ORGANOMETALLICS

Oxidative Dimerization of Aryldiynyl-Ruthenium Complexes

Michael I. Bruce,^{*,†} Karine Costuas,[‡] Frédéric Gendron,[‡] Jean-François Halet,^{*,‡} Martyn Jevric,[†] and Brian W. Skelton^{§,|}

[†]School of Chemistry & Physics, University of Adelaide, South Australia 5005, Australia

[‡]Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS, Université de Rennes 1, 35042 Rennes, France

[§]School of Biomedical, Biomolecular & Chemical Sciences, Chemistry M313, University of Western Australia, Crawley, Western Australia 6009, Australia

Supporting Information



ABSTRACT: Chemical oxidation of $Ru(C \equiv CC \equiv CR)(dppe)Cp$ with $[FeCp_2]PF_6$ affords the binuclear cations [{Ru(dppe)- $Cp_{2}C_{8}R_{2}^{2+}(PF_{6}^{-})_{2}$ (R = Ph, $7^{2+}(PF_{6}^{-})_{2}$; R = Fc, $8^{2+}(PF_{6}^{-})_{2}$) by radical coupling at electron-rich sites involving the inner and outer C=C triple bonds, to give cyclobutenediylidene derivatives. In each case, mixtures of symmetrical and asymmetrical isomers were obtained (2:1 for $7^{2+}(PF_6^{-})_2$, 1:1 for $8^{2+}(PF_6^{-})_2$), shown by single-crystal X-ray diffraction structure determinations of 7^{2+} -asym $(PF_6^-)_2$ and 8^{2+} -sym $(AsF_6^-)_2$. 8^{2+} -sym consists of a central C_4 ring with two =C=C=Ru(dppe)Cp groups in the 1,2-positions and two Fc substituents in the 3,4-positions, whereas for 7^{2+} -asym the substituent =Ru(dppe)Cp is in the 1position, =C=C=Ru(dppe)Cp is in the 2-position, Ph is in the 3-position, and $-C\equiv CPh$ is in the 4-position. DFT calculations reveal that the precursor cationic diynyl complexes show important electron density on C_{β} and C_{δ} suggesting that radical coupling $(C_{\delta} + C_{\delta})$ or $(C_{\beta} + C_{\delta})$ affords the sym and asym isomers, respectively.

■ INTRODUCTION

The chemistry of transition-metal complexes containing conjugated carbon chains continues to intrigue and surprise.^{1–3} Potential applications as components of electronic,⁴ magnetic,⁵ and optical devices⁶ and as molecular-scale wires⁷ depend upon the behavior of unpaired electrons in these systems, and much research on the redox properties of metal-ligand end-bridged compounds $\{L_nM\} - (C \equiv C)_x - \{ML_n\}$ has been carried out. The series of complexes containing a C₄ bridge has been the subject of many studies with attention being directed toward the series of oxidized derivatives $[{L_nM}-(CC)_2-{ML_n}]^{m+}$ $(ML_n = M(dppe)Cp^* (M = Fe_n^8 Ru, 9 Os^{10}), M(dppe)(\eta$ C_7H_7) (M = Mo¹¹)).

Extensive studies of the arylethynyl-metal complexes $Fe(C \equiv CAr)(dppe)Cp$ ¹² M(C $\equiv CAr)(dppe)Cp^*$ (M = Fe,¹³ Ru;¹⁴ Ar = C_6H_4X -4, X = CF₃, Br, Me, Bu^t (M = Fe), NO₂, CN, F, H, OMe, NH₂ (M = Fe, Ru)), Ru(C \equiv CAr)(PP)Cp' (Ar = Ph, C₆H₄Me-4, 1-naphthyl, 9-anthryl; (PP)Cp' = $(PPh_3)_2Cp_1$ $(dppe)Cp^*)$,¹⁵ trans-Ru $(C \equiv CAr)Cl(dppe)_2$ (Ar = C₆H₄X-4, X = NO₂, CHO, C(O)Me, F, H, OMe, NMe₂),¹⁶ $M(C \equiv$ CR)(dppe)(η -C₇H₇) (M = Mo, R = Bu^t, CO₂Me, Fc or C_6H_4X-4 , X = CO₂Me, CHO, H, Me, OMe, NH₂; M = W, R = Ph, C_6H_4Me-4),¹⁷ Mo(C \equiv CR)(CO)(dppe)Cp', and *trans*- $Mo(C \equiv CR)(CO)(PMe_3)_2Cp'$ (R = Ph, C₆H₄-4-Me, Cp' = Cp, Cp^*)¹⁸ have shown that ready 1e oxidation of these complexes occurs to give 17e monocations. Both neutral and charged species have been investigated by a variety of spectroscopic (IR, NMR, UV-vis), X-ray structural and theoretical (DFT) means. In particular, the neutral metalligand fragment, formally containing M(II), is electron-rich and behaves as an electron-releasing group to the carbon-rich ligand. It is clear that the properties of σ -alkynyl-metal complexes are best considered in terms of delocalization of electron spin density over the metal-alkynyl array.¹⁹

Whiteley and co-workers have found that similar oxidation of $Mo(C \equiv CPh)(dppe)(\eta - C_7H_7)$ afforded the bis(vinylidene) $[\{(\eta - C_7 H_7)(dppe)Mo\}(=C=CPhCPh=C=)\{Mo(dppe)(\eta - C_7 H_7)(dppe)Mo\}(=C=CPhCPh=C=)\{Mo(dppe)(\eta - C_7 H_7)(dppe)(\eta - C_7 H_7)(dppe)Mo\}$ $C_{7}H_{7}$](PF₆)₂ by coupling at C_{β} .¹⁷ Similarly, oxidation of Mo(C=CC=CR)(LL)(η -C₇H₇) (LL = bpy, R = SiMe₃; LL =

Received: June 9, 2012 Published: September 4, 2012



Scheme 2. Reactions of $Ru(C \equiv CPh)(PPh_3)_2Cp(1)$ with $[FeCp_2]PF_6$ or $Ag[PF_6]$



dppe, R = H, SiMe₃) with [FeCp₂]PF₆ produces molybdenumstabilized diynyl radicals which were characterized by extensive spectroscopic studies (IR, ESR) and by a structural study of [Mo(CCCCSiMe₃)(bpy)(η -C₇H₇)]PF₆.²⁰ Further oxidation of Mo(C≡CC≡CSiMe₃)(dppe)(η -C₇H₇) afforded a dimeric product, shown by an X-ray structure to be the bis-vinylidene [{(η -C₇H₇)(dppe)Mo}{=C=C(C≡CSiMe₃)C(C≡ CSiMe₃)C=C=}{Mo(dppe)(η -C₇H₇)}]PF₆)₂ (Scheme 1). The intermediacy of the 17e diynyl monocation was shown independently, and this evolved by C_β coupling to the branched C₈ chain-bridged product.

Related reactions have been reported for the ethynyl complexes M(C=CH)(dppe)Cp* ($\hat{M} = Fe_{,}^{8,21} Ru_{,}^{22} Os^{23'}$), which gave the bis(vinylidene) dications $[{Cp*(dppe)M}](=$ $C=CHCH=C=){M(dppe)Cp^*}]^{2+}$, from which the neutral C_4 -bridged compounds {Cp*(dppe)M}C \equiv CC \equiv C{M(dppe)-Cp*} were obtained by deprotonation with KOBu^t. Representative examples of substituted alkynyls were oxidized to 17e species (formally M(III)), either chemically or electrochemically. Paramagnetic ¹H NMR measurements have allowed the charge distribution in the aryl group to be determined, while ionization potential data correlate with electronic substituent parameters and are related to the effect of the para substituent on their electronic properties. These data and DFT calculations indicate a major difference in electronic structures of the Mo and Fe series on the one hand and the Ru compounds on the other, with the HOMO heavily weighted on the metal for the

former species but almost equally distributed on the metal and the arylalkynyl ligand for the latter.^{14,17c,24}

In the course of these studies, attempts have been made to isolate the oxidized compounds. Chemical oxidation of Fe(C \equiv CC₆H₄X-4)(dppe)Cp* with [FeCp₂]PF₆ has given [Fe-(CCC₆H₄X-4)(dppe)Cp*]PF₆ (X = NO₂, CN, CF₃, F, Br, H, Me, OBu^t, OMe, NH₂, NMe₂), and structural determinations of several of them were completed.¹³ In the ruthenium series, a major difference in reactivity is found.¹⁴ Electrochemical oxidation showed that apparently reversible or quasi-reversible le processes occur in the range 0.05–0.40 V (vs SCE), the potential correlating with the electronic properties of the substituents. However, in attempts to use chemical oxidants it was not possible to isolate any of the oxidized compounds, although in one case the vinylidene [Ru{=C=CH(C₆H₄NO₂-4)}(dppe)Cp*]PF₆ was isolated and characterized.¹⁴

In the ruthenium series, the use of $[FeCp_2]PF_6$ as the oxidant has enabled novel dimeric species to be obtained, which had been formed by radical coupling at sites shown to be electronrich, particularly involving the alkynyl C_{β} and Ph C_{para} atoms (Scheme 2).^{24,25} The product from Ru(C=CPh)(PPh_3)₂Cp (1) is the bis(vinylidene) complex 2, which during workup can be easily deprotonated to the corresponding alkynyl-(vinylidene) complex 3.

Chemical oxidation of the neutral arylalkynyl-ruthenium complexes with Ag[OTf] in dichloromethane resulted in rapid bleaching of the color of the solutions before they turned

darker, often blue.¹⁴ An earlier study described reactions of Ru(C=CPh)(PPh₃)₂Cp with Ag[PF₆] in toluene to give the silver π complex [Ag{PhC₂[Ru(PPh₃)₂Cp]}₂]PF₆ (4).²⁵ In CH₂Cl₂, the reaction affords the bis(vinylidene) 3 directly.

Related to this chemistry is the earlier report of the dimerization of the butatrienylidene W{=C=C=C=CH-(C₆H₄Bu^t)}(CO)(dppe)₂ to {(dppe)₂(OC)W}{C=C[=CH-(C₆H₄Bu^t)]C[=CH(C₆H₄Bu^t)]C=C}{W(CO)(dppe)₂} by coupling at the 3-position.²⁶ It is suggested that this reaction proceeds via a 1,2-bis(ethynyl)cyclobutenyl diradical intermediate which undergoes retro-electrocyclic ring opening (Scheme 3).

Scheme 3. Self-Coupling of W(=C=C=C= CHAr)(CO)(dppe)₂^a



 ${}^{a}[W] = W(CO)(dppe)_{2}; Ar = C_{6}H_{4}Bu^{t}-4.^{26}$

This paper describes some chemistry of the diynylruthenium complexes $\operatorname{Ru}(C \equiv CC \equiv CAr)(dppe)Cp$ (Ar = Ph (5), Fc (6)), during which binuclear complexes formed by coupling of electron-rich carbon atoms of the C₄ chains give unusual cyclobutene-centered complexes containing carbene, vinylidene, and allenylidene ligands.

RESULTS AND DISCUSSION

Electrochemical studies reveal a single irreversible oxidation at +0.46 V for 5 and at +0.32 V for 6 (CH₂Cl₂, vs SCE, referenced to internal $FeCp_2/[FeCp_2]^+ = +0.46$ V). Chemical oxidation of $Ru(C \equiv CC \equiv CAr)(dppe)Cp$ (Ar = Ph, Fc) with $[FeCp_2]PF_6$ results in the initially orange solutions darkening, eventually to give maroon $7^{2+}(PF_6^{-})_2$ (R = Ph) or intensely purple $8^{2+}(PF_6^{-})_2$ (R = Fc). The ³¹P NMR spectra of 7 showed two components (in a 2:1 ratio) containing respectively one resonance at δ 81.0 and two resonances at δ 82.0 and 86.5. The solid mixture could be precipitated, but after standing for a few minutes, a d_6 -acetone solution of $7^{2+}(PF_6)_2$ contained only the two resonances of the minor product. Although attempts to separate the mixture $7^{2+}(PF_6)_2$ by preparative TLC on silica gel resulted in the separation of two dark blue bands, the faster moving of which contained multiple ³¹P NMR resonances of decomposition products and there was no sign of the original singlet resonance at δ 81.0. The second fraction had ^{31}P resonances at δ 82.0 and 86.5, suggesting the presence of two Ru(dppe)Cp groups in different environments. In both cases, elemental analyses and ES-MS suggested that a dimeric cation had formed, which afforded the highest ions at m/z1411, assigned to $[M + OMe]^+$ and confirmed by highresolution ES-MS. Crystals satisfactory for X-ray analysis could be obtained by exchange of PF₆ for AsF₆ counterion.

For $8^{2+}(PF_6^{-})_2$, the products also contained two components, in a 1:1:1 ratio (δ 83.1, 84.1, 90.0). These data suggest that two closely related products were present in each case. In neither case were the two forms interconvertible. The complex $8^{2+}(PF_6^{-})_2$ could not be purified satisfactorily by preparative TLC, but one product could be fractionally crystallized from dichloromethane/benzene. This material exhibits a single ³¹P resonance at δ 83.1, suggesting that the two Ru(dppe)Cp groups were in identical environments ($8^{2+}(PF_6^{-})_2$, symmetric) and thus allowing assignment of the two other resonances at δ 84.1 and 90.0 to a second form ($8^{2+}(PF_6^{-})_2$, asymmetric). The ES-MS of the product showed the highest mass ion at m/z 1627, again assigned to $[M + MeOH]^+$.

The X-ray structural determinations of $7^{2+}(PF_6^{-})_2$ and $8^{2+}(AsF_6^{-})_2$ revealed that these two compounds have closely related structures (Scheme 4).

Plots of the two dications are shown in Figures 1 and 2; selected bond parameters are collected in Table 1. The dication 7^{2+} -asym contains a central four-membered ring which has as substituents Ph, C=CPh, ={Ru(dppe)Cp}, and =C=C={Ru(dppe)Cp} groups. Of the four ring C-C bonds,

Scheme 4. Oxidation of $Ru(C \equiv CC \equiv CAr)(dppe)Cp$ (Ar = Ph (5), Fc (6)) with [FeCp₂]PF₆





Figure 1. Plot of the dication of $[C_4Ph(C \equiv CPh){=Ru(dppe)Cp}{=C = C = C = Ru(dppe) Cp}](PF_6)_2$ (7^{2+} -asym(PF_6^-)_2). Ellipsoids have been drawn at the 20% probability level, with hydrogen atoms omitted for clarity.



Figure 2. Plot of the dication of $[C_4Fc_2{=}C{=}C{=}Ru(dppe)Cp_2]$ - $(AsF_6)_2$ ($8^{2^+}-sym(AsF_6^-)_2$). Ellipsoids have been drawn at the 30% probability level, with hydrogen atoms omitted for clarity.

C(4)-C(5) (1.419(13) Å) is shorter than the other three (1.475(13), 1.468(12), 1.510(12) Å), consistent with its being a C=C double bond. The Ru(2)-C(6) bond is short, at 1.920(9) Å, suggesting the multiple-bond character of a carbenic interaction (cf. Ru=C = 1.931(6) Å in [Ru{= C(CH₂Ph)(C=CPh)}(dppm)(η^{5} -C₉H₇)](BF₄)).²⁷ For Ru(1)-C(1) (1.891(8) Å) a similar shortening, together with the C(1)-C(2) and C(2)-C(3) distances of 1.271(11) and 1.341(11) Å, are consistent with an allenylidene ligand (cf. Ru-C(1), C(1)-C(2), and C(2)-C(3) distances of 1.878(5), 1.260(7), and 1.353(7) Å in [Ru(=C=C=CPh₂)(PPh₃)₂(η^{5} -C₉H₇)](PF₆)).²⁸ The separation C(7)-C(8) (1.185(12) Å) shows that the alkynyl nature of the PhC=C- group is preserved.

In contrast, the dication 8^{2+} -sym (Figure 2) contains a C₄ ring symmetrically substituted with two =C=C={Ru(dppe)-Cp} groups occupying the 1,2-positions and two Fc groups occupying the 3,4-positions. Within the C₄ ring, the C-C separations are 1.392(7) Å (C(4)–C(5)) and 1.452(6), 1.489(6), and 1.464(6) Å, the first value again consistent with the presence of a C=C double bond. The two $\{Cp(dppe)Ru\}=C=C=$ fragments are similar, with Ru(1)–C(1) and Ru(2)–C(8) being 1.913(4) and 1.898(5) Å, respectively, and C=C=C separations of 1.244(6), 1.346(6), 1.254(6), and 1.352(7) Å, consistent with the Ru–vinylidene formulations proposed (cf. Ru–C(1) and C(1)–C(2) distances of 1.839(7) and 1.30(1) Å in $[Ru(=C=CMe_2)(PPh_3)_2(\eta^5-C_9H_7)](OTf)).^{29}$

In both complexes, the Ru–P distances (range 2.268(2)– 2.2906(9) Å) are characteristic of cationic ruthenium–carbene (2.265, 2.266(2) Å),²⁷ –vinylidene (2.352, 2.367(3) Å),²⁹ and –allenylidene (2.321, 2.358(2) Å)²⁸ complexes mentioned above, rather than the somewhat shorter distances found in the neutral Ru–alkynyl species (2.240 and 2.250(1) Å in Ru(CCPh)(dppe)Cp),³⁰ as a result of weaker back-bonding from the cationic metal center and electrostatic effects.

Other spectroscopic features are in accord with the solidstate structures. The IR spectra contain ν (CC) bands at 2169, 1933, 1597, and 1563 cm⁻¹ (7²⁺-*asym*) and at 2139, 1927, 1698, and 1585 cm⁻¹ (8²⁺-*sym*). For 7²⁺-*asym*, two CpRu singlet ¹H resonances are at δ 5.50 and 5.74, whereas in 8²⁺*sym*, only a single CpRu signal is found at δ ca. 5.67 (although this is overlaid by one of the ferrocenyl C₅H₄ multiplets at δ 5.34). The ³¹P NMR spectra contain signals at δ 82.0 and 86.5 (for 7²⁺-*asym*), while 8²⁺-*sym* has a singlet at δ 83.1. The initial mixture also shows two ³¹P resonances at δ 84.1 and 89.95, which we assign to 8²⁺-*asym*. As 8²⁺-*sym* has a single resonance at δ 83.1, it is reasonable to assign the resonance at δ 84.1 to the Ru–allenylidene fragment and the signal at δ 90.0 to the Ru–carbene moiety in 8²⁺-*asym*. Limited solubility in solvents suitable for the ¹³C NMR of these complexes did not allow observation of the Ru-bonded C atoms.

These data are consistent with the reactions of 5 and 6, which give isomeric mixtures of 7^{2+} or 8^{2+} , respectively, proceeding in the same way, the two isomers shown to be present in the original product mixtures by NMR spectroscopy being the sym and asym isomers in each case. This conclusion is also supported by noting the less broadened set of signals of one of the Fc groups, which can be assigned to an Fc group extended away from the cyclobutenyl system. These signals are not present in solutions prepared from the crystalline sample. The IR spectrum of 8²⁺-asym contains a ν (C \equiv C) band at 2139 cm^{-1} , which is not present in the spectrum of 8^{2+} -sym. We cannot unequivocally rule out the possibility that the isomers of which X-ray diffraction structures could not be obtained might be the open-chain isomers containing butadienyl-based ligands, analogous to the complex reported by Berke and co-workers,²⁶ but the common features of these two isomer pairs strongly suggest that, serendipitously, we have determined the structures of the sym and asym isomers of 7^{2+} and 8^{2+} , respectively, the second isomers being the asym and sym isomers, respectively, of these complexes.

The reactions described above, which lead to cyclobutenylidene derivatives, can be understood in terms of coupling of radical species in which a significant coefficient of the spin density is found on the carbon atoms of the C₄ chain. DFT studies have shown that this is more likely to occur with alkynyl– and polyynyl–ruthenium complexes than with the corresponding iron derivatives.^{24,31} The spin density is localized on the C_β and C_δ atoms, so that coupling would be likely to

Table 1. Selected Bond Parameters for 7²⁺-asym and 8²⁺-sym

distances (Å)			angles (deg)			
	8 ²⁺ -sym	7 ²⁺ -asym		8 ²⁺ -sym	7 ²⁺ -asym	
Ru(dppe)Cp						
Ru(1) - P(1)	2.2834(11)	2.268(3)	P(1)-Ru(1)-P(2)	83.04(3)	82.77(11)	
Ru(1)-P(2)	2.2831(12)	2.280(3)	P(1)-Ru(1)-C(1)	81.5(1)	84.9(3)	
Ru(1)-C(cp)	2.212-2.236(4)	2.226-2.270(9)	P(2)-Ru(1)-C(1)	93.1(1)	91.3(3)	
av	2.227	2.244	P(3)-Ru(2)-P(4)	83.90(4)	83.58(10)	
Ru(2) - P(3)	2.2759(12)	2.286(3)	P(3)-Ru(2)-C(6)	87.3(1)	94.7(3)	
Ru(2) - P(4)	2.2908(12)	2.283(3)	P(4)-Ru(2)-C(6)	94.6(1)	91.5(3)	
Ru(2)-C(cp)	2.219-2.254(5)	2.241-2.272(9)				
av	2.237	2.260				
		$Ru-C_n$ Subs	tituents			
Ru(1)-C(1)	1.913(4)	1.891(8)	Ru(1)-C(1)-C(2)	175.8(3)	174.3(9)	
C(1) - C(2)	1.244(6)	1.271(11)	C(1)-C(2)-C(3)	179.1(5)	174.6(9)	
C(2) - C(3)	1.346(6)	1.341(11)	C(2)-C(3)-C(4)	136.5(4)	133.5(9)	
			C(2)-C(3)-C(6)	135.1(4)	136.5(9)	
Ru(2)-C(8)/C(6)	1.898(5)	1.920(9)	Ru(2)-C(8)-C(7)	171.0(4)		
C(6) - C(7)	1.352(7)		C(6) - C(7) - C(8)	173.3(5)		
C(7) - C(8)	1.254(6)					
		Exocyclic C-0	C Bonds			
C(4)-C(401)/C(41)	1.454(7)	1.386(14)	C(3)-C(4)-C(401)/C(41)	132.3(4)	132.8(8)	
			C(5)-C(4)-C(401)/C(41)	134.8(4)	138.6(8)	
C(5) - C(501)	1.423(16)		C(4)-C(5)-C(601)	143.3(8)		
			C(6)-C(5)-C(601)	125.5(8)		
			C(4) - C(5) - C(7)		132.2(9)	
			C(6)-C(5)-C(7)		133.9(9)	
C(6) - C(7)	1.352(7)		C(3)-C(6)-C(7)	134.9(4)		
C(5) - C(7)		1.413(11)	C(5)-C(6)-C(7)	136.6(4)		
			C(3)-C(6)-Ru(2)		129.0(6)	
			C(5)-C(6)-Ru(2)		142.4(6)	
			C(5)-C(7)-C(8)		177.6(12)	
C(7) - C(8)	1.254(6)	1.185(12)	C(7) - C(8) - C(81)		175.7(11)	
C(8) - C(81)		1.455(12)				
		Intra-C ₄ B	onds			
C(3) - C(4)	1.452(6)	1.475(13)	C(4) - C(3) - C(6)	87.9(4)	89.9(7)	
C(3) - C(6)	1.489(6)	1.510(12)	C(3) - C(4) - C(5)	92.6(4)	88.5(8)	
C(4) - C(5)	1.392(7)	1.419(13)	C(4) - C(5) - C(6)	91.2(4)	93.8(7)	
C(5) - C(6)	1.464(6)	1.468(12)	C(3) - C(6) - C(5)	88.3(4)	85.4(7)	

involve bond formation between these centers. In the case of the diynyl–molybdenum complex mentioned above, this occurs at the C_{β} atoms of both molecules, although in this case, only the open-chain bis(vinylidene) is formed. Berke's neutral tungsten butarienylidene complex appears to undergo a similar C_{β} – C_{β} coupling, although in this case, the postulated intermediate cyclobutane intermediate undergoes an internal redox reaction to a cyclobutene diradical, followed by ring opening to give the observed diene (Scheme 4).²⁶

We note that oxidation of the diynyl-ruthenium complexes may form a cumulene, as found with the bis(ruthenium)- C_4 species. In the latter instance, steric hindrance around the C_4 chains offered by the tertiary phosphine ligands attached to the ruthenium centers may prevent further reaction to form a cyclic derivative, such as might be formed by a [2 + 2] cycloaddition reaction. Such reactions are increasingly common, closely related examples to the present chemistry being found in the long-known [2 + 2] cycloadditions of electron-deficient alkenes, such as tetracyanoethene, to alkynyl-metal species.³² In these reactions, the first-formed (but not always observed) intermediate has been shown to be a radical salt, thus facilitating the cycloaddition.

In principle, at least three routes for [2 + 2] cycloaddition are available for the diynyl complexes studied here: namely, $(C_{\beta} +$ C_{β}), $(C_{\beta} + C_{\delta})$, and $(C_{\delta} + C_{\delta})$ coupling (Scheme 5). Alternatively, dimerization could also occur via the carbon atom in the para position of the phenyl substituent or via a carbon atom of the Cp ring, as found in the triphenylphosphine analogues (see Scheme 2). Nevertheless, no experimental evidence for these latter possible dimerizations was found. Reaction might also be expected at the metal center, although steric protection by the bulky ligands precludes this route. Similarly, the $(C_{\beta} + C_{\beta})$ coupling is unfavorable because of steric hindrance. It can be seen that the observed products correspond to the $(C_{\beta} + C_{\delta})$ and $(C_{\delta} + C_{\delta})$ routes, these affording the sym and asym isomers, respectively (Scheme 5). Although the $(C_{\beta} + C_{\beta})$ route would appear to be the most favored electronically, again steric protection by the bulky Cp and PPh₂ groups of the dppe ligand precludes this route.

A radical coupling mechanism is favored, initial reaction taking place at the C_β or C_δ atoms, as proposed for the Mo(dppe)(η -C₇H₇) system mentioned above.²⁰ Electron transfer from the metal system occurs, generating either metal–carbene or metal–allenylidene structures on the C₄

Scheme 5. Products of Oxidative Coupling at C_{β} and C_{δ}



ring. The structural parameters confirm the presence of these unsaturated carbene ligands and further suggest delocalization of the positive charge over the whole of the C_8 ligand.

DFT calculations were performed on the precursors $Ru(C \equiv$ $CC \equiv CPh)(dppe)Cp$ (5) and $Ru(C \equiv CC \equiv CFc)(dppe)Cp$ (6) in order to shed some light on the process of [2 + 2]cycloaddition which leads to the new binuclear complexes 7^{2+} and 8^{2+} . Compounds 5 and 6 were studied in two oxidation states (0/+) to understand how oxidation affects the spin density distribution in this diynyl-ruthenium compound. The geometries of 5 and 6 and their corresponding radical cations were first geometrically optimized. Pertinent computed metrical data for the Ph-containing precursors are reported in Table 2 and compared to the available X-ray data measured for the neutral complex.³³ Computed data are in reasonable agreement with the experimental values, with the largest bond length deviations found for the Ru-C(Cp) distances (0.11 Å). Upon oxidation, a substantial contraction of the Ru– C_{α} bond length (0.059 Å), a lengthening of the carbon–carbon triple bond, and a shortening of the carbon-carbon single bond lengths are computed. These slight differences are commonly observed for this kind of organometallic compound.¹⁴ As expected, $\nu(C \equiv$ C) frequencies decrease upon oxidation (see Table 2).

These bond length changes can be interpreted by looking at the nodal properties of the highest occupied molecular orbitals HOMO and HOMO-1 of the neutral compound, sketched in Figure 3. They are π -type in character, antibonding between the Ru atom and C_{α} and between C_{β} and C_{γ} and bonding between C_{α} and C_{β} and between C_{γ} and C_{δ} . These HOMOs are analogous to those generally computed for arylalkynyl-metal complexes and result from an antibonding interaction between the "t_{2g}" orbitals of the metal atom with the π -type orbitals of

Table 2. Selected Computed Data Parameters for 5 and $[5]^{+a}$

	5	5+	
	Bond Distances (Å)		
Ru–C(Cp)	Ru-C(Cp) 2.350-2.364, av 2.355 [2.238-2.251(2), av 2.244 (6)]		
Ru–P ₁	2.297 [2.2515(5)]	2.341	
Ru-P ₂	2.308 [2.2577(6)]	2.348	
$Ru-C_{\alpha}$	2.007 [1.988(2)]	1.948	
$C_{\alpha}-C_{\beta}$	1.246 [1.227(3)]	1.262	
$C_{\beta}-C_{\gamma}$	1.353 [1.367(3)]	1.333	
$C_{\gamma}-C_{\delta}$	1.234 [1.147(7)]	1.242	
$C_{\delta}-C(Ph)$	1.418 [1.438(7)]	1.408	
	Bond Angles (deg)		
P ₁ -Ru-P ₂	83.82 [82.80(2)]	82.92	
$Ru-C_{\alpha}-C_{\beta}$	174.12 [174.5(2)]	173.16	
$C_{\alpha}-C_{\beta}-C_{\gamma}$	171.24 [172.5(2)]	172.14	
$C_{\beta}-C_{\gamma}-C_{\delta}$	176.00 [167.5(3)]	174.84	
$C_{\gamma}-C_{\delta}-C(Ph)$	171.22 [172.4(6)]	173.83	
centroid(Cp)– Ru–Ph	149.96 [177.73]	162.26	
	Frequencies (cm ⁻¹)		
$\nu(C \equiv C)$	2155, 2012 [2156 m, 2017 w]	2085, 1819	
^a Experimental d	lata ³³ are given in brackets for co	mparison.	

the alkynyl ligand. As generally observed for arylalkynyl–Ru compounds, their spatial distribution is rather delocalized over the whole molecule in 5 (see Figure 3).^{14,24}

The spatial spin distribution calculated for the cationic diynyl-ruthenium complex 5^+ is plotted in Figure 4. As found in the previous calculations performed on the arylalkynyl-ruthenium compounds,²⁴ the atomic spin density of 5^+ is



Figure 3. Plot of the HOMO (left) and HOMO-1 (right) of 5 (isocontour value ± 0.05 (e/bohr³)^{1/2}). The Ru, $C_{\alpha\nu} C_{\beta\nu} C_{\gamma\nu} C_{\delta\nu} C_{ortho\nu}$ and C_{para} percentage characters are given.



Figure 4. Spatial distributions of computed spin density of 5^+ (left) and 6^+ (right) (isocontour value ± 0.005 e/bohr³). Atomic spin densities (electrons) are given.

mostly delocalized on the metal-carbon backbone. The largest part of the spin density is found on the ruthenium atom (0.33e), which is consistent with the nature of the HOMOs (see above). However, an important amount of spin density resides on the C_{β} and C_{δ} atoms (0.22e on each atom) and, to a lesser extent, on the $C_{\mbox{\scriptsize ortho}}$ and $C_{\mbox{\scriptsize para}}$ atoms of the phenyl ring (0.07e and 0.10e, respectively). Thus, several routes are electronically possible for radical coupling. However, metal center and $(C_{\beta} + C_{\beta})$ couplings are disfavored by the steric protection of the bulky dppe ligands, and we should expect the two processes shown in Scheme 5, namely $(C_{\beta} + C_{\delta})$ and $(C_{\delta} + C_{\delta})$ C_{δ} couplings, which lead to the asym and sym isomers, respectively. A process involving radical coupling between carbon atoms of the phenyl ring or the Cp ligand might also be possible, but the smaller spin density computed for these atoms (maximum of 0.10e), in comparison to those found on the C_{β} and C_{δ} atoms, suggest that these routes would occur only to a minor extent if at all. The spatial spin distribution calculated for 6^+ slightly differs from that of 5^+ (see Figure 4). The largest atomic spin densities are found on the ferrocenyl group (0.45e) and on the ruthenium atom (0.21e). However, atomic spin densities computed on the C_{β} and C_{δ} atoms (0.14e and 0.16e, respectively) are large enough to get a radical coupling process involving these atoms.

The two isomers which result from the [2 + 2] cycloaddition processes of 5^+ and 6^+ , namely 7^{2+} -asym and 7^{2+} -sym, and 8^{2+} asym and 8^{2+} -sym, respectively, were fully optimized without any geometrical constraints. These dicationic complexes were studied in two spin states (singlet and triplet). However, only results obtained for the singlet spin state, which is energetically favored over the triplet state by ca. 1 eV for both isomers, are discussed here. The major computed distances are given in Table 3 and compared to the data experimentally measured for 7^{2+} -asym and 8^{2+} -sym. The largest bond length deviations are again found for the Ru-C(Cp) distances. The computed distances for the carbon backbone match reasonably well with the experimental values, except for the $-C \equiv CPh$ substituent of the 7^{2+} -asym isomer, which is computed to have a cumulenic character more extensive than that found in the experimental compound. Interestingly, mixtures of symmetrical and asymmetrical isomers of both 7^{2+} and 8^{2+} were obtained in solution, whereas it is 7^{2+} -asym and 8^{2+} -sym that crystallize in the solid state. This indicates that the sym and asym isomers should be

Table 3. Selected Computed Distances (Å) for 7^{2+} -asym, 7^{2+} -sym, 8^{2+} -asym, and 8^{2+} -sym^a

	7^{2+} -asym	7^{2+} -sym	8 ²⁺ -asym	8 ²⁺ -sym
Ru ₁ -P ₁	2.345 [2.268(3)]	2.340	2.336	2.330 [2.2834(11)]
$Ru_1 - P_2$	2.366 [2.280(3)]	2.348	2.339	2.333 [2.2831(12)]
Ru ₂ -P ₃	2.353 [2.286(3)]	2.344	2.339	2.334 [2.2759(12)]
$Ru_2 - P_4$	2.364 [2.283(3)]	2.347	2.345	2.348 [2.2908(12)]
Ru ₁ – C(Cp)	2.354-2.369 [2.226-2.270(9)]	2.337– 2.374	2.341– 2.374	2.346-2.373 [2.212-2.236(4)]
av	2.362 [2.244]	2.360	2.359	2.363 [2.227]
Ru ₂ – C(Cp)	2.353-2.393 [2.241-2.272(9)]	2.337- 2.369	2.355- 2.380	2.338-2.365 [2.219-2.254(5)]
av	2.364 [2.260]	2.358	2.360	2.355 [2.237]
$Ru_1 - C_1$	1.952 [1.891(8)]	1.935	1.970	1.951 [1.913(4)]
$Ru_2 - C_n$		1.933 C ₈	1.989 C ₆	$\begin{array}{c} 1.951 \\ C_8 \end{array} \begin{bmatrix} 1.898(5) \\ \end{array}$
$C_1 - C_2$	1.275 [1.271(11)]	1.271	1.269	1.266 [1.244(6)]
$C_2 - C_3$	1.355 [1.341(11)]	1.349	1.364	1.359 [1.346(6)]
$C_3 - C_4$	1.470 [1.475(13)]	1.475	1.462	1.467 [1.452(6)]
$C_4 - C_5$	1.416 [1.419(13)]	1.422	1.430	1.439 [1.392(7)]
$C_{5}-C_{6}$	1.484 [1.468(12)]	1.472	1.484	1.474 [1.464(6)]
$C_{5}-C_{7}$	1.391 [1.413(11)]		1.380	
$C_{6}-C_{7}$		1.349		1.358 [1.352(7)]
$C_7 - C_8$	1.227 [1.185(12)]	1.271	1.235	1.269 [1.254(6)]
C ₄ -R	1.439 [1.386(14)]	1.444	1.425	1.429 [1.454(7)]
C_5-R		1.448		1.425 [1.423(16)]
C ₈ -R	1.421 [1.455(12)]		1.407	

^{*a*}Experimental data for 7^{2+} -*asym* and 8^{2+} -*sym* are given in brackets for comparison.

close in energy. Surprisingly, though, the computed energies for 7^{2^+} -sym and 7^{2^+} -asym (in the gas phase) differ somewhat, with the symmetric isomer being more stable than the asymmetric isomer by 59 kJ mol⁻¹. A similar energy gap (54 kJ mol⁻¹ in favor of 8^{2^+} -sym) is also computed for the two isomers of 8^{2^+} .

At first sight, such energy differences may appear important, but remember that (i) the cations 7^{2+} and 8^{2+} are large (156 atoms for the former (R = Ph) and 174 atoms for the latter (R = Fc)), (ii) several energy minima with respect to rotation of the metal end groups along the potential energy surface of these species might exist with some of them deeper in energy than others, especially for asymmetric isomers where steric hindrance might be more important than in symmetric ones, and (iii) interactions of such charged and heavy molecules (very large dipole moments are computed) with counterions and the solvent may be important (taking into account solvent effects using the COSMO formalism diminishes the energy difference between the two isomers of 7^{2+} , for instance, by ca. 10 kJ mol⁻¹). These results suggest that the *sym* forms of each complex are the thermodynamic isomers.

The DFT diagrams of the first molecular frontier orbitals for the two isomers of 7^{2+} bearing phenyl groups are shown in Figure 5 (left). The computed HOMO–LUMO energy gaps are substantial for both isomers (ca. 1.4 eV), confirming the stability of these complexes in their singlet spin states. Indeed, the nature of the HOMOs is similar to those found for the precursor **5**. The HOMO (215a) and HOMO-1 (214a) of both isomers are plotted in Figure 6. The frontier orbitals are delocalized over the entire Ru₂C₈ array, and it is not possible to draw a meaningful VB representation of the structure. They are π -type in character, being antibonding between ruthenium atoms and adjacent carbon atoms and bonding between C(1) and C(2), C(4) and C(5), and C(7) and C(8). The LUMO



Figure 5. MO energy diagram of the frontier molecular orbitals of 7²⁺-sym, 7²⁺-asym, 8²⁺-sym, and 8²⁺-asym.

and LUMO+1 (216a and 217a) are not metal-ligand antibonding in character but rather are found delocalized over the carbon chain with an important character on the four carbon atoms of the square (see Figure 6 (top)). They are reminiscent of the π -MOs of the cyclobutadiene dication $[C_4H_4]^{2+}$, with the LUMO having a bonding character between C(3) and C(4) and C(5) and C(6) and antibonding character between C(3) and C(6) and C(5).

The energy and nature of the first LUMOs (244a and 245a) of 8^{2+} -sym and 8^{2+} -asym are hardly affected by the replacement of phenyl groups by ferrocenyl groups, and they remain delocalized over the carbon chain (compare the right and left sides in Figure 5, and see also Figure 7). On the other hand, the HOMO and HOMO-1 of the 8^{2+} -sym complex, plotted in Figure 7, are not delocalized over the ruthenium-carbon skeleton as described for the 7^{2+} -sym complex. Rather, they are mainly localized on the iron atoms of the Fc donor groups and are consequently higher in energy compared to those of the 7^{2+} -sym and 7^{2+} -asym isomers. Thus, smaller HOMO-LUMO energy gaps of ca. 1 eV are computed for the former species, which should thus be easier to oxidize than the 7^{2+} -sym and 7^{2+} -asym isomers. This ferrocenyl character is computed for the first six HOMOs (" t_{2g} " d-type orbitals of the two Fc fragments). The MOs analogous to the HOMOs of the 7^{2+} isomers, which are antibonding in character between the ruthenium atoms and first adjacent carbon atoms, are HOMO-6 and HOMO-7 (236a and 237a).

CONCLUSION

In conclusion, we have demonstrated that chemical oxidation of $\operatorname{Ru}(C \equiv CC \equiv CAr)(\operatorname{dppe})Cp$ (Ar = Ph (5), Fc (6)) with $[\operatorname{FeCp}_2]\operatorname{PF}_6$ affords binuclear cations $[\{\operatorname{Ru}(\operatorname{dppe})Cp\}_2C_8Ar_2]$ - $(\operatorname{PF}_6)_2$ by radical coupling at electron-rich sites involving the inner and outer $C \equiv C$ triple bonds, to give cyclobutenediylidene derivatives. In each case, isomeric mixtures (non-interconvertible) were obtained. X-ray structural studies have shown that a central C_4 ring (cyclobutenylidene) is substituted either asymmetrically, with $=\{\operatorname{Ru}(\operatorname{dppe})Cp\}$ and =C =

C={Ru(dppe)Cp} groups in the 1,2-positions and Ar and $-C\equiv$ CAr substituents in the 3,4-positions (for Ar = Ph, 7²⁺asym), or symmetrically, with two =C=C={Ru(dppe)Cp} groups in the 1,2-positions and two Ar substituents in the 3,4-positions (for Ar = Fc, 8²⁺-sym), disposed as indicated in Scheme 4. NMR data for the second products in each case suggest that they are respectively 7²⁺-sym and 8²⁺-asym, although we cannot conclusively rule out the formation of open-chain isomers similar to Berke's W₂ complex (Scheme 2). In agreement with experiment, DFT calculations reveal that the precursor diynyl cationic complexes show important electron density on C_β and C_δ, suggesting that radical coupling (C_δ + C_δ) or (C_β + C_δ) can afford the sym and asym isomers, respectively, which are analogues of the cyclobutadiene dication. The sym forms are computed to be the thermodynamic isomers.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under dry nitrogen, although normally no special precautions to exclude air were taken during subsequent workup. 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).

Instruments. IR 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 disks. NMR spectra were recorded on a Varian Gemini 2000 instrument (¹H at 300.145 MHz, ¹³C at 75.479 MHz, ³¹P at 121.501 MHz). Unless otherwise stated, samples were dissolved in d_6 -acetone contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ¹H and ¹³C NMR spectra and external H₃PO₄ for ³¹P NMR spectra. 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 nebulizing gas. Chemical aids to ionization were used as required.³⁴ Electrochemical samples (1 mM) were dissolved in CH₂Cl₂ containing 0.5 M [NBu₄]BF₄ as the supporting electrolyte. Cyclic voltammograms were

Organometallics



Figure 6. Plots of the first HOMOs and LUMOs of 7^{2+} -sym (left) and 7^{2+} -asym (right) (isocontour value ± 0.03 [e/bohr³]^{1/2}).

recorded using a PAR Model 263 apparatus, with a saturated calomel electrode, with ferrocene as internal calibrant $(FeCp_2/[FeCp_2]^+ = +0.46 \text{ V vs SCE})$. A 1 mm path length cell was used with a Pt-mesh working electrode and Pt-wire counter and pseudo reference electrodes. Elemental analyses were carried out by Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand.

Reagents. The compounds $Ru(C \equiv CC \equiv CPh)(dppe)Cp$ and $[FeCp_2]PF_6$ were prepared as described in the literature.^{33,35}

Preparation of Ru(C=CC=CFc)(dppe)Cp (6). A mixture of RuCl(dppe)Cp (1000 mg, 2.67 mmol), KF (127 mg, 2.19 mmol), and $FcC=CC=CSiMe_3$ (550 mg, 1.80 mmol) in MeOH (50 mL, containing 1 drop of DBU, 0.10 mL of water) was heated under reflux for 1 h. After cooling, the mixture was filtered and the precipitate was washed with cold MeOH and dried under vacuum. The solid was taken up in a small amount of benzene and chromatographed (50% ether/S0% hexane, basic alumina) to give Ru(C=CC=CFc)(dppe)-



Figure 7. Plots of the first HOMOs and LUMOs of 8^{2+} -*sym* (left) and 8^{2+} -*asym* (right) (isocontour value ± 0.03 [e/bohr³]^{1/2}).

Cp (6; 430 mg, 32%) as a yellow-orange solid. FcC=CCH (170 mg, 0.73 mmol) was recovered from the filtrate. Anal. Calcd for C₄₅H₃₈FeP₂Ru: C, 67.85; H, 4.68; *M*, 798. Found: C, 67.02; H, 4.55. IR (Nujol, cm⁻¹): 2174 (m), 2024 (m), 1653 (broad w). ¹H NMR: δ 1.93–2.00 (m, 2H), 2.40–2.50 (m, 2H), 3.80 (t, *J* = 1.8 Hz, 2H), 4.03 (s, 5H), 4.28 (t, *J* = 1.6 Hz, 2H), 4.65 (s, 5H), 6.95–7.00 (m, 6H), 7.07–7.14 (m, 4H), 7.23–7.35 (m, 5H), 7.91–8.00 (m, 5H). ¹³C NMR (*d*₆-benzene): δ 28.13–28.74 (m), 60.86, 67.93, 69.81, 70.13, 71.78, 77.77, 83.33, 95.19, 115.75 (t, *J*(CP) = 99 Hz), 128.89, 129.81, 131.80–131.94 (m), 134.14–134.28 (m), 136.96–137.63 (m), 142.29–142.91 (m). ³¹P NMR: δ 86.0. ES-MS (*m*/*z*): 798, M⁺.

Oxidative Coupling of Ru(C \equiv CC \equiv CR)(dppe)Cp (R = Ph (7), Fc (8)). Preparation of [{Ru(dppe)Cp}₂C₈Ph₂](PF₆)₂ (7²⁺(PF₆⁻)₂).

- (a) [FeCp₂]PF₆ (78 mg, 0.23 mmol) was added to a stirred solution of Ru(C=CC=CPh)(dppe)Cp (104 mg, 0.15 mmol) in CH₂Cl₂ (10 mL), and the contents were stirred at ambient temperature for 5 min. The solvent was removed in vacuo and the residue separated by preparative TLC (3% acetone/97% dichloromethane) to give two main purple bands. The lower band $(R_f = 0.25)$ was isolated and crystallized (CH_2Cl_2/C_6H_6) to give the asymmetric complex 7²⁺ $asym(PF_6^-)_2$ as a maroon solid (71 mg, 57%). Anal. Calcd for C₈₂H₆₈F₁₂P₆Ru₂: C, 59.00; H, 4.08; M (dication), 1398. Found: C, 59.32; H, 4.25. IR (nujol, cm⁻¹): 1933s ν (C=C= C), 1597w, 1563 w ν (C=C), 839 s ν (PF). ¹H NMR: δ 3.27, 3.28, 3.59 and 3.85 (4 \times br s, 8H, CH₂ of dppe), 5.55 and 5.75 $(2 \times br s, 10H, CpRu)$, 7.35–7.99 (broad m, 50H, Ph). ¹³C NMR: δ 86.76, 92.97 (br s, RuCp), 93.49 (br, RuCp), 129-53-129.61 (m), 129.72-129.80 (m), 130.02-130.20 (m), 130.51, 130.93 (br), 131.75 (br), 131.84, 131.98, 132.21, 132.33, 134.05-134.13 (m), 134.72 (br), 140.26-140.77 (m). ³¹P NMR: δ –142.3 (septet, J(PF) = 706 Hz), 82.0, 86.5 (Ru– P). ES-MS (MeOH, m/z): 1411, $[M + OMe]^+$; 565, $[\operatorname{Ru}(\operatorname{dppe})\operatorname{Cp}]^+$. UV-vis (acetone): 515 nm (ε = 19 300). Xray-quality crystals were obtained from dichloromethane/ benzene.
- (b) [FeCp₂]PF₆ (20 mg, 0.060 mmol) was added to a stirred solution of Ru(C=CC=CPh)(dppe)Cp (50 mg, 0.072 mmol) in CH₂Cl₂ (10 mL), resulting in a color change to bright red. The mixture was stirred at ambient temperature for 5 min. The solution was filtered though a cotton-wool plug into stirred diethyl ether to give a precipitate which was collected on a sinter and washed several times with both Et₂O and C₆H₆ to afford the isomeric mixture $7^{2+}(PF_6^{-})_2$ as a maroon solid (41 mg, 82%). Anal. Calcd for C₈₂H₆₈F₁₂P₆Ru₂: C, 59.00; H, 4.08; M (dication), 1398. Found: C, 58.61; H, 4.07. IR (Nujol, cm⁻¹): 2164 w ν (C=C), 1929 s ν (C=C=C), 1595 w, 1573 w ν (C=C), 838 s ν (PF). ¹H NMR: δ 3.28, 3.59 and 3.86 (3 × br s, 8H, CH₂ of dppe), 5.51 and 5.74 (2 × br s, 10H, CpRu), 7.37–7.98 (broad m, 50H, Ph). ³¹P NMR: δ –142.3 (septet, J(PF) = 706 Hz, 81.0, 82.1, 86.5 (3 × Ru–P). ES-MS (MeOH-NaOMe, m/z (calcd)): 1411.256 (1411.257), [M + OMe]⁺; 690.108 (690.119), M²⁺; 593.087 (593.074), [Ru-(CO)(dppe)Cp]⁺; 565.084 (565.079), [Ru(dppe)Cp]⁺. UVvis (acetone): 464 nm (ε = 25 400), 520 (27 000).

Preparation of $[{Ru(dppe)Cp}_2C_8Fc_2](PF_6)_2 (8^{2+}(PF_6^{-})_2).$

- (a) A solution of Ru(C=CC=CFc)(dppe)Cp (68.5 mg, 0.086 mmol) and [FeCp₂]PF₆ (27.8 mg, 0.084 mmol) were stirred in THF (20 mL) at room temperature for 1 h. An excess of hexane was added, and the resulting precipitate was filtered off and washed with hexane to afford the oxidized product $8^{2+}(PF_6^{-})_2$ as a dark purple solid (48 mg, 61%). A microanalytical sample was crystallized from MeCN/benzene.
- (b) Addition of $[FeCp_2]PF_6$ (85 mg, 0.257 mmol) to a solution of $Ru(C \equiv CC \equiv CFc)(dppe)Cp$ (205 mg, 0.257 mmol) in THF (20 mL) resulted in an instantaneous color change to an intense purple. The mixture was stirred at ambient temperature for 5 min. Solvent was removed in vacuo and the residue purified by preparative TLC (5% acetone/95% dichloromethane; $R_f = 0.50$) to afford $[\{Ru(dppe)Cp\}_2C_8Fc_2](PF_6)_2$ ($8^{2+}(PF_6^{-})_2$; an inseparable 1:1 mixture of symmetric and asymmetric isomers) as a dark purple solid (210 mg, 87%). It was possible to partially separate small amounts of 8^{2+} . *sym*($PF_6^{-})_2$ from the mixture by slow fractional crystallization from CH_2Cl_2/C_6H_6 at 4 °C.

8²⁺(*PF*₆⁻)₂ (*Mixture*). Anal. Calcd for C₉₀H₇₆F₁₂Fe₂P₆Ru₂: C, 57.34; H, 4.06. Found: C, 57.99; H, 4.34. IR (Nujol, cm⁻¹) 2139 w ν (C=C), 1927 s ν (C=C=C), 1698 w ν (C=C), 1585 m ν (C=C), 839 s ν (PF). ¹H NMR: δ 2.83, 3.27, 3.35, 3.73 (4 × br s, 16H, CH₂ of dppe), 4.21 (s, 5H, FeCp), 4.32 (br s, 17H, FeCp + C_3H_4 of Fc), 4.64, 4.70 (2s, 4H, C_3H_4 of Fc), 5.31 and 5.70 (2s br, 30H, CpRu and C_5H_4 of Fc), 7.30–8.08 (m br, 80H, Ph). ¹³C NMR: δ 63.06, 69.71, 71.38, 71.69, 72.66, 73.11, 73.39, 77.91 (br, FeCp), 89.42, 91.49 (RuCp), 91.90 (RuCp), 92.98 (br, RuCp), 129.52–130.09 (br m), 130.90 (br), 131.03, 131.61 (br), 131–96–132.61 (br m), 134.04–134.22 (br m), 135.09–135.17 (m). ES-MS (MeOH + NaOMe, m/z (calcd)): 1643.156 (1643.182), [M + O + OMe]⁺; 1627.196 (1627.191), [M + OMe]⁺; 1475.202 (1475.198), [M – FeCp]⁺; 798.068 (798.086), M²⁺; 593.074 (593.074), [Ru(CO)(dppe)Cp]⁺; 565.079 (565.079), [Ru(dppe)Cp]⁺. ³¹P NMR (d_6 -acetone, 121.5 MHz): δ –142.3 (septet, J(PF) = 706 Hz, PF₆), 83.1 (PRu=C=C=C), 84.1 (PRu=C=C=C), 89.95 (PRu=C). UV–vis (acetone): 737 (ε = 15 800), 520 (27 000), 464 nm (25 400).

8²⁺-sym(PF₆⁻)₂. Anal. Calcd for C₉₀H₇₆F₁₂Fe₂P₆Ru₂: C, 57.34; H, 4.06. Found: C, 58.72; H, 4.14. IR (Nujol, cm⁻¹): 1933 s ν (C=C=C), 1590 s ν (C=C), 839 ν (PF). ¹H NMR: δ 3.28 (s br, 8H, CH₂ of dppe), 4.06, 4.31 (2s br, 13H, 2C₅H₄ + FeCp), 5.32 and 5.67 (2s br, 15H, FeCp, RuCp), 7.20–8.00 (m, 40H, Ph). ¹³C NMR: δ 70.57, 71.34, 71.65, 72.63, 73.04, 73.40, 77.77, 91.38, 91.87, 92.22, 100.80, 129.31–129.97 (m), 130.76–130.85 (m), 131.50–132.41 (m), 133.60–134.40 (m), 134.96 (t, *J*(CP) = 5.4 Hz). ³¹P NMR: δ –142.3 (septet, *J*(PF) = 706 Hz, PF₆), 83.1 (Ru(dppe)). ES-MS (MeOH + NaOMe, *m*/z): 1628, [M + OMe]⁺. UV–vis (acetone): 509 nm (ε = 26 400), 728 (20 600).

The anion could be exchanged for AsF_6 by treatment of the complex with an excess of K[AsF₆] in acetone. Removal of the solvent in vacuo followed by extraction and filtration gave *sym*-[{Ru(dpp)-Cp}₂C₈Fc₂](AsF₆)₂, which afforded X-ray-quality crystals from CH₂Cl₂/C₆H₆. The amount obtained was too small to allow elemental microanalyses.

Structure Determinations. Crystal data for 7^{2+} -*asym*(PF₆⁻)₂ and 8^{2+} -*sym*(AsF₆⁻)₂ are summarized in Table 1, with the structures being depicted in Figures 1 and 2. Selected coordination geometries are shown in Table 2. Crystallographic data for the structures were collected at 100(2) K on an Oxford Diffraction Gemini diffractometer fitted with Cu K α radiation ($\lambda = 1.541$ 78 Å). Following analytical absorption corrections and solution by direct methods, the structures were refined against F^2 with full-matrix least squares using the program SHELXL-97.³⁶

Crystal Data and Refinement Details. 7^{2+} -*asym*(PF_6^{-})₂: [$C_4Ph(CCPh){==Ru(dppe)Cp}{=C=C=Ru(dppe)Cp}]$ -($PF_6)_2$ · C_6H_6 = $C_{82}H_{68}P_4Ru_2$ · $2F_6P$ · C_6H_6 , MW = 1747.43, triclinic, space group $P\overline{1}$, a = 11.7963(4) Å, b = 16.7726(9) Å, c = 20.4211(7) Å, $\alpha = 94.253(4)^{\circ}$, $\beta = 105.569(3)^{\circ}$, $\gamma = 97.765(4)^{\circ}$, V = 3830.6(3) Å³, Z = 2, $\rho_{calcd} = 1.515$ g cm⁻³, $\mu = 5.02$, absorption correction (min/max) 0.80, crystal 0.22 × 0.09 × 0.04 mm³, 43 395 reflections measured, 13 463 unique reflections ($R_{int} = 0.063$), R1 = 0.080 ($I > 2\sigma(I)$), wR2 = 0.233 (all data). One solvent benzene molecule located adjacent to an inversion center was refined with isotropic displacement parameters; site occupancies were set at 0.5 and geometries constrained to ideal values. One PF_6^- anion was modeled as rotationally disordered over two sets of sites with occupancies constrained to 0.5 after trial refinement.

8²⁺-**sym**(AsF₆⁻)₂: [C₄Fc₂{=C=C=Ru(dppe)Cp}₂]-(AsF₆)₂·4C₆H₆ = C₉₀H₇₆Fe₂P₄Ru₂·2AsF₆·4C₆H₆, MW = 2285.5, monoclinic, space group *Pc*, *a* = 15.9391(1) Å, *b* = 11.7641(1) Å, *c* = 26.1975(2) Å, β = 95.270(1)°, V = 4891.51(6) Å³, Z = 2, ρ_{calcd} = 1.552 g cm⁻³, μ = 6.76, absorption correction (min/max) = 0.62, crystal 0.21 × 0.09 × 0.015 mm³, 56 958 reflections measured, 16 616 unique reflections (R_{int} = 0.050), R1 = 0.034 (*I* > 2σ(*I*)), wR2 = 0.075 (all data).

Computational Details. DFT calculations were carried out with the Amsterdam Density Functional (ADF) package^{37,38} without any symmetry constraints on the precursor complexes $Ru(C \equiv CC \equiv$ CR)(dppe)Cp (R = Ph, 5; R = Fc, 6) and their cations, as well as on [{Ru(dppe)Cp}₂C₈R₂]²⁺ isomers (R = Ph, 7²⁺; R = Fc, 8²⁺). Electron correlation was treated within the local density approximation (LDA) in the Vosko–Wilk–Nusair parametrization.³⁹ The nonlocal corrections of Becke and Perdew were added to the exchange and correlation

Organometallics

energies, respectively.⁴⁰ The analytical gradient method implemented by Versluis and Ziegler was used.⁴¹ The standard ADF TZP basis set was used: i.e., a triple- ζ STO basis set for the valence core augmented with a 2p polarization function for H, a 3d polarization function for C and P, and a 5p polarization function for Ru, respectively. Orbitals up to 1s, 2p, and 4p were kept frozen for C, P, and Ru, respectively. Geometry optimization convergence criteria were more drastic than default criteria (energy change <0.0005 hartree and atomic position displacement <0.005 Å). Harmonic vibrational frequency calculations were performed on the precursors (5 and 5⁺) to check that the geometries are stationary points. Molecular orbitals were plotted with the ADF-GUI package,⁴² and representations of the spin density were done using MOLEKEL4.1.⁴³

ASSOCIATED CONTENT

S Supporting Information

CIF files giving full details of the structure determinations for 7^{2+} -*asym*(PF₆⁻)₂ and 8^{2+} -*sym*(AsF₆⁻)₂ and tables containing atomic coordinates of the optimized geometries of complexes $5^{0/+}$, $6^{0/+}$, 7^{2+} , and 8^{2+} . This material is available free of charge via the Internet at http://pubs.acs.org. Full details of the structure determinations (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC 881590 (7^{2+} -*asym*(PF₆⁻)₂) and 881591 (8^{2+} -*sy*-*m*(AsF₆⁻)₂). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, + 44 1223 336 033; e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk).

AUTHOR INFORMATION

Corresponding Author

*M.I.B.: tel, +61 8 8313 5939; fax, +61 8 8303 4358; e-mail, michael.bruce@adelaide.edu.au. J.-F.H.: tel, +33 2 2323 6778; fax, +33 2 2323 6840; e-mail, halet@univ-rennes1.fr.

Present Address

^{II}CMCA, University of Western Australia, Crawley, Western Australia 6009, Australia

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Professor B. K. Nicholson, University of Waikato, Hamilton, New Zealand, for measuring mass spectra. We acknowledge financial support of this work by the ARC and Johnson Matthey plc for a generous loan of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$. F.G. and J.-F.H. acknowledge the CNRS (France) for travel grants to Australia. K.C., F.G., and J.-F.H. thank the French GENCI-CINES and GENCI-IDRIS centres for high-performance computing resources (Grant 2010-80649).

REFERENCES

(1) (a) Low, P. J.; Bruce, M. I. Adv. Organomet. Chem. 2001, 48, 71.
(b) Bruce, M. I.; Low, P. J. Adv. Organomet. Chem. 2004, 50, 179.

(2) Low, P. J. Dalton Trans. 2005, 2821.

(3) Tao, N. J. Nat. Nanotechnol. 2006, 1, 173.

(4) Paul, F.; Lapinte, C. In Unusual Structures and Physical Properties in Organometallic Chemistry; Gielen, M., Willem, R., Wrackmeyer, B., Eds.; Wiley: Chichester, U.K., 2002; p 220.

(5) Miller, J. S.; Epstein, A. Angew. Chem., Int. Ed. 1994, 33, 385.

(6) Samoc, M.; Gauthier, N.; Cifuentes, M. P.; Humphrey, M. G. Angew. Chem., Int. Ed. 2007, 45, 7376.

(7) (a) Semenov, S. N.; Taghipourian, S. F.; Blacque, O.; Fox, T.; Venkatesan, K.; Berke, H. J. Am. Chem. Soc. 2010, 132, 2584.
(b) Semenov, S. N.; Blacque, O.; Fox, T.; Venkatesan, K.; Berke, H. J. Am. Chem. Soc. 2010, 132, 3115. (9) Bruce, M. I.; Ellis, B. G.; Skelton, B. W.; White, A. H. J. Organomet. Chem. 2005, 690, 792.

(10) Bruce, M. I.; Kramarczuk, K. A.; Skelton, B. W.; White, A. H. J. Organomet. Chem. 2010, 695, 469.

(11) Fitzgerald, E. C.; Brown, N. J.; Edge, R.; Helliwell, M.; Roberts, H. N.; Tuna, F.; Beeby, A.; Collison, D.; Low, P. J.; Whiteley, M. W. *Organometallics* **2012**, *31*, 157.

(12) Sato, M.; Hayashi, Y.; Tsuda, T.; Katada, M. Inorg. Chim. Acta 1997, 261, 113.

(13) (a) Denis, R.; Toupet, L.; Paul, F.; Lapinte, C. Organometallics 2000, 19, 4240. (b) Paul, F.; Costuas, K.; Ledoux, I.; Deveau, S.; Zyss, J.; Halet, J.-F.; Lapinte, C. Organometallics 2002, 21, 5229. (c) Paul, F.; Mevellec, J.-Y.; Lapinte, C. Dalton Trans. 2002, 1783. (d) Costuas, K.; Paul, F.; Toupet, L.; Halet, J.-F.; Lapinte, C. Organometallics 2004, 23, 2053. (e) Paul, F.; Toupet, L.; Thepot, J.-Y.; Costuas, K.; Halet, J.-F.; Lapinte, C. Organometallics 2005, 24, 5464. (f) Paul, F.; da Costa, G.; Bondon, A.; Gauthier, N.; Sinbandhit, S.; Toupet, L.; Costuas, K.; Halet, J.-F.; Lapinte, C. Organometallics 2007, 26, 874.

(14) Paul, F.; Ellis, B. G.; Bruce, M. I.; Toupet, L.; Roisnel, T.;
Costuas, K.; Halet, J.-F.; Lapinte, C. *Organometallics* 2006, 25, 649.
(15) Fox, M. A.; Roberts, R. L.; Khairul, W. M.; Hartl, F.; Low, P. J. J.

Organomet. Chem. 2007, 692, 3277. (16) Gauthier, N.; Tchouar, N.; Justaud, F.; Argouarch, G.; Cifuentes,

M. P.; Toupet, L.; Touchard, D.; Halet, J.-F.; Rigaut, S.; Humphrey, M. G.; Costuas, K.; Paul, F. Organometallics **2009**, *28*, 2253.

(17) (a) Beddoes, R. L.; Bitcon, C.; Ricalton, A.; Whiteley, M. W. J. Organomet. Chem. **1989**, 367, C21. (b) Grime, R. W.; Helliwell, M.; Hussain, Z. I.; Lancashire, H. N.; Mason, C. R.; McDouall, J. J. W.; Mydlowski, C. M.; Whiteley, M. W. Organometallics **2008**, 27, 857. (c) Brown, N. J.; Collinson, D.; Edge, R.; Fitzgerald, E. C.; Helliwell, M.; Howard, J. A. K.; Lancashire, H. N.; Low, P. J.; McDouall, J. J. W.; Raftery, J.; Smith, C. A.; Yufit, D. S.; Whiteley, M. W. Organometallics **2010**, 29, 1261. (d) Lancashire, N. N.; Brown, N. J.; Carthy, L.; Collison, D.; Fitzgerald, E. C.; Edge, R.; Helliwell, M.; Holden, M.; Low, P. J.; McDouall, J. J. W.; Whiteley, M. W. Dalton Trans. **2011**, 40, 1267.

(18) Roberts, H. N.; Brown, N. J.; Edge, R.; Lewin, R.; Collison, D.; Low, P. J.; W. Whiteley, M. W. Organometallics **2011**, *30*, 3763.

(19) Schauer, P. A.; Low, P. J. Eur. J. Inorg. Chem. 2012, 390.

(20) Brown, N. J.; Collison, D.; Edge, R.; Fitzgerald, E. C.; Low, P. J.; Helliwell, M.; Ta, Y. T.; Whiteley, M. W. *Chem. Commun.* **2010**, *46*, 2253.

(21) Guillemot, M.; Toupet, L.; Lapinte, C. Organometallics 1998, 17, 1928.

(22) Bruce, M. I.; Ellis, B. G.; Low, P. J.; Skelton, B. W.; White, A. H. Organometallics **2003**, *22*, 3184.

(23) Bruce, M. I.; Costuas, K.; Davin, T.; Halet, J.-F.; Kramarczuk, K. A.; Low, P. J.; Nicholson, B. K.; Perkins, G. J.; Roberts, R. L.; Skelton, B. W.; Smith, M. E.; White, A. H. *Dalton Trans.* **2007**, 5387.

(24) Bruce, M. I.; Burgun, A.; Gendron, F.; Grelaud, G.; Halet, J.-F.; Skelton, B. W. *Organometallics* **2011**, *30*, 2861. See also: McGrady, J. E.; Lovell, T.; Stranger, R.; Humphrey, M. G. *Organometallics* **1997**, *16*, 4004.

(25) (a) Bruce, M. I.; Koutsantonis, G. A.; Liddell, M. J.; Tiekink, E. R. T. *J. Organomet. Chem.* **1991**, *420*, 253. (b) Bruce, M. I.; Zaitseva, N. N. Unpublished work.

(26) Semenov, S. N.; Blacque, O.; Fox, T.; Venkatesan, K.; Berke, H. Angew. Chem., Int. Ed. **2009**, 48, 5203.

(27) Bassetti, M.; Marini, S.; Díaz, J.; Gamasa, M. P.; Gimeno, J.; Rodriguez-Álvarez, Y.; García-Granda, S. *Organometallics* **2002**, *21*, 4815.

(28) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137.

(29) Gamasa, M. P.; Gimeno, J.; Martín-Vaca, B. M.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. Organometallics **1994**, *13*, 4045.

⁽⁸⁾ Le Narvor, N.; Toupet, L.; Lapinte, C. J. Am. Chem. Soc. 1995, 117, 7129.

(30) Bruce, M. I.; Humphrey, M. G.; Snow, M. R.; Tiekink, E. R. T. J. Organomet. Chem. 1986, 314, 213.

- (31) Bruce, M. I.; Burgun, A.; Costuas, K.; Gendron, F.; Halet, J.-F.; Lapinte, C. *Organometallics*, submitted for publication.
- (32) Bruce, M. I. Aust. J. Chem. 2011, 64, 77.

(33) Armitt, D. J.; Bruce, M. I.; Skelton, B. W.; White, A. H. J. Organomet. Chem. 2008, 693, 3571.

(34) Henderson, W.; McIndoe, J. S.; Nicholson, B. K.; Dyson, P. J. J. Chem. Soc., Dalton Trans. **1998**, 519.

(35) Connelly, N. G.; Geiger, W. E. Chem. Rev. 1996, 96, 877.

(36) Sheldrick, G. M. Acta Crystallogr. 2008, A64, 112.

(37) ADF2010.01; SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.

(38) (a) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. J. Comput. Chem. 2001, 22, 931. (b) Fonseca Guerra, C.; Snijders, J. G.;

te Velde, G.; Baerends, E. J. Theor. Chem. Acc. 1998, 99, 391.

(39) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, 58, 1200. (40) (a) Becke, A. D. *Phys. Rev. A* **1988**, 38, 3098. (b) Perdew, J. P. *Phys. Rev. B* **1986**, 33, 8822.

(41) Versluis, L.; Ziegler, T. J. Chem. Phys. 1988, 88, 322.

(42) ADF-GUI 2010; SCM, Amsterdam, The Netherlands, http://www.scm.com.

(43) Flükiger, P.; Lüthi, H. P.; Portmann, S.; Weber, J. MOLEKEL 4.1; Swiss Center for Scientific Computing (CSCS), Switzerland, 2000–2001.