



Communication

Formation of a cyclobutenylidene by cyclo-addition of an alkynyl-ruthenium complex to a cyano(alkynyl)ethene

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ABSTRACT

In contrast to the usual formal [2+2]-cycloaddition reaction, $(\text{NC})_2\text{C}=\text{C}(\text{C}\equiv\text{C}(\text{SiPr}_3)_2)$, containing bulky alkynyl substituents, reacts with $\text{Ru}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2\text{Cp}$ to give the unprecedented cyclobutenylidene complex $\text{Ru}\{\text{C}(\text{CN})_2\text{C}[\text{C}\equiv\text{C}(\text{SiPr}_3)]=\text{CC}(\text{SiPr}_3)=\text{CPhC}\}(\text{PPh}_3)\text{Cp}$, formed by addition of one of the $\text{C}\equiv\text{C}(\text{SiPr}_3)$ groups to the $\text{Ru}-\text{C}\equiv\text{CPh}$ moiety and subsequent electronic reorganisation.

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1. Introduction

Donor-substituted cyano(ethynyl)ethenes (CEEs) [1,2] are of considerable contemporary interest on account of their reactivity, showing strong intra-molecular charge-transfer effects and nonlinear optical properties. These compounds fall between tetracyanoethene on the one hand and the recently described tetraalkynylethenes [3–5] on the other. Reactions of transition metal σ -alkynyl complexes with cyano-alkenes, such as tetracyanoethene (tcne) [6,7], generally proceed by formal [2+2]-cycloaddition reactions to give substituted cyclobutenyl-metal complexes **A**, often proceeding via initial highly coloured charge transfer complexes or radical intermediates. In turn, the cyclobutenyls obtained from the alkenes undergo electrocyclic ring-opening to the butadienyl derivatives **B**, and further interaction of a $\text{C}=\text{C}$ double bond with the metal centre may occur if easily displaced ligands are present to give a 1,2,3- η^3 -butadienyl complex **C** (Scheme 1).

Some examples of substituted CEEs undergo similar [2+2]-cycloaddition and ring-opening reactions to those mentioned above [8–10]. We have recently described reactions of some substituted CEEs with several alkynyl- and diynyl-ruthenium complexes to give complexes of type **C** (e.g., **3**, Scheme 2) [11].

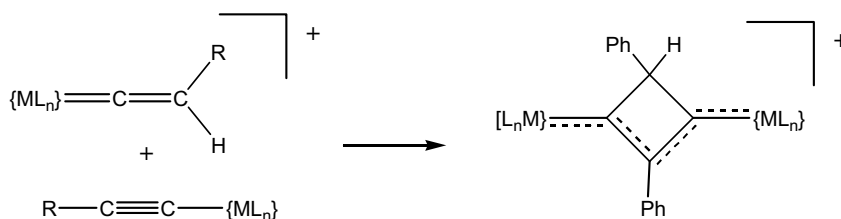
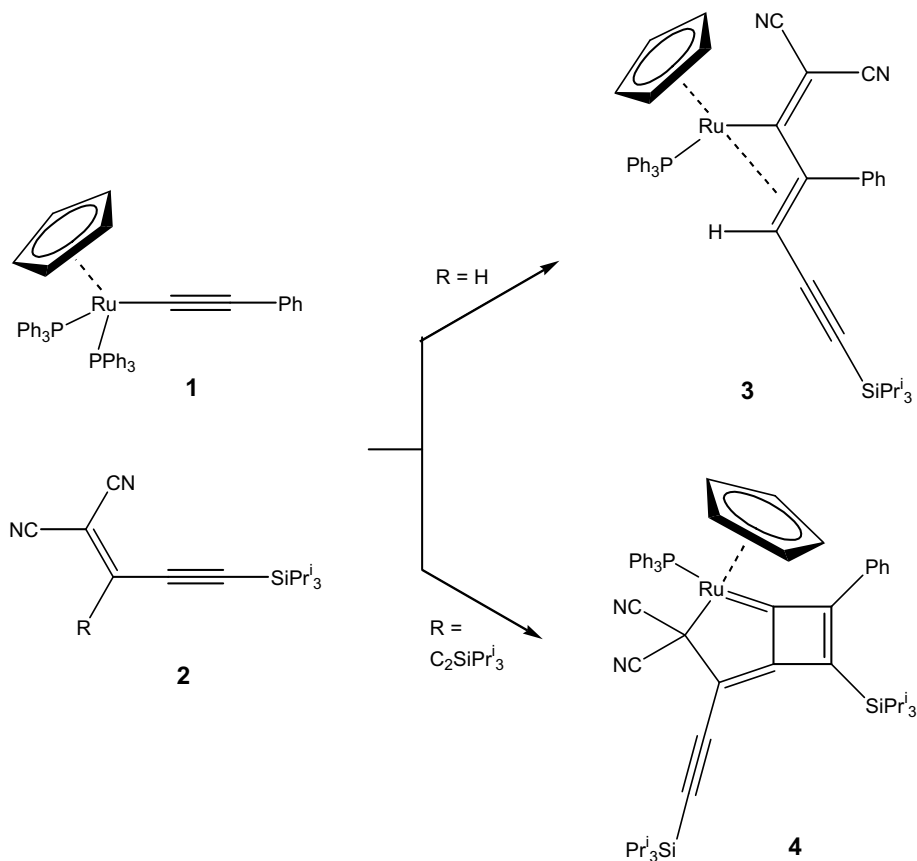
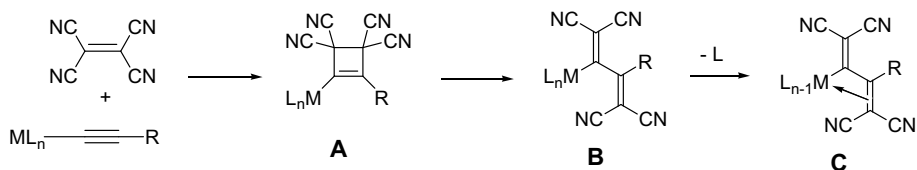
In the course of this work, we wondered whether it would be possible to encourage the addition to proceed in an alternative fashion, namely addition of a cyano(alkynyl)ethene to the alkynyl-metal complex by utilising the alkynyl group of the ethene. We recall that cycloaddition of alkynyl-metal complexes with vinylidenes affords the corresponding cationic cyclobutenylidene derivatives (Scheme 3) [12–15], but to our knowledge no similar reactions involving cycloaddition of two alkyne functionalities have been reported. Considering this approach, we decided to examine the effect of increasing the steric constraints in the cyano(alkynyl)ethene and metal-alkynyl complex beyond those employed in the previous work [11].

2. Results

The reaction between $\text{Ru}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2\text{Cp}$ **1** and $(\text{NC})_2\text{C}=\text{C}(\text{C}\equiv\text{C}(\text{SiPr}_3)_2)$ (**2**; $\text{R}=\text{C}\equiv\text{CSiPr}_3$) was carried out under irradiation with a 300 W sunlamp for 24 h and afforded a yellow-green complex **4** in 26% yield by preparative t.l.c. (Scheme 2). An XRD study demonstrated the unprecedented cyclobutenylidene structure shown in Fig. 1, with selected bond parameters given in Table 1. A $\text{Ru}(\text{PPh}_3)\text{Cp}$ fragment is chelated by C(1) of a dicyanomethylene group and C(8) [Ru–C(1,8) 1.898, 1.891(3), 2.230, 2.244(3) Å; values for molecules 1, 2] of the cyclobutenylidene formed by C(1–4), respectively, with C(3)–C(4) [1.391, 1.402(4) Å] being a $\text{C}=\text{C}$ double bond. The latter bears Ph and SiPr_3 substituents on C(4) and C(3), respectively, while C(2)–C(5) [1.340, 1.341(4) Å] is

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an *exo*-methylene group bearing the $C(CN)_2$ and $C\equiv SiPr_3^i$ substituents.

The microanalysis and ES-MS spectrum ($[2M+Na]^+$, $[M+Na]^+$ and M^+ at m/z 1959, 991 and 968, respectively) are in accord with the solid-state structure. In the NMR spectra, signals for Ph (δ_H 7.15–7.52, δ_C 123.5–135.2), Cp (δ_H 4.84, δ_C 89.2) and PPh_3 (δ_P 48.4) were present, together with resonances for the chain carbons and the CN groups between δ_C 84.3 and 107.3 and at δ_C 159.7, 171.1, 184.1. The IR spectrum contained bands assigned to $\nu(CN)$ at 2197 and $\nu(C\equiv C)$ at 2126 cm^{-1} .

We suggest that, in contrast to the usual formal [2+2]-cycloaddition of the phenylethyne group with the electron-poor alkene centre to give the corresponding cyclobutenyl, the present reaction proceeds instead by attack of C_β of phenylethyne **1** at one $C\equiv C(SiPr_3^i)$ group of the substituted CEE to give allenyl-vinylidene intermediate **D**. Cyclisation within the latter affords the cyclobutenylidene fragment, which is followed by attack of the electron-rich dicyanomethylene group on the ruthenium centre to give **4** (Scheme 4). The unusual course of this reaction can be ascribed to the presence of the two bulky $SiPr_3^i$ groups on the cyano(alky-

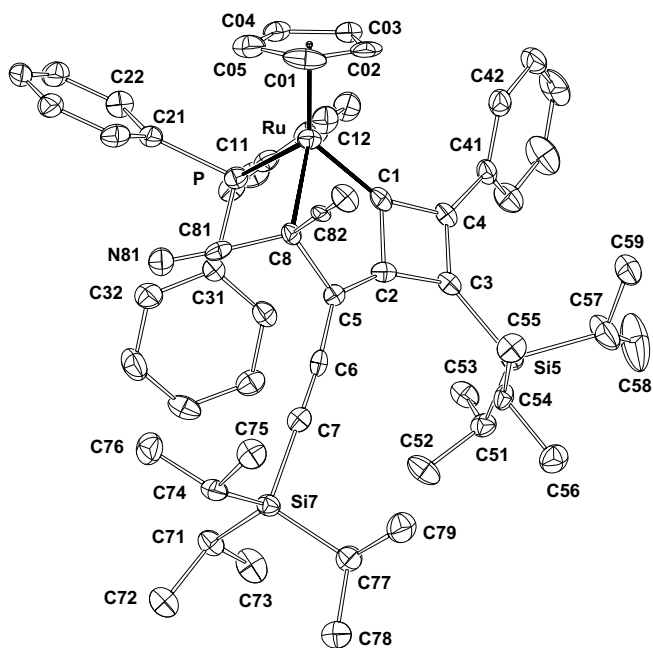
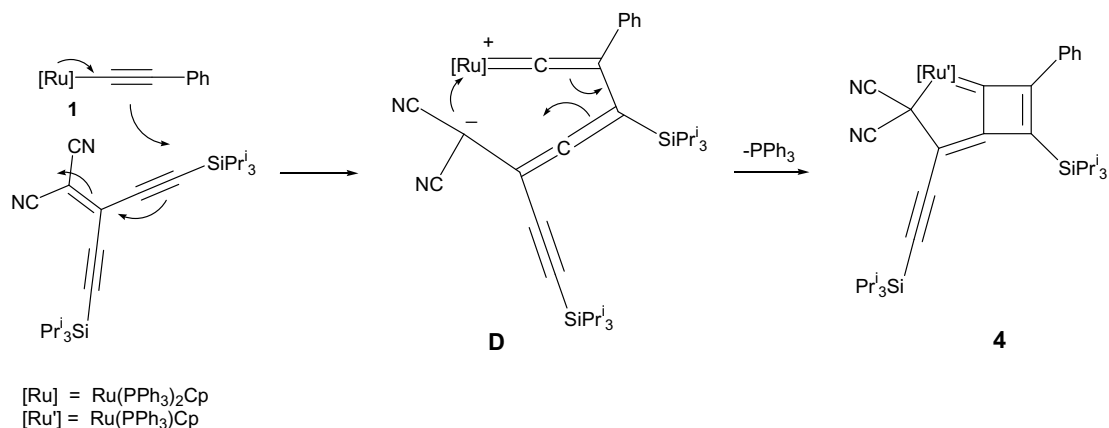


Fig. 1. Plot of a molecule of $\text{Ru}(\text{C}(\text{CN})_2\text{C}[\text{C}=\text{C}(\text{SiPr}^i_3)]=\text{CC}(\text{SiPr}^i_3)=\text{CPhC}=\text{})(\text{PPh}_3)\text{Cp}$ **4**.

Table 1

Selected bond distances (Å) and angles (°) for **4** (molecules 1 and 2).

Bond distances (Å)			
Ru–P(1)	2.3074, 2.3175(9)	C(3)–C(4)	1.391, 1.402(4)
Ru–C(cp)	2.221–2.280(4), 2.236–2.280(4)	C(4)–C(41)	1.464, 1.476(4)
(av.)	2.25(3), 2.25(2)	C(5)–C(6)	1.424, 1.415(4)
Ru–C(1)	1.898, 1.891(3)	C(5)–C(8)	1.550, 1.545(4)
Ru–C(8)	2.230, 2.244(3)	C(6)–C(7)	1.200, 1.207(4)
C(1)–C(2)	1.481, 1.479(4)	C(8)–C(81,82)	1.478, 1.496(5); 1.471, 1.486(5)
C(1)–C(4)	1.499, 1.507(4)	C(3)–Si(5)	1.880, 1.894(3)
C(2)–C(3)	1.501, 1.502(4)	C(7)–Si(7)	1.842, 1.848(4)
C(2)–C(5)	1.340, 1.341(4)		
Bond angles (°)			
P(1)–Ru–C(1)	92.52, 92.19(10)	C(5)–C(6)–C(7)	174.4, 173.9(3)
P(1)–Ru–C(8)	94.72, 92.71(9)	C(6)–C(7)–Si(7)	172.9, 178.7(3)
C(1)–Ru–C(8)	77.6, 77.3(1)	C(2)–C(5)–C(8)	110.7, 110.2(3)
Ru–C(1)–C(2)	121.1, 121.5(2)	Ru–C(8)–C(5)	110.6, 110.2(2)
Ru–C(1)–C(4)	152.6, 152.4(2)	C(2)–C(1)–C(4)	86.2, 86.1(3)
C(1)–C(2)–C(3)	90.4, 91.0(3)	C(2)–C(3)–C(4)	89.4, 89.1(3)
C(1)–C(4)–C(3)	94.0, 93.8(3)	C(2)–C(3)–Si(5)	130.2, 130.5(2)
C(3)–C(4)–C(41)	135.5, 135.2(3)	C(1)–C(4)–C(41)	130.2, 130.9(3)
C(4)–C(3)–Si(5)	138.5, 139.3(3)	C(6)–C(5)–C(8)	118.4, 119.7(3)
C(1)–C(2)–C(5)	118.4, 118.4(3)	C(2)–C(5)–C(8)	110.7, 110.2(3)
C(2)–C(5)–C(6)	130.7, 130.1(3)		



Scheme 4.

nyl)ethene, which prevent easy access to the $\text{C}=\text{C}(\text{CN})_2$ moiety, as well as the presence of an easily dissociable PPh_3 ligand at the ruthenium centre.

3. Experimental

General reaction conditions and instrumentation were similar to those described elsewhere [11].

$\text{Ru}(\text{C}=\text{CPh})(\text{PPh}_3)_2\text{Cp}$ [16] and $(\text{NC})_2\text{C}=\text{C}(\text{C}=\text{C}(\text{SiPr}^i_3)_2)$ [1] were prepared by the cited methods.

3.1. Reaction of $\text{Ru}(\text{C}=\text{CPh})(\text{PPh}_3)_2\text{Cp}$ with $(\text{NC})_2\text{C}=\text{C}(\text{C}=\text{C}(\text{SiPr}^i_3)_2)$

A mixture of $\text{Ru}(\text{C}=\text{CPh})(\text{PPh}_3)_2\text{Cp}$ **1** (79 mg, 0.10 mmol), $(\text{NC})_2\text{C}=\text{C}(\text{C}=\text{C}(\text{SiPr}^i_3)_2)$ **2** (53 mg, 0.12 mmol) in thf (4 mL) was irradiated with a 300 W sunlamp. The mixture began to reflux after ca. 15 min. After 24 h, the mixture was cooled and then concentrated under reduced pressure. Preparative t.l.c. of the residue (using acetone–hexane, 1/4) afforded cyclobutenylidene complex $\text{Ru}\{\text{C}(\text{CN})_2\text{C}[\text{C}=\text{C}(\text{SiPr}^i_3)]=\text{CC}(\text{SiPr}^i_3)=\text{CPhC}=\text{C}\}(\text{PPh}_3)\text{Cp}$ **4** as a yellow-green solid (25 mg, 26%). Anal. Calc. ($\text{C}_{57}\text{H}_{67}\text{N}_2\text{PRuSi}_2$): C, 70.70; H, 6.97; N, 2.89; M, 968. Found: C, 70.75; H, 7.04; N, 2.76%. IR (cm^{-1}): ν 3056w, 2197m, 2126m, 1433s, 1182m, 1090m, 1018m, 997m, 881m, 775m, 747m. ^1H NMR: δ 0.96–1.07 (39H, m, CHMe_2), 1.38 (3H, sept, $J = 7.6$ Hz, CHMe_2), 4.84 (5H, s,

Cp), 7.15–7.52 (20H, m, Ph). ^{13}C NMR: δ 11.4, 11.7, 18.6, 18.9 (Me), 84.3, 89.2 (Cp), 100.1, 107.3 [C(6,7)], 123.5–129.5, 129.8 [d, $J(\text{CP}) = 2.7$ Hz], 135.2 (Ph), 127.7 [d, $J(\text{CP}) = 10.3$ Hz], 132.1 [d, $J(\text{CP}) = 9.9$ Hz], 134.0 [d, $J(\text{CP}) = 11.1$ Hz] [C(1,5,8)], 159.7, 171.1, 184.1 [C(2,3,4)]. ^{31}P NMR: δ 48.4. ES-MS (m/z): 1959, [2M+Na] $^+$; 991, [M+Na] $^+$; 968, M $^+$.

3.2. Structure determination

Compound **4**. $\text{Ru}\{\text{C}(\text{CN})_2\text{C}(\text{C}(\text{SiPr}^i_3)=\text{CC}(\text{SiPr}^i_3)=\text{CPhC}=\text{C})\{\text{PPh}_3\}\text{Cp} \equiv \text{C}_{57}\text{H}_{67}\text{N}_2\text{PRuSi}_2$, $M = 968.35$. Monoclinic, $P2_1/n$, $a = 11.6703(2)$, $b = 47.6981(8)$, $c = 18.9490(3)$ Å, $\beta = 103.558(2)$, $V = 10254$ Å 3 , $Z = 8$, $\rho_c = 1.255$ g cm $^{-3}$. $2\theta_{\text{max}} = 56$, $\mu(\text{Mo K}\alpha) = 0.42$ mm $^{-1}$, $T_{\text{min/max}} = 0.98$, crystal $0.25 \times 0.18 \times 0.03$ mm.

A full sphere of diffraction data was measured at ca 100 K using a CCD area-detector instrument. 106874 reflections were merged to 23045 unique ($R_{\text{int}} = 0.076$) after “empirical”/multiscan absorption correction (proprietary software) and used in the full matrix least squares refinements on F^2 ; 11706 with $I > 2\sigma(I)$ were considered ‘observed’. All data were measured using monochromatic Mo K α radiation, $\lambda = 0.71073$ Å. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, (x , y , z , U_{iso}) $_H$ being included following a riding model [reflection weights: $(\sigma^2(F^2) + (0.030P)^2)^{-1}$, $P = (F_o^2 + 2F_c^2)/3$]; $R1$ was 0.042, $wR2$ 0.091. Neutral atom complex scattering factors were used; computation used the SHELXL 97 program [17]. Pertinent results are given in Fig. 1 (which shows non-hydrogen atoms with 50% probability amplitude displacement ellipsoids and hydrogen atoms with arbitrary radii of 0.1 Å) and in Table 1.

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Appendix A. Supplementary material

CCDC 687427 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The

Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.09.060](https://doi.org/10.1016/j.jorganchem.2008.09.060).

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