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Chiral Ruthenium–Allenylidene Complexes That Bear a Fullerene Cyclopentadienyl Ligand: Synthesis, Characterization, and Remote Chirality Transfer

Yu-Wu Zhong, Yutaka Matsuo,* and Eiichi Nakamura*[a]

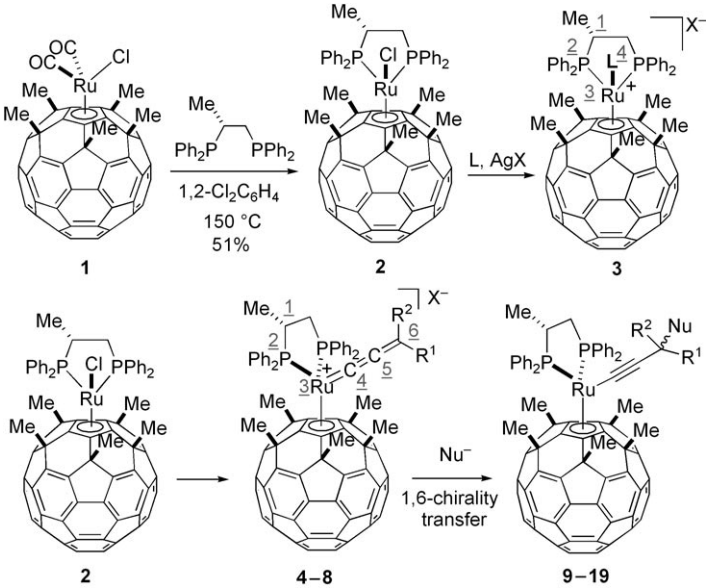
Abstract: Ruthenium complexes that bear both a fullerene and an allenylidene ligand, $[Ru(C_{60}Me_5)((R)\text{-prophos})=C=C=CR^1R^2]PF_6$ (prophos = 1,2-bis(diphenylphosphanyl)propane), were prepared by the reaction of $[Ru(C_{60}Me_5)Cl((R)\text{-prophos})]$ and a propargyl alcohol in better than 90% yields, and characterized by ^1H, ^{13}C, and ^{31}P NMR, IR, and UV/Vis/NIR spectroscopy and MS. Cyclic voltammograms of these complexes showed one reversible or irreversible reduction wave due to the allenylidene part, and two reversible reduction waves due to the fullerene core. Nucleophilic addition of RMgBr or RLi proceeded regioselectively at the distal carbon atom of the allenylidene array. The reaction took place with a 60:40–95:5 level of diastereoselectivity with respect to the original chirality in the (*R*)-prophos ligand, which is located six atoms away from the electrophilic carbon center.

Keywords: allenylidenes · fullerenes · remote chirality transfer · ruthenium

Introduction

Transition-metal allenylidene complexes are interesting organometallics due to their utility in organic transformations and in materials science.[1] Their rich reactivity arises from the nucleophilicity of the C_β atom and the electrophilicity of the C_α and C_γ atoms of the unsaturated carbon chains and has made these complexes versatile intermediates in stoichiometric[2] and catalytic conversions.[3] As part of the group of metal cumulenylidene complexes that are of interest to materials scientists,[4] allenylidene complexes have been studied widely as potential candidates for molecular wires,[5] liquid-crystalline materials,[6] and nonlinear optical materials.[7] The reactivity and the physical properties of the metal allenylidenes depend both on the metal fragments and on the ligands. For example, the regioselectivity of nucleophilic addition to the C_γ center of a ruthenium–allenylidene complex increases when electron-rich and bulky ligands are attached to the metal atom.[8] We therefore focused on the effects of fullerene ligands[9] on the reactivities of metal allenylidene complexes, as the synergy of the allenylidene and fullerene ligands may result in new chemical and physical properties that are not found in complexes with only one or none of these ligands.

An η^5-fullerene ligand, η^5-$C_{60}Me_5$ in **1** (Scheme 1), is our ligand of interest. We recently reported that this or a related



Scheme 1. Remote chirality transfer induced by the η^5-$C_{60}Me_5$ ligand.

[a] Dr. Y.-W. Zhong, Dr. Y. Matsuo, Prof. E. Nakamura
Nakamura Functional Carbon Cluster Project, ERATO
Japan Science and Technology Agency (JST)
The University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113-0033 (Japan)
Fax: (+81) 3-5800-6889
E-mail: matsuo@chem.s.u-tokyo.ac.jp
nakamura@chem.s.u-tokyo.ac.jp

η^5-$C_{60}Me_5$ ligand attached to a metal center can enhance both the stability of metal complexes and the level of chirality transfer from one chiral ligand attached to the metal to the metal center itself, or to the second achiral ligand attached to the metal atom.[10] The reaction of a ruthenium(II)–carbonyl complex, [Ru(η^5-$C_{60}Me_5$)Cl(CO)$_2$] (**1**; Scheme 1),[11] with an optically active ligand, (*R*)-prophos ((*R*)-1,2-bis(diphenylphosphinanyl)propane), takes place with excellent diastereoselectivity to give a configurationally stable chiral-at-metal complex, [Ru(η^5-$C_{60}Me_5$)Cl((*R*)-prophos)] (**2**), and also a variety of cationic complexes, [Ru($C_{60}Me_5$)((*R*)-prophos)L][SbF_6] (**3**; L = MeCN, *t*BuCN, methacrolein, acetone, CO, BnNC, 2,6-$Me_2C_6H_3$NC) (i.e., 1,3-chirality transfer). When we attached a vinylidene complex (L: =C=CPhH) to the metal atom, the stereochemistry of the chiral center on the vinylidene moiety was controlled (1,4-chirality transfer from ligand to vinylidene).

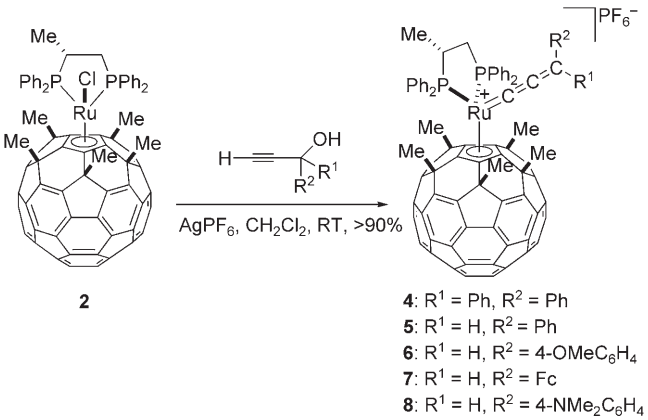
The levels of 1,3- and 1,4-chirality transfer (84–100% selective) observed for these complexes were much higher than those observed for the complexation of the corresponding simple η^5-Cp complex, [Ru(η^5-Cp)Cl(PPh_3)$_2$] (Cp = cyclopentadienyl), with (*R*)-prophos, which gave an essentially 1:1 (0–20% de) mixture of two diastereomers.[12] We ascribed the difference between the η^5-$C_{60}Me_5$ and η^5-Cp ligands to the presence of a concave cavity in the former that surrounds the metal atom.[13] We considered that if this chemistry can be extended to the corresponding ruthenium–allenylidene complexes [Ru($C_{60}Me_5$)((*R*)-prophos)=C=C=CR^1R^2]X (**4**–**8**), 1,6-chirality transfer may be achieved during nucleophilic addition to the terminal allenylidene carbon atom (Scheme 1, bottom). Though the concept of remote asymmetric induction has often been studied in the context of organic synthesis,[14] it has been less frequently studied in inorganic synthesis. We report herein the synthesis, characterization, electrochemistry, and stereochemical behavior of ruthenium complexes that bear both a fullerene and an allenylidene ligand.

Abstract in Japanese:
ペンタメチル[60]フラーレン配位子と (*R*)-prophos 配位子をもつルテニウム– アレニリデン錯体 [Ru(η^5-$C_{60}Me_5$)((*R*)-prophos)-(=C=CR^1R^2)] を合成した．この錯体はルテニウム金属中心と (*R*)-prophos 配位子に不斉中心をもつが，錯形成においては単一のジアステレオ異性体で得られる．アレニリデン錯体に対する求核付加を検討したところ，反応はガンマ位選択的に進行し，新たに構築されるガンマ炭素不斉中心におけるジアステレオ選択性は最高 95% であった．アレニリデン錯体の UV/Vis スペクトルにおいては可視部に特徴的な MLCT に由来する強い吸収が観測された．また，電気化学測定においては，アレニリデン部位で 1 電子，フラーレン部位で 2 電子の合計 3 電子還元が観測された．

Results and Discussion

Preparation and Characterization of Ruthenium–Allenylidene Complexes

We synthesized the allenylidene complexes **4**–**8** by treatment of a solution of **2** in dichloromethane with an appropriate propargyl alcohol derivative in the presence of $AgPF_6$ (Scheme 2). This reaction probably involves formation and



2

4: R^1 = Ph, R^2 = Ph
5: R^1 = H, R^2 = Ph
6: R^1 = H, R^2 = 4-$OMeC_6H_4$
7: R^1 = H, R^2 = Fc
8: R^1 = H, R^2 = 4-$NMe_2C_6H_4$

Scheme 2. Preparation of ruthenium–allenylidene complexes.

dehydration of a hydroxyvinylidene intermediate as reported by Selegue.[15] Complex **4** with two phenyl groups on the C_γ atom was first synthesized as a reference compound, which was isolated as a deep-pink solid that is stable for full characterization. To examine the 1,6-chirality transfer, we synthesized complexes **5**–**8**, which have one hydrogen atom and one aromatic group on the C_γ atom. Compound **5** was found to be unstable in $CDCl_3$ during ^{13}C NMR spectroscopic measurement overnight, but the compounds that bear an electron-donating group, such as 4-methoxyphenyl (**6**), ferrocenyl (**7**), and 4-*N*,*N*-dimethylaminophenyl (**8**), are more stable. In all cases, only one diastereomer was obtained, as proved by spectral analysis. By analogy with the stereochemistry between **2** and **3**, the stereochemistry of the ruthenium center in **4**–**8** was assumed to be the same as that in **2** and **3**.[10] Their characteristic spectral data are summarized in Table 1.

The ^1H NMR spectra of **5**–**8** showed a singlet peak at about 8.00–9.50 ppm due to the proton attached to the C_γ site of the allenylidene chain. In the IR spectra, the characteristic asymmetric stretching vibration of the C=C=C unit was found as an intense band at $\tilde{\nu}$ = 1922 (**4**), 1935 (**5**), 1935 (**6**), 1937 (**7**), 1947 (**8**) cm^{-1}. All of their $^{31}P\{^1H\}$ NMR spectra exhibited two doublet signals at about 50.0 and 77.0 ppm due to magnetically nonequivalent phosphine atoms; the values are similar to those of **2** and **3**. Furthermore, their ESI-MS (+) spectra showed peaks ascribable to $[M-PF_6]^+$. Unambiguous structure determination of the allenylidene complex was achieved by X-ray crystallographic analysis of **8** (Figure 1). The X-ray structure shows that the allenylidene plane is perpendicular to that of the Cp ring, and the phenyl

Table 1. Characteristic spectral data of ruthenium allenylidenes **4–8**.

Allenylidene	R^1, R^2	$\tilde{\nu}$ [cm^{-1}] ($\nu_{C=C=C}$)	δ (^{1}H) [ppm] (C_γH)	δ (^{31}P) [ppm]	δ (^{13}C) [ppm] C_α	C_β	C_γ	MS (ESI) m/z $[M-PF_6]^+$
4	Ph, Ph	1922	–	52.8, 77.1	287.7	206.9	162.4	1499
5	H, Ph	1935	9.54	48.4, 75.2	299.6	213.8	151.5[a]	1423
6	H, C_6H_4OMe	1935	9.00	49.4, 76.3	282.2	195.9	166.8	1453
7	H, Fc	1937	8.82	49.1, 74.3	264.8	183.1	152.9	1531
8	H, $C_6H_4NMe_2$	1947	7.96	51.3, 77.2	240.2	164.9	156.6	1466

[a] Although the ^{13}C NMR spectrum of **5** was not fully recorded, the signals of the allenylidene carbon atoms could be identified. Fc = ferrocenyl.

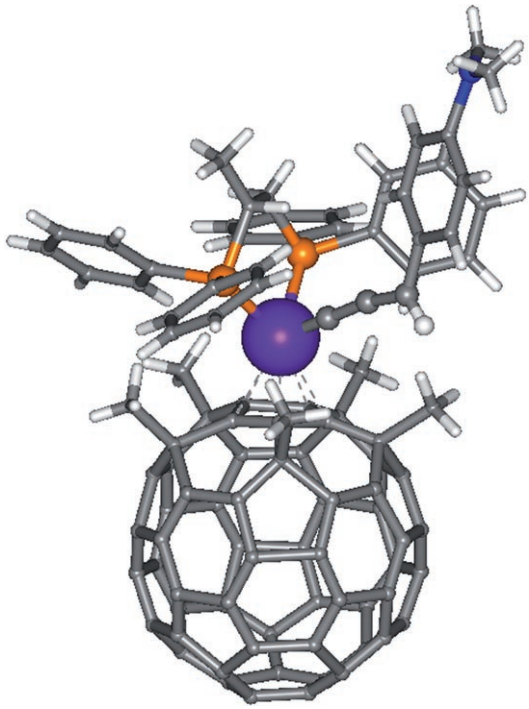
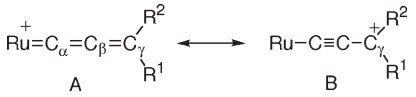


Figure 1. Crystal structure of the cationic part of **8**.

group on the allenylidene moiety points away from the fullerene core.

There are two resonance forms of transition-metal allenylidenes: an allenylidene form A and a metal-propargyl-cation form B (Scheme 3).[16] Electron-donating groups on the C_γ center (R^1 or R^2) tend to increase the contribution of form B, which is reflected in the ^{13}C NMR spectra of complexes **4–8**. The characteristic signals at 299.6 and 213.8 ppm are assigned to the C_α and C_β atoms of **5**, respectively. When an electron-donating group is attached to the C_γ center, their C_α and C_β signals shift upfield (**6–8**), suggesting increased contribution of the resonance form B. In the case of **4**, which has two phenyl groups on the C_γ site, a similar upfield shift as in **5** was observed.



Scheme 3. The two resonance forms of ruthenium allenylidenes.

Nucleophilic Addition of Grignard Reagents to Ruthenium Allenylidenes

Nucleophilic addition to electrophilic transition-metal allenylidenes is a fundamental mode of reaction, in which important issues are regioselectivity with respect to bond formation at the C_α or C_γ position and stereoselectivity at the stereogenic centers newly generated in the allenylidene moiety. There is a recent example of an asymmetric propargylic substitution catalyzed by a chiral diruthenium complex that takes place via an allenylidene intermediate.[17] High stereoselectivity has been recorded in stoichiometric additions in which the electrophilic center is located close to the stereogenic center.[18] When the electrophilic and stereogenic centers are far from each other, however, the selectivity becomes lower. For example, addition of a lithium enolate to the C_γ atom of a ruthenium allenylidene with a 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl (BINAP) ligand showed only 25% diastereomeric excess.[19] We found that addition of Grignard reagents to the ruthenium allenylidenes **4–8** takes place with moderate to high levels of chirality transfer under the influence of the bulky $C_{60}Me_5$ ligand (Table 2).

We first investigated the addition of MeMgBr to the allenylidene **4**, in which R^1 and R^2 are both phenyl groups and, hence, there exists only the issue of regioselectivity of the addition reaction (Table 2, entry 1). The reaction took place smoothly at −78 °C and exclusively on the diphenyl-substituted Cγ atom to afford the adduct **9**. The perfect regioselectivity attests to the large steering effect of the sterically demanding $C_{60}Me_5$ ligand. The product showed a characteristic triplet signal at 94.4 ppm in the ^{13}C NMR spectrum due to the alkynyl carbon directly connected to the ruthenium center and a C≡C stretching vibration band at 2065 cm^{-1} in the IR spectrum.

When a nucleophile was added to an allenylidene with two different groups on Cγ (i.e., $R^1 \neq R^2 \neq$ nucleophile), the addition reaction generated a stereogenic center at C_γ. Thus, addition of MeMgBr to **5** (R^1 = H, R^2 = Ph) gave only the C_γ-addition product with 60:40 diastereoselectivity (ds) (Table 2, entry 2). The ^{1}H NMR spectrum showed two doublets at 1.21 and 1.48 ppm respectively, which correspond to the diastereomeric methyl groups attached to the C_γ atom. We noticed that the diastereselectivity increased progressively as the R^2 phenyl group became more electron-donating from phenyl (**5**) to 4-methoxyphenyl (**6**) to 4-*N*,*N*-dimethylaminophenyl (**8**) (Table 2, entries 2, 3, and 5; 60:40, 68:32, and 88:12 ds, respectively). For reasons as yet unknown, attempted addition of EtMgBr and *i*PrMgBr to **8** gave complex mixtures.

Aryl Grignard reagents showed better diastereoselectivity than MeMgBr. The addition of PhMgBr to **6** (R^2 = 4-methoxyphenyl; Table 2, entry 6) gave the adduct **14** with 85:15

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Table 2. Nucleophilic addition to ruthenium allenylidenes.

Entry	Allenylidene	R^1, R^2	NuM	T [°C]	Product	Yield [%][a]	ds [%][b]
1	**4**	Ph, Ph	MeMgBr	−78	**9**	93	–
2	**5**	H, Ph	MeMgBr	−78	**10**	78	60:40
3	**6**	H, C_6H_4OMe	MeMgBr	−78	**11**	80	68:32
4	**7**	H, Fc	MeMgBr	−78	**12**	90	63:37
5	**8**	H, $C_6H_4NMe_2$	MeMgBr	−78	**13**	94	88:12
6	**6**	H, C_6H_4OMe	PhMgBr	0	**14**	85	85:15
7	**8**	H, $C_6H_4NMe_2$	PhMgBr	0	**15**	85	95:5
8	**8**	H, $C_6H_4NMe_2$	4-$MeOC_6H_4MgBr$	0	**16**	84	80:20
9	**8**	H, $C_6H_4NMe_2$	4-ClC_6H_4MgBr	0	**17**	85	78:22
10	**8**	H, $C_6H_4NMe_2$	1-NaphMgBr	0	**18**	91	75:25
11	**8**	H, $C_6H_4NMe_2$	PhC≡CMgBr	25	**19**	92	61:39
12	**8**	H, $C_6H_4NMe_2$	PhC≡CLi	−78	**19**	90	50:50
13	**5**	H, Ph	4-$MeOC_6H_4MgBr$	0	dia-**14**	80	25:75

[a] Yield of isolated product. [b] Determined by ^{1}H NMR spectroscopic analysis of the crude product. Naph = naphthyl.

ds, and the addition to **8** (R^2 = 4-*N*,*N*-dimethylaminophenyl) gave **15** with 95:5 ds, the highest value obtained in the present study (Table 2, entry 7). When 4-$MeOC_6H_4MgBr$, 4-ClC_6H_4MgBr, and 1-NaphMgBr were added to **8**, the ds value remained in the range 75:25–80:20 (Table 2, entries 8–10). The reaction of a less sterically demanding alkynyl nucleophile such as PhC≡CMgBr to **8** gave the product **19** with only a low ds of 61:39 at room temperature (Table 2, entry 11). It was somewhat puzzling that this Grignard reagent did not react with **8** at temperatures lower than room temperature. PhC≡CLi, however, reacted with **8** even at −78 °C, but curiously showed no diastereoselectivity (Table 2, entry 12).

The adducts described above are generally rather unstable, could not be isolated in diastereomerically pure forms, and resisted all attempts to obtain single crystals for X-ray analysis. We therefore could not determine the stereochemistry of the products. The diastereomeric ratio could, however, be determined by ^{1}H NMR spectroscopic analysis of well-resolved signals of the two diastereomers. For example, the signal assignment was achieved by comparison of a **14**-rich mixture synthesized from **6** (85:25, R^1 = H, R^2 = C_6H_4OMe, NuM = PhMgBr; Table 2, entry 6) and a mixture rich in the diastereomer dia-**14** (25:75) synthesized by alternating the sequence of introduction of the substituents on the C_γ atom, that is, addition of 4-$MeOC_6H_4MgBr$ to the allenylidene **7** (R^1 = H, R^2 = Ph; Table 2, entry 13). Spectra similar to the well-resolved ^{1}H NMR signals due to **14** and dia-**14** shown in Figure 2 were observed for other diastereomeric pairs of the adducts. We therefore assumed that the major isomer in all cases share the same stereochemistry.

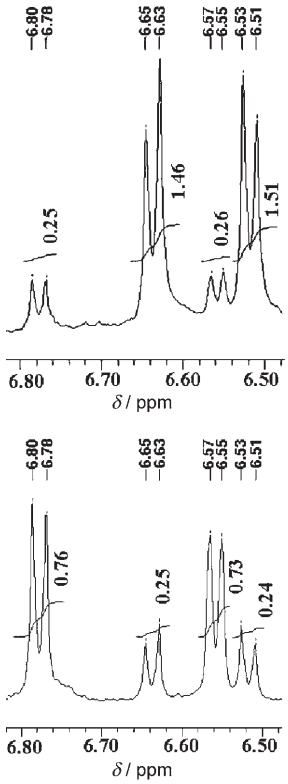


Figure 2. Partial ^{1}H NMR spectrum of **14**-rich sample obtained in Table 2, entry 6 (top) and dia-**14**-rich sample obtained in Table 2, entry 13 (bottom).

UV/Vis/NIR Measurement of the Ruthenium–Allenylidene Complexes

All the allenylidenes obtained were deep-colored compounds. Compound **4** (R^1, R^2 = Ph) is deep pink, whereas **6** (R^1 = H, R^2 = 4-$OMeC_6H_4$), **7** (R^1 = H, R^2 = Fc), and **8** (R^1 = H, R^2 = 4-$NMe_2C_6H_4$) are deep purple, deep green, and deep blue, respectively (Figure 3). Their UV/Vis/near-IR (NIR) spectra were recorded in dichloromethane at a concentration of 1×10^{-5} M. Besides the UV absorption of the fullerene group, **4**, **6**, and **8** showed an intense band in the visible region, with maximum absorption at 502, 530, and 618 nm, respectively. These bands were assigned to the metal-to-ligand charge transitions (MLCT) between the d orbital of the ruthenium centers and the π* orbital of the allenylidene ligands.[20] The ferrocene-containing **7** showed not only an MLCT absorption at 480 nm, but also a very broad absorption band at 725 nm that extends to the NIR region. As this band does not appear in the spectra of **4**, **6**, and **8**, we assume that this intriguing broad band is due to ferrocenyl-to-allenylidene charge transfer. Nearly identical bands for related systems are reported in the literature.[21] Notably, such a band was not observed in a remotely related case of a ruthenium–allenylidene complex with a ferrocene substituent connected by a saturated-carbon-chain bridge.[22]

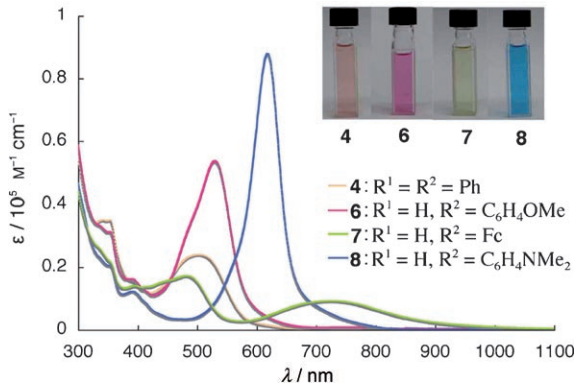


Figure 3. UV/Vis/NIR spectra of ruthenium allenylidenes. Concentration of the solutions shown is 1×10^{-5} M.

Electrochemical Studies of the Ruthenium–Allenylidene Complexes

The electrochemical behavior of these ruthenium–allenylidene complexes is of interest. Their cyclic voltammograms and redox potentials are shown in Figures 4 and 5 and

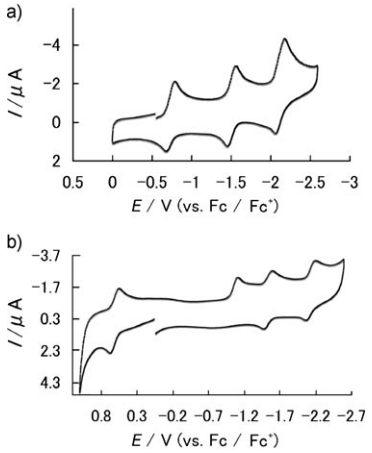


Figure 4. Cyclic voltammograms of a) **4** and b) **8** at 25 °C. Both measurements were carried out in THF (0.1 mM) containing (nBu$_4$N)(ClO$_4$) (100 mM) as supporting electrolyte.

Table 3. In the cyclic voltammogram of **4** (R^1, R^2 = Ph) in THF, three reversible reduction waves were observed, while no oxidation wave appeared within the window of the solvent (Figure 4a). The first reduction peak, with an E_{pc} value of −0.80 V, is due to reduction of the allenylidene carbon chain to the corresponding radical[23] stabilized by the two phenyl groups (Scheme 4). Two other reduction waves were assigned to the two one-electron reductions of the fullerene core. The $E_{1/2}$ values, −1.50 and −2.12 V, are comparable to those of a similar Ru–(η^5-C$_{60}$Me$_5$) complex.[11,24] In the cyclic voltammogram of **6** (R^1 = H, R^2 = 4-OMeC$_6$H$_4$), two reversible fullerene-related reduction waves were likewise observed, while the reduction of the corresponding allenylidene ligand was irreversible. We ascribe this difference to

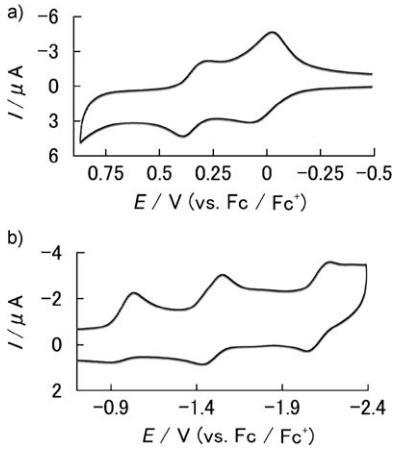
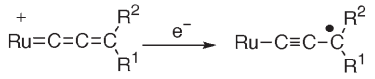


Figure 5. Cyclic voltammograms of **7** at 25 °C. a) Anodic scan in CH_2Cl_2 (0.1 mM). b) Cathodic scan in THF (0.1 mM). In both cases, (nBu$_4$N)(ClO$_4$) (100 mM) was used as supporting electrolyte.

Table 3. Redox potentials of ruthenium allenylidenes.

Allenylidene	E_{pc}^{red1} [V]	$E_{1/2}^{red1}$ [V]	$E_{1/2}^{red2}$ [V]	$E_{1/2}^{red3}$ [V]	$E_{1/2}^{ox1}$ [V]	$E_{1/2}^{ox2}$ [V]
4	−0.80	−0.72	−1.50	−2.12	–	–
6	−0.87	–	−1.53	−2.10	–	–
7	−1.03	–	−1.49	−2.11	−0.02	0.29
8	−1.14	–	−1.54	−2.13	0.61	–



Scheme 4. Reduction of a ruthenium allenylidene.

the presence of only one aryl group (R^2) in **6**, which is not enough to stabilize the radical that would have formed upon reduction (Scheme 4).

Similar behavior was observed during the reduction of **8** (R^1 = H, R^2 = 4-NMe$_2$C$_6$H$_4$), with two notable differences. One is a large cathodic shift of the irreversible reduction of the allenylidene ligand from an E_{pc} value for **4** of −0.80 V to −1.14 V (Figure 4b); the other is the reversible oxidation of the Ru^{II} center seen with an $E_{1/2}$ value of +0.61 V. We consider that the presence of an electron-donating 4-*N*,*N*-dimethylaminophenyl substituent on the allenylidene terminal was responsible for the differences. In the cathodic scan of **7** in THF (Figure 5b), electrochemical behavior similar to that of **6** and **8** was observed, with an E_{pc}^{red1} value of −1.03 V. The somewhat oddly shaped cathodic return peak is probably due to adsorption of the corresponding oxidation product onto the electrode surface. In the anodic scan in CH_2Cl_2, two well-defined one-electron reversible oxidation waves were observed (Figure 5a). The first wave is due to oxidation of the ferrocene part, whereas the second peak at $E_{1/2}$ = +0.29 V may be assigned to oxidation of the Ru^{II} center.

Conclusions

The properties of the ruthenium allenylidenes described above represent composite effects of the physical and chemical properties of the allenylidene and fullerene moieties. The regio- and stereoselectivity of the nucleophilic additions to these allenylidenes reflect the chemical reactivity of metal–allenylidene complexes modulated by the bulky $C_{60}Me_5$ ligand. The moderate to high diastereoselectivity of the reaction suggests the stereosteering effect of the concave cavity of the $C_{60}Me_5$ ligand. The intense and broad absorptions of the complexes in the visible to NIR region are of particular interest in their use in photophysical applications.[25] The availability of a variety of ligands similar to the η^5-$C_{60}Me_5$ ligand and their metal complexes[26] may allow us to tune the properties of the metal complexes.

Experimental Section

General

All experiments were carried out under argon by using standard Schlenk techniques. THF was distilled from Na/K alloy, and dichloromethane was distilled from CaH_2 before use. Compound **2** was prepared according to a previous report.[10] All ^1H (500 MHz), $^{13}C\{^1H\}$ (125 MHz), and $^{31}P\{^1H\}$ NMR (200 MHz) spectra were recorded on JEOL ECA500 spectrometers. Spectra are reported in parts per million from internal tetramethylsilane (0.00 ppm) or residual protons of the deuterated solvent for ^1H NMR, from solvent carbon (e.g., 77.0 ppm for chloroform) for $^{13}C\{^1H\}$ NMR, and from external H_3PO_4 (0.0 ppm) for $^{31}P\{^1H\}$ NMR spectroscopy. High-resolution mass spectra were recorded on a JEOL JMS-T100LC ESI-TOF mass spectrometer. IR and UV/Vis/NIR spectra were recorded on an Applied Systems Inc. React-IR 1000 and a JASCO V-570 machine. Elemental analysis was performed at the Organic Elemental Analysis Laboratory in the Department of Chemistry, University of Tokyo. Combustion data for **9**–**19** were not obtained as these compounds are very unstable.

Syntheses

Typical procedure for the preparation of **4**–**8**: Silver hexafluorophosphate (13 mg, 0.050 mmol) was added to a solution of **2** (39 mg, 0.030 mmol) and an appropriate propargyl alcohol (0.30 mmol) in dichloromethane (10 mL). The mixture was stirred at room temperature for 10 h. The solvent was then evaporated, and the residue was filtered through a silica-gel column eluted with a mixture of dichloromethane and acetonitrile (10:1 *v*/*v*). The solid obtained was recrystallized from dichloromethane/diethyl ether to give the desired allenylidene complex in greater than 90% yield.

4: IR (powder): $\tilde{\nu}$ = 3260 (br), 2927 (m, ν_{C-H}), 2360 (m), 1922 (s, $\nu_{C=C=C}$), 1583 (m), 1436 (m), 1090 (br, m), 806 (m), 746 (s), 686 cm^{-1} (s); ^1H NMR ($CDCl_3$): δ = 0.93 (dd, J = 13.75, 6.85 Hz, 3H, PCHCH_3), 1.37 (s, 3H, $C_{60}Me_5$), 1.88 (s, 6H, $C_{60}Me_5$), 2.24 (s, 3H, $C_{60}Me_5$), 2.33–2.36 (m, 1H, PCH_2), 2.45 (s, 3H, $C_{60}Me_5$), 3.21–3.24 (m, 1H, PC*H*Me), 3.38 (br, 1H, PC*H*Me), 7.35–7.63 (m, 21H, ArH), 7.72 (t, J = 7.45 Hz, 2H, ArH), 7.82 (t, J = 7.45 Hz, 2H, ArH), 7.95 (t, J = 7.20 Hz, 1H, ArH), 8.19–8.23 (m, 2H), 8.30 ppm (br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.5 (dd, J = 17.22, 5.74 Hz, *C*H$_3$CHP), 27.9 (s, 2C, $C_{60}Me_5$), 28.8 (s, 1C, $C_{60}Me_5$), 31.4 (2C, $C_{60}Me_5$), 37.3 (dd, J = 36.38, 7.66 Hz, CHP), 38.1 (dd, J = 34.47, 15.32 Hz, CH_2P), 50.5 (br, 2C, $C_{60}(sp^3)$), 51.7 (br, 3C, $C_{60}(sp^3)$), 93.5 (s, 1C, C_{60}(Cp)), 109.4 (s, 1C, C_{60}(Cp)), 113.2 (s, 1C, C_{60}(Cp)), 117.0 (s, 1C, C_{60}(Cp)), 126.1, 128.1, 128.4, 128.5, 128.8, 128.9, 129.0, 129.1, 129.2, 129.6, 129.9, 131.8, 132.1, 132.6, 132.9, 133.2, 134.1, 134.1, 134.3, 134.6, 136.6, 137.7, 138.0, 142.8, 143.3, 143.8, 147.0, 148.2, 148.4, 150.8, 151.3, 152.1, 162.4 (C=CPh$_2$), 206.9 (*C*=CPh$_2$), 287.7 ppm (t, J = 22.95 Hz, Ru=C); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 52.8 (d, J = 27.66 Hz, 1P), 77.1 (d, J = 27.66 Hz, 1P); MS (ESI) (+): m/z = 1499 $[M-PF_6]^+$; HRMS (ESI) (+): m/z calcd for $C_{107}H_{52}P_2Ru$ $[M+H-PF_6]^+$: 1500.2588; found: 1500.2618; elemental analysis: calcd (%) for $C_{107}H_{51}F_6P_3Ru$: C 78.15, H 3.13; found: C 78.26, H 3.31.

5: IR (powder): $\tilde{\nu}$ = 3259 (br), 1935 (s, $\nu_{C=C=C}$), 1584 (s), 1437 (m), 837 (s), 744 (s), 699 cm^{-1} (s); ^1H NMR ($CDCl_3$): δ = 1.32 (dd, J = 13.15, 6.30 Hz, 3H, PCHCH_3), 1.75–2.40 (m, 13H), 2.74 (br, 3H), 3.40–3.70 (m, 2H), 7.34–7.56 (m, 15H), 7.69 (t, J = 9.15 Hz, 2H), 7.78 (m, 1H), 7.84 (t, J = 6.85 Hz, 2H), 7.93 (t, J = 6.80 Hz, 1H), 8.10 (dd, J = 11.45, 8.00 Hz, 2H), 8.39 (dd, J = 10.30, 8.00 Hz, 2H), 9.54 ppm (s, 1H, C=C=CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 48.4 (d, J = 29.00 Hz, 1P), 75.2 (d, J = 29.00 Hz, 1P), −143.9 ppm (hept, J = 704.62 Hz, PF_6); MS (ESI) (+): m/z = 1423 $[M-PF_6]^+$; elemental analysis: calcd (%) for $C_{101}H_{47}F_6P_3Ru$: C 77.34, H 3.02; found: C 77.51, H 3.24.

6: IR (powder): $\tilde{\nu}$ = 2927 (s, ν_{C-H}), 1935 (s, $\nu_{C=C=C}$), 1582 (s), 1437 (m), 1270 (s), 1146 (s), 835 (s), 742 (s), 700 cm^{-1} (s); ^1H NMR ($CDCl_3$): δ = 1.32 (dd, J = 13.75, 6.30 Hz, 3H, PCHCH_3), 1.75–2.40 (m, 13H), 2.79 (br, 3H), 3.50–3.70 (m, 2H), 3.99 (s, 3H, OMe), 7.08 (d, J = 9.15, 2H), 7.36–7.56 (m, 13H), 7.73 (t, J = 9.15 Hz, 2H), 7.82 (t, J = 7.15 Hz, 2H), 7.91 (t, J = 7.45 Hz, 1H), 8.20 (dd, J = 11.45, 8.00 Hz, 2H), 8.44 (dd, J = 10.90, 8.00 Hz, 2H), 9.00 ppm (s, 1H, C=C=CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.5 (dd, J = 15.80, 4.30 Hz, *C*H$_3$CHP), 27.0 (br, 1C, $C_{60}Me_5$), 28.9 (br, 2C, $C_{60}Me_5$), 31.4 (br, 2C, $C_{60}Me_5$), 36.2 (dd, J = 33.02, 14.35 Hz, CHP), 36.8 (dd, J = 34.45, 8.56 Hz, CH_2P), 51.9 (br, 5C, $C_{60}(sp^3)$), 56.7 (OMe), 117.0, 126.6, 126.9, 128.0, 128.1, 128.3, 128.3, 128.7, 128.7, 129.0, 129.1, 131.4, 131.7, 131.9, 132.5, 132.9, 132.9, 133.3, 133.6, 133.6, 133.7, 135.3, 135.4, 137.2, 137.6, 137.7, 138.4, 138.7, 143.2, 143.7, 147.0, 148.2, 148.4, 149.7, 152.1, 166.8 (Ru=C=C=*C*), 195.9 (Ru=C=*C*), 282.2 ppm (t, J = 22.16 Hz, Ru=C); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 49.4 (d, J = 27.56 Hz, 1P), 76.3 ppm (d, J = 27.56 Hz, 1P); MS (ESI) (+): m/z = 1453 $[M-PF_6]^+$; HRMS (ESI) (+): m/z calcd for $C_{102}H_{50}OP_2Ru$: 1454.2380 $[M+H-PF_6]^+$; found: 1454.2356; elemental analysis: calcd (%) for $C_{102}H_{49}F_6OP_3Ru$: C 76.64, H 3.09; found: C 76.78, H 3.32.

7: IR (powder): $\tilde{\nu}$ = 2927 (m, ν_{C-H}), 1937 (s, $\nu_{C=C=C}$), 1492 (s), 1437 (s), 831 (s), 742 (s), 700 cm^{-1} (s); ^1H NMR ($CDCl_3$): δ = .36 (dd, J = 8.60, 6.90 Hz, 3H, PCHCH_3), 1.80–2.30 (m, 14H), 2.74 (br, 3H), 3.15–3.32 (m, 1H, PC*H*Me), 3.69 (brs, 1H, Fc), 4.45 (s, 5H, Fc), 4.91 (brs, 1H, Fc), 5.37 (s, 1H, Fc), 5.40 (s, 1H, Fc), 7.39–7.62 (m, 11H), 7.77 (t, J = 7,40 Hz, 2H), 7.85–7.89 (m, 3H), 8.08 (dd, J = 10.90, 8.00 Hz, 2H), 8.43 (dd, J = 10.30, 8.05 Hz, 2H), 8.81 ppm (s, 1H, C=C=CH); ^{13}C NMR (125 MHz, CD_2Cl_2) δ = 15.3 (dd, J = 17.24, 5.74 Hz, *C*H$_3$CHP), 29.0–31.6 (brm, 5C, $C_{60}Me_5$), 36.4 (dd, J = 36.38, 9.57 Hz, CHP), 37.5 (dd, J = 30.64, 13.40 Hz, CH_2P), 52.1 (br, 5C, $C_{60}(sp^3)$), 73.5 (5C, Fc), 80.8 (2C, Fc), 81.1 (2C, Fc), 91.1 (1C, Fc), 127.1, 127.4, 128.3, 128.3, 128.9, 129.0, 129.14, 131.7, 132.1, 132.4, 133.0, 133.4, 133.7, 133.7, 134.0, 134.1, 134.0, 136.0, 138.4, 138.5, 139.1, 139.4, 143.7, 144.0, 147.4, 148.6, 148.6, 148.7, 152.3, 152.7, 152.9 (*C*HFc), 155.6, 183.1 (*C*=CHFc), 264.8 ppm (t, J = 23.93 Hz, Ru=C); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 49.1 (d, J = 26.92 Hz, 1P), 74.3 (d, J = 26.92 Hz, 1P), −146.2 ppm (m, PF_6); MS (ESI) (+): m/z = 1531 $[M-PF_6]^+$; HRMS (ESI) (+): m/z calcd for $C_{105}H_{51}FeP_2Ru$: 1531.1859 $[M-PF_6]^+$; found: 1531.1821.

8: IR (powder): $\tilde{\nu}$ = 2926 (s, ν_{C-H}), 1947 (s, $\nu_{C=C=C}$), 1584 (s), 1380 (s), 1173 (m), 837 (s), 744 (s), 700 cm^{-1} (s); ^1H NMR ($CDCl_3$): δ = 1.30 (dd, J = 12.00, 6.30 Hz, 3H, PCHCH_3), 1.94–2.84 (m, 13H), 2.84 (br, 3H), 3.26 (s, 6H, NMe_2), 3.48 (br, 2H), 6.61–6.63 (m, 1H), 6.70–6.72 (m, 1H), 6.91–6.93 (m, 1H), 7.35–7.55 (m, 12H), 7.77-7.87 (m, 5H), 7.96 (s, 1H, C=C=CH), 8.28 (dd, J = 11.45, 7.45 Hz, 2H), 8.49 ppm (t, J = 8.60 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 14.7 (dd, J = 16.82, 4.57 Hz, *C*H$_3$CHP), 26.4–26.6 (m, 1C, $C_{60}Me_5$), 28.6–28.7 (m, 2C, $C_{60}Me_5$), 31.6–31.7 (m, 2C, $C_{60}Me_5$), 36.3 (2C, CHP and CH_2P), 41.2 (2C, NMe_2), 51.5–51.9 (m, 5C, $C_{60}(sp^3)$), 113.1, 115.8, 127.6, 127.6, 127.8, 127.9, 128.0, 128.3, 128.4, 128.6, 128.7, 130.8, 131.1, 131.4, 132.2, 133.1, 133.2, 133.2, 133.5, 133.6, 133.7, 134.6, 135.9, 136.0, 137.9, 138.0, 140.0, 140.3, 141.8, 143.4, 143.6, 144.3, 147.0, 148.1, 152.0, 152.1, 152.6, 152.7, 156.6 (Ru=C=C=*C*), 164.9 (Ru=C=*C*), 240.2 ppm (t, J = 22.93 Hz, Ru=C); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 51.3 (d, J = 30.76 Hz, 1P), 77.2 (d, J = 30.76 Hz, 1P), −144.1 ppm (hept, J = 707.5 Hz, PF_6); MS (ESI) (+): m/z = 1466

$[M-PF_6]^+$; HRMS (ESI) (+): m/z calcd for $C_{103}H_{53}NP_2Ru$: 1467.2697 $[M+H-PF_6]^+$; found: 1467.2727; elemental analysis: calcd (%) for $C_{103}H_{52}F_6NP_3Ru$: C 76.77, H 3.25, N 0.87; found: C 76.64, H 3.53, N 0.87.

Typical procedure for nucleophilic addition to ruthenium–allenylidene complexes: The corresponding organometallic reagent (0.020–0.030 mmol) was added to a solution of a ruthenium allenylidene (0.010 mmol) in THF (4.0 mL) at the temperature shown in Table 1. Complete reaction generally occurred within 5 min, as indicated by the change from the deep color of the allenylidene to orange. The solvent was evaporated, and the residue was filtered through a short silica-gel column eluted with dichloromethane to give the adduct as a mixture of two diastereomers. The diastereoselectivity was determined by ^{1}H NMR spectroscopic analysis of the sample as discussed in relation to Figure 2. All characterizations were recorded from the above-obtained mixture of two diastereomers. The ^{1}H NMR spectra typically showed a set of major and minor signals due to the major and minor diastereomers of the groups attached to the C_γ atom, as well as signals due to the methyl groups of the (*R*)-prophos ligand. Unless otherwise noted, other signals refer to the integration of the signals of the two diastereomers that are indistinguishable from each other. In general, the ^{31}P NMR spectra also showed a set of major and minor signals due to the major and minor diastereomers of the two phosphorus atoms.

9: IR (powder): $\tilde{\nu}$ = 3053, 2966, 2921, 2065 (s, $\nu_{C\equiv C}$), 1430 (s), 1260 (s), 1092, 1020 (m), 800 (s), 743 (s), 696 cm^{-1} (s); ^{1}H NMR ($CDCl_3$): δ = 0.62 (dd, J = 11.45, 6.90 Hz, 3H, PCHCH_3), 1.48 (s, 3H, $C_{60}Me_5$), 1.63 (s, 3H, $C_{60}Me_5$), 1.63 (br, 1H, overlapped, PCH_2), 1.78 (s, 3H, CPh$_2$*Me*), 1.93 (s, 3H, $C_{60}Me_5$), 2.05–2.22 (m, 1H, PC*H*Me), 2.47 (s, 3H, $C_{60}Me_5$), 3.02 (s, 3H, $C_{60}Me_5$), 3.14 (br, 1H, PCH_2), 6.60 (d, J = 8.00 Hz, 2H, ArH), 7.01–7.02 (m, 2H, AH), 7.15–7.34 (m, 11H), 7.41 (t, J = 7.45 Hz, 1H), 7.55 (t, J = 7.45 Hz, 2H), 7.63–7.68 (m, 6H), 8.13 (t, J = 8.60 Hz, 2H), 8.31 (t, J = 8.00 Hz, 2H), 8.42 ppm (t, J = 8.00 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.5 (dd, J = 15.80, 5.27 Hz, *C*H$_3$CHP), 27.3 (1C, $C_{60}Me_5$), 29.7 (2C, $C_{60}Me_5$), 30.6 (C*Me*Ph$_2$), 32.1 (2C, $C_{60}Me_5$), 34.4 (dd, J = 35.81, 10.52 Hz, CHP), 37.7 (dd, J = 29.45, 13.68 Hz, CH$_2$P), 48.3 (*C*MePh$_2$), 50.9 (1C, $C_{60}(sp^3)$), 51.5 (3C, $C_{60}(sp^3)$), 52.7 (1C, $C_{60}(sp^3)$), 94.4 (t, J = 30.55 Hz, RuC), 96.9, 101.6, 110.5, 111.0, 115.3, 116.9, 125.0, 125.9, 126.3, 126.4, 127.0, 127.2, 127.2, 127.4, 127.5, 127.5, 127.6, 128.0, 128.0, 128.6, 129.1, 129.5, 130.0, 131.4, 131.7, 131.9, 133.8, 133.9, 134.3, 134.3, 136.2, 136.3, 136.6, 136.6, 137.7, 138.0, 138.1, 139.3, 143.5, 144.3, 144.9, 145.2, 147.0, 148.1, 148.5, 148.7, 152.7, 153.3, 153.7, 154.0, 154.6 ppm; ^{31}P NMR ($CDCl_3$): δ = 58.1 (d, J = 30.60 Hz), 78.1 ppm (d, J = 34.45 Hz); MS (ESI) (+): m/z = 1514 $[M]^+$; HRMS (ESI) (+): m/z calcd for $C_{108}H_{55}P_2Ru$: 1515.2822 $[M+H]^+$; found: 1515.2826.

10 (major isomer, 60:40): ^{1}H NMR ($CDCl_3$): δ = 0.72 (dd, J = 10.85, 6.85 Hz, 1.8H, PCHCH_3, major isomer), 0.79 (dd, J = 10.90, 6.85 Hz, 1.2H, PCHCH_3, minor isomer), 1.21 (d, J = 6.85 Hz, 1.8H, C≡CCMe, major isomer), 1.38 (s, 3H, $C_{60}Me_5$), 1.48 (d, J = 6.85 Hz, 1.2H, C≡CCMe, minor isomer), 1.68 (br, 1H, overlapped, PCH_2), 1.72 (s, 3H, $C_{60}Me_5$), 1.95 (s, 3H, $C_{60}Me_5$), 2.36 (s, 3H, $C_{60}Me_5$), 2.40 (br, 1H, PC*H*Me), 3.11 (s, 3H, $C_{60}Me_5$), 3.47–3.51 (m, 1H, PCH_2), 3.79 (q, J = 6.30 Hz, 0.4H, C≡CCH, minor isomer), 3.82 (q, J = 6.30 Hz, 0.6H, C≡CCH, major isomer), 6.82 (d, J = 7.40 Hz, 2H, Ph), 7.07–7.69 (m, 17H), 8.03 (t, J = 8.00 Hz, 1.2H, major isomer), 8.16 (t, J = 8.00 Hz, 0.8H, minor isomer), 8.42–8.57 ppm (m, 4H); ^{31}P NMR ($CDCl_3$): δ = 55.9 (d, J = 27.58 Hz, major isomer), 56.0 (d, J = 30.64 Hz, minor isomer), 77.3 (d, J = 27.58 Hz, minor isomer), 77.4 ppm (d, J = 30.64 Hz, major isomer); MS (ESI) (+): m/z = 1438 $[M]^+$; HRMS (ESI) (+): m/z calcd for $C_{102}H_{50}P_2Ru$: 1438.2431 $[M]^+$; found: 1438.2415.

11 (major isomer, 68:32): ^{1}H NMR ($CDCl_3$): δ = 0.74–0.76 (m, 2.0H, PCHCH_3, major isomer), 0.82 (br, 1.0H, PCHCH_3, minor isomer), 1.18 (d, J = 7.45 Hz, 2.0H, C≡CCMe, major isomer), 1.38 (s, 3H, $C_{60}Me_5$), 1.46 (d, J = 6.85 Hz, 1.0H, C≡CCMe, minor isomer), 1.68 (br, 1H, overlapped, PCH_2), 1.70 (s, 3H, $C_{60}Me_5$), 1.96 (s, 3H, $C_{60}Me_5$), 2.36 (s, 3H, $C_{60}Me_5$), 2.47–2.57 (m, 1H, PC*H*Me), 3.11 (s, 3H, $C_{60}Me_5$), 3.50 (br, 1H, PCH_2), 3.74 (s, 3H, OMe), 3.86–3.88 (m, 1H, C≡CCH), 6.67 (d, J = 8.60 Hz, 2H, C_6H_4OMe), 6.73 (d, J = 8.60 Hz, 2H, C_6H_4OMe), 7.17–7.70 (m, 14H), 8.05 (t, J = 8.60 Hz, 1.36H, major isomer), 8.18 (t, J = 8.60 Hz, 1.64H, minor isomer), 8.43–8.57 ppm (m, 4H); ^{31}P NMR ($CDCl_3$): δ = 55.9 (d, J = 27.58 Hz, major isomer), 56.0 (d, J = 27.58 Hz, minor isomer), 77.3 (d, J = 27.58 Hz, minor isomer), 77.3 ppm (d, J = 27.58 Hz, major isomer).; MS (ESI) (+): m/z = 1468 $[M]^+$; HRMS (ESI) (+): m/z calcd for $C_{103}H_{52}OP_2Ru$: 1468.2537 $[M]^+$; found: 1468.2584.

12 (major isomer, 63:37): IR (powder): $\tilde{\nu}$ = 3259 (br), 2968, 2919, 2094 (s, $\nu_{C\equiv C}$), 1434 (s), 1092 (m), 814 (s), 743 (s), 656 cm^{-1}(s); ^{1}H NMR ($CDCl_3$): δ = 0.78 (dd, J = 10.30, 6.30 Hz, 1.9H, PCHCH_3, major isomer), 1.02 (dd, J = 10.85, 6.35 Hz, 1.1H, PCHCH_3, minor isomer), 1.10 (d, J = 6.85 Hz, 1.1H, FcCHCH_3, minor isomer), 1.34 (s, 3H, $C_{60}Me_5$), 1.47 (d, J = 6.35 Hz, 1.9H, FcCHCH_3, major isomer), 1.63 (br, 1H, overlapped, PCH_2), 1.68 (s, 3H, $C_{60}Me_5$), 1.93 (s, 3H, $C_{60}Me_5$), 2.31 (s, 3H, $C_{60}Me_5$), 2.45 (br, 1H, PC*H*Me), 3.02 (s, 3H, $C_{60}Me_5$), 3.38 (br, 1H, PCH_2), 3.41–3.43 (m, 1H, C*H*Fc) 3.71–4.14 (m, 4H, Fc), 4.03 (s, 3.15H, Fc, major isomer), 4.08 (s, 1.85H, Fc, minor isomer), 7.30–7.69 (m, 14H), 8.12 (t, J = 8.60 Hz, 1.26H, major isomer), 8.24 (t, J = 8.55 Hz, 0.74H, minor isomer), 8.37–8.48 ppm (m, 4H); ^{31}P NMR ($CDCl_3$): δ = 55.4 (d, J = 26.92 Hz, major isomer), 55.8 (d, J = 26.92 Hz, minor isomer), 76.9 (d, J = 26.92 Hz, major isomer), 77.2 ppm (d, J = 26.92 Hz, minor isomer); MS (ESI) (+): m/z = 1546 $[M]^+$; HRMS (ESI) (+): m/z calcd for $C_{106}H_{54}FeP_2Ru$: 1545.2106 $[M]^+$; found: 1545.2058.

13 (major isomer, 88:12): IR (powder): 3253 (br), 3051, 2962, 2919, 2095 (s, $\nu_{C\equiv C}$), 1517 (s), 1434 (s), 1090 (s), 816 (s), 727 (s), 696 cm^{-1} (s); ^{1}H NMR ($CDCl_3$): δ = 0.76 (dd, J = 10.90, 6.85 Hz, 2.64H, PCHCH_3, major isomer), 0.82 (dd, J = 10.90, 6.85 Hz, 0.36H, PCHCH_3, minor isomer), 1.16 (d, J = 6.85 Hz, 2.64H, C≡CCMe, major isomer), 1.38 (s, 3H, $C_{60}Me_5$), 1.45 (d, J = 6.85 Hz, 0.36H, C≡CCMe, minor isomer), 1.68 (br, 1H, overlapped, PCH_2), 1.71 (s, 3H, $C_{60}Me_5$), 1.96 (s, 3H, $C_{60}Me_5$), 2.36 (s, 3H, $C_{60}Me_5$), 2.47–2.57 (m, 1H, PC*H*Me), 2.85 (s, 0.72H, NMe$_2$, minor isomer), 2.86 (s, 5.28H, NMe$_2$, major isomer), 3.11 (s, 3H, $C_{60}Me_5$), 3.54–3.58 (m, 1H, PCH_2), 3.72 (q, 0.12H, C≡CCH, minor isomer), 3.82 (q, J = 5.15 Hz, 0.88H, C≡CCH, major isomer), 6.55 (d, J = 8.60 Hz, 2H, C_6H_4NMe$_2$), 6.71 (d, J = 8.60 Hz, 2H, C_6H_4NMe$_2$), 7.15–7.18 (m, 2H, ArH), 7.27–7.33 (m, 3H, ArH), 7.41–7.46 (m, 2H, ArH), 7.52 (t, J = 8.55 Hz, 2H, ArH), 7.59–7.60 (m, 4H), 7.66–7.69 (m, 1H), 8.06 (t, J = 8.60 Hz, 1.76H, major isomer), 8.18 (t, J = 8.55 Hz, 0.24H, minor isomer), 8.45 (t, J = 8.60 Hz, 2H), 8.54–8.58 (m, 2H); ^{31}P NMR ($CDCl_3$): δ = 56.0 (d, J = 26.92 Hz, major isomer), 56.1 (d, J = 30.76 Hz, minor isomer), 77.3 (d, J = 30.76 Hz, minor isomer), 77.3 (d, J = 30.76 Hz, major isomer); MS (ESI) (+): m/z = 1481 $[M]^+$; HRMS (ESI) (+): m/z calcd for $C_{104}H_{55}NP_2Ru$: 1481.2853 $[M]^+$; found: 1481.2817.

14 (major isomer, 85:15): IR (powder): $\tilde{\nu}$ = 3267 (br), 2921, 2096 (s, $\nu_{C\equiv C}$), 1507 (s), 1430 (s), 1245 (s, ν_{C-O}), 743 (s), 656 cm^{-1} (s); ^{1}H NMR ($CDCl_3$): δ = 0.68 (dd, J = 10.85, 6.85 Hz, 3H, PCHCH_3, overlapped), 1.47 (s, 3H, $C_{60}Me_5$), 1.66 (br, 1H, overlapped, PCH_2), 1.67 (s, 3H, $C_{60}Me_5$), 1.96 (s, 3H, $C_{60}Me_5$), 2.36 (s, 3H, $C_{60}Me_5$), 2.45 (br, 1H, PC*H*Me), 2.70 (s, 3H, $C_{60}Me_5$), 3.34–3.35 (m, 1H, PCH_2), 3.70 (s, 2.55H, OMe, major isomer), 3.80 (s, 0.45H, OMe, minor isomer), 5.02 (s, 1H, C≡C-CH), 6.52 (d, J = 8.60 Hz, 1.7H, C_6H_4OMe, major isomer), 6.56 (d, J = 8.60 Hz, 0.30H, C_6H_4OMe, minor isomer), 6.63 (d, J = 8.60 Hz, 1.7H, C_6H_4OMe, major isomer), 6.77 (d, J = 8.60 Hz, 0.30H, C_6H_4OMe, minor isomer), 7.18–7.70 (m, 19H), 8.15 (t, J = 8.00 Hz, 2H), 8.42–8.45 (m, 2H), 8.52 ppm (br, 2H); ^{31}P NMR ($CDCl_3$): δ = 56.3 (d, J = 26.92 Hz, overlapped), 77.5 (d, J = 26.92 Hz, major isomer), 77.5 ppm (d, J = 30.76 Hz, minor isomer); MS (ESI) (+): m/z = 1530 $[M]^+$; HRMS (ESI) (+): m/z calcd for $C_{108}H_{54}OP_2Ru$: 1530.2693 $[M]^+$; found: 1530.2721.

15 (major isomer, 95:5): ^{1}H NMR ($CDCl_3$): δ = 0.66 (dd, J = 11.45, 7.35 Hz, 3H, PCHCH_3), 1.47 (s, 3H, $C_{60}Me_5$), 1.66 (br, 1H, overlapped, PCH_2), 1.67 (s, 3H, $C_{60}Me_5$), 1.96 (s, 3H, $C_{60}Me_5$), 2.36 (s, 3H, $C_{60}Me_5$), 2.47 (br, 1H, PC*H*Me), 2.72 (s, 3H, $C_{60}Me_5$), 2.82 (s, 6H, NMe$_2$), 3.34–3.37 (m, 1H, PCH_2), 4.98 (s, 1H, C≡C-CH), 6.47–6.51 (m, 4H, C_6H_4NMe$_2$), 7.14–7.69 (m, 19H), 8.16 (t, J = 8.55 Hz, 2H), 8.41–8.45 (m, 2H), 8.52–8.53 ppm (m, 2H); ^{31}P NMR ($CDCl_3$): δ = 56.4 (d, J = 27.78 Hz), 77.5 ppm (d, J = 27.78 Hz); MS (ESI) (+): m/z = 1543 $[M]^+$; HRMS (ESI) (+): m/z calcd for $C_{109}H_{57}NP_2Ru$: 1543.3010 $[M]^+$; found: 1543.2988.

16 (major isomer, 80:20): ^{1}H NMR ($CDCl_3$): δ = 0.65 (dd, J = 10.90, 6.90 Hz, 3H, PCHCH_3), 1.46 (s, 3H, $C_{60}Me_5$), 1.65 (s, 3H, $C_{60}Me_5$), 1.67 (br, 1H, overlapped, PCH_2), 1.95 (s, 3H, $C_{60}Me_5$), 2.34 (s, 3H, $C_{60}Me_5$),

2.41–2.45 (m, 1H, PC*H*Me), 2.72 (s, 3H, $C_{60}Me_5$), 2.81 (s, 4.8H, NMe_2, major isomer), 2.91 (s, 1.2H, NMe_2, minor isomer), 3.31–3.35 (m, 1H, PCH_2), 3.68 (s, 0.60H, OMe, minor isomer), 3.78 (s, 2.4H, OMe, major isomer), 4.92 (s, 1H, C≡C-CH), 6.43 (d, J=8.60 Hz, 4H, $C_6H_4NMe_2$), 6.49 (d, J=8.60 Hz, 4H, $C_6H_4NMe_2$), 6.75 (d, J=8.60 Hz, 2H), 7.15–7.69 (m, 16H), 8.15 (t, J=8.60 Hz, 2H), 8.41–8.44 (m, 2H), 8.52–8.54 ppm (m, 2H); ^{31}P NMR ($CDCl_3$): δ=56.5 (d, J=27.66 Hz, major isomer), 56.6 (d, J=27.66 Hz, minor isomer), 77.7 (d, J=27.66 Hz, minor isomer), 77.7 ppm (d, J=27.78 Hz, major isomer); MS (ESI) (+): m/z=1573 $[M]^+$; HRMS (ESI) (+): m/z calcd for $C_{110}H_{60}NOP_2Ru$: 1574.3193 $[M+H]^+$; found: 1574.3169.

17 (major isomer, 78:22): ^{1}H NMR ($CDCl_3$): δ=0.65–0.69 (m, 3H, PCHC*H*$_3$), 1.46 (s, 3H, $C_{60}Me_5$), 1.67 (s, 3H, $C_{60}Me_5$), 1.68 (br, 1H, overlapped, PCH_2), 1.96 (s, 3H, $C_{60}Me_5$), 2.34 (s, 3H, $C_{60}Me_5$), 2.45 (br, 1H, PC*H*Me), 2.70 (s, 3H, $C_{60}Me_5$), 2.82 (s, 4.7H, NMe_2, major isomer), 2.93 (s, 1.3H, NMe_2, minor isomer), 3.30 (br, 1H, PCH_2), 4.95 (s, 1H, C≡C-CH), 6.44 (d, J=8.60 Hz, 4H, $C_6H_4NMe_2$), 6.50 (d, J=8.60 Hz, 4H, $C_6H_4NMe_2$), 7.16–7.69 (m, 18H), 8.14 (t, J=8.60 Hz, 2H), 8.43 (br, 2H), 8.53 ppm (br, 2H); ^{31}P NMR ($CDCl_3$): δ=56.3 (d, J=27.56 Hz, major isomer), 56.4 (d, J=27.6 Hz, minor isomer), 77.5 (d, J=27.56 Hz, minor isomer), 77.6 ppm (d, J=27.56 Hz, major isomer); MS (ESI) (+): m/z=1577 $[M]^+$; HRMS (ESI) (+): m/z calcd for $C_{109}H_{56}ClNP_2Ru$: 1577.2620 $[M]^+$; found: 1577.2594.

18 (major isomer, 75:25): ^{1}H NMR ($CDCl_3$): δ=0.14 (dd, J=10.30, 6.80 Hz, 0.75H, PCHC*H*$_3$, minor isomer), 0.57 (dd, J=10.85, 6.90 Hz, 2.3H, PCHC*H*$_3$, major isomer), 1.51 (s, 3H, $C_{60}Me_5$), 1.66 (s, 3H, $C_{60}Me_5$), 1.67 (br, 1H, overlapped, PCH_2), 1.97 (s, 3H, $C_{60}Me_5$), 2.36 (s, 3H, $C_{60}Me_5$), 2.45 (br, 1H, PC*H*Me), 2.66 (s, 3H, $C_{60}Me_5$), 2.77 (s, 4.5H, NMe_2, major isomer), 2.90 (s, 1.5H, NMe_2, minor isomer), 3.25 (br, 1H, PCH_2), 5.60 (s, 0.75H, C≡C-CH, major isomer), 5.63 (s, 0.25H, C≡C-CH, minor isomer), 6.32 (d, J=8.60 Hz, 4H, $C_6H_4NMe_2$), 6.43 (d, J=8.60 Hz, 4H, $C_6H_4NMe_2$), 6.68 (d, J=9.05 Hz, 1H), 7.15–7.88 (m, 19H), 8.11 (d, J=6.90 Hz, 1H), 8.17 (t, J=8.10 Hz, 2H), 8.45 (br, 2H), 8.59–8.63 ppm (m, 2H); ^{31}P NMR ($CDCl_3$): δ=56.4 (d, J=27.58 Hz, major isomer), 57.1 (d, J=27.58 Hz, minor isomer), 77.2 (d, J=27.58 Hz, minor isomer), 77.6 ppm (d, J=27.58 Hz, major isomer); MS (ESI) (+): m/z=1593 $[M]^+$; HRMS (ESI) (+): m/z calcd for $C_{113}H_{60}NP_2Ru$: 1594.3245 $[M]^+$; found: 1594.3268.

19 (major isomer, 61:39): IR (powder): $\tilde{\nu}$=3053, 2964, 2921, 2097 (s, $\nu_{C\equiv C}$), 1430 (s), 1090 (m), 744 (s), 696 cm^{-1} (s); ^{1}H NMR ($CDCl_3$): δ=0.77 (dd, J=11.40, 6.90 Hz, 1.2H, PCHC*H*$_3$, minor isomer), 0.81 (dd, J=11.45, 6.90 Hz, 1.8H, PCHC*H*$_3$, major isomer), 1.43 (s, 3H, $C_{60}Me_5$), 1.70–1.71 (m, 1H, overlapped, PCH_2), 1.75 (s, 3H, $C_{60}Me_5$), 1.97 (s, 3H, $C_{60}Me_5$), 2.31 (s, 3H, $C_{60}Me_5$), 2.40–2.60 (m, 1H, PC*H*Me), 2.87 (s, 2.4H, NMe_2, minor isomer), 2.89 (s, 3.6H, NMe_2, major isomer), 3.04 (s, 3H, $C_{60}Me_5$), 3.48 (br, 0.39H, PCH_2, minor isomer), 3.60 (br, 0.61H, PCH_2, major isomer), 4.86 (s, 1H, C≡C-CH), 6.56 (d, J=8.88 Hz, 0.78H, $C_6H_4NMe_2$, minor isomer), 6.58 (d, J=8.88 Hz, 1.2H, $C_6H_4NMe_2$, major isomer), 6.82 (d, J=8.88 Hz, 0.78H, $C_6H_4NMe_2$, minor isomer), 6.93 (d, J=8.88 Hz, 1.2H, $C_6H_4NMe_2$, major isomer), 7.17–7.70 (m, 19H), 8.16 (t, J=8.00 Hz, 0.78H, minor isomer), 8.21 (t, J=8.00 Hz, 1.2H, major isomer), 8.44–8.52 ppm (m, 4H); ^{31}P NMR ($CDCl_3$): δ=55.5 (d, J=30.78 Hz, minor isomer), 55.6 (d, J=30.76 Hz, major isomer), 76.8 (d, J=26.92 Hz, minor isomer), 77.4 (d, J=32.30 Hz, major isomer); MS (ESI) (+): m/z=1567 $[M]^+$; HRMS (ESI) (+): m/z calcd for $C_{111}H_{57}NP_2Ru$: 1567.3010 $[M]^+$; found: 1567.3003.

X-ray Crystallography

X-ray diffraction data were collected on a Rigaku RAXIS-RAPID II imaging plate diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (λ=0.71075 Å). As many diffraction peaks overlapped with each other owing to the large unit-cell parameters (a=47.560(10), b=19.579(4), c=17.211(3) Å, $\alpha=\beta=\gamma$=90°, V=16026.0(54) Å^3, $P2_12_12$), we are less certain of the bond distances in **8**. CCDC-628363 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Centre at www.ccdc.cam.ac.uk/data_request/cif.

Electrochemical Measurements

Electrochemical measurements were performed on a BAS CV-50W voltammetric analyzer. A glassy-carbon electrode was used as the working electrode. The counterelectrode was a platinum coil, and the reference electrode was an Ag/Ag^+ electrode. Cyclic voltammetry (CV) was performed at a scan rate of 100 mV s^{-1}. All half-wave potentials are given as $E_{1/2}=(E_{pc}+E_{pa})/2$, where E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively.

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