TRIFLUOROMETHYL SUBSTITUTED RING SYSTEMS: SYNTHESIS, AND REACTIVITY TOWARDS METAL CARBONYLS

A.R.L. BURSICS,[*] E. BURSICS-SZEKERES,[**] M. MURRAY and F.G.A. STONE

Department of Inorganic Chemistry, The University, Bristol BS8 1TS (Great Britain)

SUMMARY

Hexafluoro-but-2-yne and octafluoro-but-2-ene both readily add to cyclopentadiene. Similar Diels-Alder reactions occur between hexafluoro-but-2-yne and cycloheptatriene and cyclooctatetraene. 2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene reacts with chromium and molybdenum hexacarbonyls, and with enneacarbonyl di-iron to give metal complexes [M(diene)(CO)$_4$] (M = Cr, Mo) and [Fe(diene)(CO)$_3$], respectively. 6,7-Bis-(trifluoromethyl)tricyclo[3.2.2.0^{2,4}]nona-6,8-diene obtained from hexa-fluoro-but-2-yne and cycloheptatriene and 7,8-bis(trifluoromethyl)tri-cyclo[4.2.2.0^{2,5}]deca-3,7,9-triene formed from hexafluoro-but-2-yne and cyclooctatetraene also react with molybdenum hexacarbonyl to form complexes of molybdenum di- and tetracarbonyl groups, respectively. ^{1}H, ^{19}F and ^{13}C n.m.r. spectra of the compounds are described.

INTRODUCTION

Fluoro-olefins and -acetylenes readily function as dienophiles in 1,4-cyclo-addition reactions; their reactivity towards dienes is generally higher than that of their hydrocarbon analogues [1,2]. Hexafluoro-but-2-yne (HFB) even reacts under certain conditions with benzene, or with other aromatic compounds such as toluene, xylene and durene [3-6].

---

* Institute of Isotopes of the Hungarian Academy of Sciences, 1525 Budapest, P.O. Box 77.
** Pharmaceutical Research Institute, 1325 Budapest, P.O. Box 82.

It has been mentioned in a review [1] that HFB and octafluoro-but-2-ene (OFB) react with cyclopentadiene to give compounds (I) and (II), but no details of the reactions or properties of these compounds have been given [7]. Similarly, although the photoisomerisations of (III) and (IV) have been reported [8], compounds obtained by Diels-Alder additions of HFB to cycloheptatriene and to cyclooctatetraene, respectively, only details of the synthesis of (IV) have been published [6].

In the course of a wider study on the Diels-Alder reactions of hexafluoro-but-2-yne and fluoro-olefins [9], it seemed appropriate to re-investigate the preparation of compounds (I)-(IV) and carry out a study of some of their properties.

RESULTS AND DISCUSSION

Reaction of HFB and cyclopentadiene occurs essentially quantitatively at 100°C to give (I), characterised by analysis, and by infrared and n.m.r. spectroscopy (Tables 1 and 2). Diels-Alder addition of OFB to cyclopentadiene also occurred readily to give (II) (90% yield), a compound for which three isomers (IIa, b, c) are possible depending on the relative configuration of the F atoms and CF_3 groups in the bicycloheptene ring system. The ^{19}F n.m.r. spectrum of the product showed the presence of all three isomers, although the relative intensities of the bands showed that one was present as the major component (> 90%). The predominant isomer is assigned the trans structure (IIa), on the basis of correlations discussed elsewhere [9] for a series of related organometallic compounds in which metal atoms are substituents at the 7-position of the bicyclo-heptene ring system. The ^1H and ^{13}C n.m.r. data given in Tables 1 and 2 refer to isomer (IIa).

Reactions of HFB with cycloheptatriene and with cyclooctatetraene afford products (III) and (IV) in which a rearrangement of the cyclic polyene has occurred [10,11]. Indeed, higher temperatures are required for formation of (III) and (IV), than for (I) and (II), as might be expected if isomerisation of the polyene to its bicyclic form is necessary before addition of HFB or OFB.
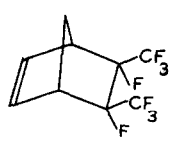
The presence of the cyclopropane ring system in (III) was confirmed by the ^1H and ^{13}C n.m.r. spectra (Tables 1 and 2) where the protons and carbon nuclei of this ring have shifts at higher field than those found in other saturated systems [12]. The n.m.r. spectra of (IV) are
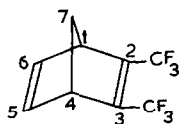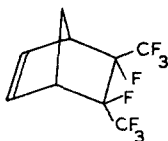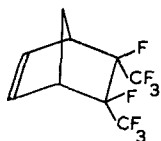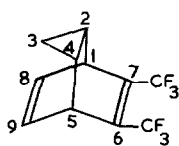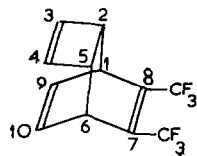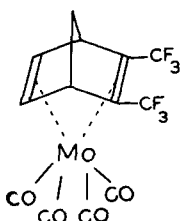
I IIa IIb

IIc III IV
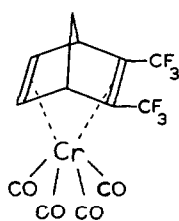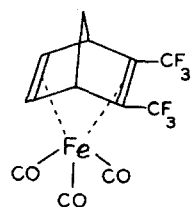
V VI VII
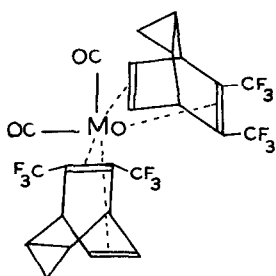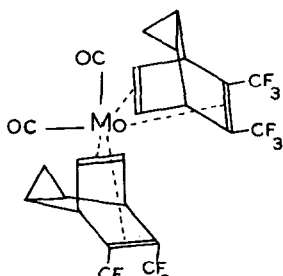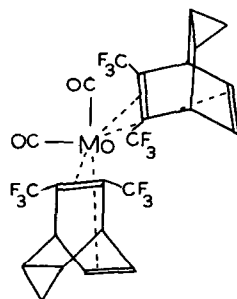
VIIIa VIIIb VIIIc
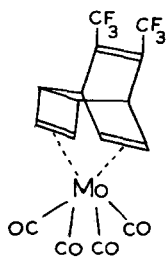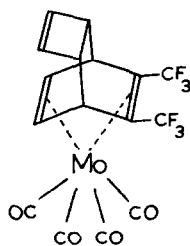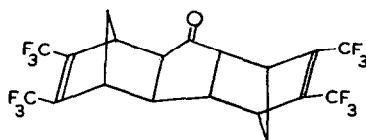
IXa IXb X

TABLE 1

^{1}H^a and ^{19}F n.m.r. data for compounds (I)-(IX)

Compound	Olefinic CH τ	Methine CH τ	Methylene CH$_2$ τ$_A$	τ$_B$	J$_{AB}$	Trifluoromethyl CF$_3$^{b} chemical shifts
I	2.99	6.02	7.67	7.87	7	61.9
II	3.61	6.65,6.72	7.69	7.95	11	73.8,74.8^c
III	3.89	5.91,8.56	9.20	9.35	7	60.8
IV	3.84,3.91	6.12,7.12	-	-	-	60.6
V	5.20	5.88	8.28	8.54	10	55.7
VI	5.69	5.96	8.28	8.54	10	55.6
VII	5.87	6.36	8.40	8.62	10	55.7
VIII	5.23,5.44	5.71,6.18,8.64	9.34	9.68	10	54.5,55.3(J$_{FF}$ = 11 Hz)^d 56.5,57.4(J$_{FF}$ = 11 Hz)^e
IX	4.97,5.26	5.90,5.33	-	-	-	60.5

^{a} The ^{1}H spectra showed the expected second order patterns for the proposed structures, but full spectral analyses were not carried out. ^{b} in p.p.m. upfield from CCl$_3$F. ^{c} Values for CF$_{3exo}$ and CF$_{3endo}$ of IIa respectively. Further data for IIa; F$_{exo}$, 168.8 p.p.m.; F$_{endo}$, 170.0 p.p.m.; J$_{CF_{3exo}F_{endo}}$ = 10.8 Hz; J$_{CF_{3exo}F_{exo}}$ = 6.8 Hz; J$_{CF_{3endo}F_{exo}}$ = 7.6 Hz; J$_{CF_{3endo}F_{endo}}$ = 16.4 Hz; J$_{CF_3CF_3}$ = 2.6 Hz; For IIb; CF$_3$, 71.8 p.p.m.; F, 162.0 p.p.m. For IIc; CF$_3$, 73.3 p.p.m.; F, 164.2 p.p.m. ^{d} Major component (> 90%). ^{e} Minor component (< 10%).

TABLE 2

^{13}C n.m.r. data for compounds (I)-(VI) and (VIII)

Compound	Olefinic C δ	Methine C δ	Methylene C δ	Trifluoromethyl C δ	$^1J_{CF}$
I	142.8(C_5,C_6) 148.7(C_2,C_3)	53.2(C_1,C_4)	73.9(C_7)	122.8	270
II	135.5(d,6Hz)}(C_5,C_6) 134.9(d,6Hz)}	49.0(d,22Hz)}(C_1,C_4) 47.2(d,21Hz)}	45.3(C_7)	122.8 122.3	283 ($^2J_{CF}$ = 32Hz) 281 ($^2J_{CF}$ = 29Hz)
III	130.1(C_8,C_9) 144.8(C_6,C_7)	40.0(C_1,C_5) 17.9(C_2,C_4)	17.2(C_3)	122.8	272
IV	129.8(C_9,C_{10}) 139.1(C_3,C_4)	43.8 42.2	-	122.3	275
V	77.6(C_5,C_6)	52.9(C_1,C_4)	59.7(C_7)		
VI	75.1(C_5,C_6)	51.0(C_1,C_4)	58.2(C_7)		
VIII	81.4,80.9(C_8,C_9)	40.6,40.3(C_1,C_5) 16.2,15.8(C_2,C_4)	3.8(C_3)		

unexceptional, and are in accord with the structure already assigned to this adduct [6]. However, none of the n.m.r. parameters afford any confirmation of the anti-configurations for the cyclopropane and cyclo-butene rings in (III) and (IV), which would normally be assumed for Diels-Alder additions of this type.

The infrared spectra (Experimental Section) of adducts (I)-(IV) show very strong bands between 1400 and 1000 cm^{-1} typical of C-F absorptions. The compounds are all colourless liquids miscible with organic solvents.

It is well known that dienes and trienes readily displace carbonyl groups from metal carbonyls to form complexes [13]. It was of interest, therefore, to study reactions of (I)-(IV) with certain metal carbonyls.

Compound (I) reacts with molybdenum and chromium hexacarbonyls, and with enneacarbonyl di-iron to afford yellow crystalline complexes (V)-(VII) characterised in the usual way (Experimental Section). The mass spectra all showed parent ions with successive loss of four carbonyl groups for (V) and (VI), and three for (VII). The ^{19}F n.m.r. spectra for each compound consisted of a single line shifted about 5 p.p.m. to low field of the signal in the free ligand (I). The ^{1}H and ^{13}C chemical resonance (Tables 1 and 2) for the CH:CH group showed the expected high field shifts for a metal co-ordinated double bond.

Reaction of (III) with molybdenum hexacarbonyl in boiling octane gave a di-carbonyl complex (VIII) for which several isomeric structures are possible. The presence in the infrared spectrum of two strong carbonyl stretching bands indicated a structure with a cis-Mo(CO)$_2$ arrangement of CO ligands (VIIIa-VIIIc). The ^{19}F n.m.r. spectrum consisted of two quartets (J_{FF} = 11 Hz), a pattern in accord with either structure (VIIIb) or structure (VIIIc). There were other weak bands in the ^{19}F spectrum indicative of the presence of another isomer in low concentration (< 10%), and in the infrared spectrum the two strong ν_{CO} bands had shoulders, suggesting that both (VIIIb) and (VIIIc) are formed, but it is not possible on the basis of the available evidence to say which is the predominant product.

The ligand behaviour of (IV) is of some interest in that there are three double bonds in the molecule of which only two are required to form the complex with the metal carbonyl fragment. Molybdenum hexacarbonyl reacted with (IV) in refluxing octane to give in low yield a yellow crystalline compound (IX), the mass spectrum of which revealed the presence of an Mo(CO)$_4$ group which was confirmed by the presence of four strong

carbonyl stretching bands in the infrared spectrum. Two structures (IXa and IXb) are possible, and a distinction between them can be made on the basis of the ^{1}H and [19]F n.m.r. data (Table 1). The ^{19}F chemical shifts for (IX) are virtually the same as in (IV) indicating that the CF_3-substituted double bonds in the tricyclodecatriene ring system are not complexed to the metal. That (IXa) is the correct formulation is supported by the ^{1}H spectrum in which the olefinic protons experience an up-field shift (~ 2 p.p.m.) relative to the free ligand. The preference for this structure is probably due more to the steric relationship of the two hydrogen substituted double bonds than to the electronic effects of the CF_3 groups, since CF_3 substituted double bonds can readily form complexes in e.g. bis(trifluoromethyl)bicyclo[2.2.2]octatrienes [14], and in (V), (VI), (VII) and (VIII) in the current work. Moreover, the fact that the hydrogen substituted double bonds are co-ordinated to the metal in complex (IX) is evidence that the adduct (IV) has the anti configuration of the cyclobutene ring system relative to the added dienophile.

In the reaction of (I) with $Fe_2(CO)_9$ we observed formation of a white crystalline material (X) as the major product. This contained no iron, but showed a carbonyl band in the infrared spectrum at 1735 cm^{-1}. The mass spectrum (molecular ion peak at 484) and analytical data suggested a composition of two molecules of (I) combined with one CO group. Examples are known for similar products from reactions of iron carbonyls with bicycloheptadienes [15,16] and bicycloheptenes [17]. These organic products have been assigned structures with dimethano-fluoren-9-one ring systems, which would imply structure (X) in our case. The ^{19}F and [13]C n.m.r. spectra are in accord with this proposal. There are two CF_3 signals (60.3 and 60.4 p.p.m.) corresponding to two very similar environments for these groups (A_3B_3 system, J_{FF} = 7 Hz). The ^{13}C spectrum reveals five signals (58.6, 51.8, 49.8, 47.3 and 44.7 p.p.m.) for carbon atoms bonded to hydrogen, suggesting that the two bicycloheptene ring systems are equivalent. The ^{1}H spectrum [τ, 6.43 (2H), 6.59 (2H), 7.22 and 7.71 (AB system, J = 7 Hz, 4H), 8.15 and 8.54 (AB system, J = 10 Hz, 4H)] is very similar to that of the dimers of bicyclo-hept-5-ene [16] and bicyclo-hept-5-ene-2-one [17] into which a carbonyl group has inserted, indicating that our product also has the exo-trans-exo configuration of the ring systems.

EXPERIMENTAL

Infrared spectra were recorded using a Perkin-Elmer 457 instrument, and n.m.r. spectra with Varian HA100 and JEOL PFT-100 spectrometers. N.m.r. spectra were measured in $CDCl_3$, and δ for ^{13}C shifts is given relative to Me_4Si. ^{19}F Chemical shifts are relative to CCl_3F (0.00 p.p.m.). Mass spectra were obtained using an AEI MS902 mass spectrometer operating at 70eV. All molecular weights were deduced from the parent ions in the mass spectra.

Cyclopentadiene, cycloheptatriene and cyclooctatetraene were freshly distilled before use. All solvents were dried and freshly distilled. Melting points are uncorrected.

General Procedure for the Synthesis of Compounds (I)-(IV)

In a representative experiment, cyclopentadiene (0.99 g, 15 mmol) was placed in a Carius tube attached to a high vacuum system. Hexafluoro-but-2-yne (2.59 g, 16 mmol) was condensed into the tube, which was then sealed and heated at 100°C for 24 hrs. After cooling, the tube was opened and the product (I) (3.2 g, 93%) isolated by distillation (b.p. 109-111°C). Analysis: Found: C, 47.3; H, 2.8; F. 49.5%. M, 228. $C_9H_6F_6$ requires C, 47.4; H, 2.7; F, 49.9%. M, 228.

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

Compound (II) (3.71 g, 92%), b.p. 117°C, from $CF_3CF:CFCF_3$ (3.20 g, 16 mmol) and cyclopentadiene (0.99 g, 15 mmol) at 100°C for 24 hrs. Analysis: Found: C, 40.9; H, 2.4; F, 57.3%. M, 266. $C_9H_6F_8$ requires C, 40.6; H, 2.3; F, 57.1%. M, 266.

Compound (III) (2.34 g, 54%), b.p. 138-140°C, from $CF_3C \equiv CCF_3$ (2.59 g, 16 mmol) and cycloheptatriene (1.48 g, 15 mmol) at 150°C for 24 hrs. Analysis: Found: C, 52.2; H, 3.3; F, 44.6%. M, 254. $C_{11}H_8F_6$ requires C, 52.0; H, 3.2; F, 44.9%. M, 254.

Compound (IV) (3.06 g, 75%), b.p. 146-150°C, from $CF_3C \equiv CCF_3$ (2.59 g, 16 mmol) and cyclooctatetraene (1.56 g, 15 mmol) at 150°C for 100 hrs. Analysis: Found: C, 53.9; H, 3.1; F. 42.5%. M, 266. $C_{12}H_8F_6$ requires C, 54.1; H, 3.0; F, 42.8%. M, 266.

Synthesis of Metal Carbonyl Complexes

(a) Molybdenum hexacarbonyl (1.32 g, 5 mmol) and 2,3-bis(trifluoromethyl)-bicyclo[2.2.1]hepta-2,5-diene (I) (1.37 g, 6 mmol) were refluxed in benzene (50 ml) for 72 hrs. under nitrogen. The black reaction mixture was filtered, and on cooling the yellow filtrate white crystals (0.47 g) of unreacted $Mo(CO)_6$ were recovered. The solution was evaporated in vacuo, and the yellow-brown residue sublimed (0.1mm/100°C) giving a yellow crystalline material (0.915 g) which was extracted with cyclohexane (30 ml) leaving further (0.10 g) unreacted $Mo(CO)_6$. The yellow solution was evaporated and complex (V) (312 mg, 14%), m.p. 132°C, was obtained by recrystallisation from cyclohexane using charcoal and Al_2O_3 as decolouriz-ing agents. Analysis: Found: C, 36.2; H, 1.6; F, 26.4%. M, 436. $C_{13}H_6F_6O_4Mo$ requires C, 35.8; H, 1.4; F, 26.1%. M, 436.

(b) Similarly, chromium hexacarbonyl (1.10 g, 5 mmol) and (I) (1.37 g, 6 mmol) were refluxed in benzene (50 ml) for 72 hrs. under nitrogen. Unreacted $Cr(CO)_6$ was recovered (0.36 g) and complex (VI) (120 mg, 6%) was obtained pure, m.p. 134°C, after crystallisation (3 times) from cyclohexane using charcoal and Al_2O_3 as decolourizing agents. Analysis: Found: C, 39.5; H, 1.7; F, 29.5%. M, 392. $C_{13}H_6F_6O_4Cr$ requires C, 39.8; H, 1.5; F, 29.1%. M, 392.

(c) Di-iron enneacarbonyl (2.18 g, 6 mmol) and (I) (1.60 g, 7 mmol) were refluxed in benzene (70 ml) for 72 hrs. under nitrogen. Filtration of the black mixture afforded a green filtrate which was evaporated in vacuo. The residue was extracted with cyclohexane, and the insoluble white solid was washed with cyclohexane and re-crystallised from boiling CH_2Cl_2 to give 888 mg (52%) of compound (X), m.p. 204-205°, Analysis: Found: C, 47.0; H, 2.5; F, 46.8%. M, 484. $C_{19}H_{12}F_{12}O$ requires C, 47.1; H, 2.5; F, 47.1%. M, 484.

The green cyclohexane extract was evaporated in vacuo and the residue recrystallised from cyclohexane, using charcoal and Al_2O_3 as decolourizing agents, giving yellow needles (30 mg) of (VII), m.p. 82-84°C. Analysis: Found: C, 39.4; H, 1.7; F, 31.2%. M, 368. $C_{12}H_6F_6O_3Fe$ requires   C, 39.2; H, 1.6; F, 31.0%. M, 368.

(d) Molybdenum hexacarbonyl (1.32 g, 5 mmol) and (III) (1.77 g, 7 mmol) were refluxed in octane (50 ml) for 96 hrs. under nitrogen. The black reaction mixture was filtered, and from the yellow filtrate compound (VIII) (92 mg), m.p. 218°C decomp., was isolated, recrystallised from cyclohexane. Analysis: Found: C, 43.9; H, 2.5; F, 34.8%. M, 660. $C_{24}H_{16}F_{12}O_2Mo$ requires C, 43.7; H, 2.4; F, 34.5%. M, 660.

(e) In a similar manner, $Mo(CO)_6$ (1.32 g, 5 mmol) and (IV) (1.61 g, 6 mmol) in refluxing octane (50 ml) for 96 hrs. gave, on crystallisation from cyclohexane, complex (IX) (75 mg), m.p. 120°C. Analysis: Found: C, 40.2; H, 1.9; F, 24.3%. M, 474. $C_{16}H_8F_6O_4Mo$ requires C, 40.5; H, 1.7; F, 24.0%. M, 474.

Infrared Spectral Bands (cm^{-1})

Liquid films.
Compound (I): 3140(w), 3085(w), 3015(m), 2998(m), 2960(s), 2890(m), 2860(sh), 2700(w), 2650(vw), 1685(vs), 1655(sh), 1565(m), 1463(m), 1403(sh), 1375(s), 1350(vs), 1302(vs,bd), 1260(vs), 1250(vs), 1240(vs), 1220(vs), 1185(vs,bd), 1155(vs,bd), 1120(vs,bd), 1095(vs), 1060(m), 1035(m), 1000(vs), 954(s), 938(s), 928(sh), 911(sh), 899(s), 894(m), 822(s), 810(s), 760(m), 749(s), 730(vs), 720(vs), 682(sh), 650(s), 626(m).

Compound (II): 3090(w), 3010(m), 2990(m), 2900(w), 1470(m), 1345(vs), 1335(vs), 1313(vs), 1285(vs), 1270(vs,bd), 1195(vs,bd), 1140(s), 1130(s), 1086(s), 1046(s), 1029(s), 1010(m), 993(m), 938(s), 925(vs), 910(m), 890(m), 804(s), 794(s), 755(s), 738(vs), 654(m), 625(w), 580(vw), 546(w), 530(m), 490(vw), 438(w), 398(s).

Compound (III): 3070(m), 3010(s), 2935(w), 1667(s), 1607(m), 1440(s), 1399(sh), 1355(vs,bd), 1285(vs,bd), 1270(vs), 1251(vs), 1215(vs), 1175(vs,bd), 1135(vs,bd), 1095(s), 1070(s), 1056(s), 1043(s), 1015(s), 995(vs), 940(s), 890(w), 862(vw), 840(s), 825(s), 794(s), 773(w), 763(m), 725(s), 710(vs,bd), 694(s), 664(m), 645(m), 620(sh), 618(m), 573(w), 540(m), 510(m).

Compound (IV): 3130(w), 3065(m), 3010(w), 2945(m), 1683(s), 1649(w), 1622(m), 1603(w), 1562(w), 1459(w), 1371(vs), 1340(vs), 1325(vs,bd), 1300(vs,bd), 1270(s), 1260(vs), 1235(s), 1155(vs,bd), 1102(s), 1055(s), 1048(vs),

1040(vs), 1022(vs), 979(m), 970(s), 940(m), 920(m), 895(m), 875(s), 845(w), 825(s), 815(sh), 795(vs), 785(vs), 766(vs), 745(m), 725(vs), 702(m), 683(m), 655(s), 614(w), 570(w), 508(w).

Cyclohexane solution.

Compound (V). ν_{CO} 2085(vs), 2062(m), 2027(sh), 2018(vs), 1998(sh), 1985(sh), 1967(vs), 1934(sh).

Other bands, 1413(w), 1335(m), 1300(m), 1250(m), 1235(sh), 1198(m), 1172(m), 1154(s), 1131(s), 1075(w), 1022(vw), 988(w), 952(m), 812(vw), 698(w), 658(w), 605(m).

Compound (VI): ν_{CO} 2079(s), 2010(m), 2000(vs), 1967(vs).

Other bands, 1388(vw), 1300(w), 1255(w), 1237(w), 1198(w), 1175(m), 1158(m), 1150(m), 1138(m), 992(vw), 952(w), 722(vw), 680(w), 655(w).

Compound (VII): ν_{CO} 2092(s), 2050(sh), 2036(m), 2010(s).

Other bands, 1425(w), 1370(w), 1347(w), 1309(m), 1285(w), 1253(w), 1240(vw), 1190(m), 1170(m). 1158(s), 1145(m), 1122(m), 1078(vw), 1040(vw), 960(w), 938(vw).

Compound (VIII): ν_{CO} 2066(s), 2048(sh), 2020(s), 2005(sh).

Other bands, 2960(vw), 2930(w), 2860(w), 1410(m), 1355(vw), 1330(m), 1295(vw), 1243(m), 1205(m), 1181(m), 1164(s), 1143(m), 1125(s), 1102(m), 1054(w), 1034(w), 1000(m), 991(w), 858(w), 822(w), 665(w).

Compound (IX): ν_{CO} 2076(vs), 2060(sh), 2026(m), 2014(sh), 1992(vs), 1955(sh), 1940(vs), 1912(sh).

Other bands, 2800(vw), 1655(w), 1380(vw), 1355(w), 1315(w), 1293(s), 1250(w), 1243(w), 1185(s), 1155(m), 1132(m), 1100(m), 1030(w), 998(w), 960(w).

Compound (X): 2960(vw), 2900(vw), 1735(s), 1675(m), 1470(w), 1461(vw), 1403(w), 1372(m), 1371(sh), 1307(vs), 1275(s,bd), 1245(sh), 1206(sh), 1188(vs), 1150(vs), 1140(sh), 1060(s), 1020(w), 988(w), 950(m), 930(w), 920(w), 890(w), 835(w), 805(vw).

REFERENCES

1   D.R.A. Perry, Fluorine Chem. Revs., 1 (1967) 253.
2   M.I. Bruce and W.R. Cullen, Fluorine Chem. Revs., 4 (1969) 79.
3   C.G. Krespan, B.C. McKusick and T.L. Cairns, J. Amer. Chem. Soc., 82 (1960) 1515.
4   C.G. Krespan, B.C. McKusick and T.L. Cairns, J. Amer. Chem. Soc., 83 (1961) 3428.
5   R.S.H. Liu, J. Amer. Chem. Soc., 90 (1968) 215.
6   R.S.H. Liu and C.G. Krespan, J. Org. Chem., 34 (1969) 1271.
7   P. Tarrant and D.R.A. Perry, unpublished results, 1966. (see Ref. 1, p. 311).
8   R.S.H. Liu, Tetrahedron Letters, (1969) 1409.
9   A.R.L. Bursics, M. Murray and F.G.A. Stone, J. Organometal. Chem., in press.
10 A.S. Onishchenko, "Diene Synthesis", Israel Program for Scientific Translations Ltd., 1964, p. 373.
11 L.T. Scott and M. Jones, Chem. Revs., 72 (1972) 181.
12 K.M. Crecely, R.W. Crecely and J.H. Goldstein, J. Phys. Chem., 74 (1970) 2680.
13 M.L.H. Green, "Organometallic Compounds. Volume 2. The Transition Elements", Methuen, 1968.
14 R.B. King, J. Amer. Chem. Soc., 84 (1962) 4705.
15 P.W. Jolly, F.G.A. Stone and K. Mackenzie, J. Chem. Soc., (1965) 6416, and references cited therein.
16 M. Green and E.A.C. Lucken, Helv. Chim. Acta, 45 (1962) 1870.
17 F. Grandjean, P. Laszlo and A. Stockis, J. Amer. Chem. Soc., 96 (1974) 1622, and references cited therein.