



Reactions of cyano(alkynyl)ethenes with some alkynyl- and diynyl-ruthenium complexes

David J. Armit^a, Michael I. Bruce^{a,*}, Brian W. Skelton^b, Allan H. White^b

^aSchool of Chemistry and Physics, University of Adelaide, Adelaide, South Australia 5005, Australia

^bChemistry M313, SBBCS, University of Western Australia, Crawley, Western Australia 6009, Australia

ARTICLE INFO

Article history:

Received 4 June 2008

Received in revised form 11 July 2008

Accepted 12 July 2008

Available online 18 July 2008

Keywords:

Cyanocarbon
Ruthenium
Cyclo-addition
Alkynyl
Diynyl
XRD structure

ABSTRACT

Reactions of $\text{Ru}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2\text{Cp}$ with $(\text{NC})_2\text{C}=\text{CR}^1\text{R}^2$ ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{C}\equiv\text{CSiPr}_3$ **8**; $\text{R}^1 = \text{R}^2 = \text{C}\equiv\text{CPh}$ **9**) have given η^3 -butadienyl complexes $\text{Ru}\{\eta^3\text{-C}[\text{C}(\text{CN})_2]\text{CPh}=\text{CR}^1\text{R}^2\}(\text{PPh}_3)\text{Cp}$ (**11**, **12**), respectively, by formal [2 + 2]-cycloaddition of the alkynyl and alkene, followed by ring-opening of the resulting cyclobutenyl (not detected) and displacement of a PPh_3 ligand. Deprotection (tba^f) of **11** and subsequent reactions with $\text{RuCl}(\text{dppe})\text{Cp}$ and $\text{AuCl}(\text{PPh}_3)$ afforded binuclear derivatives $\text{Ru}\{\eta^3\text{-C}[\text{C}(\text{CN})_2]\text{CPh}=\text{CHC}\equiv\text{C}[\text{ML}_n]\}(\text{PPh}_3)\text{Cp}$ [$\text{ML}_n = \text{Ru}(\text{dppe})\text{Cp}$ **19**, $\text{Au}(\text{PPh}_3)$ **20**]. Reactions between **8** and $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CR})(\text{PP})\text{Cp}$ [$\text{PP} = (\text{PPh}_3)_2$, $\text{R} = \text{Ph}$, SiMe_3 , SiPr_3^i ; $\text{PP} = \text{dppe}$, $\text{R} = \text{Ph}$] gave η^1 -diynyl complexes $\text{Ru}\{\text{C}\equiv\text{CC}[\text{C}(\text{CN})_2]\text{CR}=\text{CH}[\text{C}\equiv\text{C}(\text{SiPr}_3^i)]\}(\text{PP})\text{Cp}$ (**15–18**), respectively, in reactions not involving phosphine ligand displacement. The phthalodinitrile $\text{C}_6\text{H}(\text{C}\equiv\text{CSiMe}_3)(\text{CN})_2(\text{NH}_2)(\text{SiMe}_3)$ **10** was obtained serendipitously from $(\text{Me}_3\text{SiC}\equiv\text{C})_2\text{CO}$ and $\text{CH}_2(\text{CN})_2$, as shown by an XRD structure determination. The XRD structures of precursor **7** and adducts **11**, **12** and **17** are also reported.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Reactions of transition metal σ -alkynyl complexes with a variety of electron-deficient alkenes have been described, among which cyano-alkenes such as tetracyanoethene (tcne) [**1,2**], $\text{R}_2\text{C}=\text{C}(\text{CN})_2$ ($\text{R} = \text{CF}_3$ [**3**], SMe [**4**]) and dimethyl dicyanofumarate [**4**], predominate. The products are generally formed by [2 + 2]-cycloaddition reactions to give substituted cyclobutenyl-metal complexes **A** (Chart 1), often proceeding via initial highly coloured charge transfer complexes or radical intermediates. In turn, the cyclobutenyls obtained from the alkenes undergo electrocyclic ring-openings 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 1,2,3- η^3 -butadienyl complexes **C** (Scheme 1).

In the case of poly-ynyl complexes, several sites of addition are available. Previous studies have described the addition of tcne to complexes $\text{Ru}\{(\text{C}\equiv\text{C})_n\text{R}\}(\text{PP})\text{Cp}'$ [$n = 2,3$; $\text{R} = \text{Ph}$, Fc ; $\text{PP} = (\text{PPh}_3)_2$, dppe ; $\text{Cp}' = \text{Cp}$, Cp^*] [**5**]. Isomeric products formed by cycloaddition/ring-opening involve either of the $\text{C}\equiv\text{C}$ triple bonds adjacent to or one removed from the metal centre. Of some interest in these complexes is the extensive delocalisation found in the $\text{Ru}-\text{C}\equiv\text{C}-\text{C}=\text{C}(\text{CN})_2\text{CR}=\text{C}(\text{CN})_2$ fragment, in which the $\text{Ru}-\text{C}_\alpha$ bond has considerable multiple bond character.

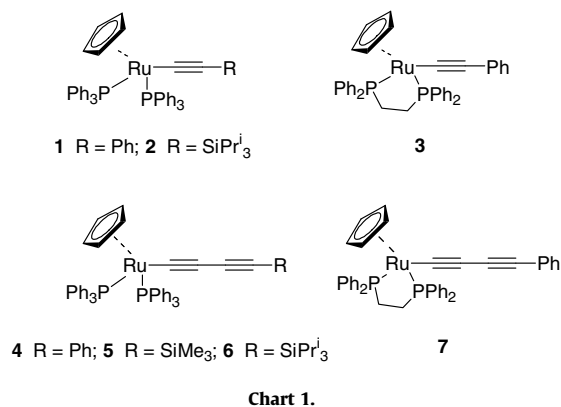
Donor-substituted 1,1,4,4-tetracyanobutadienes [**6**] and cyano(alkynyl)ethenes [**7,8**] are of considerable contemporary interest on account of their reactivity, showing strong intra-molecular charge-transfer effects and non-linear optical properties. Some examples of cyano(alkynyl)ethenes undergo similar [2 + 2]-cycloaddition and ring-opening reactions to those mentioned above [**9–11**]. These compounds fall between tetracyanoethene on the one hand and the recently described tetra-alkynylethenes [**12–14**] on the other. Some of the latter have been shown to form interesting transition metal complexes, including the tetra-cluster complex $\{[(\text{OC})_9\text{Co}_3]_2[\mu_3-(\text{C}\equiv\text{C})]_2\text{C}=\text{C}\{\text{C}\equiv\text{C}-\mu_3-\text{C}=[\text{Co}_3(\text{CO})_9]_2\}[\text{15}]$. Consequently, it is of interest to examine the reactions of several bis(alkynyl)dicyanoethenes with transition metal substrates. This paper describes the results of a brief study of the reactions of several ruthenium complexes $\text{Ru}(\text{C}\equiv\text{CR})(\text{PP})\text{Cp}$ [$\text{PP} = (\text{PPh}_3)_2$, $\text{R} = \text{Ph}$ **1**, SiPr_3^i **2**; $\text{PP} = \text{dppe}$, $\text{R} = \text{Ph}$ **3**] and $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CR})(\text{PP})\text{Cp}$ [$\text{PP} = (\text{PPh}_3)_2$, $\text{R} = \text{Ph}$ **4**, SiMe_3 **5**, SiPr_3^i **6**; $\text{PP} = \text{dppe}$, $\text{R} = \text{Ph}$ **7**] (Chart 1) with selected 1,1-dicyanobis(alkynyl)ethenes.

2. Ruthenium complexes

For the purposes of this study, we also required some ruthenium complexes which have not been described previously. The reaction between $\text{RuCl}(\text{PPh}_3)_2\text{Cp}$ and $\text{HC}\equiv\text{C}(\text{SiPr}_3^i)$ in the presence of NaOMe afforded $\text{Ru}(\text{C}\equiv\text{CSiPr}_3^i)(\text{PPh}_3)_2\text{Cp}$ (**2**) in a reaction analogous to that already described for the preparation of the related $\text{Me}_3\text{SiC}\equiv\text{C}$ complex [**16**]. The complex was obtained as a yellow

* Corresponding author. Fax: +61 8 8303 4358.

E-mail address: michael.bruce@adelaide.edu.au (M.I. Bruce).



solid, with characteristic aromatic (δ_{H} 7.52–7.58, 7.03–7.20, δ_{C} 127.1–139.5), Cp (δ_{H} 4.27, δ_{C} 97.8), alkynyl (δ_{C} 113.5, 215.9), SiPr₃ (δ_{H} 0.98–1.12, δ_{C} 12.2, 19.3) and PPh₃ resonances (δ_{P} 49.9), $\nu(\text{C}\equiv\text{C})$ at 1987 cm⁻¹ and [M + Na]⁺ and [Ru(PPh₃)_nCp]⁺ at *m/z* 895 and 691 (*n* = 2), 429 (*n* = 1), respectively.

Diyanyl-ruthenium complexes Ru(C≡CC≡CR)(PP)₂Cp [PP = (PPh₃)₂, R = SiPr₃ **6**; PP = dppe, R = Ph **7**] were obtained from similar reactions between the corresponding chloro-ruthenium complexes and HC≡CC≡CSiPr₃ (quantitative) or PhC≡CC≡CSiMe₃ (18%), respectively [17]. Both complexes were yellow solids, readily identified from characteristic features in their NMR spectra. For **6**, these include Cp at δ_{C} 4.31, δ_{C} 96.7, SiPr₃ at δ_{H} 1.08–1.12, δ_{C} at 11.8, 18.9, and PPh₃ at δ_{H} 7.18–7.23, 7.38–7.44, δ_{C} 127.3–138.8; diyanyl carbons were found at δ_{C} 63.8, 81.4, 85.5, 118.5. The ES-MS spectrum contained [M + Na]⁺, [M + H]⁺ and [Ru(PPh₃)_nCp]⁺ ions at *m/z* 919, 897, 691 (*n* = 2) and 429 (*n* = 1), respectively. For **7**, corresponding data are Cp at δ_{H} 4.67, δ_{C} 95.2; Ph at δ_{H} 6.81–7.98, δ_{C} 126.3–132.9;

diynyl C at δ_{C} 63.9, 80.4, 82.4, 83.9; dppe at δ_{P} 85.9. The ES-MS spectrum contained [M + H]⁺ and [Ru(dppe)Cp]⁺ ions at *m/z* 691 and 565, respectively.

The XRD structure of **7** was determined and a molecule is depicted in Fig. 1; selected bond parameters are listed in the caption. The Ru(dppe)Cp fragment has the usual pseudo-octahedrally coordinated ruthenium centre. The diyanyl is attached by C(1) [Ru–C(1) 1.988(2) Å] and contains alternating C=C and C–C separations along the C₄ chain from the metal [C(*n*)–C(*n* + 1) 1.227(3), 1.367(3), 1.147(7), 1.438(7) Å with angles at C(*n*) of 174.5(2)°, 172.5(2)°, 167.5(3)°, 172.4(6)°, respectively]. Overall, the molecular structure closely resembles those recently described for Ru(C≡CC≡CX)(dppe)Cp⁺ [X = H, SiMe₃, Au(PPh₃), Hg, CCo₃(μ-dppm)(CO)₇] [17–19].

3. Synthesis of cyano(alkynyl)ethenes

We prepared (NC)₂C=CH{C≡C(SiPr₃)} (**8**) as a pale yellow oil in 83% yield by condensation of SiPr₃(C≡CCHO) with malononitrile in the presence of basic alumina; the compound (NC)₂C=C(C≡CPh)₂ (**9**) is known [20] (Chart 2).

An attempted synthesis of (NC)₂C=C{C≡C(SiMe₃)₂} from bis(trimethylsilylethynyl) ketone gave instead the white 2,6-di-

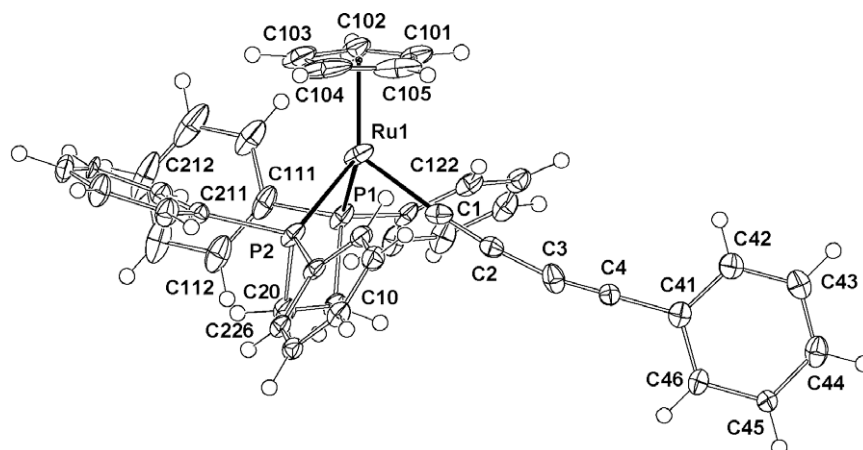
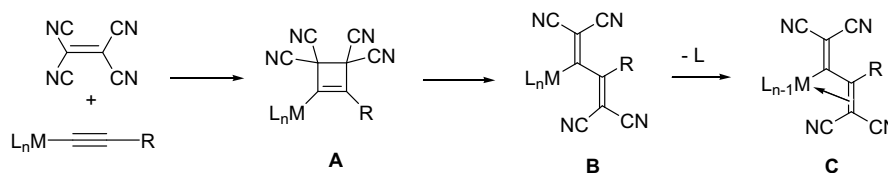
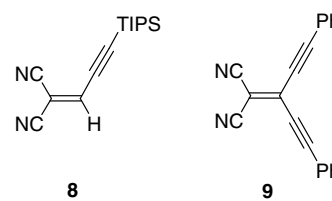


Fig. 1. Plot of a molecule of Ru(C≡CC≡CPh)(dppe)Cp (**7**). Bond distances: Ru–P(1,2) 2.2515(5), 2.2577(6), Ru–C(cp) 2.238–2.251(2), av. 2.244(6), Ru–C(1) 1.988(2), C(1)–C(2) 1.227(3), C(2)–C(3) 1.367(3), C(3)–C(4) 1.147(7), C(4)–C(41) 1.438(7) Å. Bond angles: P(1)–Ru–P(2) 82.80(2)°, P(1,2)–Ru–C(1) 84.91(6)°, 88.75(5)°, Ru–C(1)–C(2) 174.5(2)°, C(1)–C(2)–C(3) 172.5(2)°, C(2)–C(3)–C(4) 167.5(3)°, C(3)–C(4)–C(41) 172.4(6)°.

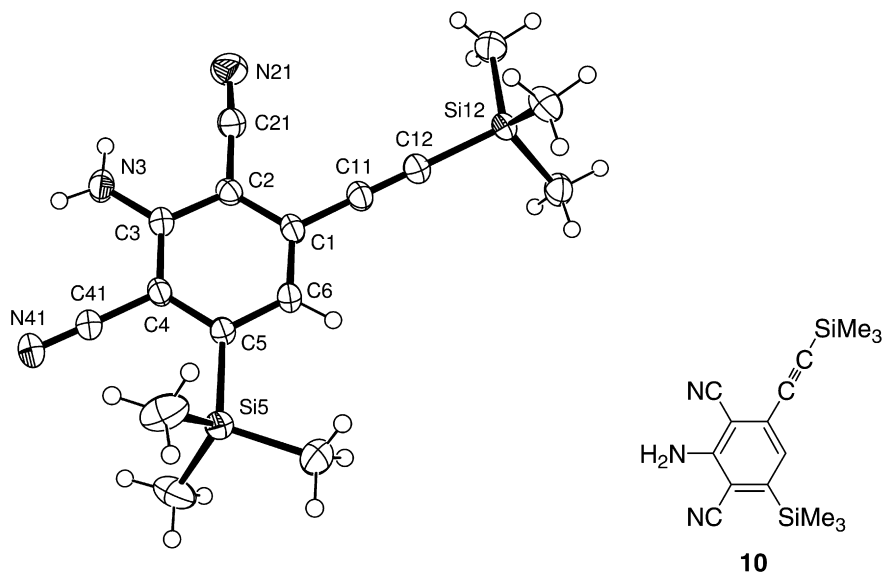


Fig. 2. Plot of a molecule of the 2,6-dicyanoaniline (**10**). Bond distances: C(1)–C(11) 1.433(1), C(11)–C(12) 1.214(2), C(12)–Si(12) 1.847(1), C(n)–C(n1) ($n=2,4$) 1.433(2), 1.438(1), C(3)–N(3) 1.359(1), C(5)–Si(5) 1.907(1) Å. Bond angles: C(1)–C(11)–C(12) 176.7(1)°, C(11)–C(12)–Si(12) 176.1(1)°, C(n)–C(n1)–N(n1) ($n=2,4$) 175.5(1)°, 178.7(1)°.

cyanoaniline **10** (2-amino-4-trimethylsilyl-6-trimethylsilylethynylisophthalonitrile) (44%), characterised by an XRD structure determination (Fig. 2). The ^1H NMR spectrum contains resonances from two non-equivalent SiMe_3 groups (δ 0.30, 0.40), the NH_2 group (δ 5.16) and a single $\text{C}(\text{sp}^2)\text{-H}$ (δ 6.96). In the ^{13}C NMR spectrum, the two CN groups appeared at δ 114.8, 116.7 and the $\text{C}\equiv\text{C}$ carbons at δ 100.4, 100.5. The IR spectrum contained $\nu(\text{C}\equiv\text{C})$ at 2163 cm^{-1} and $\nu(\text{CN})$ at 2215 cm^{-1} .

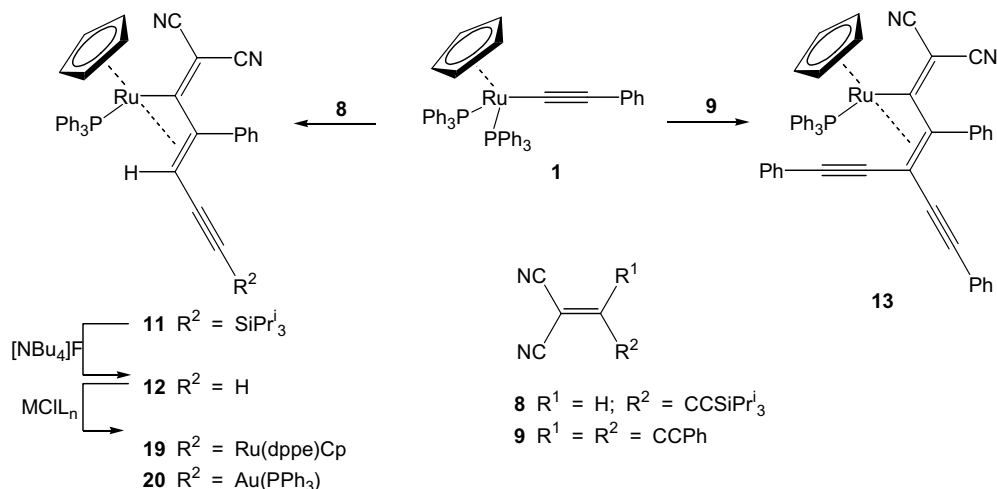
A molecule of **10** is depicted in Fig. 2, with selected bond parameters being listed in the caption thereto. The structure itself is unremarkable, except that there is a slight bending of the ethynyl group from absolute linearity, and that the SiMe_3 substituent deviates a small amount from the plane of the benzene ring. Both of these effects could be due to crystal packing constraints; inversion-related molecules pack in columns up crystallographic a . During the course of preparation of this paper, a generalised conversion of dicyanoanilines, including **10**, from ynones and malonitrile by a similar route was reported [21].

4. Cycloaddition/ring opening reactions of cyano(alkynyl)ethenes with alkynyl-Ru complexes

Reactions between the alkynyl- or diynyl-ruthenium complexes and the dicyanobis(alkynyl)ethenes afforded several complexes, the identities of which were deduced largely from their spectroscopic properties, backed up by a selection of XRD structural studies.

4.1. $\text{Ru}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2\text{Cp}$ and $(\text{NC})_2\text{C}=\text{CH}\{\text{C}\equiv\text{C}(\text{SiPr}_3^i)\}$

The reaction between $\text{Ru}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2\text{Cp}$ (**1**) and $(\text{NC})_2\text{C}=\text{CH}\{\text{C}\equiv\text{C}(\text{SiPr}_3^i)\}$ (**8**) was carried out in refluxing benzene for 24 h and the products separated to give η^3 -dienyl complex **11** as a yellow solid (32%) (Scheme 2). A larger yield (86%) was obtained by irradiation of the mixture with a 300 W sunlamp. Loss of one PPh_3 ligand during the reaction is indicated by microanalyses, ES-MS ($[\text{M} + \text{Na}]^+$ at m/z 811) and the NMR spectra. In the latter



Scheme 2.

Ph (δ_{H} 7.24–7.69, δ_{C} 128.1–137.0), Cp (δ_{H} 4.58, δ_{C} 88.8), CN (δ_{C} 111.3, 112.8), SiPr₃ (δ_{H} 1.07, δ_{C} 11.4, 18.7) and PPh₃ (δ_{P} 49.8) resonances are accompanied by signals for five carbons of the unsaturated C₆ chain at δ_{C} 28.4, 69.5, 79.4, 86.9 and 111.3. The proton attached to C(4) is found at δ_{H} 2.60 as a doublet with $J(\text{HP}) = 13.0$ Hz. The IR spectrum contains bands assigned to $\nu(\text{C}\equiv\text{C})$ at 2129 and $\nu(\text{CN})$ at 2213, 2250 cm⁻¹.

Removal of the SiPr₃ group from complex **11** was readily achieved by treatment with [NBu₄]F at 0 °C for 40 min. Conventional work-up afforded **12** as a yellow solid in quantitative yield. The molecular structure, initially established from microanalytical and spectro-

scopic data, was confirmed by an XRD structural determination. In the NMR spectra, the signals for the Ph (δ_{H} 7.27–7.66, δ_{C} 128.1–137.0), Cp (δ_{H} 4.59, δ_{C} 89.0) and the protons attached to C(4) and C(6) (δ_{H} 2.63 d, $J = 2.2$ Hz) and 2.42 (dd, $J = 2.2, 13.5$ Hz), respectively, and PPh₃ (δ_{P} 49.8) also contained signals which we have assigned to CN (δ_{C} 112.7, 118.0) and some of the carbon chain atoms (δ_{C} 26.8, 69.2, 73.4, 87.6, 89.0). The ES-MS contained [2M + Na]⁺ and [M + Na]⁺ at m/z 1287 and 655, respectively, while bands in the IR spectrum were assigned to $\nu(\text{CN})$ at 2214 and $\nu(\text{CC})$ at 2088 cm⁻¹.

The very similar XRD molecular structures of **11** and **12** are shown in Figs. 3 and 4, with selected bond parameters in Table 1,

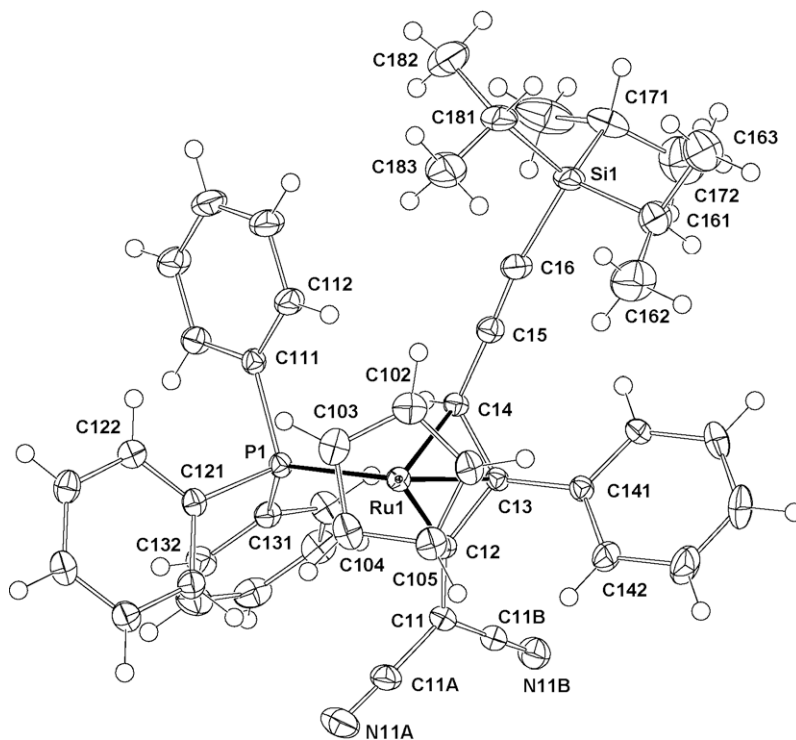


Fig. 3. Plot of a molecule of Ru(η^3 -C[=C(CN)₂]CPhCC=C(SiPr₃))(PPh₃)Cp (**11**).

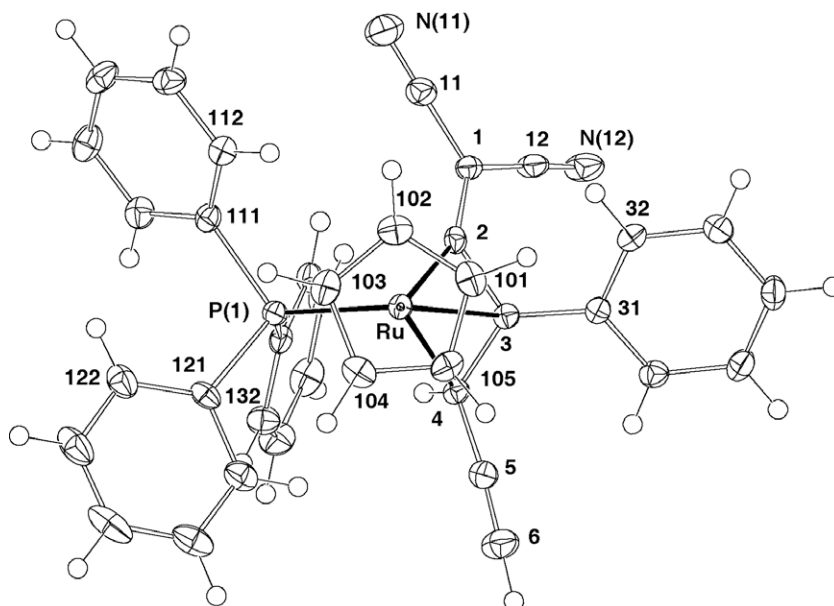


Fig. 4. Plot of a molecule of Ru(η^3 -C[=C(CN)₂]CPhCC=CH)(PPh₃)Cp (**12**).

Table 1
Selected bond distances (Å) and angles (°) for **11**, **12** and **17**

Complex	11 (molecules 1; 2)	12	17 (molecules 1; 2)
<i>Bond distances (Å)</i>			
Ru–P(1)	2.3280; 2.3272(7)	2.3215(5)	2.298; 2.312(1)
Ru–P(2)			2.319; 2.300(1)
Ru–C(cp)	2.225–2.258(3); 2.218–2.259(3)	2.217–2.258(2)	2.226–2.249(4); 2.222–2.241(4)
(av.)	2.232(15); 2.231(15)	2.234(15)	2.239; 2.234(9)
Ru–C(1)			1.976; 1.981(5)
Ru–C(2)	1.970; 1.977(3)	1.986(2)	
Ru–C(3)	2.146; 2.147(3)	2.151(2)	
Ru–C(4)	2.202; 2.204(3)	2.203(2)	
C(1)–C(2)	1.352; 1.353(4)	1.363(3)	1.221; 1.226(6)
C(1)–C(1A,1B)	1.433, 1.444(4); 1.435, 1.433(4)	1.439, 1.435(3) [C(11, 12)]	
C(2)–C(3)	1.439; 1.439(4)	1.443(3)	1.400; 1.399(6)
C(3)–C(4)	1.444; 1.438(4)	1.439(3)	1.380; 1.382(5)
C(3)–C(5)			1.501; 1.486(6)
C(3)–C(31)	1.492; 1.483(4) [C(41)]	1.489(3)	
C(4)–C(41,42)			1.424, 1.438(6); 1.434, 1.427(6)
C(4)–C(5)	1.446; 1.447(4)	1.445(3)	
C(5)–C(6)	1.202; 1.205(4)	1.173(3)	1.349; 1.341(6)
C(6)–C(7)			1.428; 1.427(6)
C(7)–C(8)			1.210; 1.187(6)
C(5)–Si(1)			1.884; 1.894(4)
C(6)–Si	1.838; 1.836(3)		
<i>Bond angles (°)</i>			
P(1)–Ru–P(2)			99.48; 99.72(4)
P(1)–Ru–C(1)			92.8; 93.1(1)
P(2)–Ru–C(1)			96.0; 95.4(1)
P–Ru–C(2)	91.03; 90.04(8)	90.71(5)	
P–Ru–C(4)	87.48; 86.92(7)	87.31(5)	
C(2)–Ru–C(4)	70.01; 69.67(11)	69.37(7)	
Ru–C(1)–C(2)			167.0; 164.0(4)
C(1)–C(2)–C(3)	136.8; 134.6(3)	130.1(2)	167.6; 162.8(4)
C(2)–C(3)–C(4)	112.7; 112.8(2)	112.1(2)	120.2; 120.3(4)
C(2)–C(3)–C(5)			121.1; 119.3(4)
C(3)–C(4)–C(5)			
C(3)–C(5)–C(6)	122.1; 121.3(2)	123.7(2)	117.1; 118.1(4)
C(4)–C(5)–C(6)	177.7; 179.4(3)	175.4(2)	
C(5)–C(6)–C(7)			125.5; 125.7(4)
C(6)–C(7)–C(8)			176.4; 175.9(5)
C(3)–C(5)–Si(1)			123.6; 121.6(3)
C(7)–C(8)–Si(2)			176.4; 163.6/171.7(6)
C(5)–C(6)–Si	171.5; 173.5(2)		

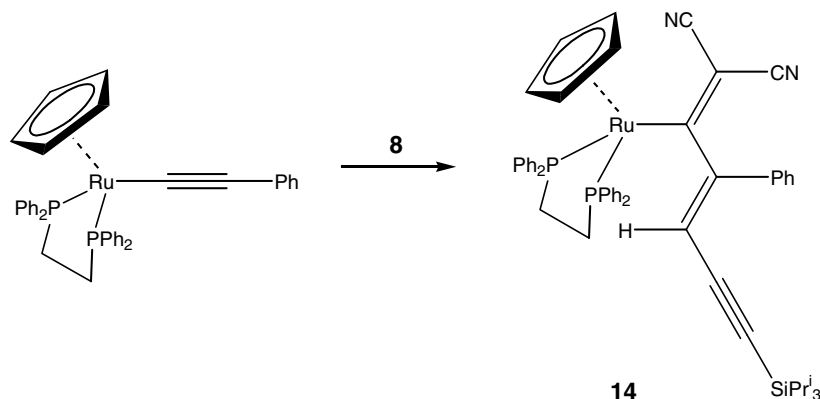
and confirm that the outer dienyl C=C double bond displaces a PPh₃ ligand with formation of a η³-butadienyl complex. In both compounds, the ruthenium atom, which is a chiral centre, is attached to the Cp [Ru–C(cp) 2.225–2.258(3), 2.218–2.259(3) (molecules 1, 2); ⟨ ⟩ 2.232, 2.231 **11**; 2.217–2.258(2), av. 2.234(15) Å **12**] and PPh₃ ligands [Ru–P 2.3280, 2.3272(7); 2.3215(5) Å, respectively]. The organic ligand is bonded to Ru by C(2) [1.970, 1.977(3); 1.986(2) Å] and C(3)–C(4) [Ru–C(3,4) 2.146, 2.147(3); 2.202, 2.204(3) **11**; 2.151, 2.203(2) Å **12**], the short former bond indicating a degree of multiple bond character. Within the carbon chain, similar C(2)–C(3) and C(3)–C(4) distances [1.439, 1.434, 1.438(4) **11**; 1.443, 1.439(3) Å **12**] indicate a degree of conjugation within the dienyl ligand, while C(1)=C(2) [1.352(5), 1.353(4); 1.363(3) Å] and C(5)–C(6) [1.202, 1.205(4); 1.173(3) Å] have the usual dimensions for unperturbed C=C and C≡C triple bonds. Other dimensions are also similar, with the exception of a slight contraction in angle C(1)–C(2)–C(3) for **12** [130.1(2)°; cf. 136.8°, 134.6(3)° for **11**]. With respect to the plane defined by C(2,3,4), C(1) lies out of plane to one side by –0.676, –0.717(6); –0.771(4) Å [**11** (molecules 1, 2); **12**], with Ru [1.566, 1.582(5); 1.595(3) Å] and C(5) [0.426, 0.395(6); 0.401(4) Å] to the other side. The C(2,3,4) planes are quasi-parallel to their companion C₅ planes [dihedrals: 8.4°, 7.7(3)°; 9.6(2)°].

4.2. Ru(C≡CPh)(PPh₃)₂Cp and (NC)₂C=C(C≡CPh)₂

The reaction between Ru(C≡CPh)(PPh₃)₂Cp (**1**) and (NC)₂C=C(C≡CPh)₂ (**9**) is similar to that with **8**, giving orange solid **13** in 54% yield. Microanalytical and ES-MS data established the η³-butadienyl formulation, with [M + H]⁺ at *m/z* 809 in the ES-MS. The NMR spectra were not well resolved as a result of low solubility, the characteristic resonances for the Ph (δ_H 6.88–7.76, δ_C 126.0–134.9), Cp (δ_H 5.11, δ_C 86.0) and PPh₃ (δ_p 52.1) groups being accompanied by signals at δ_C 29.3, 29.7, 87.9, 89.1 and 101.3 which we assign to some of the chain carbons, and one at δ_C 117.4, assigned to CN.

4.3. Ru(C≡CPh)(dppe)Cp and (NC)₂C=CH{C≡C(SiPr₃)₂}

The reaction between Ru(C≡CPh)(dppe)Cp (**3**) and (NC)₂C=CH{C≡C(SiPr₃)₂} (**8**) afforded **14** (Scheme 3) as a yellow solid in 95% yield. In this case, the microanalysis, ES-MS ([M + Na]⁺ and [M + H]⁺ at *m/z* 947, 925, respectively) and NMR spectra confirmed that the dppe ligand remained, and that the alkyndiynyl ligand was attached to the Ru centre by a σ-bond alone. The NMR parameters are similar to those of **13** (with the exception of the relative intensities of the aromatic protons), with the proton attached to C(4) now



Scheme 3.

appearing at δ_{H} 4.92. The ^{31}P resonances of the dppe ligand are 18.5 Hz doublets at δ_{P} 70.6 and 81.4, indicating the magnetic inequivalence induced by the asymmetric organic ligand. Some of the chain carbons are found at δ_{C} 28.3, 85.5, 86.0, 95.1, 105.0 and 119.8, while the SiPr₃ group gives rise to resonances at δ_{H} 1.08 and δ_{C} 11.4, 18.7.

4.4. Reactions between $(\text{NC})_2\text{C}=\text{CH}\{\text{C}\equiv\text{C}(\text{SiPr}_3^i)\}$ (**8**) and diyne complexes

The diyne complexes $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CR})(\text{PP})\text{Cp}$ [PP = (PPh₃)₂ R = Ph **4**, SiMe₃ **5**, SiPr₃ⁱ **6**; PP = dppe, R = Ph **7**] all react with **8** to give complexes in which the cyano(alkynyl)ethene has added to the outer C≡C triple bond, namely $\text{Ru}\{\text{C}\equiv\text{CC}[\text{C}(\text{CN})_2]\text{CR}=\text{CH}[\text{C}\equiv\text{C}(\text{SiPr}_3^i)]\}(\text{PP})\text{Cp}$ (**15–18**, respectively; Scheme 4), as confirmed by the XRD structure determination for **17** (Fig. 5, Table 1). The usual $\text{Ru}(\text{PPh}_3)_2\text{Cp}$ fragment [Ru–P 2.298–2.319(1); Ru–C(cp) 2.222–2.249(4), av. 2.239; 2.234(9) Å (molecules 1, 2)] is attached to the organic ligand by Ru–C(1) [1.976(3); 1.981(5) Å]. Bond lengths along the carbon chain confirm triple bonds between C(1)–C(2) and C(7)–C(8) [1.221, 1.226(6); 1.210, 1.187(6) Å] and double bonds between C(3)–C(4) and C(5)–C(6) [1.380, 1.382(5) and 1.349, 1.341(6) Å]. The differences in formal single bond lengths between C(2)–C(3), C(3)–C(5) and C(6)–C(7) [1.400; 1.399(6) and 1.501; 1.486(6) and 1.428, 1.427(6) Å] reflect the differing hybridisation [C(sp) vs. C(sp²)] and partial delocalisation along the C(1)–C(4) fragment, as found earlier in the structure of $\text{Ru}\{\text{C}\equiv\text{CC}[\text{C}(\text{CN})_2]\text{CFC}=\text{C}(\text{CN})_2\}(\text{dppe})\text{Cp}^+$ [**5c**]. Deviations in angles at individual carbon atoms [164.0–176.4(4) for C(sp), 117.1–125.7(4) for C(sp²)] probably result from “crystal packing effects”.

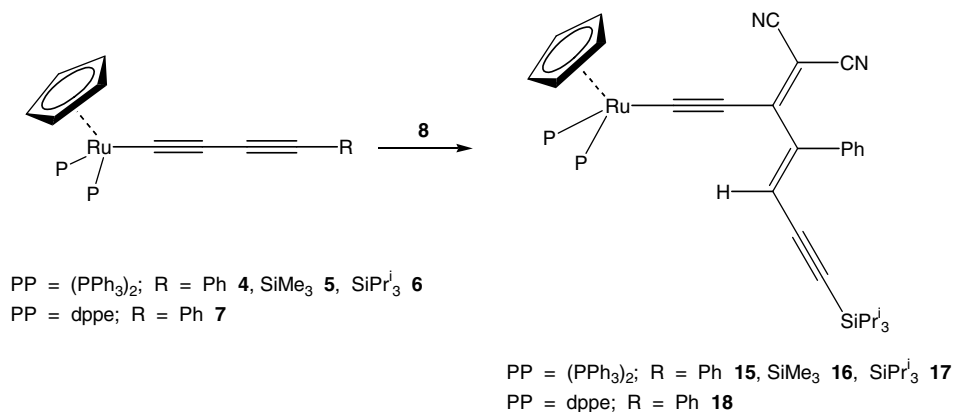
All compounds have similar spectroscopic properties (see Section 7 for details), which include $\nu(\text{CN})$ between 2208 and

2211 cm⁻¹, $\nu(\text{CC})$ between 1981 and 2002 cm⁻¹ in their IR spectra; Cp resonances between δ_{H} 4.47–4.56 (4.87 for **17**), δ_{C} 85.5–89.7, vinylic proton signals between δ_{H} 5.52 and 6.10, and PPh₃ resonances between δ_{P} 46.3 and 50.8, with the dppe at δ_{P} 83.2 in **18**. In **17**, the bulky PPh₃ groups give rise to an AB quartet at δ_{P} 46.6 ($J = 34$ Hz), possibly because of restricted rotation of the alkynyl ligand, although this is not found in any of the other complexes. Resonances for the CN groups occurred at δ_{C} 110.1–118.2. The ES-MS of solutions containing NaOMe all contained $[\text{M} + \text{Na}]^+$ and M^+ ions. The SiPr₃ groups give characteristic resonances at δ_{H} ca. 1.03–1.12 and δ_{C} ca. 11.0 and 18.0. Complex **16** showed SiMe₃ resonances at δ_{H} 0.16 and δ_{C} –1.0.

5. Further reactions of η^3 -butadienyl complexes

5.1. Addition of other metals

After deprotection of complex **11** *in situ* with $[\text{NBu}_4]\text{F}$ (as in (a) above), the resulting ethynyl derivative **12** reacts with $\text{RuCl}(\text{dppe})\text{Cp}$ in the presence of $\text{Na}[\text{BPh}_4]$ to give the binuclear derivative **19** (Scheme 2). The entering $\text{Ru}(\text{dppe})\text{Cp}$ group becomes σ -bonded to the alkynyl function of the butadienyl in **12** as indicated by the usual microanalytical and spectroscopic data. In the ^{31}P NMR spectrum, signals at δ_{P} 49.8 and 78.1 with intensity ratio 1/2 are assigned to the PPh₃ and dppe ligands, respectively. The other groups present give rise to resonances at δ_{H} 4.52 and 4.59, δ_{C} 87.3 and 87.5 ($2 \times \text{Cp}$), δ_{H} 2.17 and 2.41, δ_{C} 26.8, 29.3 (CH₂ of dppe) and δ_{H} 7.15–7.86, δ_{C} 127.8–137.0 (Ph). The proton attached to C(4) appears as a doublet at δ_{H} 2.41, while carbons of CN (δ_{C} 112.7, 117.9) and the C₆ chain appear at δ_{C} 26.6, 87.5, 141.0, 141.7 and 210.6. The ES-MS contains $[\text{M} + \text{H}]^+$ at m/z 1197, together with



Scheme 4.

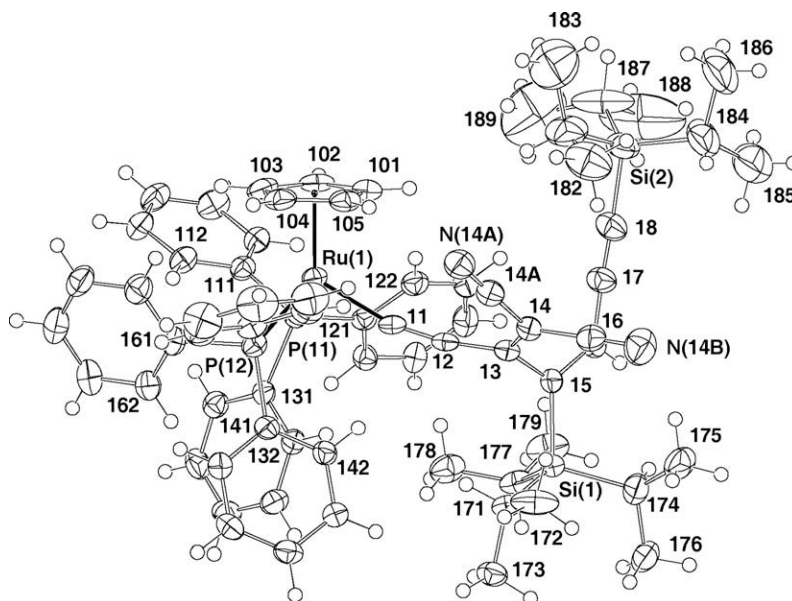


Fig. 5. Plot of a molecule of $\text{Ru}\{\text{C}\equiv\text{CC}[\text{=C}(\text{CN})_2]\text{C}(\text{SiPr}_3^t)=\text{CHC}\equiv\text{C}(\text{SiPr}_3^t)\}(\text{PPh}_3)_2\text{Cp}$ (**17**).

$[\text{Ru}(\text{dppe})\text{Cp}]^+$ at m/z 565. In the IR spectrum, $\nu(\text{CN})$ occurs at 2213 cm^{-1} .

Addition of $[\text{NBu}_4]\text{F}$ to a mixture of **11** and $\text{AuCl}(\text{PPh}_3)$ afforded a yellow solid in 90% yield, identified as the gold–ruthenium complex **20**. The ES-MS contains aggregate ions at m/z 1549 ($[\text{M} + \text{Au}(\text{PPh}_3)]^+$) and 1113 ($[\text{M} + \text{Na}]^+$), together with $[\text{Au}(\text{PPh}_3)]^+$ and $[\text{Au}(\text{PPh}_3)(\text{MeOH})]^+$ at m/z 721 and 500, respectively. In the NMR spectra, characteristic resonances for Ph (δ_{H} 7.19–7.88, δ_{C} 127.7–137.9), Cp (δ_{H} 4.55, δ_{C} 88.9), PPh_3 [δ_{P} 40.7 (Au–P) and 50.3 (Ru–P)] and the proton attached to C(4) (δ_{H} 2.70) were accompanied by signals for CN (δ_{C} 113.2, 118.5) and the chain carbons (δ_{C} 31.4, 68.3, 78.3).

6. Conclusions

This study has shown that cyano(alkynyl)ethenes, such as $(\text{NC})_2\text{C}=\text{CH}\{\text{C}\equiv\text{C}(\text{SiPr}_3^t)\}$, enter into the cycloaddition/ring-opening reactions with ruthenium alkynyl and diyne complexes which are analogous to those found earlier with tcne and other related electron-deficient alkenes. In one instance, we have demonstrated the ready deprotection of the alkynyl group and subsequent reactions of the terminal alkyne to incorporate $\text{Ru}(\text{dppe})\text{Cp}$ and $\text{Au}(\text{PPh}_3)$ groups in the resulting binuclear complexes. Inclusion of the $\text{C}\equiv\text{C}$ triple bond gives an extra functionality for construction of further examples of polynuclear complexes which may have exciting unusual optical and electronic properties.

In the course of preparing substrates for the cycloaddition reactions, we have also made and characterised $(\text{NC})_2\text{C}=\text{CH}\{\text{C}\equiv\text{C}(\text{SiPr}_3^t)\}$, while, during an attempted synthesis of 1,1-dicyano-2,2-bis(trimethylsilylethynyl)ethene, the obtained product was shown crystallographically to be 2-amino-4-trimethylsilyl-6-(trimethylsilylethynyl)isophthalonitrile (**10**).

7. Experimental

7.1. General

All reactions were carried out under dry nitrogen, although normally no special precautions to exclude air were taken during subsequent work-up. Common solvents were dried, distilled under

nitrogen and degassed before use. Separations were carried out by preparative thin-layer chromatography on glass plates ($20 \times 20\text{ cm}^2$) coated with silica gel (Merck, 0.5 mm thick).

7.2. Instruments

IR spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra were recorded on a Varian 2000 instrument (^1H at 300.13 MHz, ^{13}C at 75.47 MHz, ^{31}P at 121.503 MHz). Samples were dissolved in CDCl_3 contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to tetramethylsilane for ^1H and ^{13}C NMR spectra and external H_3PO_4 for ^{31}P NMR spectra. Electrospray mass spectra (ES-MS) were obtained from samples dissolved in MeOH, containing NaOMe to aid ionisation [22]. Solutions were injected into a Fisons VG Platform II spectrometer via a 10 mL injection loop. Nitrogen was used as the drying and nebulising gas. Ions listed are the most intense in the isotopic patterns. Elemental analyses were by CMAS, Belmont, Vic., Australia.

7.3. Reagents

The following compounds were obtained by the cited literature methods: $\text{Ru}(\text{C}\equiv\text{CPh})(\text{PP})\text{Cp}$ [$\text{PP} = (\text{PPh}_3)_2$ **1**, dppe **3** [23]], $\text{Ru}(\text{C}\equiv\text{CC}=\text{CR})(\text{PPh}_3)_2\text{Cp}$ ($\text{R} = \text{Ph}$ **4** [24], SiMe_3 **5** [17]), $\text{SiPr}_3^t(\text{C}\equiv\text{CCHO})$ [25], $\text{Br}_2\text{C}=\text{CHC}\equiv\text{C}(\text{SiPr}_3^t)$ [25], $(\text{NC})_2\text{C}=\text{C}(\text{C}\equiv\text{CPh})_2$ (**9**) [20]. Previously unknown materials were prepared as described below.

7.4. Ruthenium complexes

7.4.1. $\text{Ru}\{\text{C}\equiv\text{C}(\text{SiPr}_3^t)\}(\text{PPh}_3)_2\text{Cp}$ (**2**)

A mixture of $\text{RuCl}(\text{PPh}_3)_2\text{Cp}$ (0.70 g, 0.96 mmol) and $\text{HC}\equiv\text{C}(\text{SiPr}_3^t)$ (0.24 mL, 1.05 mmol) was heated in refluxing MeOH (30 mL) for 2 h. After cooling, NaOMe (1 M in MeOH, 3.00 mL, 3.00 mmol) was added, the solution was stirred at r.t. for 30 min, then concentrated to ca. 10 mL under reduced pressure. The resulting precipitate was collected by filtration, washed with cold MeOH (5 mL) and dried to afford $\text{Ru}\{\text{C}\equiv\text{C}(\text{SiPr}_3^t)\}(\text{PPh}_3)_2\text{Cp}$ (**2**) as a yellow solid (312 mg, 37%). Anal. Calc. for $\text{C}_{52}\text{H}_{56}\text{P}_2\text{RuSi}$: C, 71.61; H, 6.47; M, 872. Found: C, 71.58; H, 6.39%. IR (cm^{-1}): $\nu(\text{CC})$ 1987m; other bands at 1432s, 803m, 756m, 737m, 703m, 693m. ^1H NMR: δ 7.52–7.58 (12H, m),

Table 2
Crystal data and refinement details

Complex	7	10	11	12	17
Formula	C ₄₁ H ₃₄ P ₂ Ru	C ₁₆ H ₂₁ N ₃ Si ₂	C ₄₆ H ₄₇ N ₂ PRuSi	C ₃₇ H ₂₇ N ₂ PRu	C ₆₉ H ₇₈ N ₂ P ₂ RuSi ₂ · 0.25CH ₂ Cl ₂
Molecular weight	689.69	311.54	788.03	631.65	1175.76
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	C2/c	P $\bar{1}$	P $\bar{1}$	C2/c	I2/a
a (Å)	29.6151(5)	9.8992(6)	13.271(1)	17.7791(8)	46.512(6)
b (Å)	9.3742(3)	10.0452(7)	15.851(1)	9.5073(4)	13.6207(7)
c (Å)	27.6709(9)	11.0297(7)	20.848(2)	36.2525(4)	40.653(2)
α (°)		69.694(1)	74.294(2)		
β (°)	124.885(2)	63.369(1)	84.871(2)	104.358(3)	101.796(7)
γ (°)		80.071(1)	80.912(2)		
V (Å ³)	6301	919.3	4164	5936	25211
ρ_c	1.454	1.125	1.257	1.413	1.239
Z	8	2	4	8	16
2 θ _{max} (°)	65	74	70	62	53
μ (Mo-K α) (mm ⁻¹)	0.63	0.19	0.48	0.61	0.40
T _{min} /max	0.93	0.89	0.77	0.88	0.98
Crystal dimensions (mm)	0.40 × 0.19 × 0.04	0.60 × 0.40 × 0.35	0.25 × 0.25 × 0.10	0.35 × 0.12 × 0.06	0.23 × 0.18 × 0.11
N _{tot}	43 507	16 722	68 613	44 119	101 590
N (R _{int})	11 204 (0.054)	8819 (0.020)	35 719 (0.051)	9393 (0.037)	24 229 (0.061)
N _o	7201	5971	21 678	6284	12 374
R	0.040	0.052	0.066	0.033	0.049
R _w (a, b)	0.083 (0.040, –)	0.16 (0.089, 0.039)	0.16 (0.061, 3.99)	0.077 (0.036, –)	0.14 (0.067, –)
T (K)	100	150	150	100	100

7.03–7.20 (18H, m), 4.27 (5H, s), 0.98–1.12 (21H, m). ¹³C NMR: δ 215.9, 139.5, 139.1, 138.7, 133.9 [t, J(CP) = 5.3 Hz], 132.1 [d, J(CP) = 9.9], 128.3, 127.1 [t, J(CP) = 4.6 Hz], 113.5, 97.8, 85.9 [t, J(CP) = 2.3 Hz], 19.3, 12.8. ³¹P NMR: δ 49.9. ES-MS (*m/z*): 895, [M + Na]⁺; 691, [Ru(PPh₃)₂Cp]⁺; 429, [Ru(PPh₃)Cp]⁺.

7.4.2. Ru(C≡CC≡CSiPr₃)(PPh₃)₂Cp (**6**)

BuLi (2.30 M in hexanes, 2.41 mL, 5.54 mmol) was added dropwise to a solution of NHPPr₂ (0.78 mL, 5.54 mmol) in thf (4 mL) at 0 °C. The solution was stirred for 15 min at 0 °C, then added dropwise to a solution of Br₂C=CHC≡C(SiPr₃) (0.61 g, 1.68 mmol) in thf (4 mL) at –78 °C. The mixture was stirred at –78 °C for 2 h, 1 M HCl (6 mL) was added and the mixture was stirred at r.t. for a further 30 min. The organic layer was separated, washed with brine (5 mL) and water (5 mL), dried (MgSO₄), and filtered. This solution of Pr₃SiC≡CC≡CH was added to a suspension of RuCl(PPh₃)₂Cp (0.61 g, 0.84 mmol) and Na[BPh₄] (0.32 g, 0.92 mmol) in 1/1 NEt₃-thf (18 mL) and the mixture was stirred at 50 °C for 18 h. After cooling, the mixture was concentrated under reduced pressure. Flash chromatography of the residue (acetone–hexane, 1/3) afforded Ru(C≡CC≡CSiPr₃)(PPh₃)₂Cp (**6**) as a yellow solid (0.75 g, 100%). Anal. Calc. for C₅₄H₅₆P₂RuSi: C, 72.38; H, 6.30; M, 896. Found: C, 71.70; H, 6.17%. IR (cm⁻¹): ν (CC) 2162w, 2101m, 1993w; other bands at 740m, 723m, 696m. ¹H NMR: δ 7.38–7.44 (12H, m), 7.18–7.23 (6H, m), 7.08–7.13 (12H, m), 4.31 (5H, s), 1.08–1.12 (21H, m). ¹³C NMR: δ 138.8, 138.5, 138.2, 137.9, 137.7, 133.7 [t, J(CP) = 4.9 Hz], 132.1 [d, J(CP) = 9.7 Hz], 128.5, 127.3 [t, J(CP) = 4.6 Hz], 118.5 [t, J(CP) = 24.6 Hz], 96.7, 85.5, 81.4, 63.8, 18.9, 11.8. ³¹P NMR: δ 47.9. ES-MS (*m/z*): 919, [M + Na]⁺; 897, [M + H]⁺; 691, [Ru(PPh₃)₂Cp]⁺; 429, [Ru(PPh₃)Cp]⁺.

7.4.3. Ru(C≡CC≡CPh)(dppe)Cp (**7**)

A mixture of RuCl(dppe)Cp (0.85 g, 1.42 mmol), PhC≡CC≡CSiMe₃ (0.28 g, 1.42 mmol) and KF (82 mg, 1.42 mmol) was heated in refluxing MeOH (50 mL) for 1 h. After cooling, the yellow-green precipitate was filtered from the dark blue-green solution, rinsed with cold MeOH (10 mL) and dried. Chromatography of the crude product (basic alumina; acetone–hexane, 1/1) afforded Ru(C≡CC≡CPh)(dppe)Cp (**7**) as a yellow solid (176 mg, 18%). Anal. Calc. for C₄₁H₃₄P₂Ru: C, 71.40; H, 4.97; M, 690. Found: C, 71.49; H, 4.97%. IR (cm⁻¹): ν (CC) 2156m, 2017w; other bands at 1435m,

1097m, 791m, 744m, 693m. ¹H NMR: δ 7.92–7.98 (4H, m), 7.37–7.40 (2H, m), 7.23–7.28 (4H, m), 7.07–7.13 (6H, m), 6.81–7.00 (9H, m), 4.67 (5H, s), 2.47–2.59 (2H, m), 1.93–2.08 (2H, m). ¹³C NMR: δ 142.8 (m), 137.6 (m), 134.6 [t, J(CP) = 5.3 Hz], 132.9, 132.3 [t, J(CP) = 5.3 Hz], 130.2, 129.3, 128.7, 128.5, 126.3, 95.2, 83.9 [t, J(CP) = 1.9 Hz], 82.4, 80.4, 63.9, 28.9 [1:1:1 t, J(CP) = 22.9 Hz]. ³¹P NMR: δ 85.9. ES-MS (*m/z*): 691, [M + H]⁺; 565, [Ru(dppe)Cp]⁺.

7.5. 1,1-Dicyano-4-(triisopropylsilyl)but-1-en-3-yne, (NC)₂C=CH{C≡C(SiPr₃)} (**8**)

A mixture of 3-(triisopropylsilyl)propargaldehyde (1.15 g, 5.48 mmol), malononitrile (0.52 mL, 8.22 mmol), basic alumina (1.50 g, activity II) was heated in refluxing CH₂Cl₂ (25 mL) for 40 min. After cooling the alumina was filtered off and extracted with CH₂Cl₂ (3 × 10 mL). The combined filtrate and extracts were concentrated under reduced pressure. Short column chromatography of the residue (silica; CH₂Cl₂-hexane, 1/1) afforded (NC)₂C=CH{C≡C(SiPr₃)} (**8**) as a pale yellow oil (1.17 g, 83%). Anal. Calc. (C₁₅H₂₂N₂Si): C, 69.71; H, 8.58; N, 10.84; M, 259. Found: C, 69.73; H, 8.52; N, 10.85%. IR (Nujol, cm⁻¹): ν _{max} 3026w, 2234m, 2178s, 2127w, 2030w, 1561m, 1368s, 1244m, 1165m, 1106m, 1086m, 1018m, 882s, 665s, 611s. ¹H NMR: δ 6.95 (1H, s), 1.10–1.14 (21H, m). ¹³C NMR: δ 140.9, 122.7, 112.1, 110.9, 99.7, 96.3, 18.4, 11.0. ES-MS (*m/z*): 313, [M + Na + MeOH]⁺; 291, [M + MeOH]⁺.

7.6. 2-Amino-4-trimethylsilyl-6-(trimethylsilylethynyl)-isophthalonitrile (**10**)

A mixture of malononitrile (0.10 mL, 1.62 mmol), (Me₃SiC≡C)₂CO (0.24 g, 1.08 mmol), basic alumina (0.30 g, activity II) was heated in refluxing CH₂Cl₂ (5 mL) for 2 h, with addition of further portions of basic alumina every 30 min. After cooling, the alumina was filtered off and extracted with CH₂Cl₂ (3 × 10 mL). The combined filtrate and extracts were concentrated under reduced pressure. Flash chromatography of the residue (CH₂Cl₂-hexane, 2/1, then 4/1) afforded recovered ketone (84 mg, 35%) and the 2,6-dicyanoaniline (**10**) as a colourless solid (148 mg, 44%), m.p. 123–125 °C. Crystals for X-ray analysis were grown by slow evaporation

of a CH_2Cl_2 solution layered with hexane. Anal. Calc. for $\text{C}_{16}\text{H}_{21}\text{N}_3\text{Si}_2$: C, 61.69; H, 6.79; N, 13.49; M, 311. Found: C, 61.36; H, 8.17; N, 12.70%. IR (cm^{-1}): ν_{max} 3478m, 3359s, 3244m, 2215s, 2163w, 1643s, 1633s, 1563m, 1557m, 1538s, 1404m, 1267s, 1252s, 1064m, 948m, 843vs, 759m, 673m. ^1H NMR: δ 6.96 (1H, s), 5.16 (2H, br s), 0.40 (9H, s), 0.30 (9H, s). ^{13}C NMR: δ 151.3, 151.2, 130.1, 126.4, 116.7, 114.8, 105.6, 100.6, 100.5, 100.4, -0.5, -1.7. EI-MS (m/z): 311, M^+ ; 296, $[\text{M} - \text{Me}]^+$; 73, $[\text{SiMe}_3]^+$.

7.7. Reactions of $(\text{NC})_2\text{C}=\text{CH}\{\text{C}\equiv\text{C}(\text{SiPr}_3^i)\}$ (**8**)

7.7.1. With $\text{Ru}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2\text{Cp}$

(i) A mixture of $\text{Ru}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2\text{Cp}$ (**1**) (200 mg, 0.25 mmol) and $(\text{NC})_2\text{C}=\text{CH}\{\text{C}\equiv\text{C}(\text{SiPr}_3^i)\}$ (**8**) (80 mg, 0.31 mmol) was heated in refluxing benzene (10 mL) for 24 h. After cooling, the mixture was concentrated under reduced pressure and the residue was purified on a column of basic alumina. Elution with CH_2Cl_2 firstly gave an orange band containing unreacted starting materials (166 mg); further elution with CH_2Cl_2 gave a yellow band which afforded η^3 -dienyl complex **11** as a yellow solid (63 mg, 32%). Crystals suitable for X-ray analysis were grown by slow evaporation of a CH_2Cl_2 solution layered with MeOH. Anal. Calc. for $\text{C}_{46}\text{H}_{47}\text{N}_2\text{PRuSi}$: C, 70.11; H, 6.01; N, 3.55; M, 788. Found: C, 70.20; H, 6.07; N, 3.48%. IR (cm^{-1}): ν_{max} 3061w, 2250m, 2213s, 2129m, 1579s, 1494m, 1460s, 1435s, 1092s, 1011m, 998m, 881m, 812m, 765m, 732s, 694s, 660s. ^1H NMR: δ 7.66–7.69 (2H, m), 7.40–7.52 (15H, m), 7.24–7.27 (3H, m), 4.58 (5H, s), 2.60 (1H, d, J 13.0), 1.07 (21H, s). ^{13}C NMR: δ 137.0, 133.94, 133.93 [d, $J(\text{CP}) = 10.3$ Hz], 133.0, 130.6 [d, $J(\text{CP}) = 2.3$ Hz], 129.9, 128.3 [d, $J(\text{CP}) = 9.9$ Hz], 128.1, 118.0 [d, $J(\text{CP}) = 3.1$ Hz], 112.8 [d, $J(\text{CP}) = 3.1$ Hz], 111.3, 88.8 [d, $J(\text{CP}) = 1.1$ Hz], 86.9, 79.4 [d, $J(\text{CP}) = 8.0$ Hz], 69.5, 28.4 [d, $J(\text{CP}) = 2.7$ Hz], 18.7, 11.4. ^{31}P NMR: 49.8. ES-MS (m/z): 811, $[\text{M} + \text{Na}]^+$.

(ii) A mixture of **1** (200 mg, 0.25 mmol), **8** (80 mg, 0.31 mmol) and benzene (10 mL) was irradiated with a 300 W sunlamp for 24 h. The mixture began to reflux after ca. 15 min. Work-up and purification as above afforded starting materials (57 mg) and **11** (170 mg, 86%).

7.7.2. With $\text{Ru}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2\text{Cp}$

A mixture of $\text{Ru}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2\text{Cp}$ (**4**) (119 mg, 0.15 mmol) and $(\text{NC})_2\text{C}=\text{CH}\{\text{C}\equiv\text{C}(\text{SiPr}_3^i)\}$ (**8**) (47 mg, 0.18 mmol) was heated in refluxing benzene (6 mL) for 24 h. After cooling, the mixture was concentrated under reduced pressure and the residue was purified on a column of basic alumina. Elution with CH_2Cl_2 afforded $\text{Ru}\{\text{C}\equiv\text{C}[\text{C}(\text{CN})_2]\text{CPh}=\text{CHC}\equiv\text{C}(\text{SiPr}_3^i)\}(\text{PPh}_3)_2\text{Cp}$ (**15**) as a dark orange oil (102 mg, 63%) as a mixture of isomers by NMR. Anal. Calc. for $\text{C}_{66}\text{H}_{62}\text{N}_2\text{P}_2\text{RuSi}$: C, 73.79; H, 5.82; N, 2.61; M, 1074. Found: C, 73.91; H, 5.89; N, 2.57%. IR (cm^{-1}): ν_{max} 3057w, 2210m, 2125w, 1995vs, 1562m, 1434s, 1089s, 998m, 882m, 812m, 743m, 696s, 682s. ^1H NMR: δ 7.00–7.47 (35H, m), 6.95 (1H, s), 5.95 (1H, s), 4.56 (5H, s), 1.04 (21H, s). ^{13}C NMR: δ 155.3, 149.2, 138.0, 137.6, 137.1, 136.8, 136.1, 133.6, 133.5, 133.4, 132.2, 132.0, 131.9, 129.3, 129.1, 128.6, 128.4, 128.0, 127.9, 127.8, 127.7, 127.6, 127.4, 118.2, 115.3, 113.4, 112.1, 104.5, 101.9, 99.7, 88.0, 87.8, 79.4, 18.82, 18.76, 18.6, 18.4, 11.3, 11.0. ^{31}P NMR: δ 50.8. ES-MS (m/z): 1097, $[\text{M} + \text{Na}]^+$; 1074, $[\text{M}]^+$.

7.7.3. With $\text{Ru}(\text{C}\equiv\text{C}(\text{SiMe}_3))(\text{PPh}_3)_2\text{Cp}$

A mixture of $\text{Ru}(\text{C}\equiv\text{C}(\text{SiMe}_3))(\text{PPh}_3)_2\text{Cp}$ (**5**) (200 mg, 0.24 mmol) and $(\text{NC})_2\text{C}=\text{CH}\{\text{C}\equiv\text{C}(\text{SiPr}_3^i)\}$ (**8**) (77 mg, 0.30 mmol) in benzene (10 mL) was irradiated with a 300 W sunlamp for 24 h. The mixture began to reflux after ca. 15 min. After cooling,

the mixture was concentrated under vacuum and the residue was purified on a column of basic alumina. Elution with CH_2Cl_2 gave an orange band which was further purified by preparative t.l.c. to afford $\text{Ru}\{\text{C}\equiv\text{C}[\text{C}(\text{CN})_2]\text{C}(\text{SiMe}_3)=\text{CHC}\equiv\text{C}(\text{SiPr}_3^i)\}(\text{PPh}_3)_2\text{Cp}$ (**16**) as a dark orange oil (182 mg, 71%) as a mixture of isomers by NMR. Anal. Calc. for $\text{C}_{63}\text{H}_{66}\text{N}_2\text{P}_2\text{RuSi}_2$: C, 70.69; H, 6.21; N, 2.62; M, 1070. Found: C, 71.37; H, 6.71; N, 2.04%. IR (cm^{-1}): ν_{max} 3053w, 2210m, 1995vs, 1434m, 1090m, 844m, 742m, 694s. ^1H NMR: δ 7.12–7.32 (30H, m), 6.10 (1H, s), 4.52 (5H, s), 1.12 (21H, s), 0.16 (9H, s). ^{13}C NMR: δ 210.6, 195.8, 190.0, 189.6, 161.7, 157.1, 138.3, 138.0, 137.5, 137.1, 136.7, 133.5 (t, $J = 5.3$ Hz), 132.0 (d, $J = 9.9$ Hz), 129.0, 128.6, 128.3, 128.2, 128.0, 127.6 (t, $J = 4.6$ Hz), 125.5, 122.4, 117.3, 116.7, 104.9, 100.3, 87.8, 87.6, 69.4, 53.9, 31.6, 29.2, 18.6, 11.4, -1.0. ^{31}P NMR: δ 48.0. ES-MS (m/z): 1093, $[\text{M} + \text{Na}]^+$; 1071, $[\text{M} + \text{H}]^+$; 691, $[\text{Ru}(\text{PPh}_3)_2\text{Cp}]^+$; 429, $[\text{Ru}(\text{PPh}_3)\text{Cp}]^+$.

7.7.4. With $\text{Ru}\{\text{C}\equiv\text{C}(\text{SiPr}_3^i)\}(\text{PPh}_3)_2\text{Cp}$

A mixture of $\text{Ru}\{\text{C}\equiv\text{C}(\text{SiPr}_3^i)\}(\text{PPh}_3)_2\text{Cp}$ (**6**) (90 mg, 0.10 mmol) and $(\text{NC})_2\text{C}=\text{CH}\{\text{C}\equiv\text{C}(\text{SiPr}_3^i)\}$ (**8**) (31 mg, 0.12 mmol) in thf (4 mL) was irradiated with a 300 W sunlamp for 24 h. The mixture began to reflux after ca. 15 min. After cooling, the mixture was concentrated under reduced pressure. Preparative t.l.c. of the residue (silica, acetone–toluene–hexane, 1/29/30) afforded $\text{Ru}\{\text{C}\equiv\text{C}[\text{C}(\text{CN})_2]\text{C}(\text{SiPr}_3^i)=\text{CHC}\equiv\text{C}(\text{SiPr}_3^i)\}(\text{PPh}_3)_2\text{Cp}$ (**17**) as an orange solid (46 mg, 40%). Crystals suitable for X-ray were grown by slow evaporation of a CH_2Cl_2 solution. Anal. Calc. for $\text{C}_{69}\text{H}_{78}\text{N}_2\text{P}_2\text{RuSi}_2$: C, 71.78; H, 6.81; N, 2.43; M, 1154. Found: C, 71.73; H, 6.76; N, 2.49%. IR (cm^{-1}): ν_{max} 3053w, 2211m, 1981vs, 1436s, 881m, 695s. ^1H NMR: δ 7.09–7.71 (30H, m), 6.08 (1H, s), 4.47 (5H, s), 0.99–1.13 (42H, s). ^{13}C NMR: δ 221.1 [d, $J(\text{CP}) = 14.9$ Hz], 134.2, 134.1 [d, $J(\text{CP}) = 10.6$ Hz], 133.6, 132.4 [d, $J(\text{CP}) = 9.7$ Hz], 130.9, 128.7 [d, $J(\text{CP}) = 10.3$ Hz], 117.8, 112.4, 110.1, 104.0, 91.2, 89.7, 86.7, 50.7, 35.7, 31.2, 19.1, 19.0, 11.6, 11.5. ^{31}P NMR: δ 46.8 (1P, d, $J = 34$ Hz), 46.3 (1P, d, $J = 34$ Hz). ES-MS (m/z): 1177, $[\text{M} + \text{Na}]^+$; 1154, M^+ .

7.7.5. With $\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppe})\text{Cp}$

A mixture of $\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppe})\text{Cp}$ (**3**) (173 mg, 0.26 mmol) and $(\text{NC})_2\text{C}=\text{CH}\{\text{C}\equiv\text{C}(\text{SiPr}_3^i)\}$ (**8**) (83 mg, 0.32 mmol) was heated in refluxing benzene (10 mL) for 24 h. After cooling, the mixture was concentrated under reduced pressure and the residue was purified on a column of basic alumina. Elution with CH_2Cl_2 afforded $\text{Ru}\{\text{C}\equiv\text{C}[\text{C}(\text{CN})_2]\text{CPh}=\text{CHC}\equiv\text{C}(\text{SiPr}_3^i)\}(\text{dppe})\text{Cp}$ (**14**) as a yellow solid (228 mg, 95%). Anal. Calc. for $\text{C}_{54}\text{H}_{56}\text{N}_2\text{P}_2\text{RuSi}$: C, 70.18; H, 6.11; N, 3.03; M, 902. Found: C, 70.15; H, 6.19; N, 3.03%. IR (cm^{-1}): ν_{max} 3055m, 2202s, 2117m, 1484m, 1462m, 1434vs, 1096s, 1073m, 1015m, 999m, 881s, 804s, 743s, 696vs, 675s. ^1H NMR: δ 6.63–7.43 (25H, m), 4.92 (1H, br s), 4.61 (5H, br s), 2.17–2.62 (4H, m), 1.08 (21H, s). ^{13}C NMR: δ 135.8, 135.0, 132.2, 132.0, 129.6 [d, $J(\text{CP}) = 9.9$ Hz], 128.4, 128.3, 128.2, 128.1, 127.9, 127.4, 127.0, 119.8, 105.0, 95.1, 86.0, 85.5, 28.3, 18.7, 11.4. ^{31}P NMR: δ 81.4 (d, $J = 18.5$ Hz), 70.6 (d, $J = 18.5$ Hz). ES-MS (m/z): 947, $[\text{M} + \text{Na}]^+$; 925, $[\text{M} + \text{H}]^+$.

7.7.6. With $\text{Ru}(\text{C}\equiv\text{C}(\text{SiMe}_3))(\text{dppe})\text{Cp}$

A mixture of $\text{Ru}(\text{C}\equiv\text{C}(\text{SiMe}_3))(\text{dppe})\text{Cp}$ (**7**) (69 mg, 0.10 mmol) and $(\text{NC})_2\text{C}=\text{CH}\{\text{C}\equiv\text{C}(\text{SiPr}_3^i)\}$ (**8**) (31 mg, 0.12 mmol) was heated in refluxing benzene (4 mL) for 18 h. After cooling, the mixture was concentrated under reduced pressure. Preparative t.l.c. of the residue (silica, 1/19/20 acetone–toluene–hexanes) afforded $\text{Ru}\{\text{C}\equiv\text{C}[\text{C}(\text{CN})_2]\text{CPh}=\text{CHC}\equiv\text{C}(\text{SiPr}_3^i)\}(\text{dppe})\text{Cp}$ (**18**) as a dark red solid (54 mg, 57%). Anal. Calc. for $\text{C}_{56}\text{H}_{56}\text{N}_2\text{P}_2\text{RuSi}$: C, 70.94; H, 5.95; N, 2.95; M, 948. Found: C, 70.86; H, 6.03; N, 3.01%. IR (cm^{-1}): ν_{max} 3055w, 2208m, 2002vs, 1434s, 1096m, 806m, 744m, 695s, 677s. ^1H NMR: δ 7.64–7.71 (4H, m), 7.42–7.47 (6H, m), 7.14–7.36 (11H, m), 6.94–7.06 (4H, m), 5.52 (1H, s), 4.87 (5H, s), 2.19–2.30

(4H, m), 1.03 (21H, s). ^{31}P NMR: δ 83.2. ES-MS m/z 1919, $[\text{2M} + \text{Na}]^+$; 949, $[\text{M} + \text{H}]^+$; 565, $[\text{Ru}(\text{dppe})\text{Cp}]^+$.

7.8. Reaction of $\text{Ru}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2\text{Cp}$ with $(\text{NC})_2\text{C}=\text{C}(\text{C}\equiv\text{CPh})_2$

A mixture of $\text{Ru}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2\text{Cp}$ (**1**) (79 mg, 0.10 mmol), $(\text{NC})_2\text{C}=\text{C}(\text{C}\equiv\text{CPh})_2$ (**9**) (33 mg, 0.12 mmol) in thf (4 mL) was irradiated with a 300 W sunlamp for 24 h. The mixture began to reflux after ca. 15 min. After cooling, the mixture was concentrated under reduced pressure. Preparative t.l.c. of the residue (acetone-hexane, 1/3) afforded η^3 -dienyl complex **13** as an orange solid (44 mg, 54%). Anal. Calc. for $\text{C}_{51}\text{H}_{35}\text{N}_2\text{PRu}$: C, 75.82; H, 4.37; N, 3.47; M, 808. Found C, 73.65; H, 3.80; N, 2.90%. IR (cm^{-1}): ν_{max} 3055w, 2240w, 1952w, 1705s, 1608m, 1482m, 1436m, 1213m, 1091m, 909m, 730m, 693vs. ^1H NMR: δ 6.88–7.76 (30H, m), 5.11 (5H, s). ^{13}C NMR: δ 126.0–134.9 (m), 117.4, 101.3, 89.1, 87.9, 86.0 [d, $J(\text{CP}) = 2.3$ Hz], 29.7, 29.3. ^{31}P NMR: δ 52.1. ES-MS (m/z): 809, $[\text{M} + \text{H}]^+$.

7.9. Deprotection of **11** with TBAF

TBAF (1 M in thf, 0.11 mL, 0.11 mmol) was added dropwise to a solution of **11** (86 mg, 0.11 mmol) in thf (11 mL) cooled to 0 °C and the mixture was stirred at 0 °C for 40 min, then concentrated under reduced pressure. The residue was chromatographed on a short column (silica; acetone-hexane, 1/3) to afford η^3 -dienyl complex **12** as a yellow solid (69 mg, 100%). Anal. Calc. for $\text{C}_{37}\text{H}_{27}\text{N}_2\text{PRu}$: C, 70.35; H, 4.31; N, 4.43; M, 632. Found: C, 67.25; H, 4.11; N, 3.92%. IR (cm^{-1}): ν_{max} 3299s, 3055s, 2214vs, 2088w, 1970w, 1578vs, 1573vs, 1446s, 1433vs, 1408m, 1310m, 1265s, 1184s, 1158m, 1091vs, 1071s, 1028m, 1012m, 998m, 911m, 832s, 814vs, 769vs, 736vs, 697vs, 640vs, 626vs, 613s. ^1H NMR: δ 7.62–7.66 (2H, m), 7.40–7.54 (15H, m), 7.27–7.34 (3H, m), 4.59 (5H, s), 2.63 (1H, d, $J = 2.2$ Hz), 2.42 (1H, dd, $J = 2.2, 13.5$ Hz). ^{13}C NMR: δ 137.0, 134.0 [d, $J(\text{CP}) = 10.7$ Hz], 133.8, 132.9, 130.6 [d, $J(\text{CP}) = 2.3$ Hz], 129.7, 128.35 [d, $J(\text{CP}) = 10.3$ Hz], 128.3, 128.1, 118.0 [d, $J(\text{CP}) = 3.1$ Hz], 112.7 [d, $J(\text{CP}) = 3.1$ Hz], 89.0 [d, $J(\text{CP}) = 1.1$ Hz], 87.6, 73.4, 69.2, 26.8 [d, $J(\text{CP}) = 3.1$ Hz]. ^{31}P NMR: δ 49.8. ES-MS (m/z): 1287, $[\text{2M} + \text{Na}]^+$; 655, $[\text{M} + \text{Na}]^+$.

7.10. Reaction of **11** with $\text{RuCl}(\text{dppe})\text{Cp}/\text{TBAF}$

A solution of **11** (50 mg, 0.06 mmol) in thf (6 mL) was cooled to 0 °C under N_2 . TBAF (1 M in thf, 0.06 mL, 0.06 mmol) was added dropwise and the solution was stirred at 0 °C for 40 min, at which point t.l.c. indicated complete desilylation. $\text{RuCl}(\text{dppe})\text{Cp}$ (38 mg, 0.06 mmol) and NaBPh_4 (24 mg, 0.07 mmol) were added, the solution was warmed to 50 °C and stirred for 21 h. After cooling, the mixture was concentrated under vacuum. Preparative TLC (silica; acetone-hexane, 1/3) afforded binuclear complex **19** as a yellow-orange solid (46 mg, 61%). Anal. Calc. for $\text{C}_{68}\text{H}_{55}\text{N}_2\text{P}_3\text{Ru}_2$: C, 68.33; H, 4.64; N, 2.34; M, 1196. Found: C, 68.27; H, 4.69; N, 2.35%. IR (Nujol, cm^{-1}): ν_{max} 3296w, 3053w, 2213s, 1578s, 1571s, 1433s, 1091s, 814m, 744s, 696vs. ^1H NMR: δ 7.15–7.86 (40H, m), 4.59 (5H, s), 4.52 (2H, s), 3.79 (1H, br s), 2.63 (3H, s), 2.41 (2H, dd, $J = 2.2, 13.5$ Hz), 2.17 (3H, s), 1.67 (1H, br s). ^{13}C NMR: δ 210.6, 141.7, 141.0 [d, $J(\text{CP}) = 20.2$ Hz], 137.0, 135.3, 134.8, 134.4, 133.9, 133.8, 133.7, 132.8, 131.5, 131.4, 131.3, 130.6 [d, $J(\text{CP}) = 2.3$ Hz], 129.7, 129.5, 129.0, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 117.9 [d, $J(\text{CP}) = 3.1$ Hz], 112.7 [d, $J(\text{CP}) = 3.1$ Hz], 89.0 [d, $J(\text{CP}) = 1.1$ Hz], 87.5, 87.3, 79.6 [t, $J(\text{CP}) = 2.3$ Hz], 73.4, 69.5, 69.1, 53.9, 31.7, 29.3, 27.5, 27.1, 26.8, 26.7, 26.6. ^{31}P NMR: δ 78.1 (s, 2P), 49.8 (s, 1P); ES-MS m/z 1197, $[\text{M} + \text{H}]^+$; 565, $[\text{CpRu}(\text{dppe})]^+$.

7.11. Reaction of **11** with $\text{AuCl}(\text{PPh}_3)/\text{TBAF}$

A solution of **11** (79 mg, 0.10 mmol) and $\text{AuCl}(\text{PPh}_3)$ in thf (10 mL) was cooled to 0 °C under N_2 . TBAF (1 M in thf, 0.10 mL, 0.10 mmol) was added dropwise, and the mixture was stirred at 0 °C for 30 min, then at room temperature for 1 h. The mixture was concentrated under vacuum, and preparative t.l.c. of the residue (acetone-hexane, 1/2) afforded ruthenium-gold complex **20** as a yellow solid (98 mg, 90%). Anal. Calc. for $\text{C}_{55}\text{H}_{41}\text{N}_2\text{AuP}_2\text{Ru}$: C, 60.61; H, 3.79; N, 2.57; M, 1090. Found: C, 60.54; H, 3.81; N, 2.60%. IR (cm^{-1}): ν_{max} 3056w, 2249w, 2213vs, 1568s, 1436vs, 1184m, 1101s, 1091s, 998m, 910s, 814m, 732vs, 694vs, 644m, 625m, 615m. ^1H NMR: δ 7.85–7.88 (2H, m), 7.19–7.66 (33H, m), 4.55 (5H, s), 2.70 (1H, d, $J = 13.5$ Hz); ^{13}C NMR: δ 137.9, 134.2 [d, $J(\text{CP}) = 13.7$ Hz], 134.0, 131.6, 130.2 [d, $J(\text{CP}) = 2.3$ Hz], 129.7, 129.1 [d, $J(\text{CP}) = 11.5$ Hz], 128.1 [d, $J(\text{CP}) = 10.0$ Hz], 127.9, 127.7, 118.5 [d, $J(\text{CP}) = 2.9$ Hz], 113.2 [d, $J(\text{CP}) = 2.9$ Hz], 88.9 [d, $J(\text{CP}) = 1.1$ Hz], 78.3 [d, $J(\text{CP}) = 8.0$ Hz], 68.3, 31.4. ^{31}P NMR: δ 50.3 (1P, s), 40.7 (1P, br s). ES-MS (MeOH, m/z): 1549, $[\text{M} + \text{Au}(\text{PPh}_3)]^+$; 1113, $[\text{M} + \text{Na}]^+$; 721, $[\text{Au}(\text{PPh}_3)_2]^+$; 500, $[\text{Au}(\text{PPh}_3)(\text{MeOH})]^+$.

7.12. Structure determinations

Full spheres of diffraction data were measured using CCD area-detector instruments. N_{tot} reflections were merged to N unique (R_{int} cited) after “empirical”/ multiscan absorption correction (proprietary software) and used in the full matrix least squares refinements on F^2 ; N_o with $I > 2\sigma(I)$ were considered ‘observed’. All data were measured using monochromatic Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, ($x, y, z, U_{\text{iso}}\text{H}$) being included following a riding model [reflection weights: $(\sigma^2(F^2) + (aP)^2 + (bP)^2)^{-1}$, $P = (F_o^2 + 2F_c^2)/3$]. Neutral atom complex scattering factors were used; computation used the SHELXL-97 program [26]. Pertinent results are given in the figures (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids and hydrogen atoms with arbitrary radii of 0.1 Å) and in Tables 1 and 2.

Variata. **7**. The CPh group and one phenyl ring of the dppe are disordered over pairs of sites, seemingly concerted; occupancies set at 0.5 after trial refinement.

17. In molecule **2**, the SiPr_3 group was modelled as disordered over a pair of sites, occupancies refining to 0.645(5) and complement. The dichloromethane solvent lies close to an inversion centre and was modelled in terms of a pair of components, occupancies 0.25; geometries of the minor substrate component and solvent were constrained in the refinement.

Acknowledgements

We thank Professor Brian Nicholson (University of Waikato, Hamilton, New Zealand) for providing some of the mass spectra, the ARC for support of this work and Johnson Matthey plc, Reading, for a generous loan of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$.

Appendix A. Supplementary material

CCDC 687316, 687317, 687318, 687319 and 687320 contain 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 data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.07.006](https://doi.org/10.1016/j.jorganchem.2008.07.006).

References

- [1] (a) A. Davison, J.P. Solar, *J. Organomet. Chem.* 166 (1979) C13;
(b) M.I. Bruce, D.N. Duffy, M.J. Liddell, M.R. Snow, E.R.T. Tiekink, *J. Organomet. Chem.* 335 (1987) 365.
- [2] (a) M.I. Bruce, J.R. Rodgers, M.R. Snow, A.G. Swincer, *Chem. Commun.* (1981) 271;
(b) M.I. Bruce, T.W. Hambley, M.R. Snow, A.G. Swincer, *Organometallics* 4 (1985) 494;
(c) M.I. Bruce, T.W. Hambley, M.R. Snow, A.G. Swincer, *Organometallics* 4 (1985) 501;
(d) M.I. Bruce, M.P. Cifuentes, M.R. Snow, E.R.T. Tiekink, *J. Organomet. Chem.* 359 (1989) 379.
- [3] (a) M.I. Bruce, M.J. Liddell, M.R. Snow, E.R.T. Tiekink, *Organometallics* 7 (1988) 343;
(b) M.I. Bruce, T.W. Hambley, M.J. Liddell, M.R. Snow, A.G. Swincer, E.R.T. Tiekink, *Organometallics* 9 (1990) 96;
(c) M.I. Bruce, T.W. Hambley, M.J. Liddell, A.G. Swincer, E.R.T. Tiekink, *Organometallics* 9 (1990) 2886.
- [4] D.J. Armitt, M.I. Bruce, B.W. Skelton, A.H. White, *Organometallics* 27 (2008) 3556.
- [5] (a) M.I. Bruce, B.C. Hall, B.D. Kelly, P.J. Low, B.W. Skelton, A.H. White, *J. Chem. Soc., Dalton Trans.* (1999) 3719;
(b) M.I. Bruce, F. de Montigny, M. Jevric, C. Lapinte, B.W. Skelton, M.E. Smith, A.H. White, *J. Organomet. Chem.* 689 (2004) 2860;
(c) M.I. Bruce, P.A. Humphrey, M. Jevric, B.W. Skelton, A.H. White, *J. Organomet. Chem.* 692 (2007) 2564.
- [6] T. Michinobu, C. Boudon, J.-P. Gisselbrecht, P. Seiler, B. Frank, N.N.P. Moonen, M. Gross, F. Diederich, *Chem. Eur. J.* 12 (2006) 1889.
- [7] N.N.P. Moonen, W.C. Pomerantz, R. Gist, C. Boudon, J.-P. Gisselbrecht, T. Kawai, A. Kishioka, M. Gross, M. Irie, F. Diederich, *Chem. Eur. J.* 11 (2005) 3325.
- [8] I. Fernandez, G. Frenking, *Chem. Commun.* (2006) 5030.
- [9] (a) H. Hopf, M. Kreutzer, P.G. Jones, *Angew. Chem.* 103 (1991) 1148;
(b) *Angew. Chem., Int. Ed. Engl.* 30 (1991) 1127.
- [10] (a) N.R. Spreiter, C. Bosshard, G. Knopfle, P. Gunter, R.R. Tykwinski, M. Schreiber, F. Diederich, *J. Phys. Chem. B* 102 (1998) 29;
(b) R.R. Tykwinski, U. Gubler, R.E. Martin, F. Diederich, C. Bosshard, P. Gunter, *J. Phys. Chem. B* 102 (1998) 4451.
- [11] (a) U. Gubler, R. Spreiter, C. Bosshard, P. Gunter, R. Tykwinski, F. Diederich, *Appl. Phys. Lett.* 73 (1998) 2396;
(b) U. Gubler, C. Bosshard, *Adv. Polym. Sci.* 158 (2002) 123.
- [12] (a) Y. Rubin, C.B. Knobler, F. Diederich, *Angew. Chem.* 103 (1991) 708;
(b) *Angew. Chem., Int. Ed. Engl.* 30 (1991) 698.
- [13] H. Hopf, M. Kreutzer, P.G. Jones, *Chem. Ber.* 124 (1991) 1471.
- [14] O.F. Koentjoro, P. Zuber, H. Puschmann, A.E. Goeta, J.A.K. Howard, P.J. Low, *J. Organomet. Chem.* 670 (2003) 178.
- [15] M.I. Bruce, N.N. Zaitseva, P.J. Low, B.W. Skelton, A.H. White, *J. Organomet. Chem.* 691 (2006) 4273.
- [16] (a) M.I. Bruce, G.A. Koutsantonis, *Aust. J. Chem.* 44 (1991) 207;
(b) L. Dahlenburg, A. Weis, M. Moll, *J. Organomet. Chem.* 535 (1997) 195.
- [17] M.I. Bruce, B.G. Ellis, M. Gaudio, C. Lapinte, G. Melino, F. Paul, B.W. Skelton, M.E. Smith, L. Toupet, A.H. White, *Dalton Trans.* (2004) 1601.
- [18] M.I. Bruce, J.-F. Halet, B. Le Guennic, B.W. Skelton, M.E. Smith, A.H. White, *Inorg. Chim. Acta* 350 (2003) 175.
- [19] M.I. Bruce, K.A. Kramarczuk, N.N. Zaitseva, B.W. Skelton, A.H. White, *J. Organomet. Chem.* 690 (2005) 1549.
- [20] A.I. Borisova, N.S. Vyazankin, A.S. Medvedeva, I.D. Kalikhnan, *Zh. Obshch. Khim.* 48 (1978) 2800.
- [21] C. Yi, C. Blum, S.-X. Liu, G. Frei, A. Neels, P. Renaud, S. Leutwyler, S. Decurtins, *J. Org. Chem.* 73 (2008) 3596.
- [22] W. Henderson, J.S. McIndoe, B.K. Nicholson, P.J. Dyson, *J. Chem. Soc., Dalton Trans.* (1998) 519.
- [23] M.I. Bruce, C. Hameister, A.G. Swincer, R.C. Wallis, *Inorg. Synth.* 21 (1982) 78.
- [24] M.I. Bruce, B.C. Hall, B.D. Kelly, P.J. Low, B.W. Skelton, A.H. White, *Dalton Trans.* (1999) 3719.
- [25] J.D. Tovar, N. Jux, T. Jarrossan, S.I. Khan, Y. Rubin, *J. Org. Chem.* 62 (1997) 3433.
- [26] G.M. Sheldrick, SHELXL-97, A Program for Crystal Structure Refinement, University of Göttingen, 1997.