

Synthesis, structures and some reactions of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{PP})\text{Cp}$ (PP = dppe, dppm) and related compounds

Michael I. Bruce^{a,*}, Frédéric de Montigny^{a,b}, Martyn Jevric^a, Claude Lapinte^b,
Brian W. Skelton^c, Mark E. Smith^a, Allan H. White^c

^a Department of Chemistry, University of Adelaide, SA 5005, Australia

^b UMR CNRS 6509, Institut de Chimie de Rennes, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes, France

^c Department of Chemistry, University of Western Australia, Crawley, WA 6009, Australia

Received 5 March 2004; accepted 21 May 2004

Available online 22 July 2004

Abstract

The compounds $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{PP})\text{Cp}$ [PP = dppe (**1**), dppm (**2**)], have been obtained from reactions between $\text{RuCl}(\text{PP})\text{Cp}$ and $\text{FcC}\equiv\text{CC}\equiv\text{CSiMe}_3$ in the presence of KF (**1**) or $\text{HC}\equiv\text{CC}\equiv\text{CFc}$ and $\text{K}[\text{PF}_6]$ (**2**), both with added dbu. The dppe complex reacts with $\text{Co}_2(\text{CO})_6(\text{L}_2)$ [$\text{L}_2 = (\text{CO})_2$, dppm] to give **3**, **4** in which the $\text{Co}_2(\text{CO})_4(\text{L}_2)$ group is attached to the outer $\text{C}\equiv\text{C}$ triple bond. The PPh_3 analogue of **3** (**5**) has also been characterised. In contrast, tetracyanoethene reacts to give two isomeric complexes **6** and **7**, in which the cyano-olefin has added to either $\text{C}\equiv\text{C}$ triple bond. The reaction of $\text{RuCl}(\text{dppe})\text{Cp}$ with $\text{HC}\equiv\text{CC}\equiv\text{CFc}$, carried out in a thf/NEt_3 mixture in the presence of $\text{Na}[\text{BPh}_4]$, gave $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{NEt}_3)=\text{CHFc}\}(\text{dppe})\text{Cp}]\text{BPh}_4$ (**8**), probably formed by addition of the amine to an (unobserved) intermediate butatrienyliene $[\text{Ru}(\text{C}=\text{C}=\text{C}=\text{CHFc})(\text{dppe})\text{Cp}]^+$. The reaction of I_2 with **8** proceeds via an unusual migration of the alkynyl group to the Cp ring to give $[\text{RuI}(\text{dppe})\{\eta\text{-C}_5\text{H}_4\text{C}\equiv\text{CC}(\text{NEt}_3)=\text{CHFc}\}]\text{I}_3$ (**9**). Single-crystal X-ray structural determinations of **1**, **2** and **4–9** are reported.

© 2004 Published by Elsevier B.V.

Keywords: Ruthenium; Carbon chain; Alkynyl molecular wires

1. Introduction

Contemporary interest in compounds containing carbon chains linking redox-active transition metal centres stems from their possible use in nanotechnology and micro-electronics, including non-linear optics [1]. Possible uses as models for molecular-scale wires and the ease of study of such systems have resulted in a large literature describing a variety of such complexes [2]. Our

own interests, and those of others, have been centred on compounds containing C_4 chains, with groups such as $\text{Re}(\text{CO})_3(\text{bpy})$ [3], $\text{Re}(\text{NO})(\text{PPh}_3)\text{Cp}^*$ [4], $\text{Fe}(\text{CO})_2\text{Cp}^*$ [5], $\text{Fe}(\text{dppe})\text{Cp}^*$ [6], $\text{Ru}(\text{PPh}_3)_2\text{Cp}$ [7] and *trans*- $\text{PtR}(\text{PAR}_3)_2$ (R = tol, C_6F_5 ; Ar = Ph, tol) [8] as end-caps.

Previous reports from this group have described compounds containing various ML_n fragments linked to redox-active ferrocenyl (Fc) groups by carbon chains, e.g., $\{\text{Cp}(\text{OC})_3\text{W}\}(\text{C}\equiv\text{C})_n\text{Fc}$ ($n = 1\text{--}4$) [9], in which the oxidation potential of the Fc nucleus increased by ca. 0.06 V per $\text{C}\equiv\text{C}$ unit added to the chain. Related studies with $\text{Fc}(\text{C}\equiv\text{C})_n\text{Fc}$ ($n = 2, 4$) and ruthenium [10] or osmium [11] cluster carbonyls have given a variety of novel complexes, for which electrochemical studies have also

Abbreviations: dbu; 1,8-diazabicyclo[5.4.0]undec-7-ene; dppe; 1,2-bis(diphenylphosphino)ethane; dppf; 1,1'-bis(diphenylphosphino)ferrocene; Fc; ferrocenyl.

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

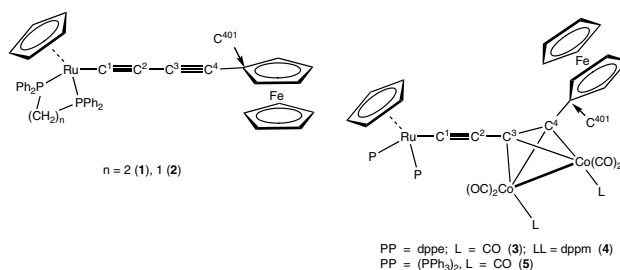
E-mail address: michael.bruce@adelaide.edu.au (M.I. Bruce).

been reported. Early papers by Sato and co-workers [12] have reported that $M(C\equiv CFc)(L)_2Cp$ [$M = Fe, Ru$; $L_2 = (PPh_3)_2, dppe, dpfp$] and some of the monocations show interesting electron delocalisation properties. Following our earlier studies, the present venture has been to make derivatives containing both Fc and $Ru(P)_2Cp$ groups linked by C_4 chains as described below.

2. Results and discussion

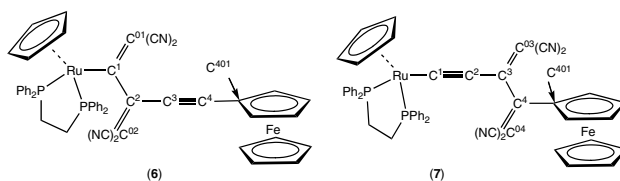
The metalla-desilylation of alkynyltrimethylsilanes has proved to be a useful source of electron-rich alkynylmetals [13] and following this protocol, the reaction between $RuCl(dppe)Cp$, $FcC\equiv CC\equiv CSiMe_3$ and KF was carried out in refluxing methanol containing dbu . Chromatographic work-up on basic alumina gave the desired $FcC\equiv CC\equiv CRu(dppe)Cp$ (**1**) in 57% yield as a yellow-orange solid, based on recovered $FcC\equiv CC\equiv CH$ (40%). Characterisation was by spectroscopy [IR, NMR, electrospray (ES) mass], together with a satisfactory elemental analysis (as for all compounds described below). Finally, a single-crystal X-ray structure determination provided confirmation of the identity of **1**. In the IR spectrum two $\nu(CC)$ bands are found at 2174 and 2024 cm^{-1} , while Cp resonances in the 1H NMR spectrum are at δ 4.03 and 4.65 (Fe, Ru, respectively) and at δ 3.80 and 4.28 (C_5H_4 of Fc). In the ^{31}P NMR spectrum, a singlet at δ 85.97 is assigned to the dppe ligand. In the ES-MS, the parent ion is found at m/z 798. The dppm complex **2** was prepared from $RuCl(dppm)Cp$, $FcC\equiv CC\equiv CH$, $K[PF_6]$ and dbu as an orange solid (28%). Its spectral properties are similar to those of **1**, including $\nu(C\equiv C)$ at 2174 and 2030 cm^{-1} . In addition to the resonances of the Cp, C_5H_4 and dppm ligands, the resonances of the C_4 chain were observed at δ_C 69.96, 77.86, 96.31 and 114.95, the latter showing triplet coupling (24.1 Hz) to the dppm P atoms and thereby assigned to the $\equiv C-Ru$ atom.

Cobalt carbonyl derivatives of **1** were obtained from its reactions with either $Co_2(CO)_8$ or $Co_2(\mu-dppm)(CO)_6$, which afforded $Ru\{C\equiv CC_2Fc[Co_2(CO)_6]\}(dppe)Cp$ (**3**) and $Ru\{C\equiv CC_2Fc[Co_2(\mu-dppm)(CO)_4]\}(dppe)Cp$ (**4**), respectively. The IR $\nu(CO)$ spectra were characteristic of the coordinated $Co_2(CO)_6L_2$ groups, between 2077 and 1976 (m-s-s-s-m pattern) and 2032–1935 (m-m-s-s-m) cm^{-1} , respectively, the latter showing the expected shift to lower energies when two CO groups are replaced by the dppm ligand. Singlet resonances in the 1H NMR spectra confirmed the retention of the Cp groups attached to Fe and Ru, while the ^{31}P NMR spectra contained resonances at δ 87.22 (dppe in **3**) or 36.30 and 86.35 (dppm, dppe in **4**). Parent ions at m/z 1084 and 1412, respectively, were found in the ES-MS. In the case of **4**, the structure was finally confirmed by a single-crystal X-ray determination.

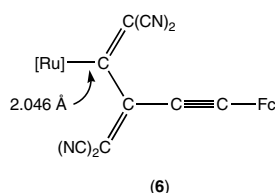


An attempt to make the PPh_3 analogue of **1** afforded an orange solid which could not be purified satisfactorily. However, derivatisation with $Co_2(CO)_8$ afforded $Ru\{C\equiv CC_2Fc[Co_2(CO)_6]\}(PPh_3)_2Cp$ (**5**) as a green crystalline solid, which exhibited three $\nu(CC)$ bands in its IR spectrum between 2077 and 2012 cm^{-1} . In the 1H NMR spectrum, characteristic resonances were found at δ 4.26 (FcCp and RuCp, overlapping) with other ferrocenyl protons at δ 4.41 and 4.47 and aromatic protons between δ 6.95 and 7.35. The ^{31}P NMR spectrum contained a singlet at δ 51.62. In the ES-MS, a molecular ion at m/z 1210 fragmented to give ions at m/z 883, 775 and 732, with the base peak at m/z 719. The structure of **5** was confirmed by an X-ray study.

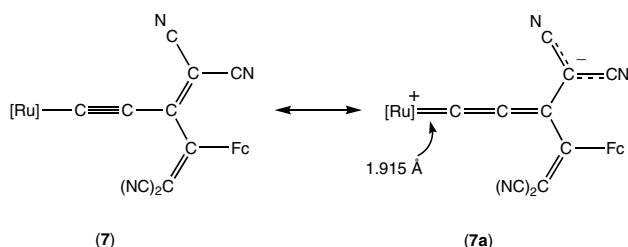
Of some interest was the reaction between **1** and tetracyanoethene (tcne). When tcne was added to a solution of **1** in thf, a deep green colouration appeared, which rapidly changed to red-violet at r.t. The deep green colour was longer lived at -78 °C, suggesting that the reaction proceeds via a radical intermediate. The solution was heated to reflux point to complete the reaction, after which a mixture of equal amounts of two isomers of the tcne adduct of **1** were obtained in a total yield of 67%. It proved difficult to separate the two complexes by t.l.c., but fractional crystallisation afforded pure samples of each, although in low yield. While the overall composition of each was ascertained from the usual analytical and spectroscopic measurements, the sites of addition were confirmed by X-ray structure determinations; crystals of each isomer were obtained by fractional crystallisation from dichloromethane/cyclohexane mixtures. Further crystallisation gave **6** as dark red crystals (from CH_2Cl_2 /hexane), while **7** formed red blocks (from acetone/hexane). No evidence for the formation of a bis-adduct was obtained when an excess of tcne was used in the reaction.



The X-ray structural determinations described below show that the tcne has added to the C≡C triple bond adjacent to the ruthenium centre in **6**, while in **7**, addition has occurred to the triple bond next to the ferrocenyl group. Of interest here is a comparison of the atom separations in the cyanocarbon moieties. While the Ru–C(1) distance in **6** [2.046(3) Å] is similar to that expected for an unperturbed Ru–C (sp²) bond, that in **7** [1.915(4) Å] is much shorter and is consistent with a significant contribution from the vinylidene structure **7a**. This is also supported by the relatively long C(1)–C(2) distance [1.230(3) Å] and the equal C(2)–C(3) and C(3)–C(03) distances [1.377(3) Å]. The shorter C(4)–C(04) distance is comparable to both C(1)–C(01) and C(2)–C(02) in **6**.



(6)

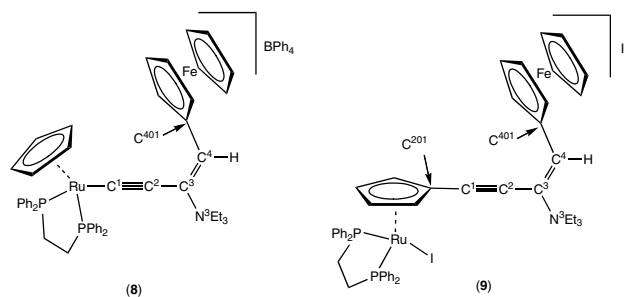


(7)

(7a)

The ³¹P NMR spectrum of a mixture of **6** and **7** contains two sets of signals which can be analysed as an AB quartet [individual doublets at δ 84.28 and 85.43, *J*(PP) 16.8 Hz] and an AX system [doublet of doublets at δ 66.06 and 82.34, *J*(PP) 21.4 Hz]. We assign these resonances to **6** and **7**, respectively, not only because of the asymmetry inherent in the cyanocarbon ligand, but also on the basis of restricted rotation about the Ru–C(1) bond, both of which lead to the observed inequivalence of the two ³¹P nuclei in each complex.

Interesting transformations were found when the synthesis of **1** from reactions of RuCl(dppe)Cp and FcC≡CC≡CH with Na[BPh₄] in the presence of NEt₃ was attempted. The product was an orange solid characterised as [Ru{C≡CC(NEt₃)=CHF₃}(dppe)Cp][BPh₄] (**8**) by an X-ray structural study. Spectroscopic properties include ν(CC) bands at 2039 and 1596 cm⁻¹, and Cp resonances at δ_H 4.06 (Fe) and 4.83 (Ru), δ_C 69.04 and 83.38; the ³¹P NMR spectrum contained the dppe resonance at δ 86.90. The parent cation was found at *m/z* 900 in the ES-MS.



(8)

(9)

During the initial attempts to characterise **8**, addition of iodine was found to give a brick-red solid, characterised as [RuI(dppe){η-C₅H₄C≡CC(NEt₃)=CHF₃}]I₃ (**9**) by X-ray crystallography, in which an unusual migration of the alkyne group from ruthenium to the C₅ ring has occurred. The spectral properties of **9** include ν(CC) at 2197 and 1979 cm⁻¹ and the ³¹P resonance at δ 79.15 (dppe). In the ¹H and ¹³C NMR spectra, the singlet for the FeCp group were observed at δ_H 4.31 overlaps both the =CH and one of the Fe(C₅H₄) resonances. The second resonance for the FeC₅H₄ group was found at δ_H 4.52. The Ru(C₅H₄) protons resonated at δ 5.09 and 5.50, these assignments being based on their higher chemical shifts. The ¹³C resonances for the C₅ rings were found at δ 70.37 (FeCp), 71.24 and 72.02 (FeC₅H₄), and 78.43 and 88.13 (RuC₅H₄). Several other resonances (see Section 4) are found between δ_C 77–120 and while not individually assigned, arise from the carbons in the C₄ chain and *ipso* carbons of the C₅ rings. In the ES-MS, an ion with *m/z* 1026 corresponds to the molecular cation.

2.1. Molecular structures

In the course of this work, single-crystal X-ray structure determinations were carried out to confirm the molecular structures. Plots of single molecules of **1**, **2** and **4–7**, and the cations of **8** and **9**, are shown in Figs. 1 and 2 while Table 1 collects significant bond distances and angles. Common features, such as the geometry about the iron or ruthenium atoms, are in accord with a myriad of related structures to be found in the Cambridge Crystallographic Data Base [14]. Within the compounds reported here, average Fe–C(cp) distances are between 2.03 and 2.04₇ Å, with Ru–P and Ru–C(cp) distances ranging between 2.2445 and 2.3129(8), and 2.21₈–2.24₆ Å, respectively. Angles subtended at ruthenium by the two P atoms and by the pair of P,C atoms are consistent with the pseudo-octahedral arrangement of ligands and depend on the bite angles of the ligands. For dppe, P(1)–Ru–P(2) and P(1,2)–Ru–C(1) are between 81.32–83.87(3)° and 81.5–98.5(1)°, respectively, while for dppe, P(1)–Ru–P(2) is 71.93(4)°.

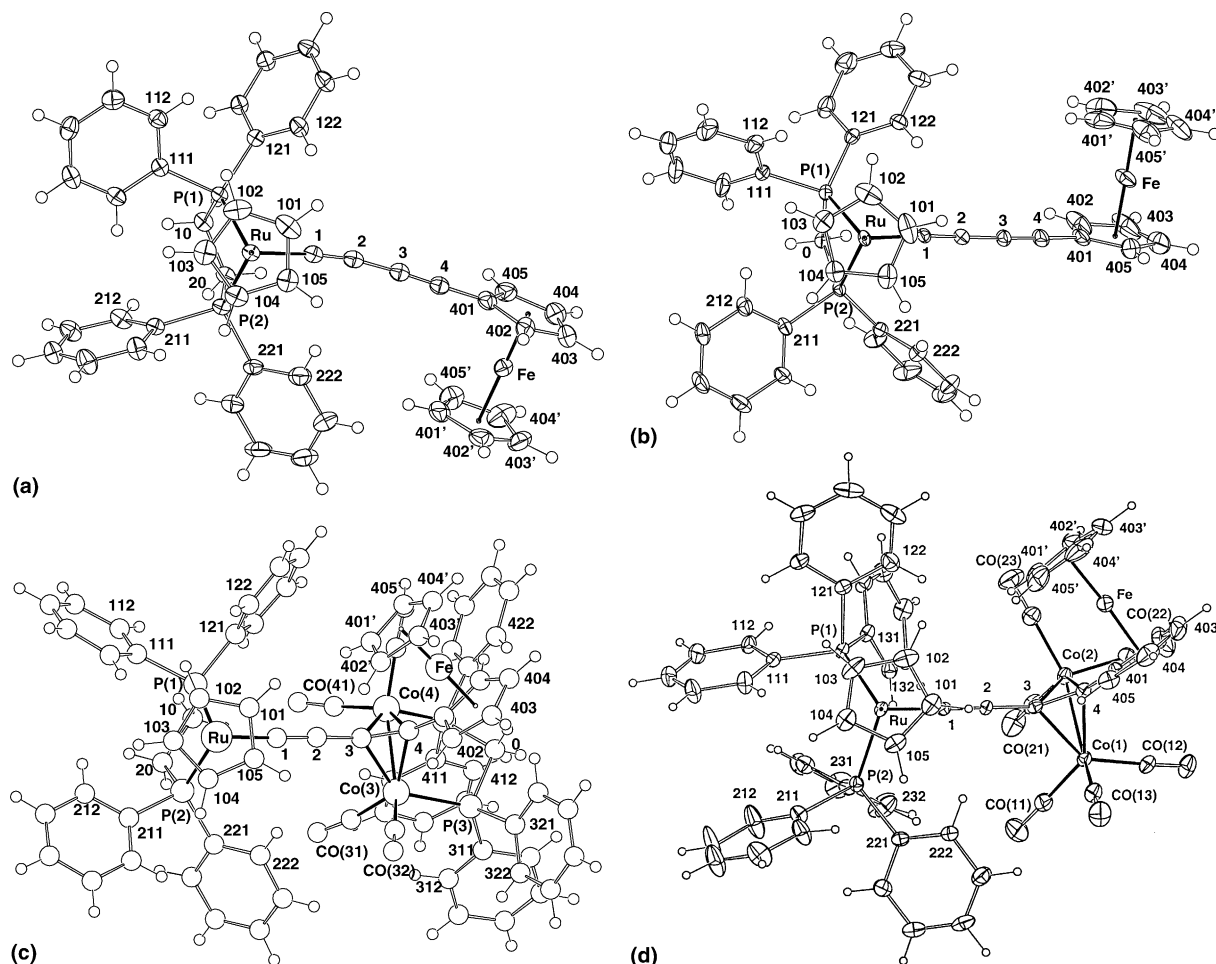


Fig. 1. Projection of molecules down the Cp(centroid)-Ru line: (a) Ru(C≡CC≡CFc)(dppe)Cp (**1**); (b) Ru(C≡CC≡CFc)(dppm)Cp (**2**); (c) Ru{C≡CC₂Fc[Co₂(μ-dppm)(CO)₄]}(dppe)Cp (**4**); (d) Ru{C≡CC₂Fc[Co₂(CO)₆]}(PPh₃)₂Cp (**5**).

Of most interest in the present study is the diyne ligand. The diyne nature of the carbon chain is shown by the short–long–short CC bond sequences [1.225(2), 1.375(3) and 1.213(3) Å], which compare well with those in similar complexes [2] and in buta-1,3-diyne itself [1.2176(14), 1.384(2) Å] [15]. Angles at individual carbons C(1–4) are close to linear [range 170.5–178.9(4)°], with a cumulative bend of ca. 20 (dppe), 6.9° (dppm). As can be seen from the plots of **1** and **2**, the overall bending results in a displacement of the terminal carbon such that the M···C(4) distances [5.235(4) (**1**), 5.771(8) Å (**2**)] are significantly less than the sum of the interatomic distances [5.765(4), 5.943(8) Å, respectively].

In **4** and **5**, addition of the Co₂ fragment to the outer C≡C triple bond has resulted in the usual C–C bond lengthening [to 1.34(1) Å] and bending about C(3) and C(4) [angles C(2)–C(3)–C(4) 148.7(13)°, 144.1(5); C(3)–C(4)–C(401) 136.1(10)°, 139.3(6)°, for **4** and **5**, respectively]. Other bond parameters for the Ru(dppe)Cp, Fc and Co₂(μ-dppm)(CO)₄ fragments are not significantly different from those found in many other reported ex-

amples [14]. In the isomeric complexes **6** and **7**, addition of tcn to one of the C≡C triple bonds has resulted in formation of tetracyanobutadiene fragments, characterised by C–C bond lengths ranging between 1.358–1.378(5) (C=C), 1.483 and 1.491(4) (C–C), and 1.414–1.451(5) Å (C–CN). In **6**, in which addition to the C≡C triple bond adjacent to the ruthenium has occurred, the Ru–C(1) distance is 2.046(3) Å, which is within the normal range for an Ru–C(sp²) bond. In contrast, in complex **7**, Ru–C(1) is short [at 1.915(4) Å] and C(1)–C(2) is long [at 1.230(5) Å], suggesting a contribution from the allenylidene tautomer **7a**, induced by the presence of the strongly electron-withdrawing polycyano-olefinic substituent on C(2) and resulting in a degree of multiple-bond character in the Ru–C(1) bond. These features have been discussed above in connection with the assignments of the ³¹P NMR spectra.

Addition of tcn to transition metal alkynyl and polyynyl complexes is a well-known reaction which has been reported for complexes containing W [16], Fe [17], Ru [18], Ni [19] and Pt [20]. It is considered to proceed via a

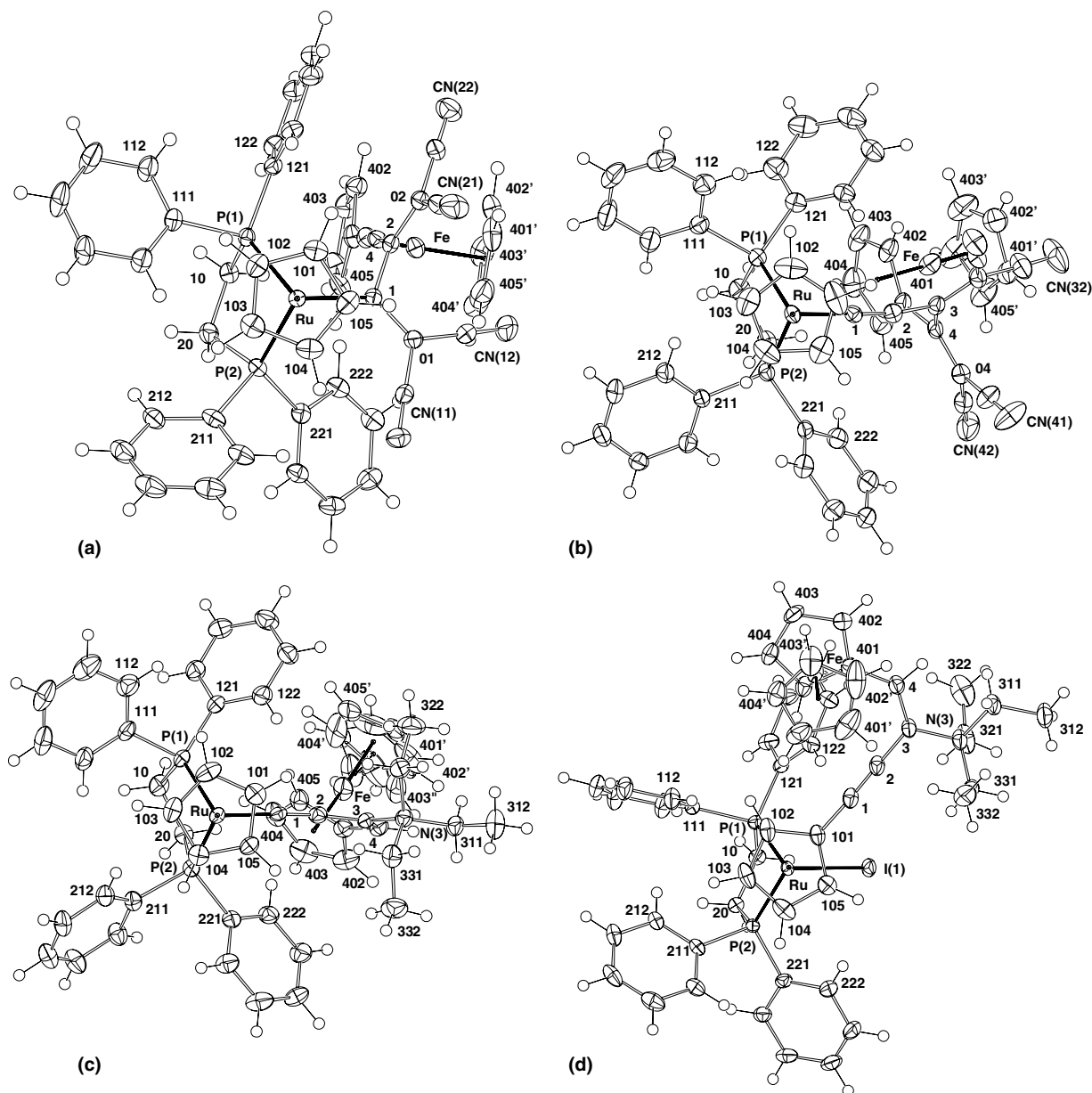


Fig. 2. Projection of molecules down the Cp(centroid)-Ru line: (a) $\text{Ru}\{\text{C}[\text{=C}(\text{CN})_2]\text{C}[\text{=C}(\text{CN})_2]\text{C}\equiv\text{CFC}\}(\text{dppe})\text{Cp}$ (**6**); (b) $\text{Ru}\{\text{C}\equiv\text{CC}[\text{=C}(\text{CN})_2]\text{CFc}=\text{C}(\text{CN})_2\}(\text{dppe})\text{Cp}$ (**7**); (c) $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{NEt}_3)=\text{CHFc}\}(\text{dppe})\text{Cp}]\text{BPh}_4$ (**8**); (d) $[\text{RuI}(\text{dppe})\{\eta\text{-C}_5\text{H}_4\text{C}\equiv\text{CC}(\text{NEt}_3)=\text{CHFc}\}]_3$ (**9**) (cations only).

radical intermediate which evolves successively to a tetracyanocyclobutenyl derivative and, via a conventional ring-opening reaction, to the isomeric tetracyanobutadienyl derivative. The radical has not been fully characterised and in the present instance, evidence for its formation was seen in the short-lived deep green colouration which developed upon addition of *tcne* to the solution of **1**, and which rapidly faded at r.t. However, the cyclobutenyls were not observed during the present reaction (spot t.l.c.), presumably because of their rapid transformation to the butadienyls. Recently, similar reactions between *tcne* and ethynylferrocene, diferrocenyne and 1,4-diferrocenylbuta-1,3-diyne to give the corresponding substituted *s-cis*-butadienes have been described [21].

The formulations of the cations in **8** and **9** were revealed by the structural determinations. While the C_4 group (on Ru in **8**, and on the C_5 ring in **9**) is the same, differences in C(1)–C(2) bond lengths [1.230(5), 1.198(5) Å, respectively] suggest that there is a contribution from the allenylidene tautomer in the former. This is supported by the relatively short Ru–C(1) distance of 1.973(3) Å. Effects of this formulation can be traced through to the C(3)–N(3) separation, which is 1.526(4) Å in **8**, but only 1.510(5) Å in **9**.

The transfer of the alkynyl group from ruthenium in **8** to the Cp ring in **9**, which occurs during the reaction with iodine, has several precedents with alkyl-transition metal complexes. Thus, the base-induced migration of organic

Table 1
Selected bond distances (Å) and angles (°)

Compound	1	2	4	5	6	7	8	9
<i>Bond distances (Å)</i>								
Ru–P(1)	2.2477(9)	2.261(1)	2.251(4)	2.313(2)	2.2899(8)	2.257(1)	2.2540(9)	2.2915(9)
Ru–P(2)	2.2551(9)	2.265(1)	2.248(4)	2.305(2)	2.3129(8)	2.2445(8)	2.2626(8)	2.2654(8)
Ru–C(cp)	2.237–2.251(4)	2.232–2.259(5)	2.22–2.26(1)	2.213–2.254(7)	2.230–2.243(4)	2.219–2.244(4)	2.224–2.249(3)	2.189–2.255(4)
⟨⟩	2.246(6)	2.245(13)	2.24(2)	2.23(2)	2.237(5)	2.23(1)	2.24(1)	2.22(2)
Fe–C(cp)	2.029–2.050(4), 2.041–2.060(6)	2.025–2.051(6)	2.02–2.04(1)	2.04, 2.03(1), 2.036(11)	2.007–2.063(4), 2.033–2.044(4)	2.016–2.046(4), 2.028–2.048(4)	2.021–2.059(3)	2.028–2.054(4), 2.024–2.070(5)
⟨⟩ ^b	2.037(8), 2.047(8); 2.042(9)	2.042(8), 2.040(10); 2.041(9)	2.030(9), 2.019(5); 2.024(9)	2.04(1), 2.03(1); 2.036(11)	2.04(2), 2.038(5); 2.039(15)	2.03(1), 2.038(8); 2.04(1)	2.03(2) [2.05(8)] ^a ; –	2.04(1), 2.05(2); 2.04(2)
Fe–C(401)	2.050(3)			2.047(6)	2.007(3)	2.028(4)	2.059(3)	
Ru–C(1)	1.979(4)	1.988(3)	1.963(10)	1.987(6)	2.046(3)	1.915(4)	1.973(3)	2.7324(4) [I]
C(1)–C(2)	1.225(5)	1.227(5)	1.24(1)	1.216(8)	1.483(4)	1.230(5)	1.219(4)	1.198(5)
C(2)–C(3)	1.373(5)	1.360(5)	1.40(1)	1.391(8)	1.403(5)	1.377(6)	1.413(4)	1.426(5)
C(3)–N(3)						1.378(5) [C(03)]	1.526(4)	1.510(5)
C(3)–C(4)	1.188(5)	1.214(6)	1.34(1)	1.348(8)	1.202(5)	1.491(4)	1.346(4)	1.349(5)
C(4)–C(401)	1.426(5)	1.430(6)	1.48(2)		1.409(5)	1.439(5)	1.459(4)	1.456(5)
C–CN					1.430–1.451(4)	1.414–1.434(5)		
<i>Bond angles (°)</i>								
P(1)–Ru–P(2)	82.77(3)	71.93(4)	83.4(1)	100.82(6)	83.22(3)	83.44(3)	83.87(3)	81.32(3)
P(1)–Ru–C(1)	88.6(1)	88.2(1)	81.9(4)	91.1(2)	98.50(9)	88.4(1)	91.86(9)	87.57(2) [I]
P(2)–Ru–C(1)	84.1(1)	81.5(1)	91.7(4)	89.1(2)	93.56(8)	82.45(9)	84.11(8)	95.03(2) [I]
Ru–C(1)–C(2)	173.1(3)	176.2(3)	173.3(12)	169.8(5)	118.8(2)	178.6(2)	174.7(3)	
C(1)–C(2)–C(3)	170.5(4)	178.9(4)	177.0(15)	178.5(6)	117.0(3)	172.6(3)	171.3(3)	175.9(4)
C(2)–C(3)–N(3)						122.6(3) [C(03)]	112.0(2)	114.1(3)
C(2)–C(3)–C(4)	176.2(5)	178.0(5)	148.7(13)	144.1(5)	177.3(3)	115.3(3)	126.4(3)	124.9(3)
C(4)–C(3)–N(3)						122.1(4) [C(03)]	121.6(2)	121.0(3)
C(3)–C(4)–C(401)	179.0(5)	174.6(5)	136.1(10)	139.3(6)	179.1(3)	115.4(3)	122.7(3)	128.1(3)

For 4: Co(3)–Co(4) 2.483(3), Co(3)–P(3) 2.235(3), Co(4)–P(4) 2.178(3), Co(3)–C(3,4) 1.98, 1.96(1), Co(4)–C(3,4) 1.98, 1.92(1), P(3,4)–C(0) 1.85, 1.82(1) Å, Co(3)–P(3)–C(0) 108.1, Co(4)–P(4)–C(0) 110.2(4), P(3)–C(0)–P(4) 105.0(5)°.

For 5: Co(1)–Co(2) 2.467(1), Co(1)–C(3,4) 1.991, 1.988(6), Co(2)–C(3,4) 2.012, 1.953(6) Å.

For 6: C(1)–C(01) 1.361(4), C(2)–C(02) 1.367(4) Å, Ru–C(1)–C(01) 126.7(2), C(1)–C(2)–C(02) 123.1(3), C(01)–C(1)–C(2) 114.3(3), C(3)–C(2)–C(02) 119.9(3)°.

For 7: C(3)–C(03) 1.378(5), C(4)–C(04) 1.358(5) Å, C(3)–C(4)–C(04) 117.9(3), C(04)–C(4)–C(401) 126.4(3)°.

For 9: Ru–C(101) 2.255(3), C(1)–C(101) 1.416(5) Å, C(101)–C(1)–C(2) 176.8(4)°.

^a Disordered ring.

^b Individual rings; global.

Table 2
Electrochemical data

Complex	Potentials (V) ^a
1	+0.32, ^b +0.76, +0.94 ^c
2	+0.31, ^b +0.73, +0.89 ^c
3	+0.45, +0.55, +0.76
4	+0.09, +0.36, +0.64
5	+0.43, +0.68, +1.11 ^c
6	−1.08, −0.92, 0.87, 1.09
7	−1.16, −0.91, +0.79, +1.06
8	+0.44, +0.86
9	+0.62

^a 1.0 mM solutions in CH₂Cl₂, 0.1M [NBu₄]BF₄, r.t., Pt-dot working, Pt counter and pseudo-reference electrodes (FcH/[FcH]⁺ = 0.46 V).

^b Irreversible.

^c Quasi-reversible.

fragments has been reported for systems such as Co(P-Me₃)₂Cp complexes bearing acyl groups [22] and transfer of SiMe₃ groups from iron [23] while similar reactions leading to amination of the Cp ring are known [24]. Extensive studies of arene-molybdenum complexes [25] and acyl-iron derivatives [26] have concluded that nucleophilic attack at the metal centre results in migration of the carbon ligand to the π -ring, followed by loss of H. A closely related example is the reaction between Ru-(C≡CPh)(PPh₃)₂Cp and C₂(CO₂Me)₂ to give RuCl-(PPh₃)₂(η -C₅H₄C≡CCO₂Me) during which, however, some process akin to alkyne metathesis has also occurred [27], while more recently, Lo Sterzo [28] has found either palladium- or LiBu-induced migrations in several cyclopentadienyl-metal carbonyl alkyls. In the present transformation of **8** into **9**, attack by iodide at the ruthenium centre prompts the migration of the alkynyl substituent to the C₅ ring.

2.2. Electrochemistry

We have determined the cyclic voltammograms for most of these complexes under standard conditions (CH₂Cl₂, 0.1 V/s, 25 °C, 0.1M [NBu₄]PF₆) and the observed redox potentials are listed in Table 2. Several one-electron processes are found, not all of which can be associated with oxidation of the ferrocenyl nucleus. As reported earlier [8], the oxidation potentials of a series of complexes Fc(C≡C)_nW(CO)₃Cp (*n* = 1–4), increase by ca. 60 mV per C₂ unit added. In these complexes, the W(CO)₃Cp group does not exhibit any redox properties. For complexes **1** and **2**, an irreversible oxidation at ca. +0.3 V occurs, followed by two quasi-reversible processes at ca. +0.75 and +0.9 V.

The Co₂(CO)_{6-2n}(dppm)_n (*n* = 0,1) adducts **3–5** show three processes, that for **4** (which contains the dppm ligand) occurring at significantly lower potentials than those found for **3** and **5**, suggesting that the dicobalt ad-

dend has a strong electron-releasing effect upon the system. For the tcne adducts **6** and **7**, two reduction waves at ca. −0.9 and −1.1 V are consistent with delocalisation of the added electrons onto the strongly electron-withdrawing dicyanomethylene groups. Two oxidation processes at ca. +0.8 and +1.05 V are close in potentials to those found for **1** and **2** and may relate to the conjugated Ru–C₄–Fc system present in all four complexes. In **8**, two waves are found at +0.44 and +0.86 V, whereas in **9**, which no longer contains the diyne-derived ligand attached to the ruthenium centre, only one process occurs, at +0.62 V. This can be compared with a value of +0.28 V for RuCl(dppe)Cp. It is not clear which centre is being oxidised in **9**.

3. Conclusions

This paper has described the syntheses of complexes containing a 4-ferrocenylbuta-1,3-diyne ligand σ -bonded to Ru(L)₂Cp (L = PPh₃, L₂ = dppm, dppe) fragments and their derivatisation by addition of Co₂(CO)₆L'₂ (L' = CO, L'₂ = dppm) or tcne to one of the C≡C triple bonds. In the case of tcne, evidence for stabilisation of the carbenoid tautomer (**7a**) of one of the adducts was obtained from ³¹P NMR and X-ray structural studies. The lack of addition of a second tcne molecule to the diyne probably results from the cyano groups of either first adduct removing electron density from the second C≡C triple bond so that the radical intermediate cannot form.

In related chemistry, the formation of a (vinylammonio)alkynyl complex (**8**) suggests the intermediacy of the cationic butatrienyldiene [Ru(=C=C=C=CHFc)-(dppe)Cp]⁺; further reaction of the cation with I₂ resulted in migration of the alkynyl group to the Ru–C₅ ring to give [Ru(dppe){ η -C₅H₄C≡CC(NEt₃)=CHFc}]I₃ (**9**).

4. Experimental

4.1. General experimental conditions

All reactions were carried out under dry, high purity argon using standard Schlenk techniques. Common solvents were dried, distilled under argon and degassed before use.

4.2. Instrumentation

Infrared spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in CH₂Cl₂ 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 Bruker AM300WB or ACP300 (¹H at

300.13 MHz, ^{13}C at 75.47 MHz, ^{31}P at 121.50 MHz) instruments. Samples were dissolved in CDCl_3 , unless otherwise stated, contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ^1H and ^{13}C NMR spectra and external H_3PO_4 for ^{31}P NMR spectra. ES-MS: VG Platform 2 or Finnigan LCQ. Solutions were directly infused into the instrument. Chemical aids to ionisation were used as required [29]. Cyclic voltammograms were recorded at 298 K as described in Table 2 using a PAR model 263 apparatus, a saturated calomel electrode, and ferrocene as internal calibrant ($\text{FeCp}_2/[\text{FeCp}_2]^+ = +0.46$ V). Elemental analyses were performed at the Centre for Micro-Analytical Services (CMAS), Belmont, Vic.

4.3. Reagents

Tetracyanoethene, $\text{Na}[\text{BPh}_4]$ and KF (Aldrich) were used as received. The compounds $\text{RuCl}(\text{PPh}_3)_2\text{Cp}$ [30], $\text{RuCl}(\text{dppe})\text{Cp}$ [31], $\text{FcC}\equiv\text{CC}\equiv\text{CH}$ [32] and $\text{Co}_2(\mu\text{-dppm})(\text{CO})_6$ [33] were prepared using the cited methods.

4.4. Synthesis of $\text{FcC}\equiv\text{CC}\equiv\text{CSiMe}_3$

A solution of LiNPr_2^i [from NHP_2^i (2.5 mL, 10 mmol) and LiBu (4.0 mL of 2.5 M) solution in light petroleum] in Et_2O (30 mL) was added to *cis*- $\text{FcC}\equiv\text{CCH}=\text{CHCl}$ (1.02 g, 3.77 mmol) in Et_2O (20 mL) at -78°C . The mixture was stirred for 4 h at -78°C and then allowed to reach r.t. After cooling again to -78°C , the solution was quenched with SiClMe_3 (2 mL, excess) and warmed to r.t. overnight. Solvent was removed in vacuo and the residue taken up in hexane and filtered. Chromatography of the reduced residue (basic alumina, hexane eluant) afforded $\text{FcC}\equiv\text{CC}\equiv\text{CSiMe}_3$ (1.05 g, 90%) as an orange solid, identified by comparison with the literature [34].

4.5. Synthesis of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{dppe})\text{Cp}$ (1)

A mixture of $\text{RuCl}(\text{dppe})\text{Cp}$ (1000 mg, 1.67 mmol), KF (127 mg, 2.19 mmol), and $\text{FcC}\equiv\text{CC}\equiv\text{CSiMe}_3$ (550 mg, 1.80 mmol) was heated in refluxing MeOH (50 mL, also containing 1 drop of *dbu*, 0.1 mL water) for 1 h. After cooling, the precipitate was filtered off, washed with cold methanol and dried under vacuum. The solid was taken up in a small amount of benzene and purified by chromatography (50% ether/hexane, basic alumina) to afford $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{dppe})\text{Cp}$ (1) (430 mg, 57% based on recovered $\text{FcC}\equiv\text{CC}\equiv\text{CH}$) as a yellow-orange solid. Crystals were obtained from benzene/hexane. $\text{FcC}\equiv\text{CC}\equiv\text{H}$ (170 mg, 31%) was recovered from the filtrate. IR (nujol) $\nu(\text{C}\equiv\text{C})$ 2174m,

2024m; other band at 1653w (br) cm^{-1} . ^1H NMR (C_6D_6): δ 1.93–2.00, 2.40–2.50 (2 \times m, 2 \times 2H, CH_2), 3.80 [t (*J* 1.8 Hz), 2H, $\text{Fe}(\text{C}_5\text{H}_4)$], 4.03 (s, 5H, FeCp), 4.28 [t (*J* 1.8 Hz), 2H, $\text{Fe}(\text{C}_5\text{H}_4)$], 4.65 (s, 5H, RuCp); 6.95–7.00 (m, 6H, Ph), 7.07–7.14 (m, 4H, Ph), 7.23–7.35 (m, 5H, Ph), 7.91–8.00 (m, 5H, Ph). ^{13}C NMR (C_6D_6): δ 28.13–28.74 (m, CH_2), 60.86, 67.93 [$\text{Fe}(\text{C}_5\text{H}_4)$], 69.81, 70.13 (FeCp), 71.78 [$\text{Fe}(\text{C}_5\text{H}_4)$], 77.77, 83.33 (RuCp), 95.19, 115.75 [t, *J* 25.2 Hz, C(1)], 128.89 (Ph), 129.81 (Ph), 131.80–131.94 (m, Ph), 134.14–134.28 (m, Ph), 136.96–137.63 (m, Ph), 142.29–142.91 (m, Ph). ^{31}P NMR (C_6D_6): δ 85.97. ES-MS (*m/z*): 798, M^+ , 100. Anal. Calc. for $\text{C}_{45}\text{H}_{38}\text{FeP}_2\text{Ru}$: C, 67.76; H, 4.80. Found: C, 67.02; H, 4.55%. *M*, 798.

4.6. Synthesis of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{dppm})\text{Cp}$ (2)

$\text{RuCl}(\text{dppm})\text{Cp}$ (98 mg, 0.162 mmol), $\text{FcC}\equiv\text{CC}\equiv\text{CH}$ (80 mg, 0.342 mmol) and $\text{K}[\text{PF}_6]$ (66 mg, 0.359 mmol) were heated overnight in refluxing *thf* (20 mL) containing *dbn* (0.25 mL). After removal of solvent, chromatography of the residue (basic alumina, $\text{Et}_2\text{O}/\text{hexane}$ 3/7) afforded $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{dppm})\text{Cp}$ (2) as an orange crystalline solid (35 mg, 28%). IR (nujol): $\nu(\text{C}\equiv\text{C})$ 2174m, 2030m; other band at 1652m (br) cm^{-1} . ^1H NMR (d_8 -toluene): δ 3.80 [m, 2H, $\text{Fe}(\text{C}_5\text{H}_4)$], 4.02 (s, 5H, FeCp), 4.18 [m, 2H, $\text{Fe}(\text{C}_5\text{H}_4)$], 4.20–4.42 (m, 2H, CH_2), 4.81 (s, 5H, RuCp), 7.12–7.20 (m, 2H, Ph), 7.28–7.46 (m, 13H, Ph), 7.95–8.01 (m, 5H, Ph). ^{13}C NMR (d_8 -toluene): δ 49.96 [t, *J*(CP) 22.6 Hz, CH_2], 60.89, 67.79 [$\text{Fe}(\text{C}_5\text{H}_4)$], 69.96, 70.09 (FeCp), 71.69 [$\text{Fe}(\text{C}_5\text{H}_4)$], 77.86, 81.05 (RuCp), 96.31, 114.95 [t, *J*(CP) 24.1 Hz, C(1)], 128.01–128.18 (m, Ph), 129.26, 129.92, 132.17 [t, *J*(CP) 5.7 Hz, Ph], 133.26 [t, *J*(CP) 5.7 Hz, Ph], 135.94 [t, *J*(CP) 25.8 Hz, Ph], 137.10–137.85 (m, Ph), 139.29 [t, *J*(CP) 19.2 Hz, Ph]. ^{31}P NMR (d_8 -toluene): δ 18.64. ES-MS (MeOH , *m/z*): 807, [$\text{M}+\text{Na}$] $^+$, 100; 784, M^+ , 36. Anal. Found: C, 67.37; H, 4.68. Calc. ($\text{C}_{44}\text{H}_{36}\text{FeP}_2\text{Ru}$): C, 67.44; H, 4.63%; *M*, 784.

4.7. Reaction of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{dppe})\text{Cp}$ with $\text{Co}_2(\text{CO})_8$

To a solution of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{dppe})\text{Cp}$ (80 mg, 0.100 mmol) in Et_2O (20 mL) was added $\text{Co}_2(\text{CO})_8$ (71 mg, 0.208 mmol) and the mixture was stirred at r.t. for 1 h. Solvent was removed in vacuo and the crude residue purified by chromatography (10% acetone/hexane, basic alumina) to afford $\text{Ru}\{\text{C}\equiv\text{CC}_2\text{Fc}[\text{Co}_2(\text{CO})_6]\}(\text{dppe})\text{Cp}$ (3) (92 mg, 81%) as a dark green solid. IR (nujol): $\nu(\text{CO})$ 2077m, 2032s, 2018s, 2000s, 1976m; other band at 1599w (br) cm^{-1} . ^1H NMR (C_6D_6): δ 2.20–2.40, 2.65–2.90 (2 \times m, 2 \times 2H, CH_2), 4.10 [s, 2H, $\text{Fe}(\text{C}_5\text{H}_4)$], 4.30 (s, 5H, FeCp), 4.38 [s, 2H, $\text{Fe}(\text{C}_5\text{H}_4)$], 4.77 (s, 5H,

RuCp), 6.91–7.38 (m, 14H, Ph), 7.93 (broad s, 6H, Ph). ^{31}P NMR (d_8 -toluene): δ 87.22. ES-MS (MeOH, m/z): 1084, M^+ , 5; 801, $[\text{M}-\text{Co}_2(\text{CO})_6]^+$, 12; 593, $[\text{M}-\text{FcC}_2\text{Co}_2(\text{CO})_6]^+$, 100. Consistent elemental analyses could not be obtained.

4.8. Reaction of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{dppe})\text{Cp}$ with $\text{Co}_2(\mu\text{-dppm})(\text{CO})_6$

$\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{dppe})\text{Cp}$ (100 mg, 0.125 mmol) and $\text{Co}_2(\mu\text{-dppm})(\text{CO})_6$ (101 mg, 0.150 mmol) were heated overnight in refluxing thf (25 ml). Solvent was removed in vacuo and the crude residue was purified by chromatography (basic alumina, 25% ether/hexane) to afford $\text{Ru}\{\text{C}\equiv\text{CC}_2\text{Fc}[\text{Co}_2(\mu\text{-dppm})(\text{CO})_4]\}(\text{dppe})\text{Cp}$ (**4**) (135 mg, 76%) as a black solid. Crystals from Et_2O /hexane. IR (nujol): $\nu(\text{CO})$ 2032m, 2000m, 1979s, 1952s, 1935m; other bands at 1585w, 1572w cm^{-1} . ^1H NMR (C_6D_6): δ 2.37–2.57, 2.39–3.05 (2 \times m, 2 \times 2H, CH_2), 3.15–3.36 (m, 3H), 4.29 [t (J 1.8 Hz), 2H, $\text{Fe}(\text{C}_5\text{H}_4)$], 4.51 [t (J 1.8 Hz), 2H, $\text{Fe}(\text{C}_5\text{H}_4)$], 4.53 (s, 5H, FeCp), 4.93 (s, 5H, RuCp), 6.65–6.77 (m, 7H, Ph), 6.84–7.06 (m, 21H, Ph), 7.15–7.22 (m, 13H, Ph), 7.39–7.44 (m, 5H, Ph), 8.07–8.13 (m, 4H, Ph). ^{13}C NMR (C_6D_6): δ 27.33–27.93 (m, CH_2), 34.71–35.23 [t, $J(\text{CP})$ 19.8 Hz, CH_2], 67.41 [$\text{Fe}(\text{C}_5\text{H}_4)$], 69.44 (FeCp), 69.76 [$\text{Fe}(\text{C}_5\text{H}_4)$], 82.92 (RuCp), 87.33, 88.22 [t, $J(\text{CP})$ 12.8 Hz, C(1)], 91.65, 111.40, 127.15–127.29 (m, Ph), 128.67 (Ph), 129.16 (Ph), 130.73–130.89 (m, Ph), 131.30–131.44 (m, Ph), 132.56–132.73 (m, Ph), 133.50–133.64 (m, Ph), 135.55 [t, $J(\text{CP})$ 15.6 Hz, Ph], 136.83 [t, $J(\text{CP})$ 25.2 Hz, Ph], 137.75–138.42 (m, Ph), 139.19 [t, $J(\text{CP})$ 22.1 Hz, Ph], 142.13–142.82 (m, Ph), 204.36, 207.95 (CO). ^{31}P NMR (C_6D_6): δ 36.30 (dppm), 86.35 (dppe). ES-MS (MeOH, m/z): 1435, $[\text{M}+\text{Na}]^+$, 48; 1412, M^+ , 100. Anal. Found: C, 63.00; H, 4.40. Calc. ($\text{C}_{74}\text{H}_{60}\text{Co}_2\text{FeO}_4\text{P}_4\text{Ru}$): C, 62.95; H, 4.28%; M , 1412.

4.9. Synthesis of $\text{Ru}\{\text{C}\equiv\text{CC}_2\text{Fc}[\text{Co}_2(\text{CO})_6]\}(\text{PPh}_3)_2\text{Cp}$ (**5**)

In a reaction similar to the synthesis of **1**, $\text{RuCl}(\text{PPh}_3)_2\text{Cp}$ (108 mg, 0.149 mmol) was treated with $\text{FcC}\equiv\text{CC}\equiv\text{CSiMe}_3$ (50 mg, 0.162 mmol) in the presence of KF (12 mg, 0.207 mmol) in MeOH (15 ml) containing dbu (1 drop). An orange solid was obtained, but could not be satisfactorily purified. Further reaction with $\text{Co}_2(\text{CO})_8$ (48 mg, 0.14 mmol) in Et_2O (10 ml) overnight was followed by removal of solvent and chromatography of the residue on basic alumina. Elution with acetone/hexane (1/9) gave green crystalline $\text{Ru}\{\text{C}\equiv\text{CC}_2\text{Fc}[\text{Co}_2(\text{CO})_6]\}(\text{PPh}_3)_2\text{Cp}$ (**5**) (52 mg, 29% overall). Crystals were obtained from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. Anal. Found: C, 60.58; H, 3.54. Calc.

($\text{C}_{61}\text{H}_{44}\text{Co}_2\text{FeO}_6\text{P}_2\text{Ru}$): C, 60.50; H, 3.66%; M , 1210. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2077m, 2037s, 2012s; also 1606w cm^{-1} . ^1H NMR (C_6D_6): δ 4.26 (br s, 10H, $\text{FeCp}+\text{RuCp}$), 4.41, 4.47 (2 \times s, C_5H_4), 6.95–7.05 (m, 6H, Ph), 7.10–7.35 (br s, 21H, Ph), 7.53–7.65 (br s, 3H, Ph). ES-MS (positive ion, m/z): 1210, M^+ ; 883, $[\text{M}-\text{PPh}_3-\text{Cp}]^+$.

4.10. Reaction of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{dppe})\text{Cp}$ with $\text{C}_2(\text{CN})_4$

A mixture of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{dppe})\text{Cp}$ (100 mg, 0.125 mmol) and $\text{C}_2(\text{CN})_4$ (16.1 mg, 0.125 mmol) was initially dark green, but changed rapidly to red, after which it was heated in refluxing thf (25 mL) for 1 h. Solvent was removed in vacuo and the residue was purified by chromatography (silica, dichloromethane) to afford a 1/1 mixture of isomers **6** and **7** (77 mg, 67%) which was further purified by fractional crystallisation (dichloromethane/cyclohexane) to give **6** and **7** as dark red (from dichloromethane/hexane) and red solids (from acetone/hexane) respectively.

6 (low R_f): IR (CH_2Cl_2): $\nu(\text{CN})$ 2223w, 2214w, 1995s; other bands at 1531w, 1480m cm^{-1} . ^1H NMR (CDCl_3): δ 2.00–2.50 (m, 4H, CH_2), 3.55–3.58 [m, 1H, $\text{Fe}(\text{C}_5\text{H}_4)$], 4.17 (s, 5H, FeCp), 4.25–4.28 [m, 1H, $\text{Fe}(\text{C}_5\text{H}_4)$], 4.62–4.66 [m, 1H, $\text{Fe}(\text{C}_5\text{H}_4)$], 4.81 (s, 5H, RuCp), 4.98–5.01 [m, 1H, $\text{Fe}(\text{C}_5\text{H}_4)$], 7.02–7.16 (m, 2H, Ph), 7.19–7.40 (m, 8H, Ph), 7.45–7.62 (m, 8H, Ph), 7.78–7.88 (m, 2H, Ph). ^{13}C NMR (CDCl_3): δ 27.27–29.66 (m, CH_2), 28.69–28.92 (m, CH_2), 70.99, 71.22, 71.26, 71.76 (FeCp), 71.80, 73.44, 74.00, 74.31, 75.25, 85.94 (RuCp), 113.23, 114.87, 115.42, 115.71 (4 \times CN), 128.32–128.51 (m, Ph), 129.45, 130.09, 130.23, 130.30, 130.83, 131.85, 131.93, 132.19, 132.26, 133.83, 134.61, 134.68, 138.48, 138.74, 141.43, 145.17, 171.99. ^{31}P NMR (d_6 -benzene): δ 84.28 [d, J 16.8 Hz], 85.4 [d, J 16.8 Hz]. ES-MS (MeOH + NaOMe, m/z): 949, $[\text{M}+\text{Na}]^+$. Anal. Found: C, 43.60; H, 3.72; N, 1.03. Calc. ($\text{C}_{51}\text{H}_{38}\text{FeN}_4\text{P}_2\text{Ru}$): C, 66.17; H, 4.14; N, 6.05; M , 926.

7 (high R_f): IR (CH_2Cl_2): $\nu(\text{CN})$ 2225w, 2213w, 2175m; $\nu(\text{C}\equiv\text{C})$ 1994s; other band at 1606w (br) cm^{-1} . ^1H NMR (CDCl_3): δ 1.90–2.20 (m, 1H, CH_2), 2.30–2.70 (m, 3H, CH_2), 4.36 (s, 5H, FeCp), 4.51, 4.54, 4.59, 4.72 [4 \times s, 4 \times 1H, $\text{Fe}(\text{C}_5\text{H}_4)$], 4.91 (s, 5H, RuCp), 6.63–6.69 (m, 2H, Ph), 7.11–7.74 (m, 16H, Ph), 7.98–8.04 (m, 2H, Ph). ^{13}C NMR (CDCl_3): δ 26.98–27.50 (m, CH_2), 29.31–29.69 (m, CH_2), 31.92, 60.12, 70.99, 71.27 (FeCp), 71.58, 71.80, 72.11, 73.92, 86.04 (RuCp), 112.16, 113.17, 113.56, 116.54, 117.92 (4 \times CN), 127.65–132.17 (m, Ph). ^{31}P NMR (C_6D_6): δ 66.06 (d, J 21.4 Hz), 82.34 (d, J 21.4 Hz). ES-MS (MeOH + NaOMe, m/z): 949, $[\text{M}+\text{Na}]^+$. Anal. Found: C, 65.63; H, 3.77; N, 5.95. Anal. Calc. ($\text{C}_{51}\text{H}_{38}\text{FeN}_4\text{P}_2\text{Ru}$): C, 66.17; H, 4.14; N, 6.05%; M , 926.

Table 3
Crystal data and refinement details

Compound	1	2	4	5	6	7	8	9
Formula	C ₄₅ H ₃₈ FeP ₂ Ru· C ₆ H ₆	C ₄₄ H ₃₆ FeP ₂ Ru	C ₇₄ H ₆₀ Co ₂ FeO ₄ P ₄ Ru	C ₆₁ H ₄₄ Co ₂ FeO ₆ P ₂ Ru	C ₅₁ H ₃₈ FeN ₄ P ₂ Ru· C ₃ H ₆ O	C ₅₁ H ₃₈ FeN ₄ P ₂ Ru· 0.5CH ₂ Cl ₂	C ₇₅ H ₇₄ BFeNP ₂ Ru	C ₅₁ H ₅₃ FeI ₄ NP ₂ Ru
MW	875.78	783.64	1411.97	1209.75	983.84	968.23	1219.10	1406.48
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>P2₁2₁2₁</i>	<i>P1</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/n</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
<i>a</i> (Å)	29.970(4)	9.1748(7)	11.365(3)	22.804(5)	9.6645(8)	14.548(3)	10.977(2)	11.800(1)
<i>b</i> (Å)	9.240(1)	18.739(1)	15.075(5)	13.240(3)	25.760(2)	18.752(3)	16.463(2)	25.876(3)
<i>c</i> (Å)	33.582(4)	21.420(2)	19.756(6)	17.428(4)	18.714(2)	16.520(3)	34.032(5)	16.559(2)
α (°)			102.747(5)					
β (°)	114.392(3)		96.467(5)	96.629(3)	101.012(2)	108.698(5)	92.212(4)	92.694(3)
γ (°)			108.560(5)					
<i>V</i> (Å ³)	8470	3683	3068	5227	4573	4269	6146	5051
<i>Z</i>	8	4	2	4	4	4	4	4
<i>D_c</i> (gcm ⁻³)	1.37 ₃	1.41 ₃	1.52 ₈	1.53 ₇	1.42 ₉	1.50 ₆	1.31 ₇	1.84 ₉
μ (cm ⁻¹)	0.81	0.92	1.16	1.29	0.76	0.87	0.58	3.1
Crystal size (mm)	0.13×0.09×0.08	0.38×0.26×0.18	0.19×0.18×0.16	0.37×0.32×0.05	0.38×0.18×0.10	0.24×0.16×0.11	0.38×0.24×0.12	0.18×0.14×0.08
<i>T</i> _{min/max}	0.74	0.86	0.74	0.87	0.89	0.84	0.81	0.79
2 θ _{max} (°)	60	75	50	50	60	60	62.5	70
<i>N</i> _{tot}	8119	76200	29115	39836	60715	48117	46322	89059
<i>N</i> (<i>R</i> _{int})	12142 (0.056)	8649 (0.039)	10739 (0.095)	9206 (0.048)	13422 (0.065)	12102 (0.067)	18089 (0.051)	22278 (0.053)
<i>N</i> _o	10011	7878	6147	6066	9845	8445	12131	14516
<i>R</i>	0.054	0.041	0.087	0.050	0.049	0.046	0.047	0.042
<i>R</i> _w	0.093	0.059	0.106	0.061	0.064	0.057	0.050	0.046

4.11. $[Ru\{C\equiv CC(NEt_3)=CHFc\}(dppe)Cp]BPh_4$ (**8**)

$RuCl(dppe)Cp$ (203 mg, 0.338 mmol), $FeC\equiv CC\equiv CH$ (79 mg, 0.338 mmol), and $Na[BPh_4]$ (163 mg, 0.463 mmol) were heated overnight at 45 °C in thf/NEt_3 (10 ml, 1:1). Solvent was removed and the residue was taken up in the minimum amount of CH_2Cl_2 , and filtered into an excess of well-stirred Et_2O . A yellow solid was filtered off, and washed with Et_2O and hexane to afford $[Ru\{C\equiv CC(NEt_3)=CHFc\}(dppe)Cp]BPh_4$ (**8**) (314 mg, 75%). Crystals were obtained from CH_2Cl_2/Et_2O . IR (nujol): $\nu(C\equiv C)$ 2039s; other bands at 1596w (br), 1580w cm^{-1} . 1H NMR ($CDCl_3$): δ 0.33 [t, J 6.6 Hz, 9H, Me], 2.24 [q, J 6.6 Hz, 6H, CH_2], 2.30–2.60 (m, 4H, CH_2), 4.06 (s, 5H, FeCp), 4.27, 4.67 [2× s, 2× 2H, $Fe(C_5H_4)$], 4.83 (s, 5H, RuCp), 5.54 (s, 1H, =CH), 6.80–6.95 (m, 4H, Ph), 7.00–7.17 (m, 12H, Ph), 7.20–7.50 (m, 20H, Ph), 7.64–7.81 (m, 4H, Ph). ^{13}C NMR ($CDCl_3$): δ 7.51 (NEt_3), 28.06–28.67 (m, CH_2), 51.52 (NEt_3), 68.95 [$Fe(C_5H_4)$], 69.04 (FeCp), 69.31 [$Fe(C_5H_4)$], 79.20, 83.38 (RuCp), 101.61, 120.52, 121.65, 121.98, 125.52 (br), 127.89, 128.28 (br), 128.83 (t, J 23.7 Hz), 129.41, 130.12, 130.64–130.78 (m, Ph), 132.69–133.83 (m, Ph), 140.93–141.47 (m, Ph), 163.18–165.15 (m, BPh_4). ^{31}P NMR ($CDCl_3$): δ 86.90. ES-MS (MeOH, m/z): 900, M^+ , 28; 799, $[M - NEt_3]^+$, 100. Anal. Found: C, 73.72; H, 6.01; N, 0.98. Calc. ($C_{75}H_{74}BF_4FeNP_2Ru$): C, 73.89; H, 6.12; N, 1.15; M , 900 (cation).

4.12. Reaction of $[Ru\{C\equiv CC(NEt_3)=CHFc\}(dppe)Cp]BPh_4$ with iodine

To a solution of $[Ru\{C\equiv CC(NEt_3)=CHFc\}(dppe)Cp]BPh_4$ (65 mg, 0.0534 mmol) in thf (10 mL) was added iodine (56 mg, 0.220 mmol), and the mixture was stirred for 20 min at r.t. Solvent was removed in vacuo and the residue was taken up in the minimum amount of CH_2Cl_2 , and filtered into an excess of well-stirred Et_2O . The precipitate was collected upon a sinter and washed successively with ether, methanol, ether, and hexane to give $[Ru(dppe)\{\eta-C_5H_4C\equiv CC(NEt_3)=CHFc\}]_3$ (**9**) (55 mg, 73%) as a brick-red solid. Crystals were obtained from $CH_2Cl_2/EtOH$ or $CHCl_3/Pr^iOH$. IR (nujol): $\nu(C\equiv C)$ 2197m, 1979w (br); other bands at 1608w, 1585w cm^{-1} . 1H NMR ($CDCl_3$): δ 1.27 [t, J 6.6 Hz, 9H, Me], 2.42–2.52 (m, 2H, CH_2), 2.83–3.02 (m, 2H, CH_2), 3.64 [q, J 6.6 Hz, 6H, CH_2], 4.31 [broad s, 8H, FeCp + $Fe(C_5H_4)+=CH$], 4.52 [s, 2H, $Fe(C_5H_4)$], 5.09, 5.50 [2× s, 2× 2H, $Ru(C_5H_4)$], 7.03–7.10 (m, 5H, Ph), 7.28–7.42 (m, 14H, Ph), 7.70–7.80 (m, 5H, Ph). ^{13}C NMR (d_6 -acetone): δ 8.61 (NEt_3), 27.89–28.99 (m, CH_2), 54.52 (NEt_3), 70.37 (FeCp), 71., 72.02 [2× $Fe(C_5H_4)$], 77.23, 78.43 [$Ru(C_5H_4)$], 80.70, 84.13, 88.13 [$Ru(C_5H_4)$], 89.34, 119.84, 128.41–128.53 (m, Ph), 128.88–129.00 (m, Ph), 130.05, 130.25,

131.60–132.48 (m, Ph), 134.57–134.82 (m, Ph). ^{31}P NMR ($CDCl_3$): δ 79.15. ES-MS (MeOH, m/z): 1026, M^+ , 100; 900, $[M+H-I]^+$, 20. Anal. Found: C, 43.60; H, 3.72; N, 1.03. Calc. ($C_{51}H_{53}FeI_4NP_2Ru$): C, 43.58; H, 3.73; N, 1.00; M , 1026 (cation).

4.13. Structure determinations

Full spheres of diffraction data were measured at ca 153 K using a Bruker AXS CCD area-detector instrument. N_{tot} reflections were merged to N unique (R_{int} cited) after “empirical”/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being used in the full matrix least squares refinements. 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_{iso})_H being constrained at estimated values. Conventional residuals R , R_w on $|F|$ are quoted at convergence [weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$]. Neutral atom complex scattering factors were used; computation used the XTAL 3.7 program system [35]. Pertinent results are given in Figs. 1 and 2 (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 3.

Individual diversities in procedure are noted as follows:

1. The benzene solvent molecule was refined as a rigid body.
4. Weak, poor quality data would support meaningful anisotropic displacement parameters for Ru, Co, Fe, P.
5. Data collection at 298 K.
7. The dichloromethane molecule of solvation was modelled as disordered about an inversion centre, C half-weighted.
8. Cp ring 40n was modelled as disordered over two sets of sites, occupancies set at 0.5 after trial refinement.

5. Supplementary material

Full details of the structure determination (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC 222413–222419 (for **9**, **8**, **1**, **4**, **6**, **7** and **2**, respectively) and 225496 (**5**). 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.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

We thank the Australian Research Council for support of this work and Johnson Matthey plc, Reading, UK, for a generous loan of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$. Provision of mass spectra by Professor B.K. Nicholson (University of Waikato, Hamilton, New Zealand) is gratefully acknowledged. These studies were facilitated by travel grants (CNRS, France, and ARC IREX, Australia).

References

- [1] F. Paul, C. Lapinte, *Coord. Chem. Rev.* 178–180 (1998) 427.
- [2] (a) P.J. Low, M.I. Bruce, *Adv. Organomet. Chem.* 48 (2002) 71; (b) M.I. Bruce, P.J. Low, *Adv. Organomet. Chem.* 50 (2004) 231.
- [3] V.W.-W. Yam, V.C.-Y. Lue, K.-K. Cheung, *Organometallics* 15 (1996) 1740.
- [4] (a) Y. Zhou, J.W. Seyler, W. Weng, A.M. Arif, J.A. Gladysz, *J. Am. Chem. Soc.* 115 (1993) 8509; (b) J.W. Seyler, W. Wang, Y. Zhou, J.A. Gladysz, *Organometallics* 12 (1993) 3802; (c) M. Brady, W. Weng, Y. Zhou, J.W. Seyler, A.J. Amoroso, A.M. Arif, M. Böhme, G. Frenking, J.A. Gladysz, *J. Am. Chem. Soc.* 119 (1997) 775.
- [5] (a) M. Akita, M.-C. Chung, A. Sakurai, S. Sugimoto, M. Terada, M. Tanaka, Y. Moro-oka, *Organometallics* 16 (1997) 4882; (b) M.-C. Chung, A. Sakurai, M. Akita, Y. Moro-oka, *Organometallics* 18 (1999) 4684; (c) M. Akita, M.-C. Chung, A. Sakurai, Y. Moro-oka, *Chem. Commun.* (2000) 1285; (d) M. Akita, M.-C. Chung, M. Terada, M. Miyauti, M. Tanaka, Y. Moro-oka, *J. Organomet. Chem.* 565 (1998) 49; (e) M. Akita, A. Sakurai, M.-C. Chung, Y. Moro-oka, *J. Organomet. Chem.* 670 (2003) 2.
- [6] (a) N. Le Narvor, L. Toupet, C. Lapinte, *J. Am. Chem. Soc.* 117 (1995) 7129; (b) F. Coat, C. Lapinte, *Organometallics* 15 (1996) 477; (c) F. Coat, M.-A. Guillevic, L. Toupet, F. Paul, C. Lapinte, *Organometallics* 16 (1997) 5988; (d) N. Le Narvor, C. Lapinte, *C.R. Acad. Sci., Paris, Ser. II* 1 (1998) 745; (e) M. Guillemot, L. Toupet, C. Lapinte, *Organometallics* 17 (1998) 1928; (f) F. Coat, M. Guillemot, F. Paul, C. Lapinte, *J. Organomet. Chem.* 578 (1999) 76.
- [7] (a) M.I. Bruce, L.I. Denisovich, P.J. Low, S.M. Peregudova, N.A. Ustynyuk, *Mendeleev Commun.* (1996) 200; (b) M.I. Bruce, P.J. Low, K. Costuas, J.-F. Halet, S.P. Best, G.A. Heath, *J. Am. Chem. Soc.* 122 (2000) 1949; (c) M.I. Bruce, B.G. Ellis, P.J. Low, B.W. Skelton, A.H. White, *Organometallics* 22 (2003) 3184.
- [8] (a) T.B. Peters, J.C. Bohling, A.M. Arif, J.A. Gladysz, *Organometallics* 18 (1999) 3261; (b) W. Mohr, J. Stahl, F. Hampel, J.A. Gladysz, *Chem. Eur. J.* 9 (2003) 3324.
- [9] M.I. Bruce, M.E. Smith, B.W. Skelton, A.H. White, *J. Organomet. Chem.* 637–639 (2001) 484.
- [10] (a) A.A. Koridze, V.I. Zdanovich, N.V. Andrievskaya, Y. Siromakhova, P.V. Petrovski, M.G. Ezernitskaya, F.M. Dolgushin, A.I. Yanovsky, Yu.T. Struchkov, *Izv. Akad. Nauk Ser. Khim.* (1996) 1261; *Russ. Chem. Bull.*, 45 (1996) 1200; (b) A.A. Koridze, V.I. Zhdanovich, V.Y. Lagunova, I.I. Petrukhova, F.M. Dolgushin, *Izv. Akad. Nauk. Ser. Khim.* (2000) 1324 *Russ. Chem. Bull.*, 49 (2000) 1321; (c) M.I. Bruce, B.W. Skelton, A.H. White, N.N. Zaitseva, *J. Organomet. Chem.* 650 (2002) 188.
- [11] (a) R.D. Adams, O.-S. Kwon, B. Qu, M.D. Smith, *Organometallics* 20 (2001) 5225; (b) R.D. Adams, B. Qu, M.D. Smith, *Inorg. Chem.* 40 (2001) 2932; (c) R.D. Adams, B. Qu, *Organometallics* 19 (2000) 2411.
- [12] (a) M. Sato, H. Shintate, Y. Kawata, M. Sekino, M. Katada, S. Kawata, *Organometallics* 13 (1994) 1956; (b) M. Sato, Y. Hayashi, S. Kumakura, N. Shimizu, M. Katada, S. Kawata, *Organometallics* 15 (1996) 721.
- [13] (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.D. Kelly, B.W. Skelton, A.H. White, *J. Organomet. Chem.* 604 (2000) 150; (c) F. Coat, P. Thominet, C. Lapinte, *J. Organomet. Chem.* 629 (2001) 39.
- [14] Cambridge Crystallographic Data Centre: ConQuest 1.5, 2000.
- [15] M. Traetteberg, L.S. Khaikin, O.E. Grikin, J.F. Liebman, M. Hulce, *J. Molec. Struct.* 559 (2001) 295.
- [16] (a) M.I. Bruce, M. Ke, P.J. Low, B.W. Skelton, A.H. White, *Organometallics* 17 (1998) 3539; (b) M.I. Bruce, M.E. Smith, B.W. Skelton, A.H. White, *J. Organomet. Chem.* 484 (2001) 637; (c) M.I. Bruce, T.W. Hambley, M.R. Snow, A.G. Swincer, *Organometallics* 4 (1985) 494.
- [17] A. Davison, J.P. Solar, *J. Organomet. Chem.* 166 (1979) C13.
- [18] (a) M.I. Bruce, J.R. Rodgers, M.R. Snow, A.G. Swincer, *J. Chem. Soc., Chem. Commun.* (1981) 271; (b) Y. Yamamoto, R. Satoh, T. Tanase, *J. Chem. Soc., Dalton Trans.* (1995) 307.
- [19] P. Hong, K. Sonogashira, N. Hagihara, *J. Organomet. Chem.* 219 (1981) 363.
- [20] (a) K. Onitsuka, S. Takahashi, *J. Chem. Soc., Chem. Commun.* (1995) 2095; (b) K. Onitsuka, N. Ose, F. Ozawa, S. Takahashi, *J. Organomet. Chem.* 578 (1999) 169.
- [21] T. Mochida, S. Yamazaki, *J. Chem. Soc., Dalton Trans.* (2002) 3559.
- [22] H. Werner, W. Hofmann, *Angew. Chem.* 90 (1978) 496 *Angew. Chem., Int. Ed. Engl.*, 17 (1978) 464.
- [23] S.R. Berryhill, B. Sharenow, *J. Organomet. Chem.* 221 (1981) 143.
- [24] P. Brun, P. Vierling, J.G. Riess, G. Le Borgne, *Organometallics* 6 (1987) 1032.
- [25] H.E. Bunting, M.L.H. Green, P.A. Newman, *J. Chem. Soc., Dalton Trans.* (1988) 557.
- [26] M. Akita, A. Kondoh, *J. Organomet. Chem.* 299 (1986) 369.
- [27] M.I. Bruce, K.R. Grundy, M.J. Liddell, M.R. Snow, E.R.T. Tiekink, *J. Organomet. Chem.* 375 (1989) 131.
- [28] (a) C. Lo Sterzo, *J. Organomet. Chem.* 408 (1991) 253; (b) C. Lo Sterzo, *J. Chem. Soc., Dalton Trans.* (1992) 1989.
- [29] W. Henderson, J.S. McIndoe, B.K. Nicholson, P.J. Dyson, *J. Chem. Soc., Dalton Trans.* (1998) 519.
- [30] M.I. Bruce, C. Hameister, A.G. Swincer, R.C. Wallis, *Inorg. Synth.* 28 (1990) 270.
- [31] A.G. Alonso, L.B. Reventos, *J. Organomet. Chem.* 338 (1998) 249.
- [32] 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.
- [33] L.S. Chia, W.R. Cullen, *Inorg. Chem.* 14 (1975) 482.
- [34] (a) E.T. Chernick, S. Eisler, R.R. Tykwinski, *Tetrahedron Lett.* 42 (2001) 8575; (b) A.L.K. Shi Shun, E.T. Chernick, S. Eisler, R.R. Tykwinski, *J. Org. Chem.* 68 (2003) 1339.
- [35] S.R. Hall, D.J. du Boulay, R. Olthof-Hazekamp (Eds.), *The XTAL 3.7 System*, University of Western Australia, Perth, 2000.