Journal of Organometallic Chemistry 696 (2011) 461–467

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Communication

Dimerisation and reactivity of $HC{\equiv}CC{\equiv}CFc$ at ruthenium centres

Michael I. Bruce [a,*], Martyn Jevric [a], Brian W. Skelton [b], Allan H. White [b]

[a] *School of Chemistry & Physics, University of Adelaide, Adelaide, South Australia 5005, Australia*
[b] *Chemistry M313, SBSSC, University of Western Australia, Crawley, Western Australia 6009, Australia*

ARTICLE INFO

Article history:
Received 22 April 2010
Received in revised form
17 September 2010
Accepted 17 September 2010
Available online 25 September 2010

Keywords:
Ferrocene
Ruthenium
Diyne
Dimerisation
Crystal structure

ABSTRACT

In contrast to the simple diynyl complexes formed in reactions between $HC{\equiv}CC{\equiv}CFc$ and $MCl(dppe)Cp^*$; ($M = Fe, Ru$), an analogous reaction with $RuCl(PPh_3)_2Cp^*$; in the presence of KPF_6 and dbu resulted in dimerisation of the diyne at the Ru centre to afford a mixture of $[Ru\{\eta^1,\eta^2\text{-}C(C{\equiv}CFc){=}C(L)CH{=}CC{=}CHFc\}(PPh_3)Cp^*]PF_6$ ($L = $ dbu **1**, PPh_3 **2**). Similar reactions with $RuCl(PR_3)_2L$ gave $[Ru\{\eta^1,\eta^2\text{-}C(C{\equiv}CFc){=}C(dbu)CH{=}CC{=}CHFc\}(PR_3)L]PF_6$ ($L = Cp$, $R = Ph$ **3**, *m*-tol **4**; $L = \eta^5\text{-}C_9H_7$, $R = Ph$ **5**). The reaction between **3** and I_2, followed by crystallization of the paramagnetic product from MeOH, afforded the dicationic $[Ru\{C(C{\equiv}CFc)C(dbu)CH{=}C(OMe)C(OMe){=}CHFc\}(PPh_3)Cp](I_3)_2$ **6**. The molecular structures of **2**$\cdot 2CH_2Cl_2$ and **6**.S ($S = 2CH_2Cl_2$, C_6H_6) were determined by single-crystal XRD studies.

1. Introduction

As a continuation of our studies of Group 8 complexes containing di- and poly-ynyl ligands [2], we earlier described the synthesis and some reactions of the complexes $Ru(C{\equiv}CC{\equiv}CFc)(dppx)Cp$ ($x = m$, e) [1]. The syntheses followed precedent by reacting $FcC{\equiv}CC{\equiv}CSiMe_3$ with $RuCl(dppx)Cp$ in the presence of KPF_6 in thf/dbu (dbu = 1,8-diazabicyclo[5.4.0]undec-7-ene) to give these complexes in 28 and 57% yields, respectively. During these studies, there was no evidence for the formation of any other product. However, when a ruthenium precursor containing a more labile monodentate phosphine ligand, namely $RuCl(PPh_3)_2Cp^*$, reacted with $FcC{\equiv}CC{\equiv}CH$, the reaction took a different course, resulting in the formal dimerisation of the diyne and subsequent reaction with nucleophiles present in the reaction mixture. Similar products were obtained with $P(m\text{-tol})_3$ or η^5-indenyl and Cp ligands. These studies are described below.

2. Results

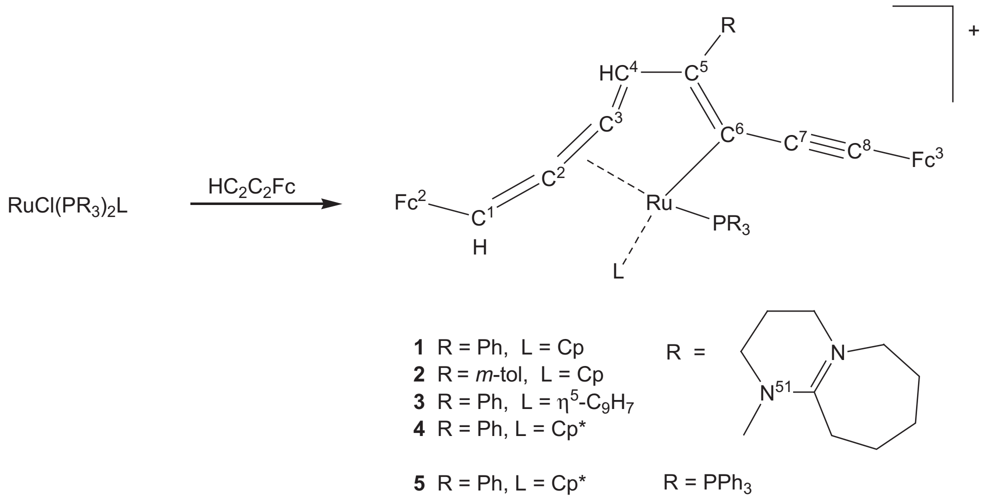
The reaction between $FcC{\equiv}CC{\equiv}CH$ and $RuCl(PPh_3)_2Cp^*$ was carried out in refluxing thf in the presence of KPF_6 (to encourage dissociation of the chloride) and dbu (as base) to afford a mixture of two complexes, which could be separated by preparative t.l.c. to give $[Ru\{\eta^1,\eta^2\text{-}C(C{\equiv}CFc){=}C(X)CH{=}CC{=}CHFc\}(PPh_3)Cp^*]PF_6$ [$X = $ dbu **1** (78%), PPh_3 **2** (14%)] (Scheme 1) as red and purple solids, respectively. Spectroscopic properties of **1** and **2** included weak $\nu(C{\equiv}C)$ and $\nu(C{=}C{=}C)$ bands at 2155 and 1778 (for **1**) and 2129 and 1881, 1782 cm^{-1} (for **2**). For **1**, resonances for the $Ru(PPh_3)Cp^*$ moiety were found at δ_H 1.33, δ_C 9.21, 98.41 ($Ru{-}Cp^*$) and δ_P 51.5, with singlets for the Fe–Cp group at δ_H 1.39, ca 4.3, δ_C 70.61, 70.75. Several signals between δ_H 1.42 and 3.70 and δ_C 20.85 and 72.04 were assigned to the dbu fragment. For **2**, signals at δ_H 1.36 and 4.07, 4.60 ($2 \times$ Fe–Cp), δ_C 6.76, 101.42 ($Ru{-}Cp^*$) and two singlets at δ_P 0.95, 25.8 ($2 \times PPh_3$) were present; the spectra were simplified by the absence of the dbu resonances in this case. In the electrospray mass spectrum (ES-MS), molecular cations were found at m/z 1119 (**1**) and 1229 (**2**). The molecular structure of **2** was determined from a single-crystal XRD study (see below).

The reaction between $RuCl(PPh_3)_2Cp$ and an excess of $FcC{\equiv}CC{\equiv}CH$ was carried out in a similar manner to that described above. Conventional work-up and final purification by preparative t.l.c. and recrystallisation from acetone–dichloromethane gave maroon $[Ru\{\eta^1,\eta^2\text{-}C(C{\equiv}CFc){=}C(dbu)CH{=}CC{=}CHFc\}(PPh_3)Cp]PF_6$ **3** (Scheme 1). The ^1H NMR spectrum contained resonances at δ 1.43 and 3.96 ($2 \times$ Cp–Fe), together with several signals between δ 1.49–2.79 (from dbu), 3.30–4.67 ($C_5H_4 + Ru{-}Cp$), 6.06–6.49 (3H on C_8 chain), and 7.00–7.80 (Ph). It was not possible to find the resonances of the vinylic protons, which were probably masked by the aromatic proton signals. Among the plethora of signals in the ^{13}C NMR spectrum, those at δ 70.00, 70.07 ($2 \times$ Cp–Fe) and 91.49 (Cp–Ru) were readily assigned. The ^{31}P NMR spectrum contained

---

[*] Corresponding author. Fax: +61 8 8303 4358.
E-mail address: michael.bruce@adelaide.edu.au (M.I. Bruce).

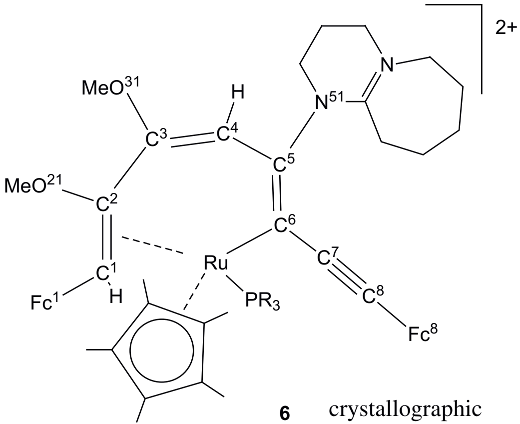
0022-328X/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2010.09.035



Scheme 1.

a singlet at δ 26.2 (PPh$_3$) and a septet at δ −142.2 (PF$_6$). The molecular cation was found at *m*/*z* 1049 in the ES-MS. Similar complexes **4** (62%) and **5** (50%) were obtained from analogous reactions of FcC≡CC≡CH with RuCl{P(*m*-tol)$_3$}$_2$Cp and RuCl(PPh$_3$)$_2$(η^5-C$_9$H$_7$), respectively, and were characterised by microanalysis and the usual spectroscopic methods, including ES-MS (molecular cations at *m*/*z* 1091, 1099, respectively). The resonances of these complexes were quite broad, possibly due to ring flips of the dbu substituent.

Prior to crystallographic characterisation, some reactions of **3** were carried out to obtain further evidence for the structure. Among these, a reaction between **3** and diiodine in thf afforded a brown paramagnetic solid for which an acceptable microanalysis for an I$_7$ salt was obtained, but no useful structural information was forthcoming from spectroscopic data. However, recrystallisation of this complex from MeOH afforded the dicationic salt [Ru{η^1,η^2-C(C≡CFc)C(dbu)CH=C(OMe)C(OMe)=CHFc}(PPh$_3$)Cp*](I$_3$)$_2$ **6**, as revealed by single-crystal XRD structure determinations of its CH$_2$Cl$_2$ and C$_6$H$_6$ solvates. Microanalysis and the ES-MS supported this formulation, with ions at *m*/*z* 1111 (M$^+$), 849 ([M − PPh$_3$]$^+$) and 697 ([M − PPh$_3$ − dbu]$^+$).



6 crystallographic numbering

2.1. Molecular structures

Fig. 1 is a plot of the cation of **2**; selected structural parameters are listed in Table 1.The usual Ru(PPh$_3$)Cp* moieties [Ru–P, 2.3155(5) Å] and Ru–C(cp) [av. 2.28(5) Å] are η^1, η^2-coordinated to the C$_8$ ligand by C(6) and C(2,3) [2.112(2), 2.136, 2.056(2) Å]. Angles P(1)–Ru–C(*n*) [*n* = 6, mid-point of C(2)–C(3)] are 90.32(5), 98.6°, and C(6)-Ru-C(2/3) are 92.3°. Along the carbon chain, the C–C separations are consistent with the structure as shown, with the C(7)–C(8) triple bond [1.215(3) Å] and the C(2)–C(3) separation [1.342(3) Å] being as expected for a coordinated C=C double bond. The Fe–C(cp) bonds for Fe(2) [av. 2.051(9) Å] and for Fe(3) [av. 2.046(7) Å] are similar.

The structure of the dication in **6** (Fig. 2, selected bond parameters in Table 1) is closely related to that of the monocation in **2**, with the exceptions of replacement of PPh$_3$ by dbu, introduction of the OMe groups on C(2) and C(3), and the coordination of C(1)–C(2)

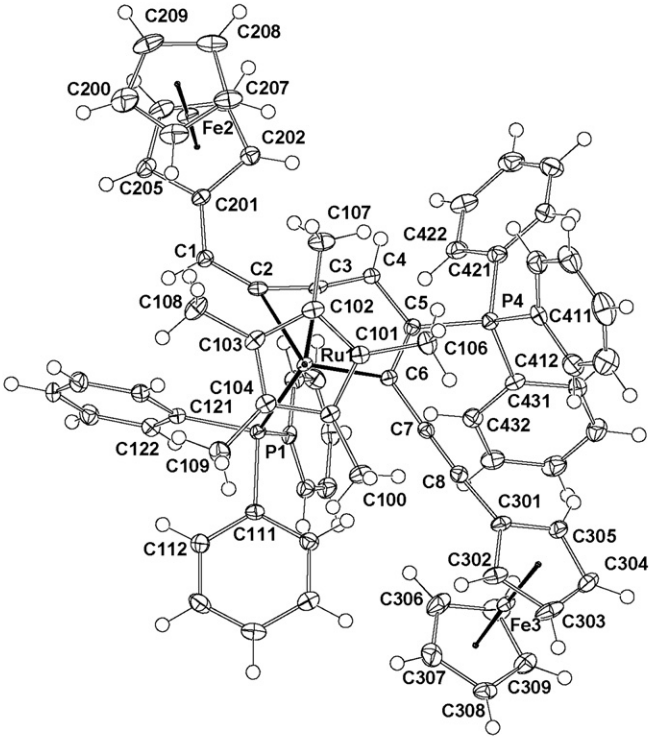


Fig. 1. Plot of the cation in [Ru{η^1,η^2-C(C≡CFc)=C(dbu)CH=CC=CHFc}(PPh$_3$)Cp*]PF$_6$ **2**.

to ruthenium [2.209(3), 2.184(3) Å]; Ru–C(6) [2.114(3) Å] is experimentally identical to that in **2** [2.112(2) Å].

There is a small but significant difference in the average Fe–C (cp) distances [Fe(2)–C(cp) 2.08(2), Fe(3)–C(cp) 2.042(8) Å] which is of interest in respect of the site of oxidation. This suggests that the former may be a ferrocenium cation, by virtue of (a) a comparison with the Fe–C distances in the ferrocenium cation in $[FeCp_2]BF_4$ [2.095 Å] [3], and (b) the similarity of the Fe(1)–Cp distances in **6** [Fe(2) 2.052, Fe(3) 2.044 Å] to those found in ferrocene itself [2.064(1) Å in the solid state [4], 2.056(2) Å in the vapour phase [5]]. However, some caution should be expressed, since accurate values for changes in the Fe–C(cp) distances can be affected by libration of the Cp ligands and any asymmetry in their coordination. Geiger, Ernst and their coworkers have suggested that "an oxidative lengthening of ca 0.04 Å seems reasonable, based upon structural data obtained for $Fe(\eta\text{-}C_5H_4SiMe_3)_2$ and its cation" [6,7]. The longer distances found in the cation could relate to the reduced back-bonding from Fe to the ring as a result of the positive charge on the metal.

Table 1
Selected bond parameters for **2**$\cdot 2CH_2Cl_2$ and **6**$\cdot 2CH_2Cl_2$.

Complex	**2**$\cdot 2CH_2Cl_2$	**6**$\cdot 2CH_2Cl_2$
Bond distances (Å)		
Fe(2)–C(cp)	2.047–2.069(3), 2.036–2.059(3)	2.027–2.178(4), 2.063–2.113(4)
(av.)	2.052, 2.050(10)	2.08, 2.09(2)
Fe(3)–C(cp)	2.035–2.058(3), 2.039–2.045(5)	2.036–2.052(4), 2.034–2.053(4)
(av.)	2.046(9), 2.046(5)	2.042, 2.045(8)
Ru(1)–C(cp)	2.232–2.343(2)	2.215–2.293(3)
(av.)	2.28(5)	2.25(3)
Ru(1)–P(1)	2.3155(5)	2.3429(9)
Ru(1)–C(2)	2.136(2)	2.184(3)
Ru(1)–C(3)	2.056(2)	2.209(3) [C(1)]
Ru(1)–C(6)	2.112(2)	2.114(3)
P(1)–C(Ph)	1.837, 1.825, 1.828(2)	
P(2)–C(5)	1.788(2)	
P(2)–C(Ph)	1.807, 1.798, 1.797(2)	1.833, 1.848, 1.838(4)
C(1)–C(201)	1.458(3)	1.467(5) [C(101)]
C(1)–C(2)	1.340(3)	1.425(4)
C(2)–C(3)	1.342(3)	1.487(4)
C(3)–C(4)	1.350(3)	1.333(6)
C(4)–C(5)	1.442(3)	1.445(5)
C(5)–C(6)	1.395(3)	1.365(4)
C(6)–C(7)	1.408(3)	1.422(5)
C(7)–C(8)	1.215(3)	1.208(5)
C(8)–C(801)	1.415(3)	1.436(5)
Bond angles (°)		
P(1)–Ru(1)–C(2)	91.80(5)	88.85(9) [C(1)]
P(1)–Ru(1)–C(3)	104.24(5)	110.12(9) [C(2)]
P(1)–Ru(1)–C(6)	90.32(5)	87.07(9)
Ru(1)–C(6)–C(5)	116.0(1)	128.6(2)
Ru(1)–C(6)–C(7)	124.7(1)	116.4(2)
P(1)–C(5)–C(4)	120.9(1)	113.7(3) [N(51)]
P(1)–C(5)–C(6)	123.4(1)	118.7(3) [N(51)]
C(201)–C(1)–C(2)	122.2(2)	124.0(3)
C(1)–C(2)–C(3)	145.1(2)	117.5(3)
C(2)–C(3)–C(4)	160.7(2)	126.3(3)
C(3)–C(4)–C(5)	111.2(2)	122.1(3)
C(4)–C(5)–C(6)	115.1(2)	127.4(3)
C(5)–C(6)–C(7)	118.7(2)	114.9(3)
C(6)–C(7)–C(8)	177.8(2)	177.5(4)
C(7)–C(8)–C(401)	175.8(3)	176.3(4)

For **6**: C(2)–O(2) 1.415(4), C(3)–O(3) 1.387(4) Å; C(1,3)–C(2)–O(2) 114.1(3), 111.5(3), C(2,4)–C(3)–O(3) 109.4(2), 124.3(3)°.

3. Discussion

The dimerisation of $FcC{\equiv}CC{\equiv}CH$ at the Ru centre contrasts with the earlier results obtained when RuCl(dppx)Cp (x = m, e), which contain a chelating diphosphine, was used, and can be rationalised by the facile loss of a bulky PR_3 ligand to generate a 16-e Ru centre. Extensive work by Kirchner [8] has shown that ready dimerisation of alkynes occurs via ruthenacyclopentatriene (dicarbene) intermediates, which undergo ready nucleophilic attack, e.g., by coordinated PPh_3, or by exterior nucleophiles (Scheme 2). In these studies, examples of complexes containing allyl- (**A**), butadienyl- (**B**) and allenyl-carbene (**C**) ligands were found. Some related work using RuCl(cod)Cp* as precursor has resulted in the formation of some binuclear derivatives which incorporated the alkyne and the cod ligand [9].

The formation of the products obtained from the reactions described above requires dissociation of chloride, which is a well-established reaction in the $Ru(PR_3)_2Cp$ series. This probably occurs after initial coordination of the first molecule of diyne and its isomerisation to a butatrienylidene intermediate. While the latter have

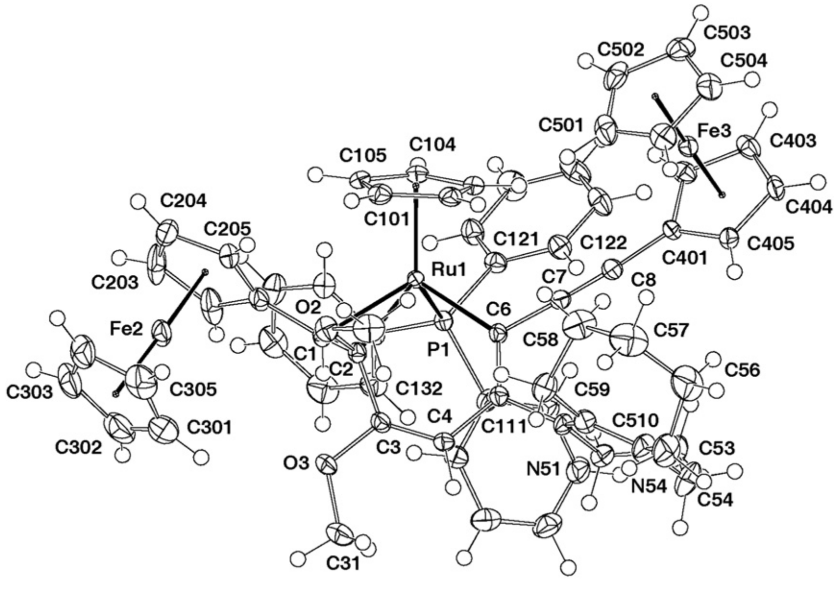
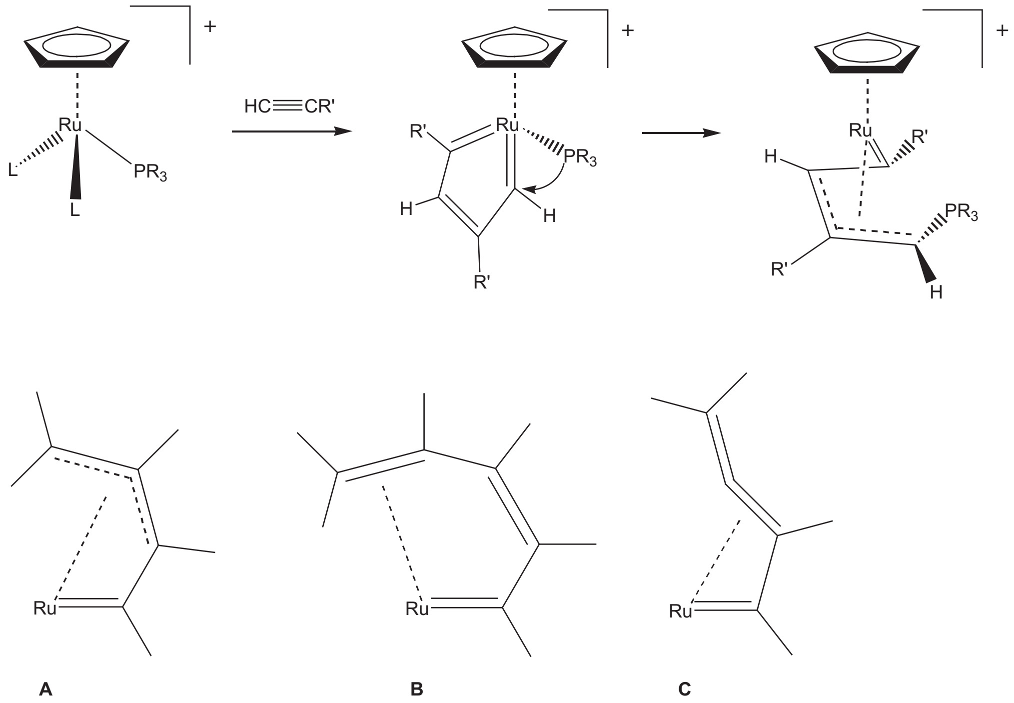


Fig. 2. Plot of the dication in $[Ru\{\eta^1,\eta^2\text{-}C(C{\equiv}CFc)C(dbu)CH{=}C(OMe)C(OMe){=}CHFc\}(PPh_3)Cp](I_3)_2$ **6**.

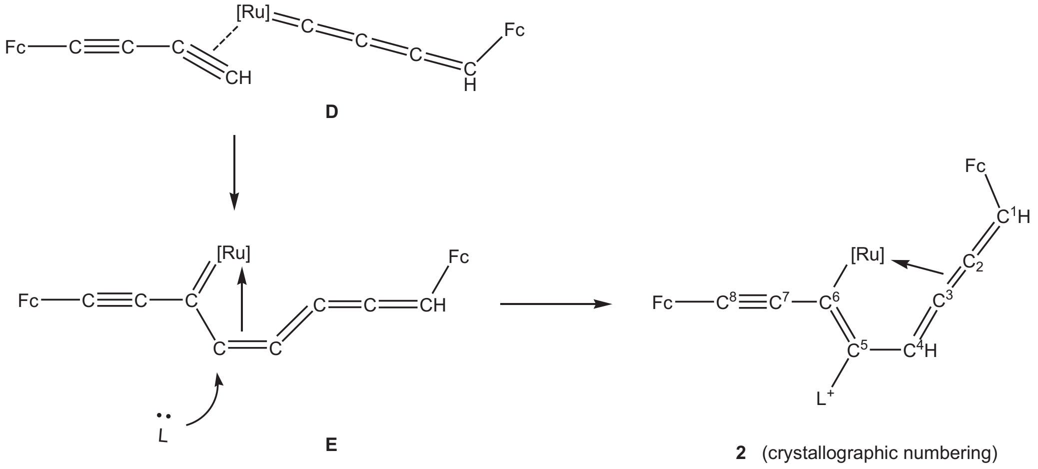


Scheme 2.

been postulated as intermediates in several examples of ruthenium chemistry [10,11], they have not been isolated or characterised in the Ru(PP)Cp series. Rare examples have been obtained with Groups 6 [12], 7 [13] and IrCl(PP) centres [14] and metallabutatrienylidene–iron complexes have been described by Lapinte [15]. Here, coordination of a second molecule of the diyne and dissociation of one PR$_3$ ligand would afford intermediate **D**, which rapidly evolves by coupling of the alkyne and trienylidene ligands to give an η^1,η^2-cumulenylcarbene **E**, for which high reactivity would be expected (Scheme 3). Related reactions have been observed with ethynylmetallocenes [8b,16]. Subsequent attack of the central carbon by the earlier displaced PPh$_3$, would afford the isolated product **3**. When the more bulky Cp* ligand is present, competing attack at the same site by dbu, present in solution as a base to remove the proton expected to be released in formation of the desired diynyl complex, and by PPh$_3$ affords a mixture of the two complexes **1** and **2**.

We were interested to study the oxidation of **3**, in particular to determine whether the electron would be lost from the electron-rich Ru centre, or from one of the Fc nuclei. Addition of I$_2$ to **3** afforded an intractable brown material which did, however, give an X-ray quality single crystals from MeOH. The structural determination revealed that the product was the bis-triiodide salt of a new dication, $[Ru\{C(C{\equiv}CFc)C(dbu)CH{=}C(OMe)C(OMe){=}CHFc\}(PPh_3)Cp](I_3)_2$ **6**. The precise mode of formation of **6** is not clear, formal double addition of methoxide to two adjacent carbons of one C=C double bond having occurred. While the double addition is unlikely to occur simultaneously at both carbons of an η^2-C=C system, migration of the metal centre along the unsaturated chain may allow attack by the second MeO group to give the observed product containing the C(OMe)C(OMe) group shown.

Of interest is the difference in structural parameters shown by the two ferrocene nuclei. Thus, the Fe(3)–C(cp) separations may be



Scheme 3.

Table 2
Crystal data and refinement details for **6**·$2CH_2Cl_2$, **2**·$2C_6H_6$ and **2**·$2CH_2Cl_2$.

Complex	**6**·$2CH_2Cl_2$	**2**·$2C_6H_6$	**2**·$2CH_2Cl_2$
Formula	$C_{62}H_{62}Fe_2N_2O_2PRu^{2+}\cdot 2I_3^-\cdot 2CH_2Cl_2$	$C_{74}H_{65}Fe_2P_2Ru^+\cdot F_6P^-\cdot 2C_6H_6$	$C_{74}H_{65}Fe_2P_2Ru^+\cdot F_6P^-\cdot 2CH_2Cl_2$
MW	2042.1	1530.2	1543.8
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	21.506(3)	14.408(7)	14.5903(9)
b/Å	12.451(2)	16.047(8)	15.651(1)
c/Å	26.608(4)	17.079(8)	16.788(1)
α/deg.		74.298(9)	74.863(2)
β/deg.	106.618(4)	74.629(9)	72.408(2)
γ/deg.		71.060(9)	69.811(2)
V/Å^3	6827(2)	3527(3)	3376.7(4)
ρ_c/g cm^{-3}	1.98_7	1.44_1	1.51_8
Z	4	2	2
$2\theta_{max}$/deg.	70	45	75
μ(Mo Kα)/mm^{-1}	3.6	0.75	0.94
$T_{min/max}$	0.72	0.70	0.90
Crystal dimensions/mm^3	0.27 × 0.15 × 0.07	0.11 × 0.06 × 0.04	0.21 × 0.17 × 0.13
N_{tot}	125549	25863	66534
N (R_{int})	30045 (0.060)	12196 (0.14)	33110 (0.046)
N_o	18297	5468	24670
$R1$	0.046	0.17	0.046
$wR2$ (a, b)	0.14 (0.078, −)	0.38 (0, 18.4)	0.15 (0.058, 4.6)

Variata. In **6**, one of the triiodide ions was modeled as disordered over two sets of sites, occupancies 0.8296(3) and complement. The two solvates of **2** are isomorphous.

somewhat shorter than Fe(2)–C(cp) bonds, suggesting that the former is an Fe(III) or ferrocenium centre, thus providing a potential answer to the mode of oxidation of the initial complex, i.e., at the ferrocene centre.

4. Conclusion

The chemistry described above is consistent with that found earlier for alkynes at similar Ru centres bearing monodentate phosphine ligands studied earlier, with a characteristic dimerisation of the alkyne, usually with incorporation of a tertiary phosphine ligand. In contrast, under similar reaction conditions, the diyne forms a simple diynyl–ruthenium complex if bidentate phosphine, such as dppe, is present, because dissociation to give a vacant coordination site is precluded.

5. Experimental

5.1. 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 × 20 cm^2) coated with silica gel (Merck, 0.5 mm thick).

5.2. Instruments

IR spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in CH_2Cl_2 were obtained using a 0.5 mm path-length solution cell with NaCl windows. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra were recorded on a Varian Gemini 2000 instrument (^{1}H at 300.145 MHz, ^{13}C at 75.479 MHz, ^{31}P at 121.501 MHz). Unless otherwise stated, samples were dissolved in $CDCl_3$ contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ^{1}H and ^{13}C NMR spectra and external H_3PO_4 for ^{31}P NMR spectra. UV–vis spectra were recorded on a Varian Cary 5 UV–vis/NIR spectrometer. Electrospray mass spectra (ES-MS) were obtained from samples dissolved in MeOH unless otherwise indicated. Solutions were injected into a Varian Platform II spectrometer via a 10 ml injection loop. Nitrogen was used as the drying and nebulising gas. Chemical aids to ionisation were used as required [17]. Electrochemical samples (1 mM) were dissolved in CH_2Cl_2 containing 0.5 M $[NBu_4]BF_4$ as the supporting electrolyte for the spectro-electrochemical experiments. Cyclic voltammograms were recorded using a PAR model 263 apparatus, with a saturated calomel electrode, with ferrocene as internal calibrant ($FeCp_2/[FeCp_2]^+ = +0.46$ V vs SCE). A 1 mm path-length cell was used with a Pt-mesh working electrode, Pt wire counter and pseudo-reference electrodes. Elemental analyses were by Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand.

5.3. Reagents

Complexes $RuCl(PPh_3)_2L$ (L = Cp [18], Cp* [19], η^5-C_9H_7 [20]), RuCl{P(m-tol)$_3$}$_2$Cp (as for the PPh_3 complex) and FcC≡CC≡CH [21] were obtained as previously described.

5.4. Reaction between HC≡CC≡CFc and $RuCl(PPh_3)_2Cp^*$

A similar reaction between $RuCl(PPh_3)_2Cp^*$ (102 mg, 0.128 mmol), HC≡CC≡CFc (73 mg, 0.312 mmol), KPF_6 (108 mg, 0.59 mmol) and dbu (5 drops) in refluxing thf (20 ml) gave two products contained in a broad maroon band, containing [Ru{C(C≡CFc)=C(dbu)CH=C=C=CHFc}(PPh_3)Cp*]PF_6 **1** (red solid, 126 mg, 78%) running below a broad blue band, containing [Ru{C(C≡CFc)=C(PPh_3)CH=C=C=CHFc}(PPh_3)Cp*]PF_6 **2** (purple solid, 25 mg, 14%).

5.4.1. [Ru{C(C≡CFc)=C(dbu)CH=C=C=CHFc}(PPh_3)Cp*]PF_6 *1*

Anal. Calcd ($C_{65}H_{66}F_6Fe_2N_2P_2Ru$): C, 61.77; H, 5.26; N, 2.22; M (cation), 1119. Found: C, 61.72; H, 5.24; N, 2.21. IR (cm^{-1}): ν(C≡C) 2155w, ν(C=C=C) 1778w, ν(C=N) 1615s; 1543w, 1509w, ν(PF) 841s. UV–vis: 409 (1308), 540 (1196). ^{1}H NMR (C_6D_6): δ 1.33 (s, 15H, Ru–Cp*), 1.39 (s, 5H, Fe–Cp), 1.42–1.50 (m, 5H, dbu), 1.63–1.73 (m, 1H, dbu), 1.80–1.82 (m, 1H, dbu), 1.96–2.02 (m, 1H, dbu), 2.08–2.10 (m, 1H, dbu), 2.47–2.51 (m, 1H, dbu), 2.70–2.74 (m, 1H, dbu), 2.88–2.91 (m, 1H, dbu), 3.28–3.32 (m, 1H, dbu), 3.44–3.46 (m, 1H, dbu), 3.65–3.70 (m, 2H, dbu), 4.24–4.31 (m, 12H, incl. s for Fe–Cp), 4.37 (s, 1H, C_5H_4), 4.57 (s, 2H, C_5H_4), 4.80–4.90, 4.95–5.15, 5.60–5.80 (br m, 3H), 6.59 (br, 2H), 7.01–7.15 (m, 2H, Ph), 7.25–7.27 (m, 9H, Ph), 7.54–7.56 (m, 2H, Ph). ^{13}C NMR (C_6D_6): δ 9.21 (Ru–C_5*Me*$_5$), 20.85, 25.07, 26.94, 29.42, 30.33, 48.38, 55.45,65.40–67.20 (br), 67.68 (br), 70.28, 70.54, 70.61, 70.75 (2 × Fe–Cp),71.43, 71.75, 71.90, 72.04, 98.41 (Ru–*C*$_5$Me$_5$), 129.77 (Ph), 130.40 (Ph), 131.59–131.93 (m, Ph), 134.57–135.60 (m, Ph), 166.26. ^{31}P NMR (C_6D_6): δ −141.9 (sept, $J = 712$ Hz, PF_6), 51.5 (br, PPh_3). ES-MS (MeOH, positive ion, *m*/*z*): 1119, M$^+$. Echem: +0.30, +0.61, +1.01 V.

5.4.2. [Ru{C(C≡CFc)=C(PPh$_3$)CH=C=C=CHFc}(PPh$_3$)Cp]PF$_6$* **2**

Anal. Calcd ($C_{74}H_{65}F_6Fe_2P_3Ru$): C, 64.69; H, 4.77; M (cation), 1229. Found: C, 64.66; H, 4.80; N, 2.39. IR (cm^{-1}): ν(C≡C) 2129w, ν(C=C=C) 1881w, 1782w, ν(PF) 840s. UV–vis: 297 (1943), 416 (864), 574 (985). ^{1}H NMR ($CDCl_3$): δ 1.36 (s, 15H, Cp*), 3.53 (s, 2H, C_5H_4), 4.07 (s, 5H, Fe–Cp), 4.14 (s 2H, C_5H_4), 4.35 (s, 2H, C_5H_4), 4.44 (s, 2H, C_5H_4), 4.60 (br s, Fe–Cp), 6.60–6.75 (m, 4H, Ph), 6.85–7.00 (m, 4H, Ph), 7.45–7.76 (m, 22H, Ph). ^{13}C NMR ($CDCl_3$): δ 6.76 (Ru–C_5*Me*$_5$), 69.61 (2 × Fe–Cp), 71.14 (C_5H_4), 71.64 (C_5H_4), 73.76 (C_5H_4), 74.46 (C_5H_4), 77.20, 101.42 (Ru–*C*$_5$Me$_5$), 123.40, 123.96, 127.38, 127.97, 129.25, 129.47–129.56 (m, Ph), 129.92, 130.21, 131.16, 131.40, 133.48–133.55 (m, Ph), 133.35, 133.78–133.80 (m, Ph). ^{31}P NMR ($CDCl_3$): δ −146.2 (sept, $J = 712$ Hz, PF_6), 0.95, 25.8 (2 × s, PPh_3). ES-MS (MeOH, positive ion, *m*/*z*): 1229, M$^+$; 967, [M − PPh_3]$^+$. Echem: +0.37, +0.67, +1.17 V. Crystals from benzene–hexane or CH_2Cl_2–hexane.

5.4.3. Synthesis of [Ru{C(C≡CFc)=C(dbu)CH=C=C=CHFc}(PPh$_3$)Cp]PF$_6$ **3**

A solution containing $RuCl(PPh_3)_2Cp$ (99 mg, 0.136 mmol), HC≡CC≡CFc (78 mg, 0.33 mmol), KPF_6 (135 mg, 0.73 mmol) and dbu (5 drops) in thf (25 ml) was heated at reflux point for 2 h, after which time solvent was removed. The residue was purified by preparative t.l.c. (acetone–CH_2Cl_2, 5/95) to give [Ru{C(C≡CFc)=C(dbu)CH=C=C=CHFc}(PPh_3)Cp]PF_6 **3** as a maroon solid (109 mg, 67%). Anal. Calcd ($C_{60}H_{56}F_6Fe_2N_2P_2Ru$): C, 60.37; H, 4.73; N, 2.35; M (cation), 1049. Found: C, 60.22; H, 4.80; N, 2.39. IR (cm^{-1}): ν(C≡C) 2196w, ν(C=C=C) 1795w, ν(C=C) 1651m, ν(C=N) 1615s; 1586w, 1546w, 1508w, ν(PF) 841s. UV–vis: 396 (866), 536 (670). ^{1}H NMR ($CDCl_3$): δ 1.43 (s, 5H, Fe–Cp), 1.49–2.79 (m, 11H, dbu), 3.30–3.64 (m, 5H, Fe–Cp), 3.79 (s, 1H), 3.90 (s, 1H), 3.96 (s, 5H, Fe–Cp), 4.02 (s, 1H), 4.14–4.67 (m, 12H, incl. Ru–Cp), 6.09–6.49 (br s, 3H), 7.00–7.80 (m, 12H, Ph). ^{13}C NMR: δ 19.99, 23.51, 26.49, 29.07, 29.86, 48.41, 49.08, 55.21, 70.00, 70.07 (2 × Fe–Cp), 70.32, 70.56, 72.70, 73.61, 91.49 (Ru–Cp), 127.95 (Ph), 128.05–128.56 (m), 130.00 (Ph), 130.11, 131.95–132.20 (m), 133.05, 168.04. ^{31}P NMR ($CDCl_3$): δ −142.2 (sept, $J = 712$ Hz, PF_6), 26.2 (s, PPh_3). ES-MS (MeOH, positive ion, *m*/*z*): 1049, M$^+$. Echem: +0.31, +0.58, +0.90 V.

5.4.4. Synthesis of [Ru{C(C≡CFc)=C(dbu)CH=C=C=CHFc}{P(m-tol)$_3$}Cp]PF$_6$ **4**

Similarly, a solution containing RuCl{P(*m*-tol)$_3$}Cp (102 mg, 0.126 mmol), HC≡CC≡CFc (79 mg, 0.34 mmol), KPF_6 (164 mg, 0.89 mmol) and dbu (5 drops) in thf (10 ml) was heated at reflux point for 2 h, [Ru{C(C≡CFc)=C(dbu)CH=C=C=CHFc}{P(*m*-tol)$_3$}Cp]PF_6 **4** was obtained as a maroon solid (97 mg, 62%). Anal. Calcd ($C_{63}H_{62}F_6Fe_2N_2P_2Ru$): C, 61.23; H, 5.06; N, 2.27; M (cation), 1091. Found: C, 61.19; H, 4.99; N, 2.15. IR (cm^{-1}): ν(C≡C) 2135w, ν(C=C=C) 1758w, ν(C=N) 1616s. UV–vis: 388 (1064), 534 (770). ^{1}H NMR ($CDCl_3$): δ 1.40–2.00 (m, 9H, dbu), 2.25 (s, 9H, tol), 2.60–2.90 (m, 3H, dbu), 3.40–3.90 (m, 4H, dbu), 4.05 (s, 5H, Fe–Cp), 4.08 (s, 1H), 4.19–4.42 (m, 8H), 4.69 (s, 1H), 4.72 (s, 5H, Fe–Cp), 6.60 (br, H, Ph), 6.90–7.21 (m, 12H, Ph). ^{13}C NMR ($CDCl_3$): δ 20.40, 21.73 (Me), 23.56, 26.49, 29.02, 30.17, 47.84, 49.12, 69.72, 69.78, 69.91, 70.00 (2 × Fe–Cp), 71.60, 71.99, 90.77 (Ru–Cp), 127.73–128.29 (m, Ph), 130.74–130.85 (m, Ph), 132.42–132.63 (m), 133.33 (Ph), 137.45–137.56 (m, Ph), 167.07. ^{31}P NMR ($CDCl_3$): δ −143.1 (sept, $J = 712$ Hz, PF_6), 30.4 [s, P(*m*-tol)$_3$]. ES-MS (MeOH, positive ion, *m*/*z*): 1091, M$^+$. Echem: +0.32, +0.59, +0.89 V.

5.4.5. Synthesis of [Ru{C(C≡CFc)=C(dbu)CH=C=C=CHFc}(PPh$_3$)(η^5-C$_9$H$_7$)]PF$_6$ **5**

Similarly, from a solution containing $RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)$ (99 mg, 0.128 mmol), HC≡CC≡CFc (83 mg, 0.355 mmol), KPF_6 (143 mg, 0.777 mmol) and dbu (5 drops) in thf (15 ml) heated at reflux point for 1 h, was obtained [Ru{C(C≡CFc)=C(dbu)CH=C=C=CHFc}(PPh_3)(η^5-C_9H_7)]PF_6 **5** as a dark red solid (79 mg, 50%). Anal. Calcd ($C_{64}H_{58}F_6Fe_2N_2P_2Ru$): C, 61.80; H, 4.70; N, 2.25; M (cation), 1099. Found: C, 61.86; H, 4.62; N, 2.28. IR (cm^{-1}): ν(C≡C) 1957w, ν(C=C=C) 1795w, ν(C=N) 1614s; 1573w, 1548w, 1508w, 840s ν(PF). UV–vis: 407 (1057), 540 (693). ^{1}H NMR ($CDCl_3$): δ 1.60–2.00 (m, 9H, dbu), 2.50–2.80 (m, 2H, dbu), 3.60–4.00 (br, 5H, dbu), 4.00–4.50 (m, 20H, incl. Fe–Cp at 4.12), 5.05 (s, 1H), 5.16 (s, 1H), 5.90–6.90 (br, 4H, Ph), 7.00–7.62 (m, 16H, Ph). ^{13}C NMR ($CDCl_3$): δ 20.00, 23.77, 26.55, 29.07, 29.69, 30.19, 47.29, 49.21, 55.29, 68.89,69.58–69.87 (m), 70.03 (2 × Fe–Cp), 70.13–70.30 (m), 71.18 (br), 71.36 (br), 72.00–73.00 (br), 79.95, 80.44, 97.08, 108.26, 112.35, 123.18 (Ph), 124.37 (Ph), 126.04 (Ph), 127.25–128.56 (m, Ph), 130.12 (Ph), 131.87–132.17 (m, Ph), 132.40–134.00 (br, Ph), 166.32. ^{31}P NMR ($CDCl_3$): δ −141.9 (sept, $J = 712$ Hz, PF_6), 20.2 (s, PPh_3). ES-MS (MeOH, positive ion, *m*/*z*): 1099, M$^+$, 837, [M − PPh_3]$^+$. Echem: +0.32, +0.61, +0.97 V.

5.5. Reaction of [Ru{C(C≡CFc)=C(dbu)CH=C=C=CHFc}(PPh$_3$)Cp]PF$_6$ with I$_2$

Iodine (35 mg, 0.14 mmol) was added to a solution of [Ru{C(C≡CFc)=C(dbu)CH=C=C=CHFc}(PPh_3)Cp]PF_6 (42 mg, 0.035 mmol) in thf (10 mL) and the mixture was stirred for 10 min. Removal of solvent, extraction of the residue with CH_2Cl_2 (10 mL) and filtration into cyclohexane (30 mL) afforded a brown solid (58 mg, 86%) which was filtered off and washed with hexane. This material was not completely characterised, with microanalyses being consistent with the formation of a bis-triiodide salt of a dication similar in composition to the precursor cation. Anal. Calcd ($C_{60}H_{55}Fe_2I_7N_2PRu$): C, 37.17; H, 2.84; N, 1.45. Found: C, 37.11; H, 2.76; N, 1.39. IR (nujol/cm^{-1}): 2106s, 1752w, 1615s, 1507m, 1500m. ^{31}P NMR ($CDCl_3$): δ 38.7. The NMR spectra of this paramagnetic solid were broad and uninformative; no satisfactory ES-MS could be obtained. Attempted recrystallisation from MeOH afforded a few well-formed crystals, shown to be [Ru{C(C≡CFc)C(dbu)CH=C(OMe)C(OMe)=CHFc}(PPh_3)Cp](I_3)$_2$ **6** by a single-crystal XRD structure determination. ES-MS (MeOH, positive ion, *m*/*z*): 1111, M$^+$; 849, [M − PPh_3]$^+$; 817, [M − PPh_3 − MeOH]$^+$; 697, [M − PPh_3 − dbu]$^+$.

5.6. Structure determinations

Full spheres of diffraction data were measured at ca 153 K using a Bruker AXS CCD area-detector instrument. All data were measured using monochromatic Mo Kα radiation, $\lambda = 0.71073$ Å. 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 $F > 4\sigma(F)$ were considered “observed”. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms; hydrogen atoms were treated with a riding model [weights: $(\sigma^2(F_o)^2 + (aP)^2\ (+bP))^{-1}$] [$P = (F_o^2 + 2F_c^2)/3$]. Neutral atom complex scattering factors were used; computation used the SHELXL 97 program [22]. 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.

Acknowledgements

We thank Professor Brian Nicholson (University of Waikato, Hamilton, New Zealand) for providing the mass spectra, the ARC for support of this work and Johnson Matthey plc, Reading, for a generous loan of $RuCl_3.nH_2O$.

Appendix A. Supplementary material

Full details of the structure determinations (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC 747080-747082. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail:deposit@ccdc.cam.ac.ukor www: http://www.ccdc.cam.ac.uk).

References

[1] 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.

[2] (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, 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;
(c) M.I. Bruce, P.A. Humphrey, M. Jevric, B.W. Skelton, A.H. White, J. Organomet. Chem. 692 (2007) 2564;
(d) M.I. Bruce, M.L. Cole, C.R. Parker, B.W. Skelton, A.H. White, Organometallics 27 (2008) 3352.

[3] (a) A.R. O'Connor, C. Nataro, J.A. Golen, A.L. Rheingold, J. Organomet. Chem. 689 (2004) 2411;
(b) S. Scholz, M. Scheibitz, F. Schodel, M. Bolte, M. Wagner, H.-W. Lerner, Inorg. Chim. Acta 360 (2007) 3323.

[4] (a) P. Seiler, J.D. Dunitz, Acta Crystallogr. B 38 (1982) 1741;
(b) R. Martinez, A. Tiripicchio, Acta Crystallogr. C 46 (1990) 202.

[5] R.K. Bohn, A. Haaland, J. Organomet. Chem 5 (1966) 470.

[6] D. Chong, W.E. Geiger, N.A. Davis, A. Weisbrich, Y. Shi, A.M. Arif, R.D. Ernst, Organometallics 27 (2008) 430.

[7] D.A. Foucher, C.H. Honeyman, A.J. Lough, I. Manners, J.M. Nelson, Acta Crystallogr. C 51 (1995) 1795.

[8] (a) R. Schmid, K. Kirchner, Eur. J. Inorg. Chem. (2004) 2609;
(b) E. Rüba, K. Mereiter, R. Schmid, V.N. Sapounov, K. Kirchner, H. Schottenberger, M.J. Calhorda, L.F. Veiros, Chem. Eur. J. 8 (2002) 3948;
(c) R. Schmid, K. Kirchner, in: G. Meyer, D. Naumann, L. Wesemann (Eds.), Inorganic Chemistry in Focus II, Wiley-VCH, Weinheim, 2005, p. 221 (Chapter 13).

[9] L. Zhang, H.H.-Y. Sung, I.D. Williams, Z. Lin, G. Jia, Organometallics 27 (2008) 5122.

[10] (a) M.I. Bruce, P. Hinterding, E.R.T. Tiekink, B.W. Skelton, A.H. White, J. Organomet. Chem. 450 (1998) 209;
(b) M.I. Bruce, B.G. Ellis, B.W. Skelton, A.H. White, J. Organomet. Chem. 690 (2005) 1772.

[11] (a) R.F. Winter, F.M. Hornung, Organometallics 16 (1997) 4248;
(b) R.F. Winter, F.M. Hornung, Organometallics 18 (1997) 4005.

[12] S.N. Semenov, O. Blacque, T. Fox, K. Venkatesan, H. Berke, Angew. Chem. Int. Ed. 48 (2009) 5203.

[13] K. Venkatesan, F.J. Fernandez, O. Blacque, T. Fox, M. Alfonso, H.W. Schmalle, H. Berke, Chem. Commun. (2003) 2006.

[14] (a) K. Ilg, H. Werner, Angew. Chem. Int. Ed. 39 (2000) 1632;
(b) K. Ilg, H. Werner, Chem. Eur. J. 8 (2002) 2812.

[15] F. Coat, M. Guillemot, F. Paul, C. Lapinte, J. Organomet. Chem. 578 (1999) 76.

[16] E. Rüba, K. Mereiter, R. Schmid, K. Kirchner, H. Schottenberger, J. Organomet. Chem. 637–639 (2001) 70.

[17] W. Henderson, J.S. McIndoe, B.K. Nicholson, P.J. Dyson, J. Chem. Soc., Dalton Trans. (1998) 519.

[18] M.I. Bruce, C. Hameister, A.G. Swincer, R.C. Wallis, Inorg. Synth. 28 (1990) 270.

[19] M.I. Bruce, B.C. Hall, N.N. Zaitseva, B.W. Skelton, A.H. White, Dalton Trans. (1998) 1793.

[20] L.A. Oro, M.A. Ciriano, M. Campo, C. Foces-Foces, F.H. Cano, J. Organomet. Chem. 289 (1985) 117.

[21] Z. Yuan, G. Stringer, I.R. Jobe, D. Kreller, K. Scott, L. Koch, N.J. Taylor, T.B. Marder, J. Organomet. Chem. 452 (1993) 115.

[22] (a) G.M. Sheldrick, SHELXL-97: A Program for Crystal Structure Refinement. University of Göttingen, Göttingen, Germany, 1997;
(b) G.M. Sheldrick, Acta Crystallogr. A 64 (2008) 112.