

Reactions of transition-metal σ -acetylide complexes

XII *. Formal insertion of CS_2 into the $\text{M}-\text{C}(sp)$ bond of $\text{Ru}(\text{C}_2\text{Ph})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$. X-Ray crystal structure of $\text{Ru}(\eta^2\text{-S}_2\text{CC}_2\text{Ph})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$

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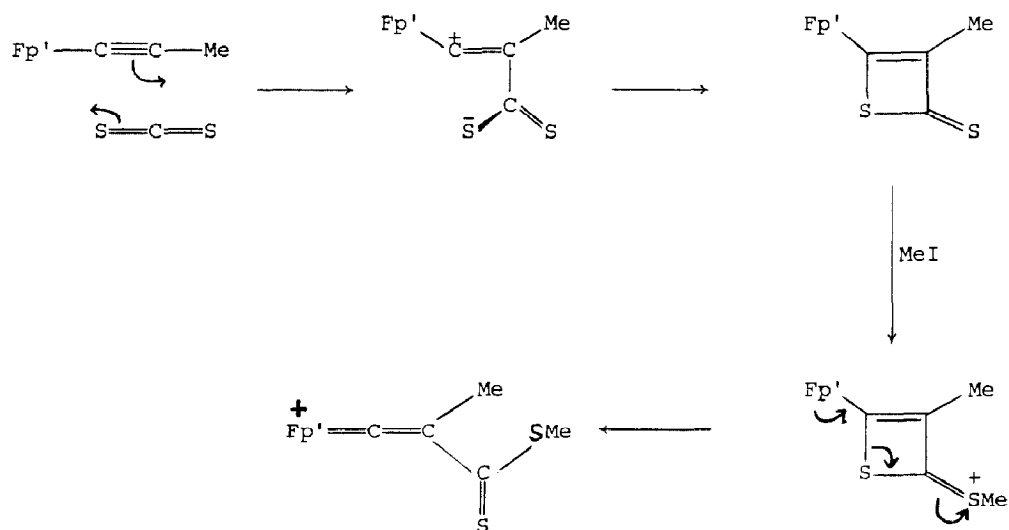
Abstract

The prolonged reaction between $\text{Ru}(\text{C}_2\text{Ph})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ and CS_2 afforded $\text{Ru}(\eta^2\text{-S}_2\text{CC}_2\text{Ph})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$, characterised by X-ray crystallography, which contains the novel phenyldithiopropiolate ligand, $\text{S}_2\text{CC}_2\text{Ph}$. Crystals of $\text{Ru}(\eta^2\text{-S}_2\text{CC}_2\text{Ph})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ are orthorhombic, space group $P2_12_12_1$, with unit cell dimensions a 9.676(6), b 14.414(6) and c 19.836(12) Å, U 2766.5 Å³, and $Z = 4$. Full-matrix least-squares refinement on 1430 reflections with $I \geq 2.5\sigma(I)$ converged to $R = 0.049$ and $R_w = 0.054$.

Introduction

Insertions of CS_2 into transition metal-hydride and -carbon bonds are well known [1], but examples involving $\text{M}-\text{C}(sp^2)$ and $\text{M}-\text{C}(sp)$ bonds are rare. We have earlier described the reaction of a ruthenium hydrido-olefin complex with CS_2 to give a novel example of a β -dithiocarboxylato ligand [2]. Previously Selegue [3] found that the reaction between CS_2 and $\text{Fe}(\text{C}_2\text{Me})(\text{dppe})(\eta\text{-C}_5\text{H}_5)$ gave $\text{Fe}\{\overline{\text{C}}=\text{CMeC}(\text{S})\overline{\text{S}}\}(\text{dppe})(\eta\text{-C}_5\text{H}_5)$, containing a 2*H*-thiete-2-thione ligand. This complex reacts with MeI to give the cationic vinylidene complex $[\text{Fe}\{\overline{\text{C}}=\text{CMeC}(\text{S})\text{SMe}\}(\text{dppe})(\eta\text{-C}_5\text{H}_5)]^+$. This unusual reaction was suggested to proceed via an initial (2 + 2)-cycloaddition of the CS_2 with the acetylide, followed by ring closure

* For Part XI, see ref. 4d.



Scheme 1. $\text{Fp}' = \text{Fe}(\text{dppe})(\eta\text{-C}_5\text{H}_5)$.

(Scheme 1), in a reaction which is related to those between metal acetylides and certain electron-deficient olefins [4].

Results

We have now found that formal insertion of CS_2 into the $\text{M}-\text{C}(\text{sp})$ bond in the related ruthenium complex $\text{Ru}(\text{C}_2\text{Ph})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ (**1**) occurs on extended heating of a solution of the reactants in benzene. With a large excess of CS_2 , the dark red crystalline $\text{Ru}(\eta^2\text{-S}_2\text{CC}_2\text{Ph})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ (**2**) was obtained in 56% yield. The FAB mass spectrum of **2** showed the parent ion centred on m/z 606, which loses SCC_2Ph , $\text{S}_2\text{CC}_2\text{Ph}$ and PPh_3 groups. Analytical and NMR data provided further evidence for formulation of **2** as $\text{Ru}(\eta^2\text{-S}_2\text{CC}_2\text{Ph})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$. In the ^{13}C NMR spectrum the CS_2 resonance is found at δ 211.9 ppm; in dithiocarbamates, for example, the corresponding resonances are found between δ 185–220 ppm. The UV/visible spectrum contains a broad band at 488 nm, assigned to charge-transfer absorption within the $\text{RuS}_2\text{CC}_2\text{Ph}$ system. Other features are a shoulder at 324 nm, and peaks at 302 and 234 nm; comparison with $\text{RuX}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ ($\text{X} = \text{Cl}$ or C_2Ph) suggest that these result from a $\pi \rightarrow \pi^*$ transition in the phenylethynyl group, and intraligand transitions in the $\text{Ru}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ group, respectively [6].

An X-ray structure determination of **2** was carried out to establish the mode of incorporation of the CS_2 molecule into the complex. The molecular structure of **2** is shown in Fig. 1. Only one of the two orientations found for the phenyl group of the $\text{S}_2\text{CC}_2\text{Ph}$ ligand is shown for clarity (see Experimental). The ruthenium atom has distorted octahedral coordination with three facial coordination sites being occupied by the $\eta\text{-C}_5\text{H}_5$ group (av. $\text{Ru}-\text{C}$ 2.205(6) Å). The remaining three positions are occupied by the PPh_3 ligand ($\text{Ru}-\text{P}$ 2.279(4) Å) and the two sulphur atoms of the phenyldithiopropiolate ligand ($\text{Ru}-\text{S}$ 2.336(3), 2.353(4) Å). The latter compare with the $\text{Ru}-\text{SR}_2$ and $\text{Ru}-\text{SR}$ distances of 2.323(4) and 2.379(4) Å, respectively, found in

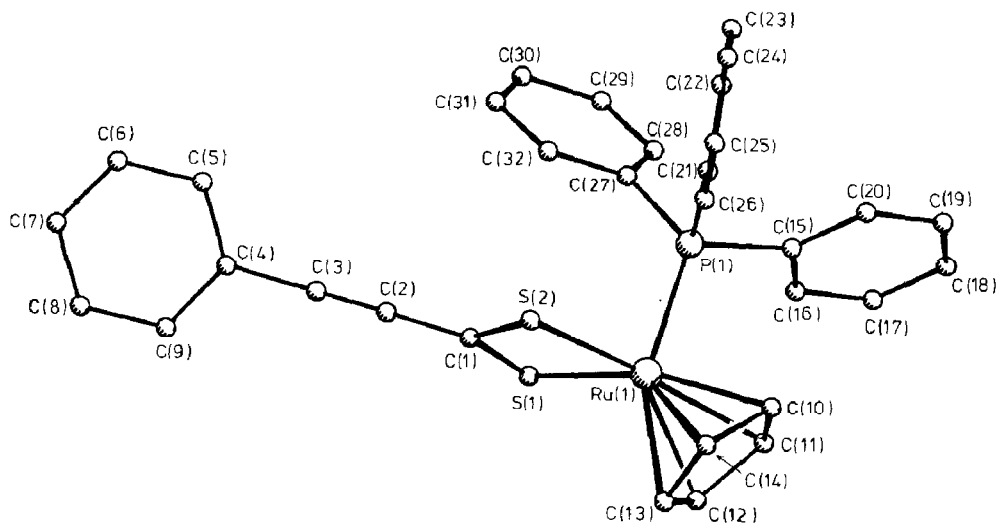
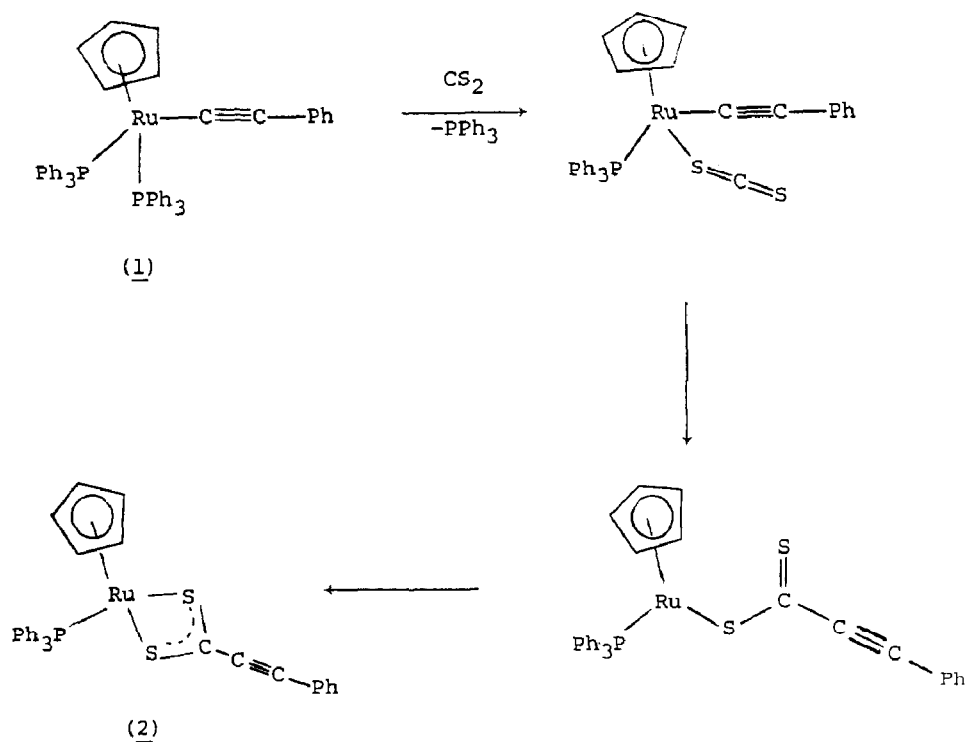


Fig. 1. Molecular structure of $\text{Ru}(\eta^2\text{-S}_2\text{CC}_2\text{Ph})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ (**2**), showing atom numbering scheme. Only one orientation of the phenyl group of the $\text{S}_2\text{CC}_2\text{Ph}$ ligand is shown for clarity.

$\text{Ru}(\text{CO})(\text{SC}_6\text{H}_3\text{Me-2-SC}_6\text{H}_4\text{Me})(\eta\text{-C}_5\text{H}_5)$, which contains a five-membered RuSC_2S chelate ring [7]. The major distortion from octahedral geometry results from the restricted bite of the sulphur chelate ligand ($\text{S-Ru-S } 71.7(1)^\circ$). Within this ligand, the C-S bond distances of 1.71(1) and 1.68(1) Å are equivalent within experimental



Scheme 2

error and indicate substantial delocalisation of π -electron density over the S_2C moiety. Further delocalisation into the $C\equiv C$ triple bond is indicated by the shortening of C(1)–C(2) (1.35(2) Å) and lengthening of C(2)–C(3) (1.23(2) Å) from the normal values associated with C–C single and $C\equiv C$ triple bonds, respectively.

The novel phenyldithiopropiolato ligand has been formed by a formal insertion of CS_2 into the Ru–C(*sp*) bond of the precursor phenylacetylide complex. We

Table 1

Fractional coordinates (Ru $\times 10^5$, others $\times 10^4$) of non-hydrogen atoms in $Ru(\eta^2-S_2CC_2Ph)(PPh_3)(\eta-C_5H_5)(2)^a$

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Ru	25872(11)	19141(6)	10087(5)
P(1)	1781(3)	2289(2)	2054(2)
S(1)	4234(3)	3097(2)	963(2)
S(2)	1549(4)	3232(3)	525(2)
C(1)	3031(15)	3824(9)	615(7)
C(2)	3217(16)	4733(9)	486(8)
C(3)	3424(17)	5557(12)	355(8)
C(4)	3587(20)	6524(13)	205(15)
C(5)	2574(20)	7158(13)	401(15)
C(6)	2728(20)	8097(13)	249(15)
C(7)	3895(20)	8402(13)	–100(15)
C(8)	4907(20)	7769(13)	–296(15)
C(9)	4754(20)	6829(13)	–144(15)
C(5')	3891(35)	7163(19)	731(12)
C(6')	3988(35)	8106(19)	582(12)
C(8')	3398(35)	7785(19)	–579(12)
C(9')	3301(35)	6842(19)	–429(12)
C(10)	1712(17)	515(9)	1034(10)
C(11)	3199(18)	463(9)	1206(8)
C(12)	3930(17)	773(9)	650(8)
C(13)	3034(21)	985(11)	153(8)
C(14)	1624(19)	824(11)	378(9)
C(15)	2175(7)	1374(6)	2658(4)
C(16)	3565(7)	1175(6)	2775(4)
C(17)	3929(7)	446(6)	3202(4)
C(18)	2903(7)	–84(6)	3512(4)
C(19)	1513(7)	115(6)	3394(4)
C(20)	1149(7)	844(6)	2967(4)
C(21)	–90(10)	2443(7)	2124(4)
C(22)	–666(10)	2816(7)	2709(4)
C(23)	–2087(10)	2967(7)	2748(4)
C(24)	–2934(10)	2745(7)	2202(4)
C(25)	–2358(10)	2371(7)	1617(4)
C(26)	–937(10)	2220(7)	1578(4)
C(27)	2410(12)	3351(7)	2476(5)
C(28)	3162(12)	3317(7)	3076(5)
C(29)	3577(12)	4138(7)	3389(5)
C(30)	3240(12)	4992(7)	3103(5)
C(31)	2488(12)	5026(7)	2504(5)
C(32)	2073(12)	4206(7)	2190(5)

^a Note that atoms C(5), C(6), C(8) and C(9) have fractional occupancy. Unprimed atoms: 0.74(1); Primed atoms: 0.26(1).

cannot say how this reaction proceeds, although the obvious route of displacement of one of the PPh₃ ligands from **1** by CS₂ and subsequent migration and rearrangement is a possibility (Scheme 2). The ready loss of PPh₃ from Ru(PPh₃)₂(η-C₅H₅) complexes may be the determining feature leading to the observed difference in the reactions of the Fe-dppe and Ru-PPh₃ complexes.

Experimental

Synthesis

A solution of Ru(C₂Ph)(PPh₃)₂(η-C₅H₅) (110 mg, 0.14 mmol) in a mixture of CS₂ (10 ml) and C₆H₆ (15 ml) was refluxed for 4 d. The solvent was removed under reduced pressure and the residue chromatographed (Florisil, eluant 1/1 petroleum spirit/CH₂Cl₂). The major red band was collected and crystallized (petroleum spirit/CH₂Cl₂) to give dark red crystalline Ru(η²-S₂CC₂Ph)(PPh₃)(η-C₅H₅) (47 mg, 56%), m.p. 202–203 °C. Anal. Found: C, 63.21; H, 4.15. C₃₂H₂₅PRuS₂ calc: C, 63.45; H, 4.16; *M*, 606. *M*⁺ (FAB MS), 606. IR (Nujol): ν(CC) 2170w, ν(CS) 971w, other peaks at 1431w, 1312w, 1180w, 1157w cm⁻¹. ¹H NMR: δ (CDCl₃) 7.6–7.2 (m, 20H, Ph), 4.58 (s, 5H, C₅H₅) ppm. ¹³C NMR: δ (CDCl₃) 211.9 (s, CS₂), 136.1–122.5 (m, Ph), 78.5 (s, C₅H₅) ppm. UV/VIS (nm, (ε); CH₂Cl₂): 488 (3511), 324 (3485), 302 (4541), 234 (10532).

Structure determination

Intensity data for 2146 reflections ($\theta_{\max} = 22.5^\circ$) were measured at room temperature on an Enraf–Nonius CAD4 diffractometer fitted with graphite-monochromated Mo-K_α radiation (λ 0.7107 Å) with the use of the $\omega:2\theta$ scan technique. No decomposition of the crystal occurred during the data collection. Corrections were applied for Lorentz and polarisation effects [8] but not for absorption.

Crystal data. C₃₂H₂₅PRuS₂, *M* = 605.7, orthorhombic, space group *P*2₁2₁2₁, *a* 9.676(6), *b* 14.414(6), *c* 19.836(12) Å, *U* 2766.5 Å³, *D*_c 1.454 g cm⁻³ for *Z* = 4, *F*(000) = 1232, μ 7.43 cm⁻¹.

The structure was solved by normal heavy-atom methods and refined by full-matrix least-squares procedures using 1430 reflections with $I \geq 2.5\sigma(I)$. Phenyl groups

Table 2

Selected bond distances (Å) and angles (°) for Ru(η²-S₂CC₂Ph)(PPh₃)(η-C₅H₅) (**2**)

Ru–P(1)	2.279(4)	Ru–S(1)	2.336(3)
Ru–S(2)	2.353(4)	Ru–C(10)	2.19(1)
Ru–C(11)	2.21(1)	Ru–C(12)	2.21(2)
Ru–C(13)	2.21(2)	Ru–C(14)	2.21(2)
P(1)–C(15)	1.822(9)	P(1)–C(21)	1.83(1)
P(1)–C(27)	1.85(1)	S(1)–C(1)	1.71(1)
S(2)–C(1)	1.68(1)	C(1)–C(2)	1.35(2)
C(2)–C(3)	1.23(2)	C(3)–C(4)	1.43(3)
P(1)–Ru–S(1)	95.5(1)	P(1)–Ru–S(2)	91.9(1)
S(1)–Ru–S(2)	71.7(1)	Ru–S(1)–C(1)	89.9(5)
Ru–S(2)–C(1)	90.1(5)	S(1)–C(1)–S(2)	108.3(7)
S(1)–C(1)–C(2)	126 (1)	S(2)–C(1)–C(2)	126 (1)
C(1)–C(2)–C(3)	178 (2)	C(2)–C(3)–C(4)	177 (2)

were refined as rigid hexagonal groups, the remaining non-hydrogen atoms being refined anisotropically; hydrogen atoms (except for those on the disordered phenyl group) were included in the model at their calculated positions. The phenyl group of the phenyldithiopropiolate ligand was disordered over two positions, refinement leading to fractional occupancies of 0.74(1) and 0.26(1) for the two orientations. The refinement converged to final R 0.049, R_w 0.054 for $w = [\sigma^2(F) + 0.0068F^2]^{-1}$; the correct enantiomer was determined from differences in Friedel pairs included in the data set. Atomic coordinates and selected bond parameters are given in Tables 1 and 2, respectively, and the numbering scheme used is shown in Fig. 1; other crystallographic data are available from the authors.

Acknowledgements

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Note added in proof

The molecular structure of $\text{Ru}(\text{S}_2\text{CNMe}_2)(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ (A.W. Cordes and M. Dragagnac, *Acta Crystallogr.*, C44 (1988) 363) has Ru-S 2.394(3) and 2.397(3)Å.