Remote Chirality Transfer within a Coordination Sphere by the Use of a Ligand Possessing a Concave Cavity

Yutaka Matsuo,[†] Yuichi Mitani,[‡] Yu-Wu Zhong,[†] and Eiichi Nakamura*[,†,‡]

Nakamura Functional Carbon Cluster Project, ERATO, Japan Science and Technology Agency, and Department of Chemistry, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

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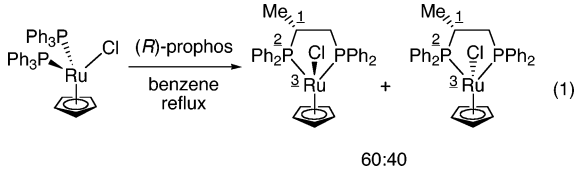
The possibility to enhance the effect of a modest chiral element in a metal ligand by the use of a second ligand possessing a concave cavity has been examined for the examples of 1,3- and 1,4-chirality transfer within the metal coordination sphere. Complexation of $Ru(C_{60}Me_5)Cl(CO)_2$ with (*R*)-prophos [(*R*)-1,2-bis(diphenylphosphino)propane] took place with excellent diastereoselectivity to give a configurationally stable chiral-at-metal complex, $Ru(C_{60}Me_5)Cl$((*R*)-prophos). This complex was converted, with good to perfect diastereoselectivity, into a variety of cationic complexes, [$Ru(C_{60}Me_5)$((*R*)-prophos)L]-[SbF_6] (L = MeCN, ^{t}BuCN, methacrolein, acetone, CO, BnNC, 2,6-$Me_2C_6H_3NC$), and a vinylidene complex, [$Ru(C_{60}Me_5)$(=C=CPhH)((*R*)-prophos)][SbF_6]. The chirality transfer to the reactants reacting in the outer sphere of the coordination resulted in an asymmetric Diels−Alder reaction, albeit with modest selectivity.

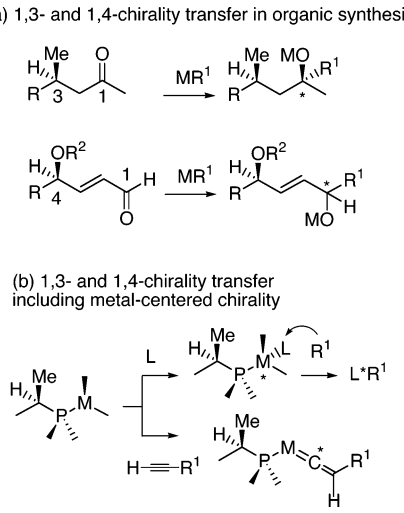
Introduction

Diastereoselective creation of a new stereogenic center under the influence of an existing stereogenic center in some remote location of the same molecule (chirality transfer) is a rather difficult task, and its feasibility was studied extensively by organic chemists in the 1980s and 1990s in the context of synthesis of complex organic molecules. For instance, nucleophilic addition to a ketone shown in Scheme 1a (top) may take place diastereoselectively under the influence of the stereogenic center at the 3-position.[1] Chirality transfer to a more remote position such as 1,4-transfer is less straightforward, but can also be achieved in some cases (Scheme 1a, bottom).[1,2]

Similar chirality transfer can be envisaged in inorganic chemistry; for instance, addition of a ligand L to a coordinatively unsaturated metal may induce metal-centered chirality in a 1,3-manner under the influence of a stereogenic center in the phosphine ligand attached to the metal (Scheme 1b, top). The reaction of L with a second reactant R^1 may create a new molecule L*R^1, which may be optically active if the chiral phosphine ligand is nonracemic. Such chirality transfer to external reactants constitutes the basic principle of metal-assisted asymmetric synthesis.[3] Chirality transfer may occur during formation of an organometallic compound as in Scheme 1b, bottom, where the new stereogenic center on the added carbon ligand may be controlled in a 1,4-manner.[4,5]



Scheme 1. 1,*n*-Chirality Transfer in Organic and Organometallic Chemistry



Achieving high diastereoselectivity in remote chirality transfer within an organometallic complex however has not been an easy issue[6,7] because of the thermodynamic and kinetic instability of the configuration of the metal-centered chirality.[8] For instance, the reaction of $Ru(\eta^5\text{-Cp})Cl(PPh_3)_2$ with a chiral diphosphine ligand of modest steric demand, (*R*)-prophos [(*R*)-1,2-bis(diphenylphosphino)propane], gives an essentially 1:1 (0−20% de) mixture of two diastereomers (eq 1).[9] The

* To whom correspondence should be addressed. E-mail: nakamura@chem.s.u-tokyo.ac.jp.

[†] ERATO, Japan Science and Technology Agency.

[‡] The University of Tokyo.

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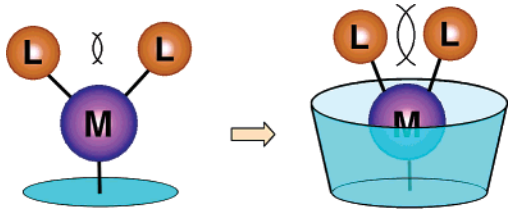
Scheme 2

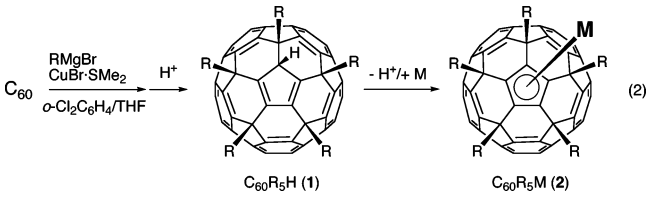


diastereoselectivity may be improved by the use of a sterically more demanding pentamethylcyclopentadienide ligand (up to 95:5 for Ru(η^5-C_5Me_5)Cl(PPh_3)$_2$).[10]

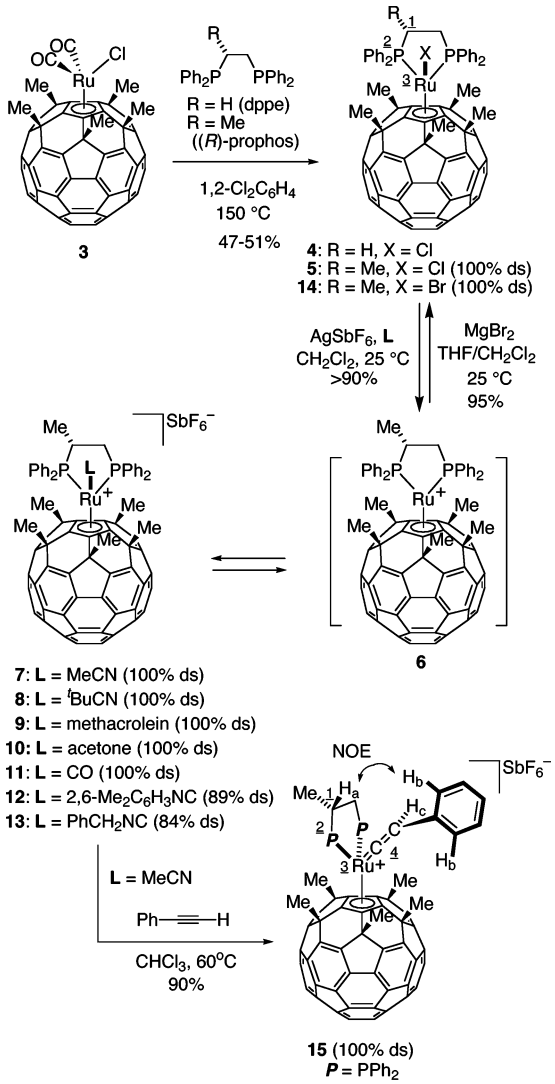
One can consider that installation of a ligand with a concave structural motif on the metal center (Scheme 2) would limit the conformational mobility of the other ligands (e.g., L^1 and L^2) and hence would enhance the steric effect of one ligand to the other. In other words, even a modest chirality element in L^1 would be reflected much more on the stereochemistry in L^2 or that of the metal center. However, metal ligands possessing a clearly defined concave cavity are rare (e.g., pyrazolylborate[11]). We recently created a new class of cyclopentadienide ligands where the cyclopentadienide (Cp) moiety is enclosed in a concave cavity built on the skeleton of a fullerene molecule (eq 2). Herein we report the first application of this concave ligand for stereocontrol as illustrated for the coordination behavior of ruthenium complexes (Scheme 3). The new ligand much enhances the degree of the remote chirality transfer in the case shown in eq 1.

Results and Discussion

Regioselective addition of an organocopper compound to [60]-fullerene has made available a wide variety of pentaorgano fullerene metal complexes that feature a cyclopentadiene or a metal cyclopentadienide moiety embedded in the fullerene framework (eq 2). When the added R groups are large enough (e.g., biphenyl), the molecule resembles the shape of a badminton shuttlecock and forms supramolecular one-dimensional stacks in crystals or in liquid crystals.[12]



Scheme 3



The underlined numbers in **4**, **5**, **14**, and **15** refer to the positions relative to the original chirality that is defind as 1.

In addition to the supramolecular effect, the concave cavity offers possibilities for organometallic chemistry; for instance, the protruding R groups provide a new type of environment for the metal group M. Unlike conventional cyclopentadienide ligands that are flat and symmetric with regard to the plane involving the 6π-aromatic five-membered ring, the fullerene cyclopentadienide (FCp) is not. When the conical cavity around the cyclopentadienide of **2** is deep enough (e.g., R = phenyl), the cavity provides steric protection of the center metal against attachment of external reactants. For instance, a Ni(η^3-C_3H_5) complex of **2** (R = Ph) is very stable to air (i.e., molecular oxygen), whereas the corresponding ordinary Ni(η^3-C_3H_5)(η^5-C_5H_5) complex is too unstable to be isolated (immediate oxidative decomposition).[13] We therefore conjectured that modulation of the height of the wall (i.e., the size of the R group)

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would control the coordination chemistry of the metal atom by limiting the mobility of the ligand molecules (Scheme 2).

Diastereoselective Synthesis of Ru(η^5-$C_{60}Me_5$)Cl((*R*)-prophos). A previously described complex, Ru(η^5-$C_{60}Me_5$)Cl$(CO)_2$ (**3**),[14] was synthesized, and the 1,3-chirality transfer during the course of ligand exchange from CO to (*R*)-prophos was examined. As a reference, the corresponding achiral diphosphine, 1,2-bis(diphenylphosphino)ethane (dppe), was also studied.

The reaction of **3** with dppe proceeds in 1,2-dichlorobenzene at 150 °C to give the diphosphine complex Ru(η^5-$C_{60}Me_5$)Cl(dppe) (**4**) as air-stable orange microcrystals in 47% yield (Scheme 3). We examined the reaction with (*R*)-prophos under the same conditions. To our pleasant surprise, the reaction even at such a high temperature afforded Ru(η^5-$C_{60}Me_5$)Cl((*R*)-prophos) (**5**) as a single diastereomer in 51% yield. We carefully determined the diastereomeric excess of **5** in the crude mixture and found that the reaction is completely selective as determined by ^{1}H, ^{13}C, and ^{31}P NMR and HPLC analyses (Cosmosil Buckyprep and Develosil RPFullerene). Thus, unlike the normal Cp ligand, which gave a 60:40 diastereomeric mixture (eq 1), the FCp ligand destabilizes one isomer more than the other.

The ^{1}H NMR of **4** and **5** at room temperature displayed three signals due to the methyl groups at δ 2.24, 2.25, and 2.36 and five singlet signals at δ 1.44, 1.61, 2.06, 2.48, and 2.86, respectively. Therefore, **4** and **5** are C_s and C_1 symmetric, respectively, indicating that the diphosphine ligands are fixed in their location relative to the FCp methyl groups. The ^{13}C NMR spectra also supported this conclusion. The ^{31}P{^{1}H} NMR spectrum of **4** exhibited a singlet signal due to the phosphine ligand at δ 63.44, while **5** showed two doublet signals at 45.8 and 69.0 due to magnetically nonequivalent phosphine atoms.

The ^{31}P signals of **4** and **5** appear at a lower field than that of the free ligands (**4**, δ −12.70; **5**, δ −20.98 and 1.35), indicating that the diphosphine ligands are coordinated in a bidentate fashion. Variable-temperature ^{1}H and ^{31}P NMR measurements of **5** in a temperature range between 80 and −45 °C did not show any significant signal broadening, strongly suggesting that the metal-centered chirality of **5** is very stable both conformationally and configurationally.

The structures of **4** and **5** were unambiguously determined by X-ray crystallographic analysis. Slow diffusion of ethanol to a toluene solution of **4** and **5** gave single crystals having centrosymmetric ($P2_1/c$) and chiral ($P2_1$) space groups, respectively (Figures 1 and 2). The two structures are very similar to each other except the presence of an extra methyl group of the (*R*)-prophos ligand in **5** and twisting of the phenyl group (shown by an arrow) next to the methyl group. The absolute configuration at the Ru center of **5** was determined to be S_{Ru}, and the methyl substituent on the ligand backbone was found to point away from the chlorine atom on the Ru atom. All Ru−P and Ru−C(fullerene-Cp moieties) bond distances of **4** and **5** (shown in the caption of Figure 1) are slightly longer than those of the normal CpRu-prophos complex, (*S*)-Ru(η^5-C_5H_5)Cl{(*R*)-prophos} [Ru−P = 2.276 and 2.278 Å, Ru−C(Cp, averaged) = 2.20 Å],[9] while the Ru−Cl distances of **4** and **5** are not very different from that of (*S*)-Ru(η^5-C_5H_5)Cl{(*R*)-prophos} (Ru−Cl = 2.444 Å). The long bond distances of Ru−P and Ru−C(fullerene-Cp) can be ascribed to the steric repulsion between the methyl groups of the $C_{60}Me_5$ ligand and the phenyl groups of the diphosphine ligands. Taking into account the NMR and X-ray data, we conclude that the concave shape of the $C_{60}Me_5$ ligand is responsible for the perfect 1,3-chiral induction from the chiral center of the carbon atom of (*R*)-prophos to the ruthenium center.

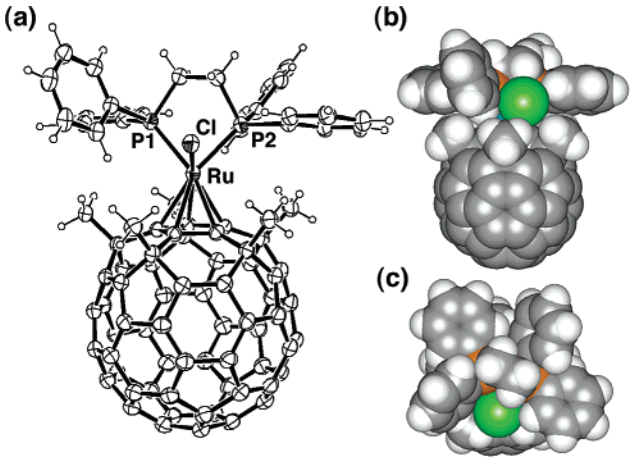

Figure 1. Molecular structure of **4**. Selected bond distances (Å) and angles (deg): Ru−C(fullerene Cp, average) = 2.27, Ru−centroid(MeFCp) = 1.92, Ru−Cl = 2.44, Ru−P1 = 2.37, Ru−P2 = 2.35, P1−Ru−P2 = 82.3, Cl−Ru−P1 =84.3, Cl−Ru−P2 = 82.5.

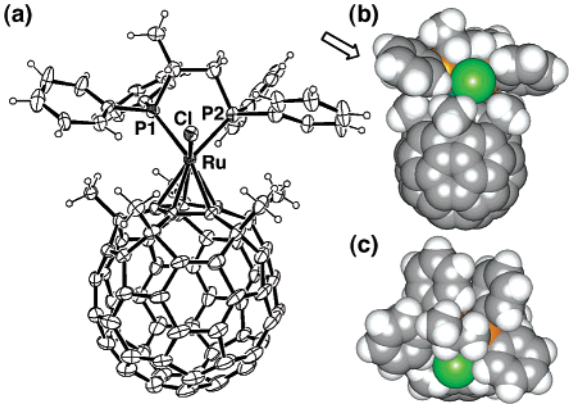

Figure 2. Molecular structure of **5**. Selected bond distances (Å) and angles (deg): Ru−C(fullerene Cp, average) = 2.28 Å, Ru−centroid(fullerene Cp) = 1.92 Å, Ru−Cl = 2.437(3) Ru−P1 = 2.344(3), Ru−P2 = 2.341(3), P1−Ru−P2 = 80.5(1), Cl−Ru−P1 = 86.2(1), Cl−Ru−P2 = 81.4(1). The phenyl group indicated by an arrow is tilted due to the methyl group in the prophos ligand.

Diastereoselective Conversion to Cationic Complexes. Having found excellent diastereoselectivity of the (*R*)-prophos complex formation, we examined the reaction of the corresponding cationic complex **6** with a nucleophile to see whether 1,3-chirality transfer to the metal center also occurs here with high selectivity. To this end, the chlorine atom in **5** was removed by $AgSbF_6$ in CH_2Cl_2 to generate in situ a cationic complex **6**, which was allowed to react with neutral molecules, CO, methacrolein, acetone, nitriles, and isonitriles to form complexes **7**−**13** in essentially quantitative yields. All reactions produced one diastereomer in excess of another, and the diastereomeric selectivity ranged from 84% to 100%.

The sense of the diastereoselectivity of the complex formation was assigned for the ^{t}BuCN complex **8**. The 2D NOESY spectrum of **8** exhibited a strong NOE effect between the *tert*-butyl nitrile and the proton bound to the chiral center of (*R*)-prophos. As can be seen in Figure 2, such proximity indicates that the stereochemistry of **8** is the same as that of **5**, that is, S_{Ru}. The major diastereomers of other complexes showed NMR spectra, ^{31}P NMR, in particular,[15] essentially the same as those of **8**, suggesting that all are in the same configuration. In

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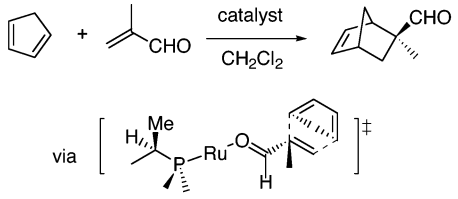
addition, when the acetonitrile complex **7** was treated with $MgBr_2$ in a mixture of THF and CH_2Cl_2, the neutral complex **14** was obtained in 100% ds (Scheme 3), and the absolute configuration of the ruthenium center was the same as that in **5** as determined by the X-ray analysis. The ligand exchange thus took place with overall retention of the stereochemistry at the metal center. Only when the ligands were strong coordinating isonitriles (**12** and **13**) did the selectivity erode to about 80%. The similarity in the steric bulk of nitriles and isonitriles suggests that the observed diastereoselectivity is related to both the thermodynamics and kinetics of the complexation reaction.

We also found that 1,4-chirality transfer takes place with excellent selectivity. Treatment of **7** with phenylacetylene in $CHCl_3$ at 60 °C afforded **15** as a single diastereomer.[16] Its ^{13}C NMR spectrum showed a characteristic low-field phosphorus-coupled triplet at δ 343.92, which attests to the presence of the vinylidene motif. The ^1H NMR exhibited a singlet at δ 5.19 for the β-H of vinylidene. 2D NOESY measurement showed a strong NOE effect between the proton bound to the chiral center of (*R*)-prophos (H_a) and the aryl proton H_b. In addition, a weak NOE was observed between H_b and the methyl groups of the fullerene core, which in turn showed a weak NOE with H_c (β-H of vinylidene). All these pieces of information indicated the major conformation of **15** in solution as that illustrated in Scheme 3, in which the plane containing the vinylidene ligand is orthogonal to the plane containing the centroid of the fullerene Cp ligand/the ruthenium atom/the α-carbon of the vinylidene ligand, with the phenyl group of vinylidene directed toward the chiral center of (*R*)-prophos. The spatial orientation of the phenyl group is consistent with the steric environment found in the X-ray structure of **5** (Figure 2), where the tilted phenyl group (indicated by an arrow) provides a chiral space to accommodate the vinylidene group above it. Overall, the suggested conformation corroborates with previous theoretical analyses[17] and X-ray analyses of similar structures bearing a cyclopentadienyl,[16b,18] pentamethyl cyclopentadienyl,[19] or indenyl ligand.[20]

The chiral space in which the chlorine atom of **5** or the vinylidene group of **15** is located is not particularly conspicuous because of the lack of any intentional design at this stage. Nonetheless, we examined if this modest steric effect can induce any chirality in the reaction in the outer sphere of coordination. Following the lead by Kündig, we examined the asymmetric Diels−Alder reaction between cyclopentadiene and methacrolein (Scheme 4).[21] The reaction was very slow by itself and was

Scheme 4



catalyst (mol %)	temp, h	%yield	exo:endo	%ee
none	rt, 24	10	5.5:1	--
BF_3•Et_2O (10)	0°C, 1/3	95	5:1	--
Ru•CH_3CN **5** (5)	rt, 72	85	9:1	5
Ru•methacrolein **7** (5) 2,6-di-*tert*-butylpyridine	rt, 48	80	23:1	20

accelerated by BF_3 etherate, but *exo*/*endo* selectivity was modest in both cases. The CH_3CN complex **7** accelerated the reaction to a small degree, but diastereo- and enantioselectivities were poor. We suspected that it is due to the sluggishness of CH_3CN/methacrolein exchange and instead used the methacrolein complex **9**. The reaction took place faster indeed and with much enhanced *exo*:*endo* ratio (23:1) and enantioselectivity (20% ee; absolute stereochemistry of major isomer as indicated). The high *exo*/*endo* selectivity suggests that the FCp complex is acting as a bulky ligand, but the low enantioselectivity indicates that the design of the chiral environment is yet to be improved.

The basic principle of the enhancement of the effect of the modest chiral element in the prophos ligand by the use of the concave FCp ligand has been proved. The availability of numerous chiral ligands and η^5-FCp complexes[22] combined with the preliminary data on asymmetric catalysis suggests that suitable modification of the substituents in the ligand chirality as well as that of the R groups on the fullerene would provide us with new opportunities in asymmetric synthesis of organic and inorganic compounds.

Experimental Section

General Procedures. All experiments were carried out under argon using standard Schlenk techniques. THF and toluene were distilled from Na/K alloy, and 1,2-dichlorobenzene was distilled

(15) ^{31}P NMR signals of major diastereomers (**5**, **7**−**15**) appear around δ 45 and 70. See Exparimental Section.

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from CaH_2 before use. All solvents were thoroughly degassed by trap-to-trap distillation and stored under argon. $Ru(C_{60}Me_5)Cl(CO)_2$ (**3**) was prepared according to the previous report.[14] A THF solution of KO^{t}Bu and (*R*)-1,2-bis(diphenylphosphino)propane were purchased from Sigma-Aldrich Co. and were used as received.

HPLC analyses were performed on Shimadzu LC-10A system equipped with SPD-M10A diode array detector and a Cosmosil-Buckyprep column (4.6 × 250 mm, Nacalai Tesque Co.). Preparative HPLC separations were performed by the use of a Buckyprep column (20 mm × 250 mm) using toluene/2-propanol (7:3 or 1:1) as eluent. All ^{1}H (400 MHz, 500 MHz), ^{13}C{^{1}H} (100 MHz, 125 MHz), and ^{31}P{^{1}H} NMR (200 MHz) spectra were recorded on JEOL ECX400 and ECA500 spectrometers. Spectra were reported in parts per million from internal tetramethylsilane (δ 0.00 ppm) or residual protons of the deuterated solvent for ^{1}H NMR, from solvent carbon (e.g., δ 77.00 ppm for chloroform) for ^{13}C{^{1}H} NMR, and from external H_3PO_4 (δ 0.00 ppm) for ^{31}P{^{1}H} NMR. High-resolution mass spectra were measured on a JEOL JMS-T100LC APCI/ESI-TOF mass spectrometer. IR and UV−vis spectra were recorded on Applied Systems Inc. React-IR 1000 and JASCO V-570.

Preparation of Ru(η^5-$C_{60}Me_5$)Cl(dppe) (4). To a solution of Ru(η^5-$C_{60}Me_5$)Cl(CO)$_2$ (**3**; 50 mg, 0.051 mmol) in 1,2-dichlorobenzene (10.0 mL) was added 1,2-bis(diphenylphosphino)ethane (dppe) (101 mg, 0.25 mmol). The mixture was stirred and heated at 150 °C for 4 days, and the progress of the reaction was monitored by HPLC. After the solvent was evaporated under reduced pressure, purification by preparative HPLC afforded orange crystals of **4** (31 mg, 47% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.18 (m, 2H, $Ph_2PCH_2CH_2PPh_2$), 2.25 (s, 6H, $C_{60}Me_5$), 2.36 (s, 9H, $C_{60}Me_5$), 3.01−3.05 (m, 2H, $Ph_2PCH_2CH_2PPh_2$), 7.40−7.53 (m, 12H, P*Ph*$_2$), 7.81 (t, 4H, P*Ph*$_2$), 8.30 (t, 4H, P*Ph*$_2$); ^{13}C NMR (125 MHz, CS_2/C_6D_6) δ 30.92 (br, 2C, PCH_2CH_2P), 31.96 (s, $C_{60}Me_5$), 32.18 (s, $C_{60}Me_5$), 32.18 (s, $C_{60}Me_5$), 32.39 (s, $C_{60}Me_5$), 51.68 (br, $C_{60}Me_5$), 136.40 (s, P*Ph*$_2$), 137.65 (s, P*Ph*$_2$), 144.25 (br, C_{60}), 147.79 (br, C_{60}), 148.81 (br, C_{60}); ^{31}P NMR (200 MHz, $CDCl_3$) δ 63.44 (s, 2P, $Ph_2PCH_2CH_2PPh_2$); IR (powder, cm^{-1}) 2964 (m), 2923 (m), 2854 (m) (ν_{C-H}), 1459 (m), 1447 (m), 1434 (m), 1414 (m), 1090 (m), 1067 (m), 1027 (m) (ν_{P-C}); APCI-HRMS (−) calcd for $C_{91}H_{39}ClP_2Ru$ (M^-) 1330.1259, found 1330.1307.

Preparation of Ru(η^5-$C_{60}Me_5$)Cl((*R*)-prophos) (5). To a solution of **3** (50 mg, 0.051 mmol) in 1,2-dichlorobenzene (10.0 mL) was added [*R*-(+)-1,2-bis(diphenylphosphino)propane] ((*R*)-prophos) (104 mg, 0.25 mmol). The mixture was stirred and heated at 150 °C for 16 h, and the progress of the reaction was monitored by HPLC. After the solvent was evaporated under reduced pressure, purification by preparative HPLC afforded orange crystals of **5** (28 mg, 41% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.09 (dd, $^3J_{H-H}$ = 6.9 Hz, $^3J_{P-H}$ = 10.6 Hz, 3H, PCH*Me*), 1.44 (s, 3H, $C_{60}Me_5$), 1.61 (s, 3H, $C_{60}Me_5$), 1.87−1.95 (m, 1H, PC*H*$_2$), 2.06 (s, 3H, $C_{60}Me_5$), 2.48 (s, 3H, $C_{60}Me_5$), 2.57−2.73 (m, 1H, PC*H*Me), 2.86 (s, 3H, $C_{60}Me_5$), 3.54−3.57 (m, 1H, PC*H*$_2$), 7.33−7.96 (m, 14H, P*Ph*$_2$), 8.24 (t, $^3J_{H-H}$ = 8.0 Hz, 2H, P*Ph*$_2$), 8.39 (t, $^3J_{H-H}$ = 8.0 Hz, 2H, P*Ph*$_2$), 8.46 (t, $^3J_{H-H}$ = 8.6 Hz, 2H, P*Ph*$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.53 (dd, $^2J_{P-C}$ = 15.9 Hz, $^3J_{P-C}$ = 5.7 Hz, 1C, *C*H$_3$), 23.62 (s, 1C, $C_{60}Me_5$), 24.59 (s, 1C, $C_{60}Me_5$), 27.37 (s, 1C, $C_{60}Me_5$), 31.77 (s, 1C, $C_{60}Me_5$), 32.06 (s, 1C, $C_{60}Me_5$), 32.67 (dd, $^1J_{P-C}$ = 32.3 Hz, $^2J_{P-C}$ = 11.7 Hz, 1C, Ph_2PC), 37.92 (dd, $^1J_{P-C}$ = 27.2 Hz $^2J_{P-C}$ = 16 Hz 1C, Ph_2PC), 51.05 (s, 1C, $C_{60}(sp^3)$), 51.29 (s, 1C, $C_{60}(sp^3)$), 51.36 (s, 1C, $C_{60}(sp^3)$), 51.54 (s, 1C, $C_{60}(sp^3)$), 53.62 (s, 1C, $C_{60}(sp^3)$), 87.62 (s, 1C, C_{60}(Cp)), 92.51 (s, 1C, C_{60}(Cp)), 108.37 (s, 1C, C_{60}(Cp)), 110.02 (s, 1C, C_{60}(Cp)), 110.43 (s, 1C, C_{60}(Cp)), 126.82 (d, $^2J_{P-C}$ = 9.3 Hz, 2C, *o*-Ph), 127.04 (d, $^2J_{P-C}$ = 9.5 Hz, 2C, *o*-Ph), 127.73 (d, $^2J_{P-C}$ = 8.2 Hz, 2C, *o*-Ph), 127.81 (d, $^2J_{P-C}$ = 8.2 Hz, 2C, *o*-Ph), 129.62 (s, 1C, *p*-Ph), 129.91 (s, 1C, *p*-Ph), 130.53 (s, 1C, *p*-Ph), 131.37 (s, 1C, *i*-Ph), 131.68 (s, 1C, *i*-Ph), 131.75 (s, 1C, *p*-Ph), 133.45 (s, 1C, *i*-Ph), 133.82 (s, 1C, *i*-Ph), 134.12 (d, $^3J_{P-C}$ = 8.6 Hz, 2C, *m*-Ph), 134.88 (d, $^3J_{P-C}$ = 6.3 Hz, 2C, *m*-Ph), 137.58 (d, $^3J_{P-C}$ = 10.9 Hz, 2C, *m*-Ph), 138.83 (d, $^3J_{P-C}$ = 12.8 Hz, 2C, *m*-Ph), 143.06−143.89, 144.21, 147.20, 148.10−148.40, 151.44, 152.75, 152.91, 153.08, 153.46, 153.80, 154.03, 154.92 (50C, $C_{60}(sp^2)$); ^{31}P NMR (200 MHz, $CDCl_3$) δ 45.8 (d, $^2J_{P-P}$ = 32.3 Hz, 1P, Ru*P*Ph$_2$), 69.0 (d, $^2J_{P-P}$ = 32.3 Hz, 1P, Ru*P*Ph$_2$); IR (powder, cm^{-1}) 2923 (m), 2892 (m), 2865 (m) (ν_{C-H}), 1459 (m), 1447 (m), 1432 (m), 1090 (m), 1067 (m), 1027 (m) (ν_{P-C}); UV−vis (4.46 × 10^{-6} M in CH_2Cl_2; λ_{max}/nm (ϵ)) 276 (1.22 × 10^5), 348 (3.13 × 10^4), 392 (1.82 × 10^4); APCI-HRMS (−) calcd for $C_{92}H_{41}ClP_2Ru$ (M^-) 1344.1416, found 1344.1457.

Preparation of [Ru(η^5-$C_{60}Me_5$)((*R*)-prophos)(CH_3CN)]$^+$-[SbF_6]$^-$ (7). In the presence of $AgSbF_6$ (3.8 mg, 0.0111 mmol) acetonitrile (7.8 μL, 0.1486 mmol) was added to a solution of **5** (10 mg, 0.00743 mmol) in dichloromethane (2 mL), and the mixture was stirred at room temperature for 1 h. The mixture was diluted with dichloromethane and poured onto a silica gel column eluted with dichloromethane to obtain complex **7** (9.0 mg, 90% yield) as a brown solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.11 (m, 3H, CHC*H*$_3$), 1.19 (s, 3H, $C_{60}Me_5$), 1.91 (s, 3H, $C_{60}Me_5$), 1.92 (m, 1H, C*H*$_2$PPh$_2$), 2.08 (s, 3H, C*H*$_3$CN), 2.12 (s, 3H, $C_{60}Me_5$), 2.23 (s, 3H, $C_{60}Me_5$), 2.40 (s, 3H, $C_{60}Me_5$), 2.70 (m, 1H, C*H*$_2$PPh$_2$), 2.75−2.91 (m, 1H, C*H*CH$_3$), 7.38−7.87 (m, 14H, P*Ph*$_2$), 7.86 (t, $^3J_{H-H}$ = 8.30 Hz, 2H, P*Ph*$_2$), 8.14 (t, $^3J_{H-H}$ = 8.87 Hz, 2H, P*Ph*$_2$), 8.36 (t, $^3J_{H-H}$ = 9.18 Hz, 2H, P*Ph*$_2$); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 5.33 (s, 1C, *C*H$_3$CN), 15.10 (dd, $^2J_{P-C}$ = 16.69 Hz, $^3J_{P-C}$ = 4.76 Hz, PPh_2CHCH_3), 25.97 (s, 1C, $C_{60}Me_5$), 27.24 (s, 1C, $C_{60}Me_5$), 28.73 (s, 1C, $C_{60}Me_5$), 31.74 (s, 2C, $C_{60}Me_5$), 32.10 (dd, $^1J_{P-C}$ = 29.81, $^2J_{P-C}$ = 10.74 Hz, 1C, *C*H$_2$PPh$_2$ or PPh$_2$*C*HCH$_3$), 35.40 (dd, $^1J_{P-C}$ = 29.81, $^2J_{P-C}$ = 15.50 Hz, *C*H$_2$PPh$_2$ or PPh$_2$*C*HCH$_3$), 50.61 (s, 1C, $C_{60}(sp^3)$), 51.89 (s, 4C, $C_{60}(sp^3)$), 92.78 (s, 1C, $C_{60}(C_{Cp})$), 95.63 (s, 1C, $C_{60}(C_{Cp})$), 108.27 (s, 1C, $C_{60}(C_{Cp})$), 114.50 (s, 1C, $C_{60}(C_{Cp})$), 118.29 (s, 1C, $C_{60}(C_{Cp})$), 127.67−153.52 (C_{60} and Ph); ^{31}P NMR (200 MHz, $CDCl_3$) δ 44.16 (d, $^2J_{P-P}$ = 32.28 Hz, 1P), 71.43 (d, $^2J_{P-P}$ = 32.28 Hz, 1P); IR (powder, cm^{-1}) 2973 (m) (ν_{C-H}), 1958 (m) (ν_{C-N}), 1437 (m), 1096 (m) (ν_{P-C}); APCI-HRMS (+) calcd for $C_{94}H_{44}NP_2Ru$ [M − SbF_6^-]$^+$ 1350.1975, found 1350.1926.

Preparation of [Ru(η^5-$C_{60}Me_5$)((*R*)-prophos)(^{t}BuCN)]$^+$[SbF_6]$^-$ (8). This compound was prepared in a manner similar to that for **7**. Complex **8** was isolated in 95% yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.21 (s, 9H, t-*Bu*CN), 1.30 (dd, $^3J_{P-H}$ = 11.45 Hz, $^3J_{H-H}$ = 6.85 Hz, 3H, CHC*H*$_3$), 1.37 (s, 3H, $C_{60}Me_5$), 1.97 (m, 1H, PC*H*), 1.98 (s, 6H, $C_{60}Me_5$), 2.37 (s, 3H, $C_{60}Me_5$), 2.62 (m, 1H, PC*H*), 2.67 (s, 3H, $C_{60}Me_5$), 3.13 (m, 1H, PC*H*), 7.43 (m, 5H), 7.69 (m, 3H), 7.79−7.94 (m, 8H), 8.36 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.00 (dd, $^2J_{P-C}$ = 16.27 Hz, $^3J_{P-C}$ = 5.74 Hz, CH_3(prophos)), 26.41 (s, 1C, $C_{60}Me_5$), 27.17 (s, 3C, NCC*Me*$_3$), 27.60 (s, 1C, $C_{60}Me_5$), 27.98 (1C, $C_{60}Me_5$), 31.51 (2C, $C_{60}Me_5$), 32.70 (dd, $^1J_{P-C}$ = 29.68 Hz, $^2J_{P-C}$ = 10.54 Hz, CH(prophos)), 34.65 (dd, $^1J_{P-C}$ = 28.73 Hz, $^2J_{P-C}$ = 15.31 Hz, CH_2(prophos)), 50.21 (s, 1C, $C_{60}(sp^3)$), 51.16 (s, 1C, $C_{60}(sp^3)$), 51.52 (s, 3C, $C_{60}(sp^3)$), 92.88 (s, 1C, $C_{60}(C_{Cp})$), 95.33 (s, 1C, $C_{60}(C_{Cp})$), 110.03 (s, 1C, $C_{60}(C_{Cp})$), 113.05 (s, 1C, $C_{60}(C_{Cp})$), 116.99 (s, 1C, $C_{60}(C_{Cp})$), 127.29, 127.60, 128.01, 128.09, 128.66, 128.74, 129.53, 129.63, 129.70, 129.87, 130.19, 131.26, 131.91, 132.42, 132.61, 132.66, 133.25, 133.32, 133.53, 135.26, 135.35, 137.42, 137.52, 138.51, 138.84, 141.31, 142.50−143.90 (m), 147.15, 148.31, 151.12, 151.76, 153.13 (C_{60} and Ph); ^{31}P NMR (200 MHz, $CDCl_3$) δ 44.90 (d, $^2J_{P-P}$ = 38.30 Hz, 1P), 70.48 (d, $^2J_{P-P}$ = 38.30 Hz, 1P); IR (powder cm^{-1}) 2930 (m), 2868 (m) (ν_{C-H}), 2210 (m) (ν_{C-N}), 1440 (m), 1090 (m) (ν_{P-C}); ESI-HRMS (+) calcd for $C_{97}H_{50}NP_2Ru$ [M − SbF_6^-]$^+$ 1392.2462, found 1392.2472.

Preparation of [Ru(η^5-$C_{60}Me_5$)((*R*)-prophos)(methacrolein)]$^+$-[SbF_6]$^-$ (9). This compound was prepared in a manner similar to that for **7**. Complex **9** was isolated in 80% yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (m, 3H), 1.36 (dd, $^3J_{P-H}$ = 13.75 Hz, $^3J_{H-H}$

= 6.3 Hz, 3H), 2.00 (m, 15H, $C_{60}Me_5$), 2.40 (m, 1H), 2.67 (m, 1H), 2.80 (m, 1H), 4.30−5.07 (m, 2H), 7.50−8.43 (m, 20H, H_{Ar}), 9.58 (br, 1H); ^{31}P NMR (200 MHz, $CDCl_3$) δ 38.71 (d, $^2J_{P-P}$ = 48.46 Hz, 1P), 68.38 (d, $^2J_{P-P}$ = 53.82 Hz, 1P).

Preparation of [Ru(η^5-$C_{60}Me_5$)((*R*)-prophos)(acetone)]$^+$-[SbF_6]$^-$ (10). This compound was prepared in a manner similar to that for **7**. Complex **10** was isolated in 80% yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (dd, $^3J_{P-H}$ = 13.20 Hz, $^3J_{H-H}$ = 6.30 Hz, 3H), 1.95 (m, 15H, $C_{60}Me_5$), 2.02 (s, 6H, CH_3COCH_3), 2.38 (m, 1H, CH_2PPh$_2$), 2.66 (m, 1H, CH_2PPh$_2$), 2.74−2.85 (m, 1H, CHCH$_3$), 7.48−7.86 (m, 16H, PPh$_2$), 8.03 (m, 2H, PPh$_2$), 8.38 (m, 2H, PPh$_2$); ^{31}P NMR (200 MHz, $CDCl_3$) δ 45.90 (d, $^2J_{P-P}$ = 48.44 Hz, 1P), 72.35 (d, $^2J_{P-P}$ = 53.84 Hz, 1P).

Preparation of [Ru(η^5-$C_{60}Me_5$)((*R*)-prophos)(CO)]$^+$[SbF_6]$^-$ (11). This compound was prepared in a manner similar to that for **7** under 1 atm of CO. Complex **11** was isolated in 81% yield: ^{1}H NMR (500 MHz, $CDCl_3$, −40 °C) δ 1.13 (s, 3H, $C_{60}Me_5$), 1.22 (dd, $^3J_{P-H}$ = 12.80 Hz, $^3J_{H-H}$ = 6.00 Hz, 3H, CHCH_3), 1.86(s, 6H, $C_{60}Me_5$), 2.06 (m, 1H, CH_2PPh$_2$), 2.16 (s, 3H, $C_{60}Me_5$), 2.81 (s, 3H, $C_{60}Me_5$), 2.81 (m, 1H, CH_2PPh$_2$), 2.96−3.07 (m, 1H, CHCH$_3$), 4.76−8.30 (20H, Ph); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ 14.90 (dd, $^2J_{P-C}$ = 17.88 Hz, $^3J_{P-C}$ = 4.76 Hz, PPh$_2$CH*C*H$_3$), 28.48 (s, 2C, $C_{60}Me_5$), 30.94 (s, 3C, $C_{60}Me_5$), 35.70 (dd, $^1J_{P-C}$ = 32.80 Hz, $^2J_{P-C}$ = 12.52 Hz, *C*H$_2$PPh$_2$ or PPh$_2$*C*HCH$_3$), 37.15 (dd, $^1J_{P-C}$ = 34.50 Hz, $^2J_{P-C}$ = 8.35 Hz, *C*H$_2$PPh$_2$ or PPh$_2$*C*HCH$_3$), 51.58 (s, 5C, $C_{60}(sp^3)$), 123.78−150.62 (C_{60} and Ph), 203.74 (dd, $^2J_{P-C}$ = 20.2 Hz, $^2J_{P-C}$ = 17.9 Hz, *C*O); ^{31}P NMR (200 MHz, $CDCl_3$) δ 44.26 (d, $^2J_{P-P}$ = 26.92 Hz, 1P), 72.35 (d, $^2J_{P-P}$ = 21.54 Hz, 1P); IR (powder, cm^{-1}) 2930 (ν_{C-H}), 2864 (m), 2162 (m), 1972 (s) (ν_{C-O}), 1440 (m), 1090 (m) (ν_{P-C}); APCI-HRMS (+) calcd for $C_{93}H_{41}OP_2Ru$ [M − SbF_6^-]$^+$ 1337.1676, found 1337.1689.

Preparation of [Ru(η^5-$C_{60}Me_5$)((*R*)-prophos)(2,6-$Me_2C_6H_3$-NC)]$^+$[SbF_6]$^-$ (12). This compound was prepared in a manner similar to that for **7**. Complex **12** was isolated in 91% yield as a mixture of two diastereomers: ^{1}H NMR (500 MHz, $CDCl_3$, major isomer) δ 1.24 (dd, $^3J_{P-H}$ = 12.9 Hz, $^3J_{H-H}$ = 6.3 Hz, 3H, CHCH_3), 1.45 (s, 3H, $C_{60}Me_5$), 1.58 (s, 3H, $C_{60}Me_5$), 1.96 (s, 3H, $C_{60}Me_5$), 2.22 (m, 1H, CH_2PPh$_2$), 2.45 (s, 3H, $C_{60}Me_5$), 2.49 (s, 6H, Ph-(*Me*)$_2$NC), 2.86 (s, 3H, $C_{60}Me_5$), 3.08 (m, 1H, CH_2PPh$_2$), 3.19 (m, 1H, CHCH$_3$), 7.15−7.96 (23H, Ph); ^{31}P NMR (200 MHz, $CDCl_3$) δ 53.12 (d, $^2J_{P-P}$ = 21.54 Hz, 1P, major), 56.53 (d, $^2J_{P-P}$ = 26.92 Hz, 1P, minor), 64.80 (d, $^2J_{P-P}$ = 21.54 Hz, 1P, minor), 74.30 (d, $^2J_{P-P}$ = 26.92 Hz, 1P, major); IR (powder, cm^{-1}) 3290 (m), 3250 (m), 2972 (m) (ν_{C-H}), 2362 (m), 2061 (s) (ν_{N-C}), 1741 (s), 1430 (s), 1370 (m), 1204 (s), 745 (s); APCI-HRMS (+) calcd for $C_{101}H_{50}NP_2Ru$ [M − SbF_6^-]$^+$ 1440.2445, found 1440.2426.

Preparation of [Ru(η^5-$C_{60}Me_5$)((*R*)-prophos)(PhCH$_2$NC)]$^+$-[SbF_6]$^-$ (13). This compound was prepared in a manner similar to that for **7**. Complex **13** was isolated in 68% yield as a mixture of two diastereomers. ^{1}H NMR (500 MHz, $CDCl_3$, major isomer) δ 0.93 (dd, $^3J_{P-H}$ = 12.3 Hz, $^3J_{H-H}$ = 6.9 Hz, 3H, CHCH_3), 1.93−2.34 (m, 15H, $C_{60}Me_5$), 2.78−2.93 (m, 3H, CH_2CH), 4.74 (AB, δ_A = 4.70, δ_B = 4.78, J_{AB} = 14.85 Hz, PhCH_2NC), 6.82 (d, $^3J_{H-H}$ = 6.85 Hz, 2H), 7.20−8.37 (m, 23H); ^{31}P NMR (200 MHz, $CDCl_3$) δ 47.50 (d, $^2J_{P-P}$ = 21.52 Hz, 1P, major), 56.81 (d, $^2J_{P-P}$ = 1.52 Hz, 1P, minor), 65.26 (d, $^2J_{P-P}$ = 21.52 Hz, 1P, minor), 73.78 (d, $^2J_{P-P}$ = 26.92 Hz, 1P, major); IR (powder, cm^{-1}) 3255 (br), 2126 (s) (ν_{N-C}), 1437 (s), 1096 (s) (ν_{P-C}); APCI-HRMS (+) calcd for $C_{100}H_{48}NP_2Ru$ [M − SbF_6^-]$^+$ 1426.2306, found 1426.2264.

Preparation of Ru(η^5-$C_{60}Me_5$)Br((*R*)-prophos) (14). To a solution of 1 mL of CH_2Cl_2 containing compound **7** (2.3 mg, 0.00170 mmol) was added 36 mg of magnesium bromide diethyl etherate complex in 1 mL of THF. After stirring for 5 h at 40 °C, the mixture was concentrated and subjected to flash column chromatography to afford 2.0 mg of the desired product as a yellow solid, **14** (85% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.09 (dd, $^3J_{H-H}$ = 6.9 Hz, $^3J_{P-H}$ = 10.3 Hz, 3H, CHCH_3), 1.58 (s, 3H, $C_{60}Me_5$), 1.64 (s, 3H, $C_{60}Me_5$), 1.87 (m, 1H, CH_2PPh$_2$), 2.07 (s, 3H, $C_{60}Me_5$), 2.50 (s, 3H, $C_{60}Me_5$), 2.60−2.80 (m, 1H, CH_2PPh$_2$), 2.97 (s, 3H, $C_{60}Me_5$), 3.83 (m, 1H, CHCH$_3$), 7.17−7.73 (14H, Ph), 8.28 (t, $^3J_{H-H}$ = 7.70 Hz, 2H, Ph), 8.39 (t, $^3J_{H-H}$ = 8.50 Hz, 2H, Ph), 8.43 (t, $^3J_{H-H}$ = 8.50 Hz, 2H, Ph); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 16.00 (dd, $^2J_{P-C}$ = 15.50 Hz, $^3J_{P-C}$ = 5.95 Hz, CH_3(prophos)), 24.75 (s, 1C, $C_{60}Me_5$), 27.31 (s, 1C, $C_{60}Me_5$), 27.41 (s, 1C, $C_{60}Me_5$), 31.80 (s, 1C, $C_{60}Me_5$), 32.28 (s, 1C, $C_{60}Me_5$), 34.40 (dd, $^1J_{P-C}$ = 33.38 Hz, $^2J_{P-C}$ = 11.92 Hz, CH(prophos)), 37.48 (dd, $^1J_{P-C}$ = 26.23 Hz, $^2J_{P-C}$ = 16.70 Hz, CH_2(prophos)), 50.87 (s, 1C, $C_{60}(sp^3)$), 51.29 (s, 1C, $C_{60}(sp^3)$), 51.34 (s, 1C, $C_{60}(sp^3)$), 51.71 (s, 1C, $C_{60}(sp^3)$), 53.90 (s, 1C, $C_{60}(sp^3)$), 88.58 (s, 1C, C_{60}-(C_{Cp})), 92.62 (s, 1C, $C_{60}(C_{Cp})$), 107.83 (s, 1C, $C_{60}(C_{Cp})$), 109.79 (s, 1C, $C_{60}(C_{Cp})$), 110.52 (s, 1C, $C_{60}(C_{Cp})$), 126.77 (d, $^2J_{P-C}$ = 9.53 Hz, 2C, *o*-Ph), 126.91 (d, $^2J_{P-C}$ = 9.53 Hz, 2C, *o*-Ph), 127.50 (d, $^2J_{P-C}$ = 8.34 Hz, 2C, *o*-Ph), 127.69 (d, $^2J_{P-C}$ = 8.35 Hz, 2C, *o*-Ph), 129.56 (s, 1C, *p*-Ph), 129.92 (s, 1C, *p*-Ph), 130.44 (s, 1C, *p*-Ph), 131.64 (s, 1C, *p*-Ph), 133.68 (d, $^3J_{P-C}$ = 5.96 Hz, 1C, *i*-Ph), 134.00 (d, $^3J_{P-C}$ = 4.76 Hz, 1C, *i*-Ph), 134.13 (d, $^3J_{P-C}$ = 8.35 Hz, 2C, *m*-Ph), 134.68 (d, $^1J_{P-C}$ = 2.39 Hz, 1C, *i*-Ph), 135.00 (d, $^1J_{P-C}$ = 2.38 Hz, 1C, *i*-Ph), 135.10 (d, $^2J_{P-C}$ = 5.96 Hz, 2C, *m*-Ph), 137.76 (d, $^3J_{P-C}$ = 10.76 Hz, 2C, *m*-Ph), 138.65 (d, $^3J_{P-C}$ = 11.92 Hz, 2C, *m*-Ph), 142.87−144.24, 147.13−147.33, 148.03−148.40 (C_{60}), 151.37, 152.54, 152.67, 152.79, 152.89, 153.40, 153.55, 153.79, 154.83 (s, $C_{60}(C_\beta)$); ^{31}P NMR (200 MHz, $CDCl_3$) δ 45.99 (d, $^2J_{P-P}$ = 30.64 Hz, 1P), 67.89 (d, $^2J_{P-P}$ = 27.58 Hz, 1P); IR (powder, cm^{-1}) 2923 (m, ν_{C-H}), 1432 (m), 1260 (s), 1054 (m) (ν_{P-C}); APCI-HRMS (−) calcd for $C_{92}H_{41}BrP_2Ru$ [M]$^-$ 1390.0921, found 1390.0962.

Table 1. Crystal Data and Data Collection Parameters for 4, 5 and 14

	4	5	14
formula	$C_{91}H_{39}ClP_2Ru$	$C_{92}H_{41}ClP_2Ru$	$C_{92}H_{41}BrP_2Ru$
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1$ (No. 4)	$P2_1$ (No. 4)
R, R_w ($I > 2\sigma(I)$)	0.0714, 0.1865	0.0774, 0.2104	0.057, 0.1461
R_1, wR_2 (all data)	0.0808, 0.1979	0.0846, 0.2219	0.062, 0.1517
GOF on F^2	1.061	1.049	1.039
a, Å	12.919(9)	10.615(5)	10.5860(3)
b, Å	23.937(18)	29.500(5)	26.7560(13)
c, Å	17.951(9)	19.502(5)	21.8930(9)
α, deg	90	90	90
β, deg	99.741(4)	95.533(5)	94.366(3)
γ, deg	90	90	90
V, Å^3	5471.2(6)	6078(3)	6183.0(4)
Z	4	2	2
T, K	153(2)	153(2)	153(2)
cryst size, mm	0.85, 0.42, 0.2	0.80, 0.30, 0.20	0.45, 0.40, 0.20
D_{calcd}, g/cm^{-3}	1.615	1.469	1.591
$2\theta_{min}$, $2\theta_{max}$, deg	2.29, 25.56	2.05, 25.62	2.21, 25.72
no. reflns (total)	42 910	39 175	44 838
no. reflns (unique)	10 127	9781	11 858
no. reflns ($I > 2\sigma(I)$)	8575	8719	10 890
no. params	857	1705	1856
Δ, e Å^{-3}	1.01, −0.941	1.377, −0.84	1.133, −1.015

Preparation of [Ru(η^5-$C_{60}Me_5$)((*R*)-prophos)(β-Ph-vinylidene]$^+$-[SbF_6]$^-$ (15). A solution of ruthenium cation complex **7** (20 mg) and phenylacetylene (0.5 mL) in chloroform (4 mL) was heated at 60 °C for 24 h. The solvent was then removed under vacuum. The residue was dissolved in 2 mL of dichloromethane, and 20 mL of *n*-hexane was added to precipitate the product **15** (19 mg, 90%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.38 (m, 3H, CHCH_3), 1.39 (s, 3H, $C_{60}Me_5$), 1.71 (s, 3H, $C_{60}Me_5$), 1.93 (s, 3H, $C_{60}Me_5$), 2.33 (s, 3H, $C_{60}Me_5$), 2.43 (m, 1H, CH_2PPh$_2$), 2.91(s, 3H, $C_{60}Me_5$), 3.36−3.46 (m, 1H, CH_2PPh$_2$), 3.64 (m, 1H, CHCH$_3$), 5.19 (s, 1H, PhCH), 6.50 (d, J_{H-H} = 6.90 Hz, Ph), 7.13 (m, 3H, Ph), 7.42−7.99 (m,

16H), 8.15 (t, J_{H-H} = 8.00 Hz, 2H), 8.27 (t, J_{H-H} = 8.00 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.87 (d, $^2J_{P-C}$ = 16.78 Hz, prophos), 27.15 (s, 1C, $C_{60}Me_5$), 28.20 (s, 1C, $C_{60}Me_5$), 29.00 (1C, $C_{60}Me_5$), 31.55 (s, 2C, $C_{60}Me_5$), 31.63 (s, 1C, $C_{60}Me_5$), 35.40 (d, $^1J_{P-C}$ = 30.20 Hz, prophos), 36.20 (d, $^1J_{P-C}$ = 33.55 Hz, prophos), 51.04 (s, 1C, $C_{60}(sp^3)$), 51.36 (s, 1C, $C_{60}(sp^3)$), 51.77 (s, 2C, $C_{60}(sp^3)$), 51.95 (s, 1C, $C_{60}(sp^3)$), 108.38 (s, 1C, $C_{60}(C_{Cp})$), 116.48 (s, 2C, $C_{60}(C_{Cp})$), 119.73 (s, 1C, $C_{60}(C_{Cp})$), 120.99 (s, 1C, *C*HPh), 126.23 (s, 1C, $C_{60}(C_{Cp})$), 124.88−151.73 (C_{60}, Ph), 343.92 (dd, $^2J_{P-C}$ = 23.48, $^2J_{P-C}$ = 13.42 Hz, 1C, Ru*C*); ^{31}P NMR (200 MHz, $CDCl_3$) δ 49.57 (d, $^2J_{P-P}$ = 24.52 Hz, 1P), 72.78 (d, $^2J_{P-P}$ = 24.52 Hz, 1P); IR (powder, cm^{-1}) 3256 (br), 2929 (m) (ν_{C-H}), 1652 (m) ($\nu_{C=C}$), 1436 (s), 1094 (m) (ν_{P-C}); ESI-HRMS (+) calcd for $C_{101}H_{48}P_2Ru$ [M + H − SbF_6^-]$^+$ 1412.2275, found 1412.2269.

Catalytic Diels−Alder Reaction of Methacrolein and Cyclopentadiene.[20] To a solution of 0.01 mmol of **9** and 2,6-di-*tert*-butylpyridine in 1 mL of dichloromethane were added 0.02 mL (0.2 mmol) of methacrolein and 0.033 mL (0.4 mmol) of cyclopentadiene. After stirring at room temperature for 48 h, the reaction was quenched by addition of 10 mL of *n*-hexane. The resulting precipitate was removed by filtrating through a pad of silica gel. ^{1}H NMR analysis of the concentrated residue showed an *exo*/*endo* ratio of the adduct of 23:1 (δ 9.69 for CHO of the *exo* isomer, δ 9.40 for that of the *endo* isomer). Flash column chromatography afforded 30 mg of the adduct in 80% yield. The ee value was determined by ^{1}H NMR analysis after conversion to the acetal of (2*R*,4*R*)-2,4-pentanediol (δ 4.70 for CHO_2 of the major *exo* isomer, δ 4.68 for that of the minor *exo* isomer).

X-ray Crystallographic Analysis. Single crystals of **4**, **5**, and **14** suitable for X-ray diffraction studies were grown and subjected to data collection. The data sets were collected on a MacScience DIP2030 imaging plate diffractometer using Mo Kα (graphite monochromated, λ = 0.71069 Å) radiation. Crystal data and data statistics are summarized in Table 1. The structures of **4**, **5**, and **14** were solved by the direct method (SIR97).[23] The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares method, using SHELXL-97.[24] Hydrogen atoms were placed at calculated positions and refined with the riding mode on their corresponding carbon atoms. In the subsequent refinement, the function $\sum w(F_o^2 - F_c^2)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^4)]^{1/2}$.

Supporting Information Available: Crystallographic data of **4**, **5**, and **14** (CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

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