixture of isomers (see text). [f] No molecular peak observed.

TABLE 2

ANALYTICAL AND ^{1}H NMR SPECTROSCOPIC DATA FOR ADDUCTS OF SILYL- AND STANNYL-COMPOUNDS

Dienophiles	Dienes	Products	B.p. °C/ mm Hg	Analysis [a]			Mol. wt. [a,b]	^{1}H NMR (τ, ppm) [c]			
				C	H	F		1,4	5,6	7	Others
$CF_3C{\equiv}CCF_3$	$Me_3SiC_5H_5$	VIII	30/0.5	48.1 (48.0)	4.6 (4.7)	37.9 (37.9)	300 (300.32)	6.15	3.04 (tr,2)	7.75 (tr, 1)	10.14
$CF_3C{\equiv}CCF_3$	$(Me_3Si)_2C_5H_4$	IX	67/1.1	48.7 (48.4)	6.1 (6.0)	30.4 (30.6)	372 (372.51)	5.88, 5.98	2.82 (d,3)	7.67	9.88, 10.08
$CF_3C{\equiv}CCF_3$	$Me_3SnC_5H_5$	X	46—48/0.4	37.0 (36.9)	3.6 (3.6)	29.4 (29.2)	392 (390.93)	6.00	3.02 (tr,3)	7.61 (tr,1)	9.99
$CF_3C{\equiv}CCF_3$	$(Me_3Sn)_2C_5H_4$	XI	84—86/0.5	32.7 (32.6)	4.1 (4.0)	21.0 (20.6)	554 (553.73)	5.91, 6.08	3.00 (d,3)	7.64 (tr,1)	9.90 (sat., 56) 10.09 (sat., 54)
$CF_3CF{=}CFCF_3$	$Me_3SiC_5H_5$	XII [d]	42—45/0.7	42.9 (42.6)	4.2 (4.2)	44.5 (44.9)	337 (338.32)	6.71, 6.82	3.73	7.96 (d,6)	9.96
$CF_3CF{=}CFCF_3$	$(Me_3Si)_2C_5H_4$	XIII [d]	55—56/0.2	44.0 (43.9)	5.6 (5.4)	37.3 (37.0)	410 (410.51)	6.68, 6.80	3.47	8.00 (d,6)	9.89, 10.00

[a] Calculated in brackets. [b] Molecular weight from mass spectra. [c] For the position of protons of bicyclo[2.2.1]heptene ring see footnote d of Table 1. Coupling constants (Hz) in brackets. [d] Mixture of isomers (see text).

TABLE 3

^{13}C NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS (IN PARENTHESES) FOR BICYCLO[2.2.1]HEPTENE AND BICYCLO[2.2.1]HEPTADIENE DERIVATIVES

Compound	C(1) [a]	C(4) [a]	C(2)	C(3)	C(5) [b]	C(6) [b]	C(7)	CF_3	Other carbons
I	59.1	59.1	156.6	156.6	145.9	145.9	109.5		51.9(OCH_3), 166.1(CO)
II	58.1	58.1	*c*	*c*	146.0	146.0	109.8	*c*	
XVI	53.2	53.2	148.7	148.7	142.8	142.8	73.9	122.8(270 [d])	
VIII	55.3	55.3	*c*	*c*	142.6	142.6	82.7	122.3(270 [d])	−0.8($SiCH_3$)
IX	58.3	56.5	151.7 [j]	150.3 [j]	155.0	152.7	83.0	122.3(270 [d])	−0.9($SiCH_3$), −1.6($SiCH_3$)
XI	62.0(39 [e])	58.6(46 [e], 89 [e])	*c*	*c*	157.1	154.3(37 [c])	82.1(385 [f], 370 [g])	122.3(269 [d])	−9.2($SnCH_3$), −9.6(361 [f], 347 [g]) ($SnCH_3$)
XVIIa	49.0(22 [h])	47.2(21 [h])	*c*	*c*	135.5(6 [h])	134.9(6 [h])	45.3	122.8(283 [d], 32 [h]) 122.3(281 [d], 29 [h])	
XIIa	51.1(22 [h])	48.2(19 [h])	*c*	*c*	134.9	134.1(6 [h])	45.6	*c*	−0.5($SiCH_3$)
XIIIa	52.2(20 [h])	51.7(20 [h])	*c*	*c*	149.8	143.6(6 [h])	45.9	*c*	−0.4($SiCH_3$) −1.6($SiCH_3$)

[a] Where C(1) and C(4) are not equivalent, there is ambiguity as to which signal should be assigned to which carbon. Only in the case of XI was a tentative assignment possible on account of satellites observed from both tin nuclei for C(4). [b] For IX, XI and XIII assignment of these two signals was possible due to the greater intensity of the C(6) signal (N.O.E.). For XVII and XII the assignment is ambiguous. [c] Signals for these carbon atoms were not measurable due to low intensity and multiplicity (C—F coupling). [d] $^1J(CF)$ for CF_3 groups. [e] $^2J(CSn)$; ^{117}Sn and ^{119}Sn not resolved. [f] $^1J(C^{119}Sn)$. [g] $^1J(C^{117}Sn)$. [h] $^2J(CF)$ or $^3J(CF)$. [j] The assignment of these two signals could possibly be reversed.

XV. Consistent assignments of all peaks in the ^{19}F spectra were then possible on the basis that fluorine atoms in *exo*-positions had higher shifts than those in *endo*-positions.

In the case of compounds III, XII and XIII their ^{19}F spectra revealed the presence of three isomers, the major component (~85%) of each isomeric mixture having a *trans* arrangement of CF_3 groups as in IIIa.

As expected this configuration gives rise to two signals for the *exo*- and *endo*-CF_3 groups and two signals for the *exo*- and *endo*-F atoms, which are assigned on the basis of the correlation established for IV. The remaining signals are attributed to the two possible *cis*-configurations for the substituents in the bicyclo[2.2.1]hept-5-ene rings, viz. IIIb and IIIc for the mercury compound. The more intense of these two sets of signals (~10% of the product for III) was assigned, on the basis of a relatively lower field CF_3 signal and higher field F signal, a configuration in which the two CF_3 groups are both in *exo*-configurations at the 2- and 3-positions of the bicyclic system (viz. IIIb for the mercury compound). The presence of all three configurations is consistent with a *cis*-addition mechanism for the Diels—Alder process, as the perfluorobut-2-ene used was shown by ^{19}F NMR studies to be a mixture of *trans*- (70%) and *cis*- (30%) isomers. Separation of the isomers was not possible in any of these cases.

The ^{13}C NMR spectra for several of the compounds were recorded and results are summarised in Table 3, together with those for the two compounds XVI and XVII unsubstituted at the 7-position [14], included for comparison purposes.

Assignment of all peaks was generally straightforward, except for the ambiguities mentioned in the footnotes to Table 3. Most of the trends observed are comparable with those observed for other bicyclo[2.2.1]hepta-2,5-diene and bicyclo[2.2.1]hept-5-ene derivatives [15]. Thus the C(7) resonance in the bicyclo[2.2.1]hepta-2,5-diene derivatives is at much lower field than in the bicyclo[2.2.1]hept-5-ene derivatives, but there is an additional low field shift of this resonance observed for the mercury compounds. While a downfield shift is also observed on substitution of silicon and tin in the 7-position (VIII, IX, XI and XVI), the magnitude of the shift is much greater on substitution by mercury. Similar downfield shifts are observed for straight-chain alkylmercury derivatives [16]. The other shifts observed on substitution at the 7-position are less remarkable, and are generally paralleled by the proton shifts.

As might be expected, the infrared spectrum of compound I shows strong carbonyl bands (at 1727 and 1710 cm^{-1}). A corresponding band in the spectrum of VII was measured at 1725 cm^{-1}. In the spectra of compounds II—V, and VIII—XIII very strong bands were observed between 1000 and 1350 cm^{-1} typical of the presence of carbon—fluorine bonds. In V and VI bands at 2210, 2110 and 2210, 2130 cm^{-1}, respectively, are assigned to the cyano-group vibrations. In X strong bands at 550 and 530 cm^{-1} are assigned to $\nu(SnC)$, the corresponding absorptions in the spectrum of XI being observed at 545 and 528 cm^{-1}. Infrared data for the various compounds is given in the Experimental section.

The mercury compounds (Table 1) are all solids which tend to decompose only after several months storage at ambient temperature in day light. The silicon and tin compounds are colourless liquids, miscible with most organic solvents.

Formation of the 5,7-bis(trimethylsilyl)- and 5,7-bis(trimethylstannyl) derivatives (IX, XI and XIII) from compounds $C_5H_4(MMe_3)_2$ (M = Si, Sn) prepared as

5,5-isomers clearly involves a metallotropic migration. These rearrangements occur at elevated temperatures in the cyclopentadiene derivatives and have been well studied [6—11,17]. In the present study we are unable to say at which stage migration of Me_3Si or Me_3Sn groups occur.

We are uncertain of the stereochemistry at the 7-position in the products. Our NMR studies reveal that only one configuration is present, and we have chosen to assume that the substituent (Hg or MMe_3) is in an *anti*-configuration with respect to the added dienophile.

In contrast to the results with $CF_3C{\equiv}CCF_3$, $C_2(CO_2Me)_2$, and the other dienophiles shown in Table 1, bis(cyclopentadienyl)mercury did not undergo Diels—Alder additions with $PhC{\equiv}CH$ or $CF_3C{\equiv}CH$. Instead the following reactions occurred to give the known compounds XVIII and XIX [18—20] in low yield (<5%):

$$\mathrm{Hg(C_5H_5)_2} \begin{cases} \xrightarrow{\mathrm{PhC{\equiv}CH}} \underset{\mathrm{(XVIII)}}{\mathrm{Hg(C{\equiv}CPh)_2}} + \mathrm{Hg} + \mathrm{C_{10}H_{12}} \\[2ex] \xrightarrow{\mathrm{CF_3C{\equiv}CH}} \underset{\mathrm{(XIX)}}{\mathrm{Hg(C{\equiv}CCF_3)_2}} + \mathrm{Hg} + \mathrm{C_{10}H_{12}} \end{cases}$$

Experimental

Infrared spectra were recorded using a Perkin—Elmer 457 instrument, and NMR spectra with Varian HA100 and JEOL PFT100 spectrometers. NMR spectra were measured in $CDCl_3$, and δ for ^{13}C shifts is measured relative to Me_4Si. ^{19}F chemical shifts are relative to CCl_3F (0.00 ppm), positive values indicating a shift to high field. Mass spectra, for molecular weight determinations, were obtained using an AEI MS902 mass spectrometer operating at 70 eV.

The compounds $Hg(C_5H_5)_2$ [23], $C_5H_5MMe_3$, and $C_5H_4(MMe_3)_2$ (M = Si, Sn) [9,10,21,22] were prepared by published methods. ^1H NMR studies revealed that as prepared the silicon and tin compounds were the 5- and 5,5-isomers. Solvents were dried and freshly distilled before use.

Reactions of bis(cyclopentadienyl)mercury

(a) With dimethyl acetylenedicarboxylate. Bis(cyclopentadienyl)mercury (331 mg, 1 mmol) and $C_2(CO_2Me)_2$ (284 mg, 2 mmol) were refluxed in tetrahydrofuran (20 ml) for 140 h. The clear pale yellow solution so produced was evaporated under vacuum and 50 ml of n-hexane was added. The solution was refrigerated for 48 h and the white solid obtained was filtered off and washed twice with a diethyl ether/tetrahydrofuran (1 : 1) mixture. Recrystallisation from methylene chloride afforded compound I (328 mg, 53%).

In CH_2Cl_2, infrared bands were observed at 3050w, 3000w, 2960w, 2910(sh), 2850vw, 1727vs, 1710vs, 1625m, 1555vw, 1437s, 1425(sh), 1315s, 1255vs, 1245s, 1225m, 1200s, 1140m, 1096s, 1050m, 953w, 920vw, 900s, 870(sh), 845vw, 755vs, 710vs cm^{-1}.

(b) With hexafluorobut-2-yne. Bis(cyclopentadienyl)mercury (662 mg, 2 mmol) and 20 ml of tetrahydrofuran were placed in a Carius tube which was attached to a high vacuum system. Hexafluorobut-2-yne (648 mg, 4 mmol) was condensed

into the tube which was sealed and heated (100° C, 40 h). The tube was opened, solvent removed in vacuo, and the white solid recrystallised from dichloromethane to give II (1.18 g, 90%). In other experiments it was found that the Diels—Alder addition of $CF_3C_2CF_3$ to $Hg(C_5H_5)_2$ occurs at room temperature over a period of four days to give II in 86% yield.

The infrared spectrum of II in CH_2Cl_2 showed bands at 3010w(br), 2890w(br), 1680s, 1559vw, 1340vs, 1295vs, 1262(sh), 1245s, 1232vs, 1205vs, 1178vs, 1135vs, 1090s, 1001s, 985m, 934w, 892w, 839w, 811w cm^{-1}. The ^{19}F NMR spectrum showed a sharp signal at 61.8 ppm.

(c) With octafluorobut-2-ene. As described in *b*, bis(cyclopentadienyl)mercury (662 mg, 2 mmol) and octafluorobut-2-ene (800 mg, 4 mmol) in tetrahydrofuran (20 ml) were reacted in a sealed tube at 100° C for 40 h. The resultant brown solid was isolated from methylene chloride and gave compound III (780 mg, 53%).

The infrared spectrum of III in CH_2Cl_2 showed bands at 3080vw, 3000vw, 2980(sh), 2870vw(br), 1344m, 1330s, 1310s, 1290m, 1270(sh), 1195vs, 1175(sh), 1114w, 1085w, 1070w, 1050m, 1018s, 990m, 965vw, 948m, 926m, 882vw, 815m, 780vw cm^{-1}. The ^{19}F NMR spectrum showed peaks corresponding to the presence of three isomers (see earlier) at 73.1 (CF_3 *exo*), 74.0 (CF_3 *endo*), 165.5 (F *exo*) and 162.9 (F *endo*) ppm for IIIa; at 71.0 (CF_3) and 158.4 (F) ppm for IIIb; and at 72.4 (CF_3) and 156.7 (F) ppm for IIIc.

(d) With hexafluoropropene. In a similar procedure to that followed in *b* above, bis(cyclopentadienyl)mercury (662 mg, 2 mmol) and hexafluoropropene (600 mg, 4 mmol) in tetrahydrofuran (20 ml) at 100° C for 40 h gave compound IV (258 mg, 28%), crystallised from methylene chloride.

The infrared spectrum of IV in CH_2Cl_2 showed bands at 3070vw, 2960(sh), 2930w, 2860(sh), 1715w(br), 1605w(br), 1550vw(br), 1464(sh), 1440(sh), 1425s, 1380(sh), 1330s, 1307s, 1267vs, 1235s, 1200vs, 1138m, 1100m, 1075m, 1065m, 1048m, 1005(sh), 995m, 970m, 959m, 930m, 900s, 860w, 810m, 735vs cm^{-} The ^{19}F NMR spectrum showed peaks corresponding to the presence of two isomers (see earlier). The relative intensity of the bands indicated an isomer distribution of 40% for IVa and 60% for IVb. Assignments were as follows: Isomer IVa: 73.5 (CF_3), 107.3 (F_a), 103.1 (F_b) and 162.0 (F_c) ppm; $J(F_aF_b)$ 235, $J(F_cF_b) = J(F_bCF_3) = 0$ Hz. Isomer IVb: 74.6 (CF_3), 105.9 (F_a), 103.7 (F_b) and 166.0 (F_c) ppm; $J(CF_3F_a) = 0$, $J(CF_3F_b) = 10$, $J(CF_3F_c) = 4$, $J(F_aF_b) = 232$ and $J(F_aF_c) = 12.5$ Hz.

(e) With 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene. Bis(cyclopentadienyl)mercury (662 mg, 2 mmol), 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (856 mg, 4 mmol) and tetrahydrofuran (50 ml) were placed in a flask and stirred at room temperature over night. A pale brown solid was filtered off and crystallised from pyridine to give V (461 mg, 30%).

The infrared spectrum of compound V (Nujol mull) showed bands at 2385 vw, 2210s, 2110vs, 1722w(br), 1650w(br), 1575vw(br), 1310(sh), 1275s, 1260s, 1230s, 1205s, 1195s, 1145m, 1110w, 1055w, 1032vw, 992w, 980(sh), 965m, 948(sh), 932w, 918(sh), 852m, 845w, 838m, 755m, 745(sh), 705vw, 650vw, 600vw, 582vw(br), 565vw(br), 555vw(br), 508w cm^{-1}.

(f) With tetracyanoethylene. Reaction occurred immediately when a solution of bis(cyclopentadienyl)mercury (662 mg, 2 mmol) in tetrahydrofuran (10 ml)

TABLE 4

SPECTROSCOPIC PROPERTIES OF COMPOUNDS VIII—XIII

(a) Infrared Spectra (liquid film) (cm^{-1})

Compound VIII:	3100vw, 3025m, 2980s, 2920m, 2900m, 1795m, 1745w, 1735(sh), 1695(sh), 1690s, 1575w, 1570w, 1435w, 1423w, 1353vs, 1310vs, 1300(sh), 1265vs, 1255(sh), 1240s, 1215vs, 1185vs(br), 1140vs(br), 1100s, 1065m, 1050m, 1040(sh), 1014s, 994s, 942s, 930s, 905s, 874vs, 852vs, 822m, 815(sh), 798w, 772s, 750(sh), 735vs, 729(sh), 719s, 704w, 645w, 627m.
Compound IX:	3060vw, 2995(sh), 2960s, 2905m, 2865m, 1940vw(br), 1880vw(br), 1867(sh), 1675s, 1655(sh), 1553m, 1543(sh), 1445(sh), 1427(sh), 1410m, 1340vs, 1300vs, 1254vs, 1230s, 1208vs, 1170vs(br), 1130vs(br), 1035s, 996m, 958s, 935s, 890(sh), 880s, 835vs(br), 815s, 792m, 756s, 743m, 728m, 716(sh), 698m, 658w, 630m, 578vw, 556w, 518vw, 460w, 415m.
Compound X:	3027m, 2984s, 2910m, 1799s, 1750m, 1700s, 1695s, 1582w, 1575(sh), 1428m, 1358vs, 1315vs, 1307(sh), 1220vs, 1185vs, 1140vs(br), 1106s, 1056m, 1020s, 1000s, 949s, 934s, 910s, 874vs, 856vs, 825m, 802w, 780s, 740vs, 733(sh), 724s, 650w, 627m, 550s, 530s, 495vw.
Compound XI:	3070(sh), 3030s, 2960s(br), 2700w, 2300w(br), 1967(sh), 1687s, 1665(sh), 1550m, 1347vs, 1307vs(br), 1245vs, 1200vs, 1180vs(br), 1138vs(br), 1038m, 1028vs, 1012w, 998s, 948m, 930m, 912m, 890w, 865s, 842s, 820(sh), 785vs(br), 746s, 736s, 661m, 645m, 630vw, 545vs, 528s, 473m, 462m.
Compound XII:	3090w, 3000m, 2960s, 2910(sh), 1440(sh), 1425m(br), 1345vs, 1329vs, 1315vs, 1295vs, 1255vs, 1245vs, 1220vs(br), 1190vs(br), 1145(sh), 1120m, 1088s, 1073s, 1055s, 1020s, 1005m, 990s, 970m, 948s, 939s, 926s, 885(sh), 865vs, 845vs, 802m, 795m, 768s, 740vs, 730(sh), 725s, 698w, 670m, 638w, 624m, 600vw, 580vw, 550w, 533m, 500vw, 490vw, 464vw, 440w.
Compound XIII:	3060w, 2960vs, 2908s, 2810(sh), 1940w(br), 1880w(br), 1575m, 1425(sh), 1410m, 1335vs, 1313vs, 1292vs, 1280vs, 1255vs(br), 1230vs(br), 1190vs(br), 1118m, 1085s, 1060s, 1025vs, 985s, 950s, 940s, 910s, 870vs(br), 830vs(br), 793s, 758vs, 748vs, 726vs, 698s, 678s, 645(sh), 625s, 582vw, 560m, 535m, 522(sh), 490m, 475(sh), 446w, 418m.

(b) ^{19}F NMR Chemical shifts (ppm) and coupling constants (Hz).

Compound VIII:	61.6
Compound IX:	60.0 and 62.1. $J(CF_3—CF_3)$ 8.8
Compound X:	61.8
Compound XI:	61.20 and 61.15. $J(CF_3—CF_3)$ 2.4
Compound XII:	Isomer XIIa, 73.4 (CF$_3$ *exo*), 74.3 (CF$_3$ *endo*), 166.4 (F *exo*) and 165.5 (F *endo*). $J(CF_3—CF_3)$ 2.4, J(CF$_3$ *endo*—F *endo*) 14.4 and J(CF$_3$ *endo*—F *exo*) 7.6. Isomer XIIb, 71.2 (CF$_3$) and 159.3 (F). Isomer XIIc, 72.6 (CF$_3$), peaks for F too weak and broad to be observed.
Compound XIII:	Isomer XIIIa, 73.4 (CF$_3$ *exo*), 74.3 (CF$_3$ *endo*), 166.9 (F *exo*) and 164.7 (F *endo*). $J(CF_3—CF_3)$ 2.4, J(CF$_3$ *endo*—F *endo*) 14.2, J(CF$_3$ *endo*—F *exo*) 7.6, J(CF$_3$ *exo*—F *exo*) 8.1 and J(CF$_3$ *exo*—F *endo*) 13.0. Isomer XIIIb, 72.3(CF$_3$). Isomer XIIIc, 72.6(CF$_3$). For isomers XIIIb and XIIIc concentrations were too low for high field fluorine signals to be observed (see text).

was added to a solution of tetracyanoethylene (512 mg, 4 mmol) in the same solvent (10 ml). The yellow solid which precipitated was filtered off and washed with diethyl ether/tetrahydrofuran (1 : 1) to give compound VI (1.06 g, 90%).

The infrared spectrum of VI (Nujol mull) showed bands at 2360vw, 2265(sh), 2210m(br), 2130w(br), 1575w(br), 1332s, 1310m, 1275(sh), 1265m, 1255(sh), 1208w, 1170m, 1156m, 1100vw, 1085vw, 1035vw(br), 975w(br), 935w, 915vw, 895vw(br), 868s, 790m, 780s cm^{-1}.

(g) With 4-phenyl-1,2,4-triazoline-3,5-dione. Bis(cyclopentadienyl)mercury

(331 mg, 1 mmol) and 4-phenyl-1,2,4-triazoline-3,5-dione (350 mg, 2 mmol) in tetrahydrofuran (50 ml) were stirred at room temperature for 15 h. The dark red solution was evaporated in vacuo, and the residue was treated with petroleum ether (40—60° C) from which dark red crystals of VII (450 mg, 66%) were recovered.

The infrared spectrum of VII (CH_2Cl_2 solution) showed bands at 2920w(br), 2345vw, 1725s, 1700(sh), 1603w, 1507m, 1495(sh), 1430(sh), 1415m, 1385(sh), 1370(sh), 1300vw(br), 1263vw(br), 1235m, 1165m, 1068vs, 1030vs, 970w, 948vw, 920sh, 910w, 840vw(br), 825vw cm^{-1}.

General procedure for the synthesis of the organo-silicon and -tin compounds VIII—XIII.

In a representative experiment, 5-trimethylsilylcyclopentadiene (1.38 g, 10 mmol) was placed in a Carius tube attached to a high vacuum system. Hexafluoro-but-2-yne (1.78 g, 11 mmol) was condensed into the tube which was sealed, and heated at 100° C for 40 h. After cooling the tube was opened and the liquid removed, and distilled under reduced pressure, giving compound VIII (1.36 g, 45%).

Using a similar technique the other compounds were prepared from reactants as follows:

Compound IX. (3.05 g, 82%) from $CF_3C{\equiv}CCF_3$ (1.78 g, 11 mmol) and $(Me_3Si)_2C_5H_4$ (2.11 g, 10 mmol) at room temperature for 60 h.

Compound X. (1.01 g, 52%) from $CF_3C{\equiv}CCF_3$ (0.92 g, 6 mmol) and $Me_3SnC_5H_5$ (1.59 g, 5 mmol) at room temperature for 120 h.

Compound XI. (1.46 g, 53%) from $CF_3C{\equiv}CCF_3$ (0.92 g, 6 mmol) and $(Me_3Sn)_2C_5H_4$ (1.96 g, 5 mmol) at room temperature for 110 h.

Compound XII. (2.37 g, 70%) from $CF_3CF{=}CFCF_3$ (2.2 g, 11 mmol) and $Me_3SiC_5H_5$ (1.38 g, 10 mmol) at 100° C for 40 h.

Compound XIII. (1.44 g, 70%) from $CF_3CF{=}CFCF_3$ (1.2 g, 6 mmol) and $(Me_3Si)_2C_5H_4$ (1.05 g, 5 mmol) at 100° C for 12 h.

The spectroscopic properties of compounds VIII—XIII are given in Table 4.

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