

COORDINATION CHEMISTRY OF SILOLES: VINYL-, ALLYL- AND ALKYNYL-SILOLES; SYNTHESIS AND STRUCTURE OF η^4, η^2 -1-ALLYL- AND 1-VINYL-2,5-DIPHENYLSILACYCLOPENTADIENE COMPLEXES *

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Summary

The reactions of 1-allyl-1-methyl- (**8**), 1-vinyl-1-methyl- (**10**), 1,1-diallyl- (**14**), 1,1-divinyl- (**16**), 1-ethynyl-1-methyl- (**2a**) and 1-propynyl-1-methyl-2,5-diphenylsilacyclopentadiene (**2b**) (or siloles) with transition metals are described. Competition between complexation of the diene and that of the triple bond of the propynylsilole is observed with $\text{Co}_2(\text{CO})_8$, but with $\text{Fe}_2(\text{CO})_9$, the η^4 -complexes are obtained in all cases. $\text{Co}_2(\text{CO})_8$ reacts with the vinyl- and allyl-siloles to give η^4 -complexes, but $\text{Mo}(\text{CO})_4(\text{COD})$ ($\text{COD} = 1,5$ -cyclooctadiene) or $\text{W}(\text{CO})_3(\text{CH}_3\text{CN})_3$ gives η^4, η^2 -complexes. The crystal structures of (η^4 -(η^2 -endo-1-allyl)-exo-1-methyl)- (**9a**) and (η^4 -(η^2 -endo-1-vinyl)-exo-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyl molybdenum (**12a**) have been determined. They show that the dihedral angle between the diene and the C(1)–Si–C(2) plane is 28° in the case of the allyl derivative **9a** but only 8.9° in the vinyl complex **12a**.

Introduction

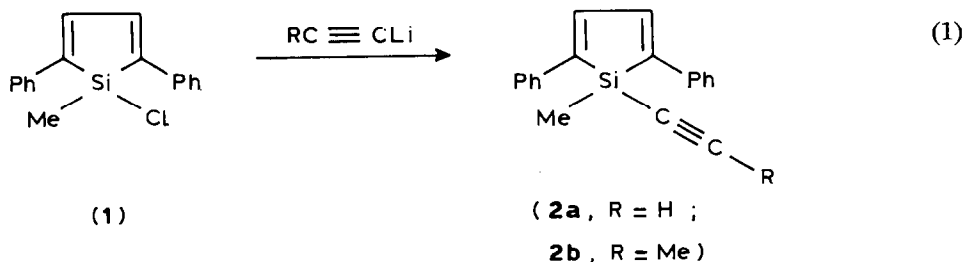
We have shown previously that 2,5-diphenylsilacyclopentadienes (or siloles) are good ligands for transition metals [1]. We report here results obtained with 2,5-diphenylsilacyclopentadienes bearing an unsaturated group, vinyl, allyl or alkynyl, on silicon. These groups are interesting from two points of view: first they may coordinate to the transition metal leading to other different geometries or polymetallic compounds, and secondly they are "pseudofunctional" groups which can be cleaved by electrophiles with possible formation of reactive functional groups

* Dedicated to Professor Jean Tirouflet in recognition of his outstanding contributions to organometallic chemistry.

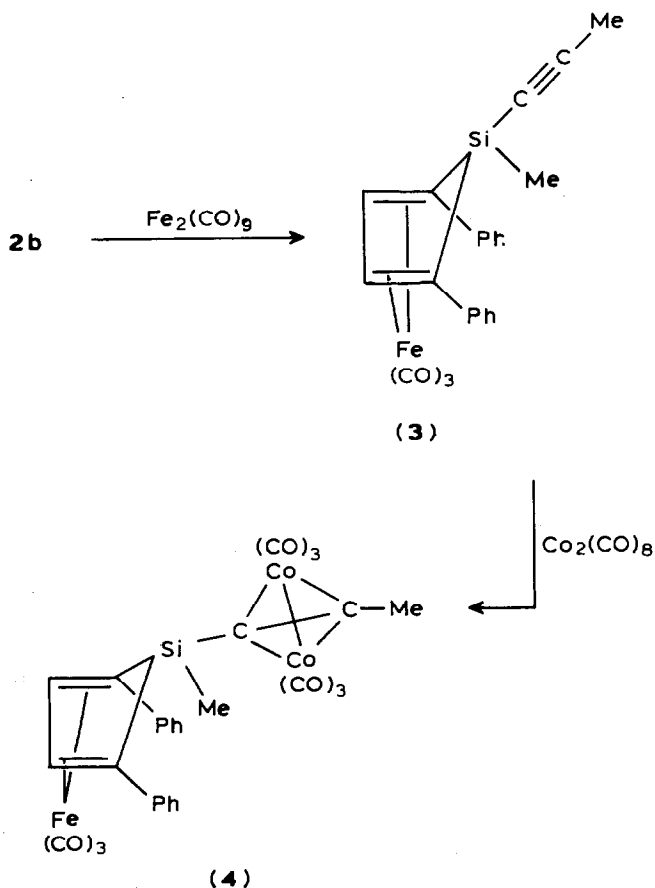
(such as halides) at silicon. In the case of an alkynyl group bonded to silicon, the possibility arises of competition between complexation of the triple bond and that of the diene of the silole.

Results and discussion

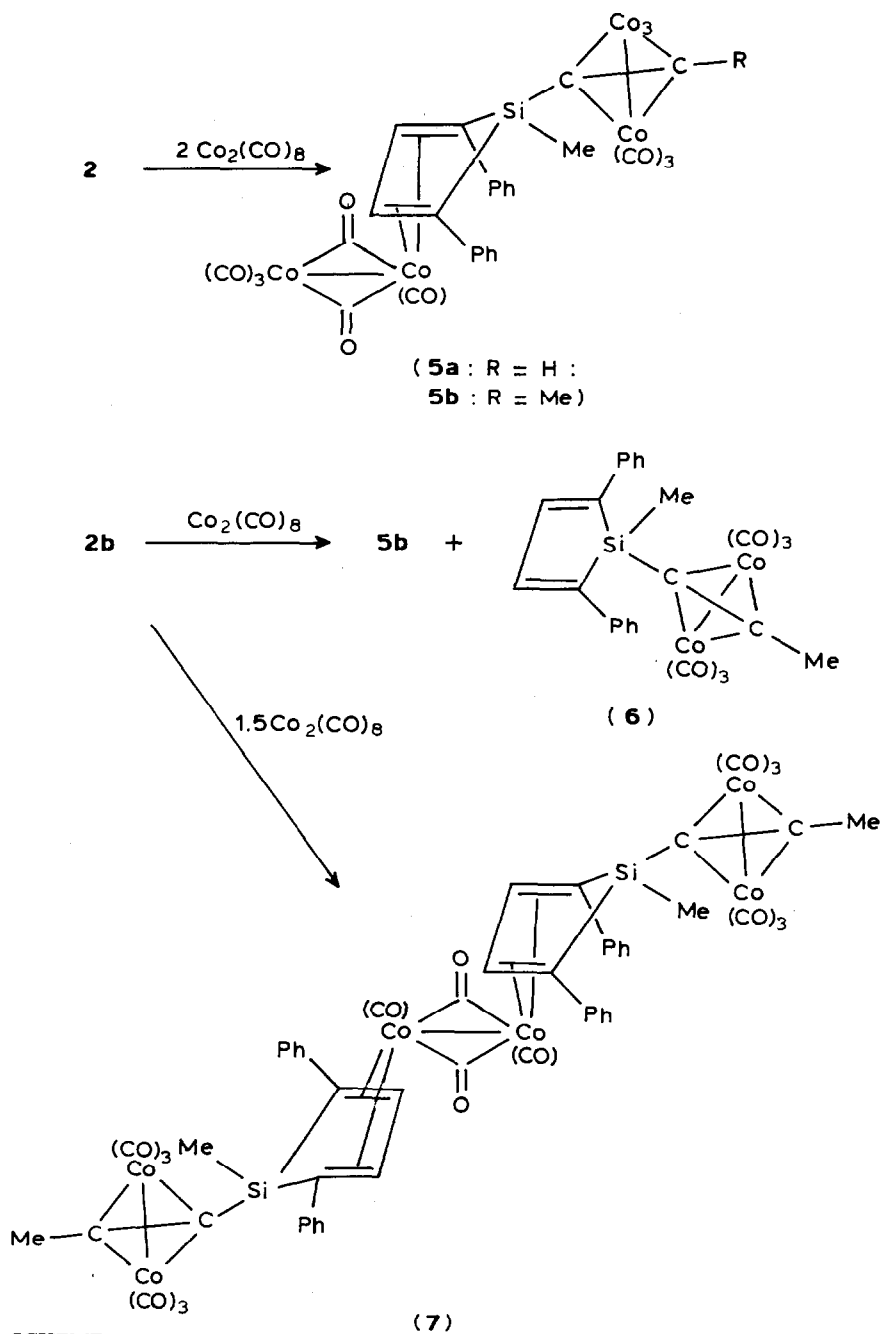
The ethynylsilole **2a** and propynylsilole **2b** were prepared (eq. 1) from methylchlorosilole **1**. These compounds have three possible modes of coordination, via the



diene or the triple bond or both. All three modes are observed, depending on the transition metal (Schemes 1 and 2).

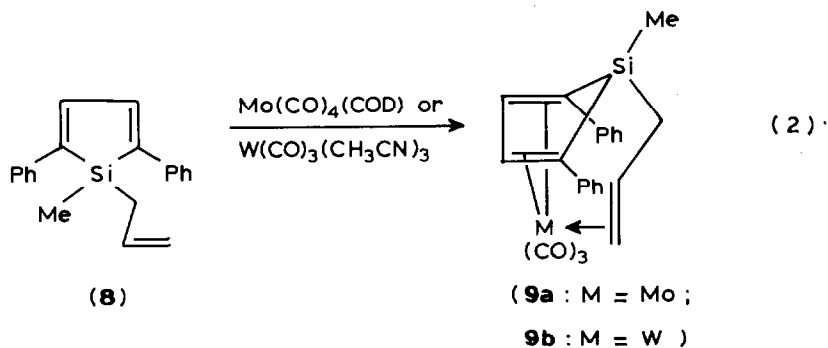


SCHEME 1



The reaction of **2b** with $\text{Fe}_2(\text{CO})_9$ gave the η^4 -complex **3** with the methyl group in *endo*-position. The triple bond was not affected but complex **3** reacted further with $\text{Co}_2(\text{CO})_8$ to give **4**, which contains one iron and two cobalt atoms.

The alkynyl derivatives **2** reacted with 2 moles of $\text{Co}_2(\text{CO})_8$ to give **5** in which both the diene and the triple bond are complexed to the metal. But **2b** reacted with 1 mole of $\text{Co}_2(\text{CO})_8$ to give complex **5b** together with a compound having only the triple bond complexed to the cobalt. Reaction of **2b** with 1.5 moles of $\text{Co}_2(\text{CO})_8$ gave a low yield of the symmetric derivative **7**, which has six cobalt atoms in the molecule; two of these are complexed with the dienes and the remaining four with the two triple bonds (Scheme 2).



Reaction of 1-methyl-1-allyl-2,5-diphenylsilacyclopentadiene (**8**) with $\text{Mo}(\text{CO})_4(\text{COD})$ or $\text{W}(\text{CO})_3(\text{CH}_3\text{CN})_3$ gave the complexes **9** (eq. 2). The structures of

TABLE 1

^1H NMR DATA (C_6D_6 , δ (ppm)) FOR COMPOUNDS **9a** AND **9b**

	9a , M = Mo		9b , M = W	
Ph	7.3–6.7	m	7.6–6.7	m
$\text{H}^x(\text{H}^{x'})$	6.0	d, $J_{xx'}$ 2 Hz	5.7	d, $J_{xx'}$ 2 Hz
$\text{H}^x(\text{H}^{x'})$	5.8	d, $J_{x'x}$ 2 Hz	5.45	d, $J_{x'x}$ 2 Hz
H^B	5.8	m	5.6–5.1	m
H^C	4.3	d, J_{CB} 6 Hz	3.95	d, J_{CB} 6 Hz
H^D	3.9	d, J_{DB} 11 Hz	3.45	d, J_{DB} 10 Hz
$\text{H}^A(\text{H}^{A'})$	2.3	dd, J_{AB} 6 Hz $J_{AA'}$ 9 Hz	2.3	dd, J_{AB} 5.5 Hz $J_{AA'}$ 9 Hz
$\text{H}^{A'}(\text{H}^A)$	1.95	dd, $J_{A'B}$ 6 Hz $J_{A'A}$ 9 Hz	1.7	dd, $J_{A'B}$ 5 Hz $J_{A'A}$ 9 Hz
Me	0.1	s	0.0	s

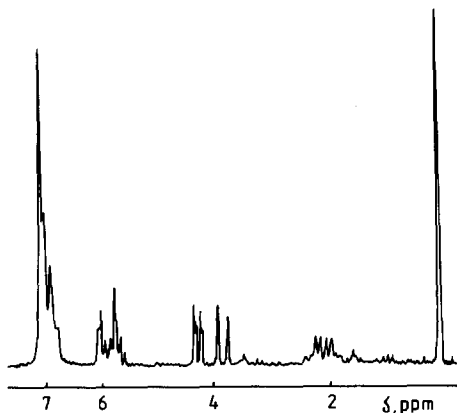
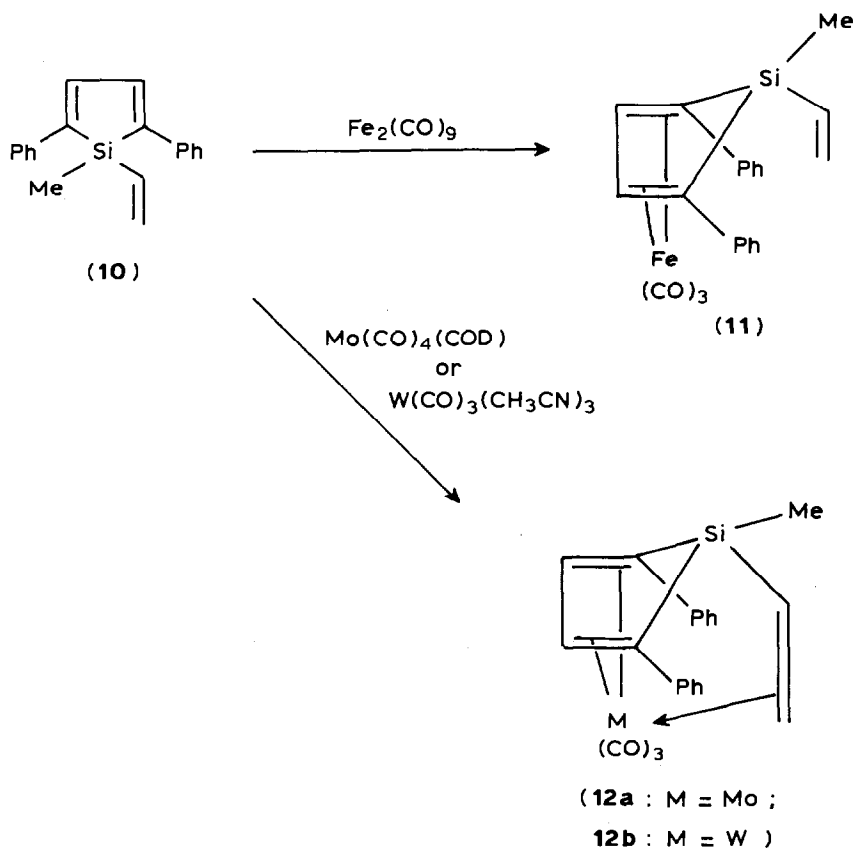


Fig. 1. ^1H NMR (C_6D_6) spectrum of complex **9a**.

complexes **9** were determined by IR, ^1H and ^{13}C NMR spectroscopy (see Table 1 and Fig. 1 for ^1H NMR of **9a**) and by X-ray analysis of **9a** (vide infra), which gave the dihedral angle between the diene plane and the (C(1)–Si–C(2)) plane. This angle



SCHEME 3

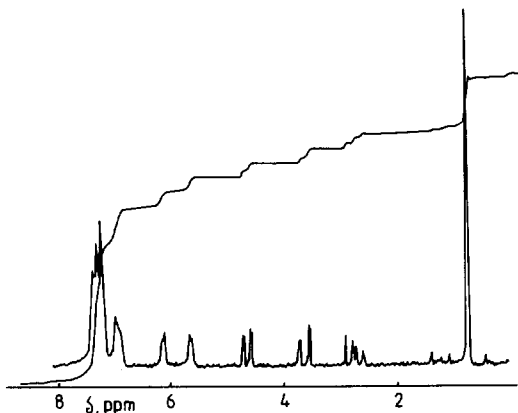
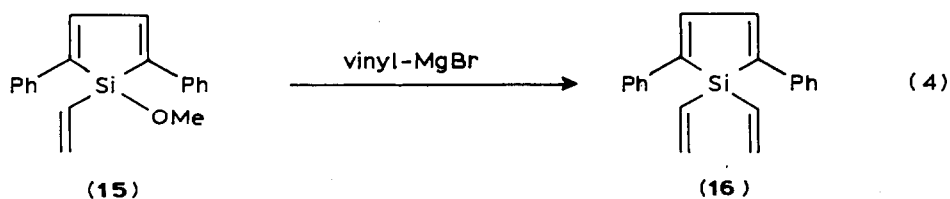
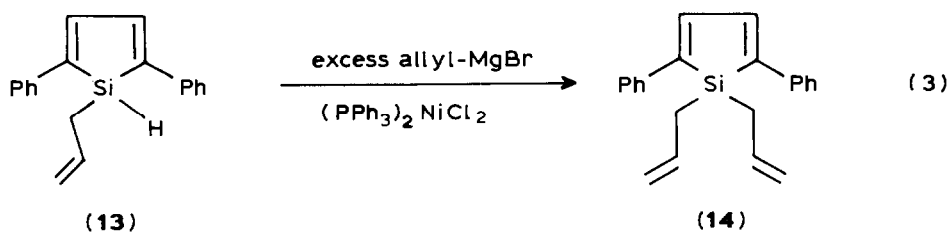


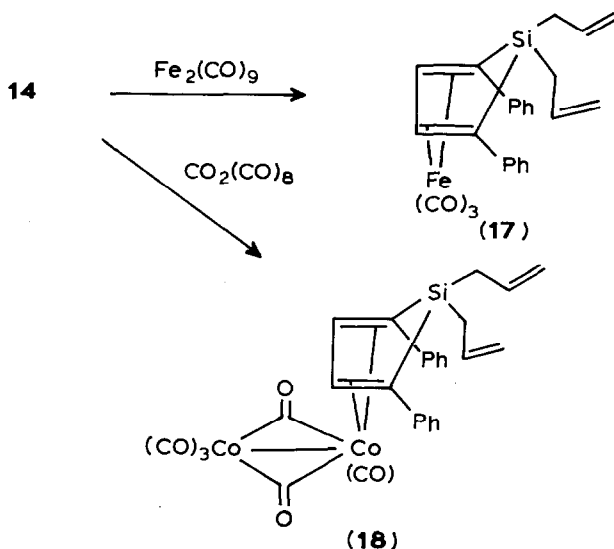
Fig. 2. ^1H NMR (C_6D_6) spectrum of complex **12b**.

of 28° , is similar to that of 32° observed by Muir [2] in the case of $(\eta^4\text{-1,1-dimethyl-2,5-diphenylsilacyclopentadiene})\text{tricarbonylruthenium}$, but it is larger than the 20° observed for $\text{bis}(\eta^4\text{-1,1-dimethyl-2,5-diphenylsilacyclopentadiene})\text{nickel}$ [1].

In order to reduce the dihedral angle, vinyl derivatives were prepared (Scheme 3). Compound **10** reacted with $\text{Fe}_2(\text{CO})_9$ to give the $(\eta^4\text{-}exo\text{-1-methyl-}endo\text{-1-vinyl-2,5-diphenylsilacyclopentadiene})\text{tricarbonyliron}$ complex **11**. The exocyclic vinyl group is not coordinated to the iron atom, as observed in the case of allyl [1]. But, in the case of molybdenum and tungsten, the spectroscopic data for complexes **12** and crystal structure of **12b** showed that the vinyl double bond is coordinated to the metal (Fig. 2 shows the ^1H NMR spectrum of **12b**). In **12a** (vide infra) the dihedral angle is only 8.9° showing that it is possible to make the silacyclopentadiene ring flatter, and perhaps in that way permit aromaticity of the silacyclopentadiene ring.

The change in the dihedral angle results in the modification of the position of the R group, to *exo* with respect to the metal, and the reactivity of the R group should





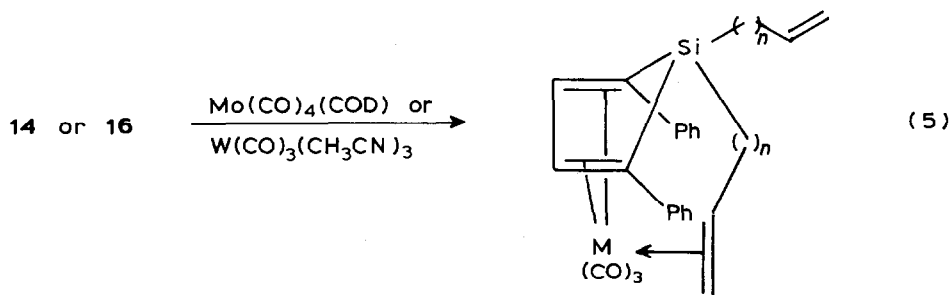
SCHEME 4

thus be different. In order to check this, the disubstituted allyl- and vinyl-silicon derivatives were prepared (eq. 3, 4).

The diallyl derivative **14** reacted with $\text{Fe}_2(\text{CO})_9$ or $\text{Co}_2(\text{CO})_8$ to give the corresponding η^4 -complexes **17** and **18** (Scheme 4), as observed in the case of the methyl(allyl)silole [1].

The ^1H NMR spectra showed that the *endo*-allyl group of complexes **17** and **18** were not coordinated to the metal; however, treatment of **14** and **16** with $\text{Mo}(\text{CO})_4(\text{COD})$ or $\text{W}(\text{CO})_3(\text{CH}_3\text{CN})_3$ gave, as expected, the corresponding complexes **19** and **20** (eq. 5), with the exocyclic double bond complexed to the metal.

We tried to cleave the *exo*-silicon-carbon bond of complexes **19** and **20**. $\text{Me}_3\text{SiOSO}_2\text{Cl}$ normally brings about insertion of SO_3 into silicon-carbon bonds



(19a : M = Mo , n = 1 ;

19b : M = W , n = 1 ;

20a : M = Mo , n = 0 ;

20b : M = W , n = 0)

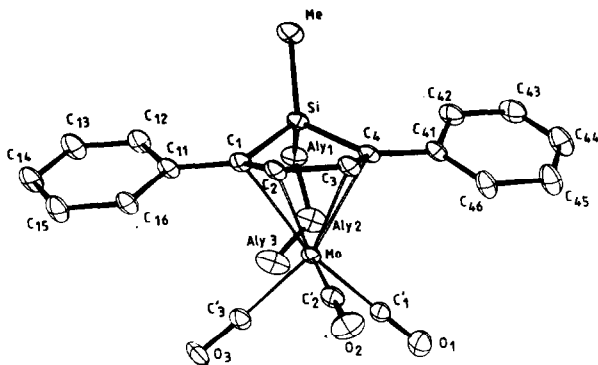
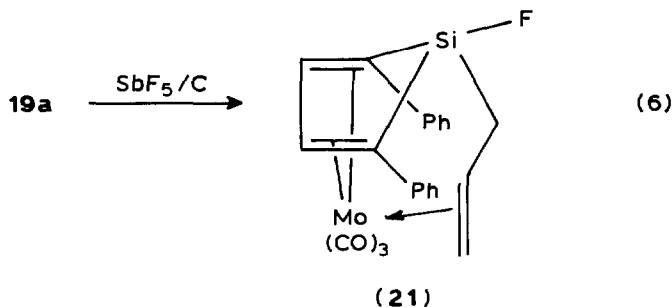


Fig. 3. ORTEP drawing of complex **9a** with the numbering of the atoms. The thermal ellipsoid encloses 20% of the electron density.

such as Si-aryl or Si-allyl [3], but **19a**, gave a mixture of unidentified products. Reactions of **19a** with HCl gas, SbCl₅ intercalated in graphite, or SnCl₄ (which is known to cleave the bond between the *exo*-methyl group and silicon in the tetraphenylsilole series [4]), gave intractable mixtures. With SbF₅ intercalated in graphite [5], the *exo*-fluoro complex **21** was obtained in good yield (eq. 6). The corresponding reaction with the vinyl complex **20a** was unsuccessful, as was that



of CH₃COCl/AlCl₃ [6].

We are undertaking a study of the reactions of these new complexes.

Crystal structures: results and comments

Structure of complex 9a. The labelling of the atoms is given in Fig. 3. The molecular configuration is best seen in Fig. 4. Bond lengths and bond angles are listed in Tables 2 and 3. The overall octahedral geometry is retained, with the three carbonyl groups *trans* to the three carbon-carbon double bonds. The mirror plane observed by Muir [2] in the free ligand, and even in the ruthenium tricarbonyl complex, is not retained here, owing to the configuration of the allyl group. Another feature is the fact that the C'(3)-Mo-C'(1) angle is > 14° larger than the other OC-Mo-CO angles. This is due to steric hindrance of the allyl group *trans* to the carbonyl group C'(2)O(2), though the coordination distance of the vinyl ligand is much larger.

Within the silole ring, the C(2)-C(3) distance, 1.457(8) Å, remains longer than the formal double bond distances (av. 1.42(1) Å), thus suggesting a weaker coordi-

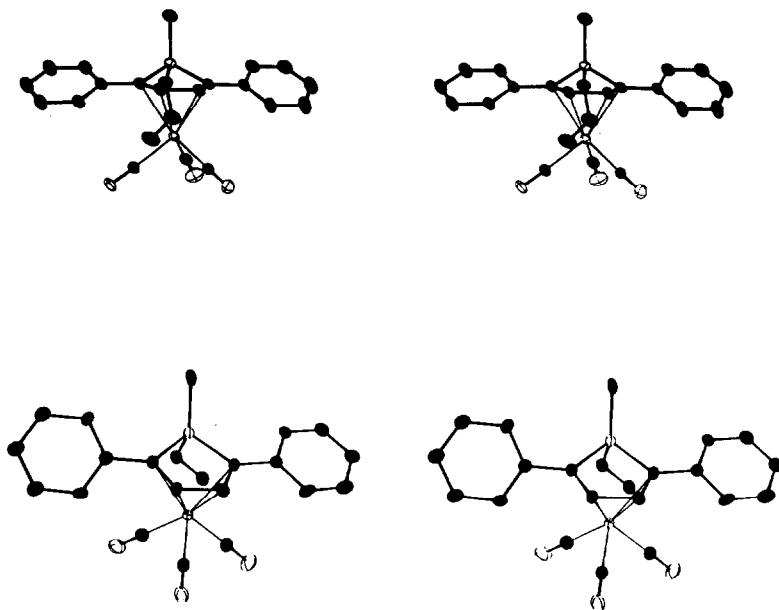


Fig. 4. Stereoscopic diagram of the molecules of (a) compound **9a** and (b) compound **12a**. All carbon atoms are plain black ellipsoids.

nation for molybdenum than for ruthenium (see ref. 2), the result is comparable to that we noted previously [1] for bis(η^4 -1,1-dimethyl-2,5-diphenylsilacyclopentadiene)nickel.

TABLE 2

BOND LENGTHS (Å) FOR COMPLEX **9a**, e.s.d.s. IN PARENTHESES

Mo-C(1)	2.410(7)	C(1)-C(2)	1.416(8)
Mo-C(2)	2.308(7)	C(2)-C(3)	1.457(8)
Mo-C(3)	2.316(7)	C(3)-C(4)	1.425(8)
Mo-C(4)	2.442(7)	C(1)-C(11)	1.471(8)
Mo-Allyl(2)	2.666(7)	C(4)-C(41)	1.466(8)
Mo-Allyl(3)	2.527(8)		
Mo-C'(1)	1.988(8)	C(11)-C(12)	1.400(9)
Mo-C'(2)	1.961(7)	C(12)-C(13)	1.401(9)
Mo-C'(3)	1.987(8)	C(13)-C(14)	1.402(11)
		C(14)-C(15)	1.403(10)
Si-C(1)	1.879(6)	C(15)-C(16)	1.397(9)
Si-C(4)	1.875(6)	C(16)-C(11)	1.406(9)
Si-Me	1.886(9)	C(41)-C(42)	1.402(10)
Si-Allyl(1)	1.882(7)	C(42)-C(43)	1.416(10)
Allyl(1)-Allyl(2)	1.525(14)	C(43)-C(44)	1.380(14)
Allyl(2)-Allyl(3)	1.308(13)	C(44)-C(45)	1.405(12)
		C(45)-C(46)	1.416(10)
C'(1)-O(1)	1.141(10)	C(46)-C(41)	1.393(10)
C'(2)-O(2)	1.163(8)		
C'(3)-O(3)	1.140(9)	Mo...Si	3.042(2)

TABLE 3
SELECTED BOND ANGLES (deg) FOR COMPLEX 9a

C'(1)–Mo–C'(2)	82.4(3)	Mo–C'(1)–O(1)	176.8(6)
C'(2)–Mo–C'(3)	82.1(3)	Mo–C'(2)–O(2)	178.4(7)
C'(3)–Mo–C'(1)	96.9(3)	Mo–C'(3)–O(3)	176.5(7)
Allyl(2)–Mo–Allyl(3)	29.0(3)		
C(1)–Mo–C(2)	34.8(2)	Si–Allyl(1)–Allyl(2)	104.3(5)
C(2)–Mo–C(3)	36.7(2)	Allyl(1)–Allyl(2)–Allyl(3)	125.0(8)
C(3)–Mo–C(4)	34.7(2)		
C(1)–Mo–C(4)	66.3(2)	Si–C(1)–C(2)	105.8(4)
		C(1)–C(2)–C(3)	114.7(5)
C(1)–Si–C(4)	89.9(3)	C(2)–C(3)–C(4)	115.1(5)
C(1)–Si–Me	115.3(3)	C(3)–C(4)–Si	105.4(4)
C(4)–Si–Me	115.8(3)	C(11)–C(1)–Si	129.1(5)
C(1)–Si–Allyl(1)	111.2(3)	C(11)–C(1)–C(2)	122.4(5)
C(4)–Si–Allyl(1)	108.9(3)	C(41)–C(4)–Si	130.0(5)
Me–Si–Allyl(1)	113.4(3)	C(41)–C(4)–C(3)	121.6(5)

The phenyl rings are not coplanar with the butadiene unit; the phenyl rings C(11–16) and C(41–46) are rotated in the same sense (ca. 23.2 and 29.4°, respectively), with atoms C(12) and C(42), nearest to silicon, both lying away from the Mo(CO)₃ moiety. The coordination of the allyl group decreases slightly the fold angle of the silole ring: the planar butadiene unit C(1)–C(2)–C(3)–C(4) and the C(1)–Si–C(4) plane make a dihedral angle of 28.0°; this value is smaller than that observed for the molybdenum complex (Me₄Silole)₂Mo(CO)₂ [7], in which the fold angle is 36.6°.

The mean Si–C(silole) bond length, 1.88(1) Å, is identical with literature values [1,2] and longer than that observed for the disilole molybdenum complex [7] (1.86(1) Å). The carbonyl group C'(2)O(2), *trans* to the vinyl group, looks slightly different from the two other CO groups: although the Mo---O(2) distance remains about 3.13(1) Å, the C'(2) atom is nearer to the Mo atom by 0.024(8) Å.

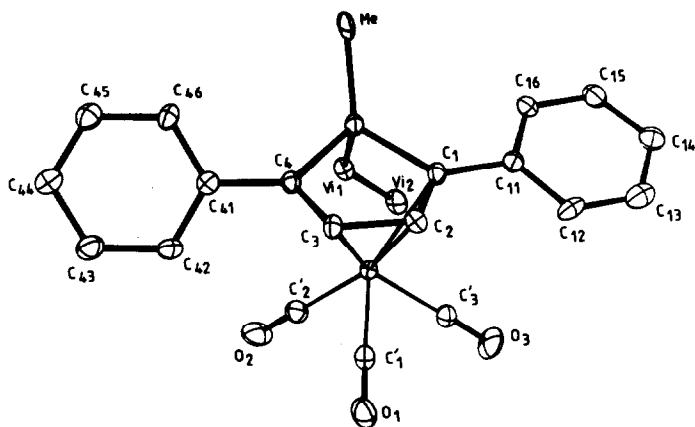


Fig. 5. Perspective view of complex 12a showing the labelling of the atoms, with the thermal ellipsoids at the 20% probability level.

TABLE 4
BOND LENGTHS (Å) FOR COMPLEX **12a**, e.s.d.s., IN PARENTHESES

Mo–C(1)	2.416(7)	C(1)–C(2)	1.396(10)
Mo–C(2)	2.331(7)	C(2)–C(3)	1.461(10)
Mo–C(3)	2.359(7)	C(3)–C(4)	1.410(10)
Mo–C(4)	2.500(7)	C(1)–C(11)	1.496(11)
Mo–Vinyl(1)	2.498(7)	C(4)–C(41)	1.483(11)
Mo–Vinyl(2)	2.527(7)		
Mo–C'(1)	1.975(8)	C(11)–C(12)	1.414(11)
Mo–C'(2)	1.991(8)	C(12)–C(13)	1.394(12)
Mo–C'(3)	1.962(8)	C(13)–C(14)	1.410(12)
Mo...Si	2.803(2)	C(14)–C(15)	1.412(13)
		C(15)–C(16)	1.393(12)
Si–C(1)	1.895(8)	C(16)–C(11)	1.405(10)
Si–C(4)	1.868(7)		
Si–Me	1.879(9)	C(41)–C(42)	1.400(12)
Si–Vinyl(1)	1.876(7)	C(42)–C(43)	1.425(13)
Vinyl(1)–Vinyl(2)	1.388(11)	C(43)–C(44)	1.402(13)
		C(44)–C(45)	1.388(14)
C'(1)–O(1)	1.145(10)	C(45)–C(46)	1.410(2)
C'(2)–O(2)	1.127(10)	C(46)–C(41)	1.391(11)
C'(3)–O(3)	1.147(10)		

Structure of complex 12a. Figure 5 gives a perspective view of the molecule with the atom numbering. A stereoscopic view is given in Fig. 4. Interatomic distances and main bond angles are listed in Tables 4 and 5. The overall geometry is the same as in complex **9a**, but there is stronger coordination of the double bond of the vinyl group to the transition metal atom: Mo–C distances are 2.666 and 2.527(8) Å in the “allyl”-complex discussed above; in **12a** these distances are shorter at 2.498 and 2.527(7) Å, and fall in the range of Mo-to-butadiene distances (Mo–C(4): 2.500(7) Å). As a consequence, the carbonyl ligand C'(1)O(1) *trans* to the vinyl group does not differ from the other carbonyl groups: the Mo–C'(1) distance is equal to the average of the two other Mo–CO bond lengths, 1.976(8) Å.

TABLE 5
IMPORTANT BOND ANGLES (deg) FOR COMPLEX **12a**

C'(1)–Mo–C'(2)	85.2(3)	Mo–C'(1)–O(1)	177.5(5)
C'(2)–Mo–C'(3)	95.5(4)	Mo–C'(2)–O(2)	177.9(6)
C'(3)–Mo–C'(1)	82.5(3)	Mo–C'(3)–O(3)	175.8(5)
Vinyl(1)–Mo–Vinyl(2)	32.1(3)		
C(1)–Mo–C(2)	34.2(2)	Si–Vinyl(1)–Vinyl(2)	121.6(4)
C(2)–Mo–C(3)	36.3(3)		
C(3)–Mo–C(4)	33.6(2)	Si–C(1)–C(2)	109.6(5)
C(1)–Mo–C(4)	65.4(2)	C(1)–C(2)–C(3)	114.7(6)
		C(2)–C(3)–C(4)	115.8(6)
C(1)–Si–C(4)	89.8(3)	C(3)–C(4)–Si	109.3(5)
C(1)–Si–Me	120.5(4)		
C(4)–Si–Me	119.5(3)	C(11)–C(1)–Si	125.9(5)
C(1)–Si–Vinyl(1)	102.2(3)	C(11)–C(1)–C(2)	124.3(7)
C(4)–Si–Vinyl(1)	98.8(3)	C(41)–C(4)–Si	129.5(5)
Me–Si–Vinyl(1)	120.1(3)	C(41)–C(4)–C(3)	120.9(6)

As would be expected, the absence of the CH₂ link to silicon and a slight shortening of the vinyl carbon atoms to molybdenum distance lead to markedly smaller fold angle for the silole ring: the butadiene unit and the C(1)–Si–C(4) plane make a dihedral angle of 8.9°, leaving the Si atom only 0.21 Å above the plane of the butadiene. Consequently, the Mo---Si Van der Waals contact shortens by about 0.24 Å to fit the constrained geometry. This value for the fold angle is to our knowledge the smallest reported for a coordinated silole ring [1,2,7].

Another feature of the structure of complex **12a** is the different conformations, at least in the solid state, of the phenyl rings; they are rotated in the same way, as for complex **9a**, but not to the same extent: phenyl group C(11–16) makes an angle of ca. 14.1° with the butadiene plane, whereas for phenyl group C(41–46) the angle is 52.2°. However, there are no significant differences in the C(1)–C(2) and C(3)–C(4) conjugated double bonds of the silole ring, i.e. the bond lengths are equal when the standard deviations are taken into account.

Experimental

All reactions were carried out under nitrogen, a vacuum line and Schlenk tubes being used in the case of transition metal complexes. Solvents were dried and distilled before use. The preparations of the following starting materials have been described previously [1]: 1-chloro-1-methyl-, **1**, 1-methyl-1-allyl-, **8**, 1-methyl-1-vinyl-, **10**, 1-hydro-1-allyl-, **13**, 1-methoxy-1-vinyl-2,5-diphenylsilacyclopentadiene, **15**. Melting points were determined with an oil-circulating apparatus. IR spectra were recorded with a Perkin–Elmer 298 spectrophotometer, ¹H NMR spectra with a Varian EM 360 or EM 390, ¹³C NMR spectra with a Bruker WP 200 SY spectrometer (chemical shifts, δ (ppm), are relative to TMS). The mass spectra recorded with a JEOL JMS-D100 spectrometer, are electronic impact unless otherwise noted.

1-Methyl-1-ethynyl-2,5-diphenylsilacyclopentadiene (2a). A mixture of an excess of HC≡CMgBr [8] and **1** in THF was stirred at room temperature for 20 h. After standard work up, the solvent was removed under vacuo and the residue chromatographed on florisil with 30/70 toluene/hexane as eluant. Recrystallisation from hexane at –20°C gave the product in 40% yield; m.p. 118–119°C; ¹H NMR (CCl₄): δ 7.6–7.0 (m, 12H, aromatic and ethylenic), 2.5 (s, 1H, ≡C–H), 0.6 (s, 3H, SiMe); IR (CCl₄): ν(C≡C) 2030 cm⁻¹, ν(≡C–H) 3280 cm⁻¹; mass spectrum, *m/e* (assignment) 272 (molecular peak). Found: C, 83.75; H, 5.89, C₁₉H₁₆Si calcd.: C, 83.82, H, 5.88%.

1-Methyl-1-propynyl-2,5-diphenylsilacyclopentadiene (2b). A solution of **1** in ether was added dropwise to one of CH₃C≡CLi in the same solvent at –30°C. The mixture was allowed to warm up to room temperature with stirring during 0.5 h. After standard work up, the yellow residue was recrystallised from 1/9 CH₂Cl₂/hexane at –78°C. 15% yield; m.p. 101–102°C; ¹H NMR (CCl₄): δ 7.6–7.1 (m, 12H, aromatic and ethylenic), 1.9 (s, 3H, Me), 0.5 (s, 3H, SiMe); IR (CCl₄): ν(C≡C) 2160 cm⁻¹; mass spectrum, *m/e* (assignment) 286 (molecular peak). Found: C, 83.62; H, 6.17. C₂₀H₁₈Si calcd.: C, 83.86; H, 6.33%.

1,1-Diallyl-2,5-diphenylsilacyclopentadiene (14). A ten-fold excess of allyl-MgBr (33 ml, 1 M) in diethyl ether was added dropwise to a solution of **13** (0.9 g, 3.25 mmol) with (PPh₃)₂NiCl₂ (0.042 g, 2%). The mixture was stirred at room tempera-

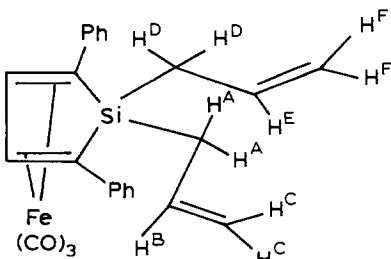
ture (20 h) (the disappearance of SiH was monitored by IR). After hydrolysis (cold NH_4Cl solution) and standard work up, the solvent was pumped off and the remaining oil dissolved in hexane and kept at -20°C to give yellow crystals of **14**. 40% yield; m.p. $45\text{--}46^\circ\text{C}$. ^1H NMR (CCl_4): δ 7.5–7.0 (m, 12H, aromatic + ethylenic), 5.8–4.5 (m, 6H, $\text{CH}=\text{CH}_2$), 2.2–1.95 (d, 8Hz, 4H, CH_2). Found: C, 84.10; H, 7.19. $\text{C}_{22}\text{H}_{22}\text{Si}$ calcd.: C, 84.07; H, 7.00%.

1,1-Divinyl-2,5-silacyclopentadiene (16). To a solution of vinylmethoxysilole **15** in diethyl ether was added dropwise a ten-fold excess of vinyl-MgBr. The mixture was stirred for 20 h (disappearance of SiOMe monitored by TLC, toluene/hexane 10/90). After standard work up, the remaining yellow oil was purified by preparative TLC with 30/70 toluene/hexane as eluant. 61% yield; ^1H NMR (CCl_4): δ 7.5–7.0 (m, 12H, aromatic + ethylenic), 6.5–6.0 (m, 6H, $\text{CH}=\text{CH}_2$). Found: 83.55; H, 6.70. $\text{C}_{20}\text{H}_{18}\text{Si}$ calcd.: C, 83.88; H, 6.33%.

(η^4 -*exo-1-Propynyl-endo-1-methyl-2,5-diphenylsilacyclopentadiene*)tricarbonyliron (**3**). A solution of **2b** (0.2 g, 7 mmol) in 20 ml of toluene was added to a suspension of $\text{Fe}_2(\text{CO})_9$ (0.3 g, 7 mmol) in 30 ml of the same solvent, and the mixture was stirred at $40\text{--}50^\circ\text{C}$ for 20 h. (IR monitoring). The solvent was pumped off and the residue extracted with hexane. The extract was filtered and kept at -20°C to give red crystals of **3**. 35% yield. m.p. $150\text{--}152^\circ\text{C}$ dec.; ^1H NMR (CCl_4): δ 7.7–6.8 (m, 10H, aromatic), 5.5 (s, 2H, ethylenic), 1.6 (s, 3H, Me), 0.4 (s, 3H, SiMe). IR (hexane) $\nu(\text{C}\equiv\text{C})$: 2180 $\nu(\text{CO})$ 2050, 1990, 1980 cm^{-1} .

(η^4 -*exo-1-Methyl-endo-1-vinyl-2,5-diphenylsilacyclopentadiene*)tricarbonyliron (**11**). The procedure as for **3** but with a reaction time 17 h. Yellow crystals. 41% yield; m.p. 152.5°C ; ^1H NMR (CDCl_3): δ 7.40–7.0 (m, 10H, aromatic), 6.7–6.2 (m, 3H, vinyl), 6.0 (s, 2H, cyclic H), 0.15 (s, 3H, SiMe); IR (hexane): $\nu(\text{CO})$ 2050 (s), 1982 (s, br) cm^{-1} ; mass spectrum, m/e (assignment, relative intensity) 414 (M^+ , 4), 386 ($M^+ - \text{CO}$, 11), 358 ($M^+ - 2\text{CO}$, 14), 330 ($M^+ - 3\text{CO}$, 100). Found: C, 64.03; H, 4.40. $\text{C}_{22}\text{H}_{18}\text{FeO}_3\text{Si}$ calcd.: C, 63.78; H, 4.38%.

(η^4 -*exo-1-Allyl-endo-1-allyl-2,5-diphenylsilacyclopentadiene*)tricarbonyliron (**17**). The procedure was as for **3** but with a reaction time of 24 h. Red crystals. 15% isolated yield, m.p. $110\text{--}111^\circ\text{C}$; ^1H NMR (CDCl_3): δ 7.6–7.05 (m, 10H, phenyl), 6.8 (s, 2H, H^{C}), 6.2 (s, 2H, H^{X}), 6.0–5.3 (m, 2H, $\text{H}^{\text{B}} + \text{H}^{\text{E}}$), 4.9–4.5 (m, 2H, H^{F}), 2.1 (d, 3 Hz, H^{A}), 1.6 (d, 5–6 Hz, H^{D}). IR (hexane): $\nu(\text{CO})$ 2050(s), 1980(s, br)



cm^{-1} . Found: C, 65.71; H, 5.08. $\text{C}_{25}\text{H}_{22}\text{FeO}_3\text{Si}$ calcd.: C, 66.07; H, 4.84%.

(η^4 -*exo-1-(Propyne hexacarbonyldicobalt)-endo-1-methyl-2,5-diphenylsilacyclopentadiene*)tricarbonyliron (**4**). A solution of complex **3** (0.213 g, 0.5 mmol) and $\text{Co}_2(\text{CO})_8$ (0.17 g, 0.5 mmol) in 20 ml hexane was stirred at room temperature for 20 h, then filtered and cooled at -20°C to give brown crystals of **4**. 45% yield; m.p.

170–175 °C dec. $^1\text{H NMR}$ (C_6H_6): δ 7.1 (s, broad, 10H, aromatic), 5.2 (s, cyclic H), 2.9 (s, 3H, CMe), 0.35 (s, 3H, SiMe). IR (hexane) $\nu(\text{CO})$ 2090 (m), 2054 (s), 2028 (s), 2009 (w), 1989 (m), 1977 (s); mass spectrum, m/e (assignment, relative intensity) 426 ($M^+ - \text{Co}_2(\text{CO})_6$, 2), 398 ($M^+ - \text{Co}_2(\text{CO})_6 - \text{CO}$, 33) 370 ($M^+ - \text{Co}_2(\text{CO})_6 - 2\text{CO}$, 57), 343 ($M^+ - \text{Co}_2(\text{CO})_6 - 3\text{CO}$, 100). Found: C, 48.97; H, 2.47. $\text{C}_{29}\text{H}_{18}\text{Co}_2\text{FeO}_6\text{Si}$ calcd.: C, 48.90; H, 2.55%.

(η^4 -*exo*-1-(Propyne hexacarbonyldicobalt)-endo-1-methyl-2,5-diphenylsilacyclopentadiene)hexacarbonyldicobalt (**5b**). A solution of silole **2b** (0.286 g, 1 mmol) and $\text{Co}_2(\text{CO})_8$ (0.684 g, 2 mmol) in 30 ml hexane was stirred at room temperature for 20 h, then filtered and cooled at -20°C , to give brown crystals of **5b**. 72% yield; m.p. 117°C dec.; $^1\text{H NMR}$ (C_6D_6): δ 8.0–6.9 (m, 10 H, aromatic), 5.85 (s, 2H, cyclic H), 1.55 (s, 3H, CMe), 0.1 (s, 3H, SiMe). IR (hexane): $\nu(\text{CO})$ 2088 (m), 2075 (s), 2053 (s), 2028 (s), 1870 (w), 1853 (m) cm^{-1} . Found: C, 44.45; H, 2.09. $\text{C}_{32}\text{H}_{18}\text{Co}_4\text{O}_{12}\text{Si}$ calcd.: C, 44.75; H, 2.09%.

1-Methyl-1-(Propyne hexacarbonyldicobalt)-2,5-diphenylsilacyclopentadiene (**6**). The procedure was as for **5b** but with a 1/1 silole/ $\text{Co}_2(\text{CO})_8$ ratio. The $^1\text{H NMR}$ spectrum of the crude product indicated it to be a mixture (60/40) of **5b** and **6**, and from this brown crystals of the latter were obtained. 22% yield; m.p. 117°C dec. $^1\text{H NMR}$ (C_6D_6) δ 7.8–7.2 (m, 12H, aromatic + cyclic H), 2.3 (s, 3H, C–Me), 0.8 (s, 3H, SiMe); IR (hexane): $\nu(\text{CO})$ 2088 (m), 2050 (s), 2028 (s), 1995 (sh) cm^{-1} . Found: C, 53.97; H, 3.13. $\text{C}_{26}\text{H}_{18}\text{Co}_2\text{O}_6\text{Si}$ calcd.: C, 54.54; H, 3.14%.

Bis{(η^4 -*exo*-1-(propyne hexacarbonyldicobalt)-endo-1-methyl-2,5-diphenylsilacyclopentadiene)}dicarbonylcobalt (**7**). The procedure was as for **5b** but with a 1/1.5 silole/ $\text{Co}_2(\text{CO})_8$ ratio and a reaction temperature of 40 – 50°C . Brown crystals; 13% yield; m.p. 120 – 130°C dec. $^1\text{H NMR}$ (C_6D_6): δ 7.7–7.1 (m, 20 H, aromatic), 6.0 (s, 2H, cyclic H), 2.25 (s, 6H, CMe), 1.3 (s, 6H, SiMe). IR (hexane): $\nu(\text{CO})$ 2060 (m), 2050 (s), 2040 (s), 1850 (w) cm^{-1} . Found: C, 48.86; H, 2.82. $\text{C}_{56}\text{H}_{36}\text{Co}_6\text{O}_{16}\text{Si}_2$ calcd.: C, 48.92; H, 2.64%.

(η^4 -*exo*-1-(Acetylene hexacarbonyldicobalt)-endo-1-methyl-2,5-diphenylsilacyclopentadiene)hexacarbonyldicobalt (**5a**). The procedure described for **5b** gave brown crystals; 83% yield; m.p. 120 – 125°C dec. $^1\text{H NMR}$ (C_6D_6): δ 7.85–7.0 (m, 10H, aromatic), 6.2 (s, 2H, cyclic H), 5.65 (s, 1H, C–H), 1.35 (s, 3H, SiMe). IR (hexane): $\nu(\text{CO})$ 2088 (m), 2070 (s), 2050 (s), 2020 (s), 1865 (w), 1850 (m) cm^{-1} . Found: C, 44.03; H, 2.19; Co, 28.24. $\text{C}_{31}\text{H}_{16}\text{Co}_4\text{O}_{12}\text{Si}$ calcd.: C, 44.07; H, 1.89; Co, 27.96%.

(η^4 -*exo*-1-Allyl-endo-1-allyl-2,5-diphenylsilacyclopentadiene)hexacarbonyldicobalt (**18**). The same procedure was as for **5b** but with a 1/1 silole/ $\text{Co}_2(\text{CO})_8$ ratio. Reaction time 3 h. Brown crystals; 44% yield; m.p. 78°C dec. $^1\text{H NMR}$ (C_6D_6): δ 7.5–6.8 (m, 10H, aromatic), 5.8 (s, 2H, cyclic H), 6.0–4 (m, 6H, $\text{CH}=\text{CH}_2$), 2.65 (broad d, 2H, 8 Hz, CH_2 -endo), 1.3 (broad d, 2H, 8 Hz, CH_2 -exo). IR (hexane): $\nu(\text{CO})$ 2080 (s), 2063 (m), 2020 (s), 1865 (w), 1854 (s), 1830 (w) cm^{-1} . Found: C, 55.92; H, 3.69. $\text{C}_{28}\text{H}_{22}\text{Co}_2\text{O}_6\text{Si}$ calcd.: C, 56.00; H, 3.66%.

(η^4 -(η^2 -endo-1-Allyl)-*exo*-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyl-molybdenum (**9a**). A solution of **8** (0.864 g, 3.0 mmol) in hexane (40 ml) was added to $\text{Mo}(\text{CO})_4\text{COD}$ [**9**] (0.945 g, 3 mmol) and the mixture was stirred under reflux for 24 h (IR monitoring). The yellow solution turned light red. Filtration followed by cooling at -20°C , gave white crystals of $\text{Mo}(\text{CO})_6$ together with red ones. Recrystallisation from the same solvent gave red crystals of **9a**. 0.690 g, 49% yield; m.p. 151 – 156°C (dec.). $^1\text{H NMR}$ (C_6D_6) see Table 1; $^{13}\text{C NMR}$ (CDCl_3) see Fig.

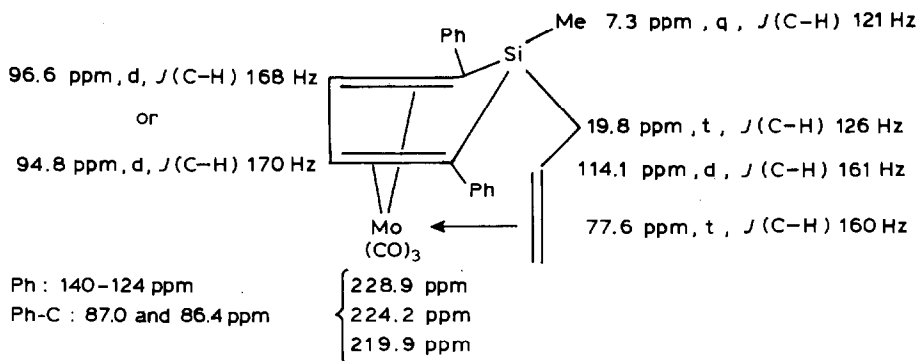
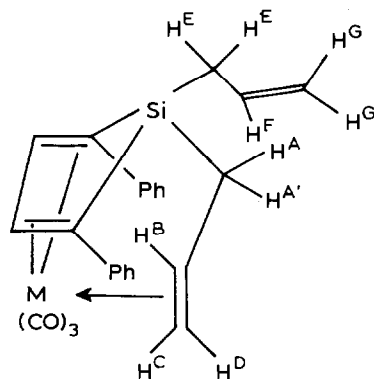


Fig. 6.

6. IR (hexane): $\nu(\text{CO})$ 2000 (s), 1928 (m), 1918 (s) cm^{-1} ; mass spectrum, m/e , (assignment for ^{98}Mo , intensity) 469.8 (M^+ , 14), 441.8 ($M^+ - \text{CO}$, 22), 413.8 ($M^+ - 2\text{CO}$, 28), 385.8 ($M^+ - 3\text{CO}$, 100), 287.9 ($M^+ - \text{Mo}(\text{CO})_3$, 16). Found: C, 58.74; H, 4.41. $\text{C}_{23}\text{H}_{20}\text{O}_3\text{MoSi}$ calcd.: C, 58.97; H 4.30%.

TABLE 6

^1H NMR DATA (C_6D_6 , δ , ppm) FOR COMPOUNDS **19a** AND **19b**



	19a , M = Mo		19b , M = W	
Ph	7.6–6.7	m	7.3–6.5	m
H ^x H ^{x'} H ^B H ^F	6.1–5.25	m	5.8–5.0	m
H ^G	4.9–4.5	m	4.8–4.5	m
H ^C	4.1	d, J_{BC} 6 Hz	3.8	d, J_{BC} 9 Hz
H ^D	3.8	d, J_{BD} 14 Hz	3.4	d, J_{BD} 14 Hz
H ^A (H ^{A'})	2.1	dd, J_{AB} 5 Hz	2.4–1.2	m
H ^A (H ^A)	1.65	dd, $J_{\text{A'A'}}$ 9 Hz $J_{\text{A'B}}$ 5 Hz $J_{\text{A'A'}}$ 9 Hz		
H ^E	1.5	d, J_{EF} 5 Hz		

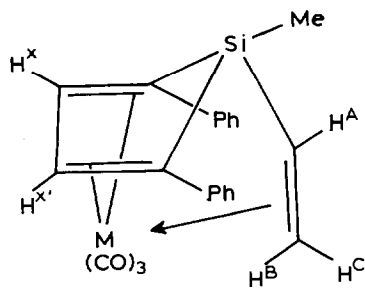
(η^4 -(η^2 -endo-1-Allyl)-exo-1-allyl-2,5-diphenylsilacyclopentadiene)tricarbonylmolybdenum (**19a**). The procedure was as for **9a**. Red brown crystals, 53% yield; m.p. 107–108°C; $^1\text{H NMR}$ (C_6D_6) (see Table 6); IR (hexane): $\nu(\text{CO})$ 2000 (s), 1930 (s), 1920 (s) cm^{-1} . Found: C, 60.34; H, 4.37. $\text{C}_{25}\text{H}_{22}\text{O}_3\text{MoSi}$ calcd.: C, 60.72; H, 4.48%.

(η^4 -(η^2 -endo-1-Allyl)-exo-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyltungsten (**9b**). A solution of silole **8** (0.556 g, 2 mmol) and $\text{W}(\text{CO})_3(\text{CH}_3\text{CN})_3$ [10] (0.752 g, 2 mmol) in 10 ml CH_2Cl_2 was stirred at room temperature for 16 h. (IR monitoring). The solvent was pumped off from the red solution, and the residue extracted with 35/65 toluene/hexane, then filtered, and cooled at -20°C , to give red crystals of **9b**. 0.632 g, 57% yield; m.p. 175°C; $^1\text{H NMR}$ see Table 1; IR (hexane): $\nu(\text{CO})$ 2000 (s), 1926 (m), 1912 (s) cm^{-1} ; mass spectrum, chemical ionisation m/e (assignment for ^{184}W , relative intensity) 557 ($M+1$, 100), 289 ($M+1-\text{W}(\text{CO})_3$, 60). Found: C, 49.56; H, 3.51. $\text{C}_{23}\text{H}_{20}\text{O}_3\text{SiW}$ calcd.: C, 49.65; H, 3.62%.

(η^4 -(η^2 -endo-1-Allyl)-exo-1-allyl-2,5-diphenylsilacyclopentadiene)tricarbonyltungsten (**19b**). The same procedure was as for **9b**. Reaction time 20 h. Red crystals, 12% isolated yield; m.p. 142–143°C dec.; $^1\text{H NMR}$: see Table 6; IR (hexane): $\nu(\text{CO})$ 2000 (s), 1925 (m), 1912 (s) cm^{-1} ; mass spectrum, m/e (assignment for ^{184}W , relative intensity), 582 (M^+ , 20), 554 ($M^+ - \text{CO}$, 62), 526 ($M^+ - 2\text{CO}$, 5), 496 ($M^+ - 3\text{CO}$, 100). Found: C, 51.66; H, 3.66. $\text{C}_{25}\text{H}_{22}\text{O}_3\text{SiW}$ calcd.: C, 51.55; H, 3.78%.

(η^4 -(η^2 -endo-1-Vinyl)-exo-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonylmolybdenum (**12a**). A solution of silole **10** (0.825 g, 2.55 mmol) and $\text{Mo}(\text{CO})_4(\text{COD})$ (0.805 g, 2.55 mmol) in 20 ml hexane was kept at 50°C for 22 h. The orange

TABLE 7

 $^1\text{H NMR}$ DATA (CDCl_3 , ppm) FOR COMPOUNDS **12a** AND **12b**


	12a , M = Mo		12b , M = W	
Ph	7.4–6.7	s	7.7–6.7	m
$\left. \begin{array}{l} \text{H}^x(\text{H}^x') \\ \text{H}^x'(\text{H}^x) \end{array} \right\}$	6.3–5.8	br s	5.6	br
H^C	4.9	dd, J_{AC} 12 Hz J_{BC} 3 Hz	4.6	dd, J_{AC} 12 Hz J_{BC} 2.5 Hz
H^B	3.8	dd, J_{BA} 17 Hz J_{BC} 3 Hz	3.6	dd, J_{BA} 17 Hz J_{BC} 2.5 Hz
H^A	2.9	dd, J_{AC} 12 Hz J_{AB} 17 Hz	2.7	dd, J_{AC} 12 Hz J_{AB} 17 Hz
SiMe	0.8	s	0.8	s

solution was then filtered and cooled at -20°C to give after removal of some white crystals of $\text{Mo}(\text{CO})_6$ orange crystals of **12a**, 0.521 g, 45% yield; m.p. 141°C dec.; ^1H NMR: see Table 7. IR (hexane): $\nu(\text{CO})$ 2000 (s), 1935 (m), 1920 (s) cm^{-1} ; mass spectrum, m/e (assignment for ^{98}Mo , relative intensity): 456 (M^+ , 6), 428 ($M^+ - \text{CO}$, 4), 400 ($M^+ - 2\text{CO}$, 6), 372 ($M^+ - 3\text{CO}$, 18), 274 ($M^+ - \text{Mo}(\text{CO})_3$, 100), 259 ($M^+ - \text{Mo}(\text{CO})_3 - \text{Me}$, 27). Found: C, 58.00; H, 3.98. $\text{C}_{22}\text{H}_{18}\text{MoO}_3\text{Si}$ calcd.: C, 58.15; H, 3.99%.

(η^4 -(η^2 -endo-1-Vinyl)-exo-1-vinyl-2,5-diphenylsilacyclopentadiene)tricarbonyl-molybdenum (**20a**). The procedure used for **12a** gave orange crystals, 33% yield, m.p. 180°C dec.; ^1H NMR (C_6D_6) 7.2–6.8 (2 pics, 10H, aromatic), 5.8 (s, 2H, H^{X}), 6.4–5.4 (m, 3H, $\text{H}^{\text{D}} + \text{H}^{\text{E}} + \text{H}^{\text{F}}$), 4.6 (dd, 1H, H^{C} , $J_{\text{CA}} 12$ Hz, $J_{\text{CB}} 3$ Hz), 3.75 (dd, 1H, H^{B} , $J_{\text{BA}} 17$ Hz, $J_{\text{BC}} 3$ Hz), 2.6 (dd, 1H, H^{A} , $J_{\text{AB}} 17$ Hz, $J_{\text{AC}} 12$ Hz) (see Fig. 7). IR (hexane): 1998 (s), 1932 (m), 1917 (s) cm^{-1} . Found: C, 60.01; H, 4.32. $\text{C}_{23}\text{H}_{18}\text{MoO}_3\text{Si}$ calcd.: 59.22; H, 3.86%.

(η^4 -(η^2 -endo-1-Vinyl)-exo-1-methyl-2,5-diphenylsilacyclopentadiene)tricarbonyl-tungsten (**12b**). The procedure described as for **9b**, with a reaction time of 22 h, gave red crystals, 64% yield; m.p. 172°C ; ^1H NMR (CDCl_3) see Table 7. IR (hexane):

TABLE 8

SUMMARY OF CRYSTAL DATA, INTENSITY COLLECTION AND REFINEMENT

	9a	12a
Formula	$\text{C}_{23}\text{H}_{20}\text{MoO}_3\text{Si}$	$\text{C}_{22}\text{H}_{18}\text{MoO}_3\text{Si}$
Cryst system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/a$
a , Å	8.8077(18)	14.6799(37)
b , Å	14.9791(13)	9.3038(25)
c , Å	8.4049(7)	14.6581(27)
α , deg	98.013(7)	
β , deg	107.736(11)	100.64(2)
γ , deg	79.894(11)	
vol, Å ³	1035.4	1967.6
mol. wt	468.2	454.4
Z	2	4
d_{calcd} , g cm^{-3}	1.504	1.534
d_{measd} , g cm^{-3}	1.51(2)	1.52(2)
Cryst size, mm ³	0.15 × 0.30 × 0.40	0.10 × 0.30 × 0.45
Cryst color	red	orange-red, hexagonal plates
Recrystn solv	hexane	hexane
M.p. ($^{\circ}\text{C}$)	151–156, dec.	141, dec
Method of data collectn	moving crystal, moving counter	moving crystal, moving counter
Radiation (graphite monochromated)	Mo- K_{α}	Mo- K_{α}
μ , cm^{-1}	6.28	6.31
2θ limits, deg	4–44	4–50
No. of unique reflections	2703	3292
No. of observed reflections	1991	1973
Final no. of variables	253	244
R	0.0337	0.0344
R_w	0.0354	0.0395
Residual electron density	0.58	0.57

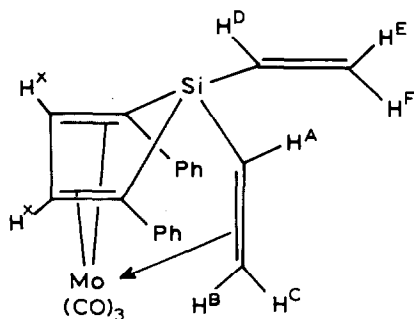


Fig. 7.

$\nu(\text{CO})$ 1997 (s), 1930 (m), 1917 (s) cm^{-1} ; mass spectrum, chemical ionisation, m/e , (assignment for ^{184}W , relative intensity), 543 ($M^+ + 1$, 28), 515 ($M^+ + 1 - \text{CO}$, 4), 275 ($M^+ + 1 - \text{W}(\text{CO})_3$, 100). Found: C, 48.97; H, 3.27. $\text{C}_{22}\text{H}_{18}\text{O}_3\text{SiW}$ calcd.: 48.72; H, 3.35%.

TABLE 9

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR COMPLEX 9a, WITH e.s.d.s. IN PARENTHESES

Atom	x	y	z
Mo	2871.3(7)	2282.8(4)	144.4(7)
Si	181(2)	2681(1)	1821(2)
C(1)	606(7)	1661(4)	365(8)
C(2)	2083(7)	1176(4)	1251(8)
C(3)	3070(7)	1712(4)	2634(8)
C(4)	2394(7)	2638(4)	2892(8)
Me	-1090(9)	2524(5)	3178(9)
Allyl(1)	-557(8)	3739(5)	676(9)
Allyl(2)	782(10)	3814(5)	-77(11)
Allyl(3)	859(11)	3461(6)	-1569(12)
C'(1)	4449(8)	3126(4)	370(8)
O(1)	5405(7)	3585(4)	552(7)
C'(2)	4805(9)	1371(5)	458(9)
O(2)	5971(6)	846(3)	639(7)
C'(3)	2618(8)	1851(5)	-2255(9)
O(3)	2468(7)	1560(4)	-3613(7)
C(11)	-506(7)	1247(4)	-1127(8)
C(12)	-2128(8)	1630(5)	-1622(9)
C(13)	-3217(9)	1256(5)	-3042(9)
C(14)	-2705(9)	491(5)	-4014(9)
C(15)	-1075(9)	113(5)	-3527(9)
C(16)	7(8)	477(4)	-2098(8)
C(41)	3266(8)	3274(4)	4195(8)
C(42)	2399(10)	4007(5)	4924(9)
C(43)	3239(12)	4608(5)	6213(11)
C(44)	4899(12)	4485(6)	6772(10)
C(45)	5778(11)	3762(6)	6029(10)
C(46)	4943(9)	3159(5)	4740(9)

Crystal structures of complexes 9a and 12a

Crystal preparation. Crystals of complexes **9a** and **12a** were grown at -20°C from hexane solutions under nitrogen. Preliminary X-ray photography revealed a triclinic unit cell for complex **9a**, and a monoclinic one for complex **12a**, with space group $P2_1/a$ (systematic absences: $0k0$, $k = 2n + 1$; $h0l$, $h = 2n + 1$). The hexagonal plates were mounted inside Lindeman glass capillaries with the [100] and [011] directions, respectively, parallel to the Φ axis of the diffractometer.

X-Ray data collection. Data were collected on a CAD-4 automated diffractometer. For both compounds, the lattice constants given in Table 8 came from a least-squares refinement of 25 reflections. The intensities of three standard reflections were monitored after intervals of 60 min. In neither case was there a significant change in these intensities during data collection. The usual Lorentz and polarization corrections were applied. No absorption corrections were made because of the relatively small values of μ .

Of the 2703 reflections collected for compounds **9a**, 1991 were found to have $I > 2.5\sigma(I)$ and were used in solving and refining the structure. A total of 4031 scans, including 739 redundant data, were measured for compound **12a**. Equivalent reflections were averaged, to give 1973 unique observed intensities ($I > 1.5\sigma(I)$).

TABLE 10

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR COMPLEX **12a**, WITH e.s.d.s. IN PARENTHESES

Atom	x	y	z
Mo	396.4(5)	-2047.8(7)	2152.1(4)
Si	-390(2)	357(2)	2860(2)
C(1)	834(5)	385(8)	2617(5)
C(2)	1380(5)	-598(8)	3196(5)
C(3)	870(5)	-1508(8)	3741(5)
C(4)	-91(5)	-1252(8)	3619(4)
Me	-891(5)	1993(9)	3335(5)
Vinyl(1)	-1046(5)	-568(8)	1802(5)
Vinyl(2)	-713(5)	-608(8)	976(5)
C'(1)	1357(5)	-3514(9)	2564(5)
O(1)	1917(4)	-4371(6)	2770(4)
C'(2)	-451(6)	-3714(9)	1819(6)
O(2)	-916(4)	-4680(7)	1653(5)
C'(3)	922(5)	-2105(9)	1016(5)
O(3)	1281(4)	-2160(8)	385(4)
C(11)	1197(5)	1400(8)	1979(5)
C(12)	2094(5)	1196(9)	1776(5)
C(13)	2417(6)	2153(10)	1176(6)
C(14)	1882(6)	3333(8)	781(5)
C(15)	980(6)	3500(9)	972(6)
C(16)	647(6)	2544(7)	1565(5)
C(41)	-686(5)	-2109(9)	4129(4)
C(42)	-650(6)	-3612(9)	4122(6)
C(43)	-1187(6)	-4385(9)	4675(6)
C(44)	-1745(6)	-3660(10)	5204(5)
C(45)	-1788(6)	-2170(1))	5171(5)
C(46)	-1273(5)	-1387(9)	4618(5)

Structure determination and refinement. The centric space group ($P\bar{1}$) was initially chosen for the complex **9a**, and confirmed by the successful refinement of the structure. The molybdenum atom position was determined by the Patterson method. The remaining non-hydrogen atoms were located by Fourier syntheses. The scale factor and the positional and anisotropic thermal parameters were refined by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/(\sigma^2(F) + 0.0019F^2)$. The final values of the positional atomic parameters are listed in Table 9.

The structure of the complex **12a**, was solved by direct methods. The position of the Mo so obtained was first checked by the heavy atom method and then used to phase a Fourier map calculation, which revealed all the 26 non-hydrogen atoms. After two cycles of refinement with isotropic thermal parameters, all atoms were given anisotropic thermal parameters. The weighting scheme was $w = 0.011/(\sigma^2(F) + 1.728F^2)$. The residuals R and R_w and the residual electron density are given in Table 8. The final atomic coordinates are listed in Table 10.

Lists of anisotropic thermal parameters and observed and calculated structure factors for compounds **9a** and **12a** are available from the authors.

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