

# Articles

## Ruthenium(II) Complexes of Pentamethylated [60]Fullerene. Alkyl, Alkynyl, Chloro, Isocyanide, and Phosphine Complexes

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A ruthenium chloro dicarbonyl complex bearing a pentamethylated [60]fullerene ligand,  $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)\text{Cl}(\text{CO})_2$  (**1**), was prepared by the reaction of  $[\text{RuCl}_2(\text{CO})_3]_2$  with  $\text{C}_{60}\text{Me}_5\text{K}$  in THF. A variety of ligand exchange reactions involving the carbonyl and chloro ligands took place on the ruthenium metal attached directly to the exterior of the fullerene framework. Treatment of **1** with a phosphine ligand afforded phosphine complexes,  $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)\text{Cl}(\text{PET}_3)(\text{CO})$  (**2**) and  $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)\text{Cl}(\text{PPh}_3)(\text{CO})$  (**3**). Isocyanide complexes,  $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)\text{Cl}(\text{t-BuNC})(\text{CO})$  (**4**),  $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)\text{Cl}(\text{MeNC})(\text{CO})$  (**5**), and  $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)\text{Cl}(\text{XylNC})(\text{CO})$  (**6**; Xyl = 2,6-dimethylphenyl), were also prepared by reaction with an appropriate isocyanide ligand, while the use of a large excess of the same isocyanides gave bis(isocyanide) complexes,  $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)\text{Cl}(\text{t-BuNC})_2$  (**7**) and  $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)\text{Cl}(\text{XylNC})_2$  (**8**). Metathetic replacement of the halogen atom on the transition-metal fullerene complexes was achieved: methyl and (trimethylsilyl)methyl Grignard reagents reacted with **1** to give a methyl complex,  $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)\text{Me}(\text{CO})_2$  (**9**), and a (trimethylsilyl)methyl complex,  $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)(\text{CH}_2\text{SiMe}_3)(\text{CO})_2$  (**10**), respectively. Alkynylation reactions gave various alkynyl complexes,  $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)(\text{C}\equiv\text{C}^n\text{Bu})(\text{CO})_2$  (**11**),  $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)(\text{C}\equiv\text{C}^n\text{Bu})(\text{CO})_2$  (**12**),  $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)(\text{C}\equiv\text{C}^n\text{SiMe}_3)(\text{CO})_2$  (**13**),  $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)(\text{C}\equiv\text{C}^n\text{SiMe}_3)(\text{CO})_2$  (**14**), and  $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)(\text{C}\equiv\text{CH})(\text{CO})_2$  (**15**). X-ray single-crystal structure analyses and electrochemical studies of a series of new ruthenium fullerene complexes were performed.

### Introduction

Metal fullerene complexes and related compounds have attracted much interest, owing to their potential applications to catalysis, to electrochemical<sup>1</sup> and photochemical<sup>2</sup> reactions, to materials of nonlinear optical<sup>3</sup> and electron transfer<sup>4</sup> properties, and to the construction of nanoscale molecular and supramolecular architectures.<sup>5</sup> These compounds may be classified into three classes, alkali-metal fulleride salts,<sup>1,6</sup> endohedral metal fullerene compounds,<sup>7</sup> and exohedral transition-metal fullerene complexes.<sup>8</sup> While alkali-metal fulleride salts have surprised scientists for quite some time due to

their high-temperature superconductivity,<sup>1</sup> the current attention of chemists is focused more on the transition-metal fullerene complexes. The most readily available metal complexes are  $\eta^2$ -[60]fullerene complexes, in which an electron-rich transition metal coordinates to a fullerene core that serves as an electron-deficient olefinic  $\eta^2$  ligand.<sup>8–10</sup> A major problem of such transition-metal fullerene complexes has thus far been the inflexibility of molecular design, owing to their instability toward various transformations that are mandatory for derivatization. For instance, while some polymetallic  $\eta^2$ : $\eta^2$ - and  $\eta^2$ : $\eta^2$ : $\eta^2$ -fullerene complexes are quite stable,<sup>11</sup> the mononuclear metal  $\eta^2$ -fullerene complexes easily release the fullerene ligand upon addition of a donor/ $\pi$ -acidic ligand such as a triorganophosphine.<sup>8,12</sup>

We recently reported the syntheses of transition-metal  $\eta^5$  complexes,  $\text{Rh}(\eta^5\text{-C}_{60}\text{Me}_5)(\text{CO})_2$ <sup>13</sup> and  $\text{Fe}(\eta^5\text{-C}_{60}\text{Me}_5)\text{Cp}$ ,<sup>14</sup> which bear an  $\eta^5$ -pentamethylated [60]-fullerene ligand,  $\eta^5\text{-C}_{60}\text{Me}_5$  (to be abbreviated as MeFCp).<sup>15</sup> These  $\eta^5$ -cyclopentadienide complexes were

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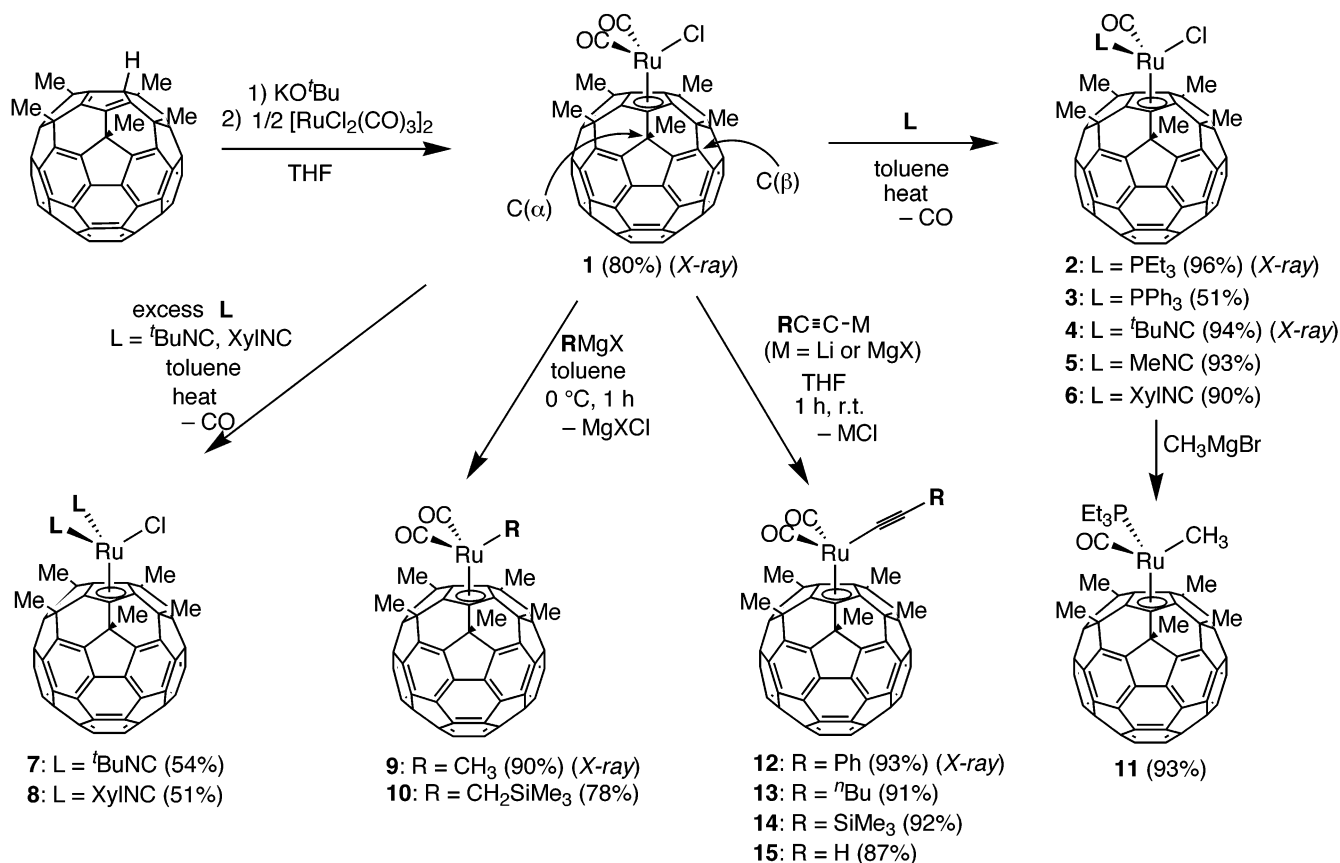
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Scheme 1



found to be stable compounds. In these complexes, there is electronic communication between the metal and the bottom 50- $\pi$ -electron system through the cyclopentadienide moiety.<sup>16</sup> We therefore considered it necessary as the second stage of our studies to examine whether one can perform synthetically useful transformations on a transition-metal fullerene  $\eta^5$ -complex. To this end, we focused on Ru(II)-MeFCp complexes bearing a metal-halogen bond and on their transformations. We report, in this article, the synthesis and the characterization of a ruthenium chloro complex bearing the FCp ligand,

Ru( $\eta^5$ -C<sub>60</sub>Me<sub>5</sub>)Cl(CO)<sub>2</sub> (**1**), as well as substitution reactions of the carbonyl and the chloro ligands on the ruthenium center with phosphine, isocyanide, alkyl, and alkynyl ligands. The alkylation and alkynylation reactions of a halide atom on transition metal fullerene complexes. The present results also provide the first example of a successful ligand exchange reaction of the carbonyl ligand on the metal center of mononuclear fullerene complexes.<sup>17</sup> We anticipate that the new half-sandwich Ru-MeFCp complexes will expand the platform for the organometallic extension of fullerene chemistry and that for catalysis and materials science in general.<sup>18</sup>

## Results and Discussion

**Synthesis and Characterization of Chloro Dicarbonyl Complexes of Ruthenium.** The reaction of [RuCl<sub>2</sub>(CO)<sub>3</sub>]<sub>2</sub> with a potassium salt of the MeFCp ligand in THF led to the formation of a half-sandwich complex of ruthenium, Ru( $\eta^5$ -C<sub>60</sub>Me<sub>5</sub>)Cl(CO)<sub>2</sub> (**1**), in 80% yield on a gram scale (Scheme 1). Other ruthenium complexes were examined as the starting material without success: e.g., RuCl<sub>3</sub>·*n*H<sub>2</sub>O, Ru<sub>3</sub>(CO)<sub>12</sub>, [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub>, [RuCl<sub>2</sub>(cod)]<sub>n</sub> (cod = 1,5-cyclooctadiene), RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, RuCl<sub>2</sub>(MeCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, and RuCl<sub>2</sub>(nbd)(PPh<sub>3</sub>)<sub>2</sub> (nbd = norbornadiene). For the successful complexation of **1**, therefore, we must avoid the presence

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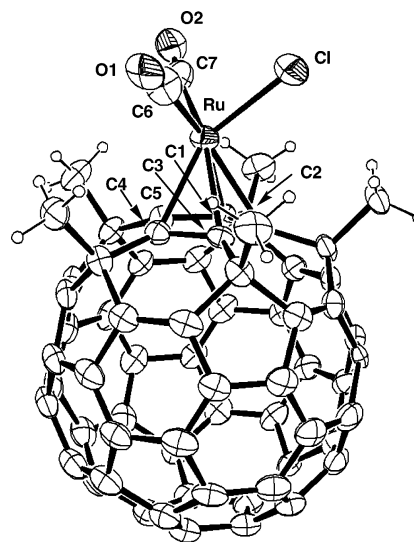
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of a strongly coordinating ligand such as phosphine and arene ligands. Complex **1**, which is reasonably soluble in toluene, was easily separated from byproducts, the salt KCl and a small amount of oxidation products derived from the MeFCp ligand, with the aid of a short silica gel column (toluene eluent). Orange crystals of **1** are stable in air and also in solution (hydrocarbon and halogenated solvents).

Identification of **1** was achieved first by spectroscopic and combustion analyses. The  $^1\text{H}$  NMR spectrum of **1** displayed a singlet signal at  $\delta$  2.18 due to five magnetically equivalent methyl groups, suggesting that the  $\text{C}_{60}\text{-Me}_5$  ligand is coordinated to the ruthenium metal in an  $\eta^5$  fashion. The  $^{13}\text{C}$  NMR spectrum displayed only a small number of signals due to the  $\text{C}_{5v}$ -symmetric fullerene skeleton: the cyclopentadienyl moiety ( $\delta$  111.69), the  $\text{sp}^3$  fullerene carbon atom ( $\text{C}(\alpha)$ ;  $\delta$  51.19), the  $\text{sp}^2$  carbon atom next to  $\text{C}(\alpha)$  ( $\text{C}(\beta)$ ;  $\delta$  152.28), and five other types of fullerene  $\text{sp}^2$  carbon atoms ( $\delta$  143.83, 144.17, 147.42, 148.60, and 148.98), together with a methyl group signal ( $\delta$  30.82) and a carbonyl signal on the metal ( $\delta$  196.93). The asymmetric and symmetric stretching vibrations of the carbonyl groups,  $\nu(\text{CO})$ , in the IR spectrum of **1** were observed at 2052 and 2006  $\text{cm}^{-1}$ . These wavenumbers are similar to those found for a ruthenium  $\eta^5\text{-Cp}$  chloro carbonyl complex,  $\text{RuCpCl}(\text{CO})_2$  (2059 and 2008  $\text{cm}^{-1}$ ),<sup>19</sup> and are larger than those of the  $\text{Cp}^*$  (=pentamethylcyclopentadienyl) analogue  $\text{RuCp}^*\text{Cl}(\text{CO})_2$  (2030 and 1988  $\text{cm}^{-1}$ ).<sup>20</sup> The fact that the CO stretching frequencies of **1** are higher than those of the  $\text{Cp}^*$  analogue may suggest that the MeFCp ligand is a more electron deficient ligand. The UV/visible spectrum ( $\lambda$  370 (sh), 395 nm) is similar to those of [60]-fullerene and related organic derivatives.<sup>15a,21</sup>

To conclusively determine the structure of the half-sandwich complex **1**, a single-crystal X-ray diffraction study was performed. Recrystallization of **1** from a toluene/ethanol mixture gave single crystals composed of a 1:1 mixture of **1** and toluene. Figure 1 shows the molecular structure of **1**, and selected metrical parameters are summarized in Table 1. A feature of interest in the structure of **1** is the "fold-back angle" of the fullerene carbon atoms ( $\text{C}(\alpha)$ ) out of the Cp mean plane. This angle (average 17.5°) is much larger than that in a cyclopentadienyl ruthenium complex such as  $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{Cl})\text{Cl}(\text{CO})_2$  (average <4.8°).<sup>22</sup> Nonetheless, an averaged interatomic distance between the ruthenium atom and the  $\eta^5\text{-Cp}$  carbon atoms (average 2.27 Å) in **1** is comparable to that found for  $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{Cl})\text{Cl}(\text{CO})_2$  (average 2.23 Å) and other related complexes (ca. 2.2–2.3 Å).<sup>22,23</sup> The sum of the three angles around  $\text{C}(\alpha)$



**Figure 1.** Molecular structure of **1** with 30% probability level ellipsoids. The toluene molecule found in the unit cell is omitted for clarity.

**Table 1.** Selected Bond Distances and Angles for **1**

Bond Distances (Å)			
Ru–C1	2.285(9)	Ru–Cl	2.387(9)
Ru–C2	2.304(10)	Ru–C6	1.97(2)
Ru–C3	2.247(9)	Ru–C7	1.92(4)
Ru–C4	2.246(10)	O1–C6	0.955(19)
Ru–C5	2.284(10)	O2–C7	0.93(4)
Ru–C(Cp) (av)	2.273		
Ru–(centroid of Cp)	1.919		
C(Cp)–C(Cp) (av)	1.433		
C(Cp)–C( $\alpha$ ) (av)	1.502		
C( $\alpha$ )–C( $\beta$ ) (av)	1.542		
C( $\beta$ )–C( $\beta$ ) (av)	1.366		
Bond Angles (deg)			
Cl–Ru–C6	84.6(6)	C6–Ru–C7	86.3(13)
Cl–Ru–C7	83.7(14)		
hold-back angle	17.47		
sum of three angles around C(Cp) (av) <sup>a</sup>	356.22		
sum of three angles around C( $\alpha$ ) (av) <sup>a</sup>	312.64		
sum of three angles around C( $\beta$ ) (av)	353.69		

<sup>a</sup> Within the fullerene core.

(included in the fullerene core, excluding those related to the methyl group) (average 312.6°) is smaller than the 316° value for a usual  $\text{sp}^3$  carbon atom and the 324° value of [60]fullerene, indicating that the  $\text{C}(\alpha)$  atoms protrude out of the mean sphere of the fullerene core. Intercarbon distances in the Cp moiety ( $\text{C}(\text{Cp})\text{--C}(\text{Cp})$ ) are normal for a Cp ligand (average 1.43 Å; 1.40–1.45 Å for  $\text{RuCp}_2$ )<sup>24</sup> and are shorter than those of the corresponding 5:6 ring junction found in [60]fullerene (1.467 Å).<sup>25</sup>

**Ligand Exchange Reaction of 1.** The carbonyl ligands in **1** can be replaced with phosphine and isocyanide ligands. Treatment of **1** with a slight excess of  $\text{PEt}_3$  in toluene at 70 °C resulted in quantitative formation of the desired phosphine complex,  $\text{Ru}(\eta^5\text{-C}_{60}\text{-Me}_5)\text{Cl}(\text{PEt}_3)(\text{CO})$  (**2**) (Scheme 1). This finding stands

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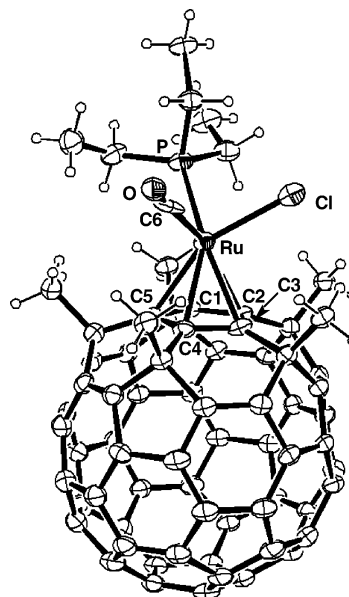


in sharp contrast to the reported observation that the  $C_{60}$  ligand on an  $\eta^2$  complex,  $Ru(C_{60})(CO)_4$ , is lost upon addition of a phosphine ligand.<sup>12</sup> In the MeFCp complex, a basic alkylphosphine ligand is expected to stabilize coordination of the MeFCp ligand to the ruthenium center, because the latter may act as an acceptor of electron donation by the phosphine ligand. Complex **2** was air- and moisture-stable in toluene at ambient and boiling temperatures. When the arylphosphine  $PPh_3$  was allowed to react with **1**, the triphenylphosphine complex  $Ru(\eta^5-C_{60}Me_5)Cl(PPh_3)(CO)$  (**3**) was obtained only in moderate (51%) yield, even in the presence of 10 equiv of  $PPh_3$  at reflux temperature.<sup>26</sup> This unfavorable exchange is consistent with the relatively low basicity and steric bulk of the triarylphosphine ligand. Complexes **2** and **3** were found to be inert to further ligand exchange with a phosphine ligand, even at reflux temperature. The  $^1H$  NMR spectra of **2** and **3** showed singlet signals at  $\delta$  2.47 and 2.22, respectively, due to the  $C_{5v}$  symmetry of the MeFCp ligand. The  $^{31}P\{^1H\}$  NMR spectra exhibited a singlet signal due to the phosphine ligands at  $\delta$  32.28 and 37.23 for **2** and **3**, respectively. The presence of a carbonyl group in **2** and **3** was confirmed by the  $^{13}C$  NMR spectra ( $\delta$  204.84 for **2** and  $\delta$  201.93 for **3**), the signal possessing a coupling constant  $J_{P-C}$  of 25 Hz for **2** and 24 Hz for **3**, and also by the IR spectra ( $\nu(CO)$  1937  $cm^{-1}$  for **2** and  $\nu(CO)$  1950  $cm^{-1}$  for **3**).

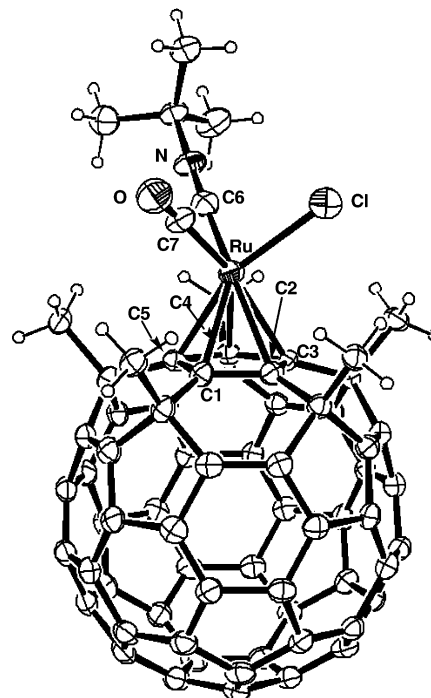
A similar exchange reaction with isocyanides gave the corresponding ruthenium isocyanide complexes  $Ru(\eta^5-C_{60}Me_5)Cl(BuNC)(CO)$  (**4**),  $Ru(\eta^5-C_{60}Me_5)Cl(MeNC)(CO)$  (**5**), and  $Ru(\eta^5-C_{60}Me_5)Cl(XylNC)(CO)$  (**6**; Xyl = 2,6-dimethylphenyl). Isocyanide ligands are expected to form stable complexes, owing to their large  $\sigma$ -donor properties<sup>27</sup> and their small steric bulk. In fact, complexes **4** and **5** formed much more smoothly than the phosphine complexes. Heating **1** in toluene with 1.5 equiv of *tert*-butyl and methyl isocyanide ligands gave orange microcrystals of **4** and **5** in 94% and 93% yields, respectively. Xylyl isocyanide was less reactive, and hence, the maximum yield (90%) was obtained by the use of 4.5 equiv of XylNC. These isocyanide carbonyl mixed ligand complexes were identified by the  $^1H$  and  $^{13}C$  NMR spectra as well as IR spectra. In particular, the IR spectra of **4–6** showed strong absorptions due to both the CO groups ( $\nu$  1976, 1978, and 1978  $cm^{-1}$ , respectively) and the NC groups ( $\nu$  2159, 2178, and 2140  $cm^{-1}$ , respectively). In contrast to the phosphine ligands, an excess amount of isocyanide ligands afforded bis(isocyanide) complexes,  $Ru(\eta^5-C_{60}Me_5)Cl(^tBuNC)_2$  (**7**) and  $Ru(\eta^5-C_{60}Me_5)Cl(XylNC)_2$  (**8**). When a toluene solution of **1** was treated with 10 equiv of  $^tBuNC$  and XylNC at 100 °C for 24 h, the bis(isocyanide) complexes **7** and **8** formed as predominant products in two steps via the mono(isocyanide) complex. These bis(isocyanide) complexes decomposed gradually during isolation and, hence, were characterized in solution with NMR spectroscopy; the  $^1H$  NMR spectra of these complexes exhibited one set of signals due to both MeFCp and isocyanide ligands in an exactly 1:2 integral ratio.

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**Figure 2.** Molecular structure of **2** with 30% probability level ellipsoids. The toluene molecule found in the unit cell is omitted for clarity.



**Figure 3.** Molecular structure of **4** with 30% probability level ellipsoids. The toluene molecule found in the unit cell is omitted for clarity.

Molecular structures of the phosphine complex **2** and the isocyanide complex **4** were determined by X-ray crystallographic analysis (Figures 2 and 3). The selected bond distances and angles are listed in Tables 2 and 3, respectively. The structural features of **2** and **4** are similar to those of the dicarbonyl complex **1**. The chloro ligands of both **2** and **4** are set in the space between two methyl groups of the MeFCp ligand, while the carbonyl and the phosphine/isocyanide ligands sit above the methyl groups. The ruthenium–Cp carbon (C(Cp)) bond distances of **2** ( $Ru-C(Cp) = 2.296$  Å (average)),  $Ru-(\text{centroid of Cp}) = 1.947$  Å) are longer than those of **4** ( $Ru-C(Cp) = 2.273$  Å (average),  $Ru-(\text{centroid of$

**Table 2.** Selected Bond Distances and Angles for **2**

Bond Distances (Å)			
Ru–C1	2.334(6)	Ru–P	2.3417(19)
Ru–C2	2.312(6)	Ru–Cl	2.425(3)
Ru–C3	2.267(6)	Ru–C6	1.965(11)
Ru–C4	2.269(6)	C6–O	0.879(10)
Ru–C5	2.275(7)		
Ru–C(Cp) (av)	2.291		
Ru–(centroid of Cp)	1.943		
C(Cp)–C(Cp) (av)	1.429		
C(Cp)–C(α) (av)	1.520		
C(α)–C(β) (av)	1.542		
C(β)–C(β) (av)	1.370		
Bond Angles (deg)			
P–Ru–Cl	82.53(8)	Cl–Ru–C6	95.4(3)
P–Ru–C6	84.4(2)		
hold-back angle			18.38
sum of three angles around C(Cp) (av) <sup>a</sup>			355.78
sum of three angles around C(α) (av) <sup>a</sup>			313.08
sum of three angles around C(β) (av)			353.87

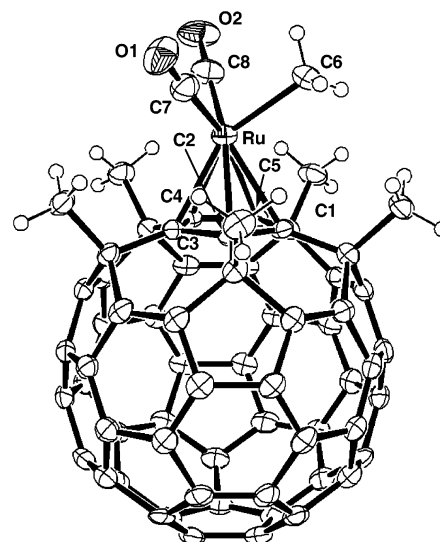
<sup>a</sup> Within the fullerene core.**Table 3.** Selected Bond Distances and Angles for **4**

Bond Distances (Å)			
Ru–C1	2.243(6)	Ru–Cl	2.409(2)
Ru–C2	2.267(6)	Ru–C6	1.953(7)
Ru–C3	2.298(5)	Ru–C7	2.004(6)
Ru–C4	2.279(5)	N–C6	1.164(8)
Ru–C5	2.236(5)	O–C7	0.946(8)
Ru–C(Cp) (av)	2.265		
Ru–(centroid of Cp)	1.909		
C(Cp)–C(Cp) (av)	1.432		
C(Cp)–C(α) (av)	1.505		
C(α)–C(β) (av)	1.542		
C(β)–C(β) (av)	1.373		
Bond Angles (deg)			
Cl–Ru–C6	87.0(2)	C6–Ru–C7	85.2(2)
Cl–Ru–C7	86.7(2)		
hold-back angle			17.52
sum of three angles around C(Cp) (av) <sup>a</sup>			356.18
sum of three angles around C(α) (av) <sup>a</sup>			313.38
sum of three angles around C(β) (av)			353.47

<sup>a</sup> Within the fullerene core.

Cp) = 1.919 Å), because of steric repulsion between the phosphine ligands and the methyl group on the [60]-fullerene. The methyl group near the phosphine group is pushed down due to steric effects. Consistent with the higher reactivity of **4** relative to **2**, the ruthenium–C(CO) bond length in **4** is elongated to 2.004 Å, which is longer than those of **1** (1.92(4) and 1.97(2) Å), **2** (1.965–(11) Å), and the usual terminal carbonyl–ruthenium bond (ca. 1.85–1.90 Å).<sup>28</sup>

**Alkylation and Alkynylation of Ruthenium Chloro Complexes.** The chloro ligand on the ruthenium center can also be exchanged readily with an alkyl or an alkynyl ligand with the aid of a nucleophilic alkylation or alkynylation reagent. The reaction of **1** with 1.2 equiv of alkyl Grignard reagents such as MeMgBr and Me<sub>3</sub>SiCH<sub>2</sub>MgCl in toluene at 0 °C afforded the alkyl complexes Ru(η<sup>5</sup>-C<sub>60</sub>Me<sub>5</sub>)(CH<sub>3</sub>)(CO)<sub>2</sub> (**9**) and Ru(η<sup>5</sup>-C<sub>60</sub>Me<sub>5</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>)(CO)<sub>2</sub> (**10**) as orange microcrystals in 90% and 78% yields, respectively (Scheme 1). The reactions performed in THF at low temperature (–78

**Figure 4.** Molecular structure of **9** with 30% probability level ellipsoids. The chlorobenzene molecule found in the unit cell is omitted for clarity.

°C) gave the alkylated complexes in lower yield (ca. 50%). The metal–carbon bond was characterized by the <sup>1</sup>H and <sup>13</sup>C NMR spectra: the signals due to the CH<sub>3</sub>–Ru group in **9** and the CH<sub>2</sub>–Ru group in **10** appear at high field (δ 1.17 and 1.03) as singlet signals, and the carbon signals of the CH<sub>3</sub>–Ru and the CH<sub>2</sub>–Ru groups appear also at high field (δ –28.23 and –28.50, respectively). The CO stretching frequencies of the MeFCp compound **9** (ν<sub>asym</sub> 2014 and ν<sub>sym</sub> 1955 cm<sup>–1</sup>) are similar to those of a Cp analogue, RuCp(CH<sub>3</sub>)(CO)<sub>2</sub> (ν<sub>asym</sub> 2019 and ν<sub>sym</sub> 1958 cm<sup>–1</sup>),<sup>29</sup> and larger than those of a Cp\* analogue, RuCp\*(CH<sub>3</sub>)(CO)<sub>2</sub> (ν<sub>asym</sub> 1998 and ν<sub>sym</sub> 1935 cm<sup>–1</sup>).<sup>30</sup> The phosphine complex **2** was similarly converted to a methyl complex. The reaction of Ru(η<sup>5</sup>-C<sub>60</sub>Me<sub>5</sub>)Cl(PET<sub>3</sub>)(CO) (**2**) with 1.5 equiv of MeMgBr in toluene afforded the methyl complex Ru(η<sup>5</sup>-C<sub>60</sub>Me<sub>5</sub>)(CH<sub>3</sub>)(PET<sub>3</sub>)(CO) (**11**) in 93% yield. The methyl complex **11** is thermally stable both in solution and as a solid. The <sup>1</sup>H NMR spectrum of **11** in CDCl<sub>3</sub> exhibits a doublet signal (δ 0.77, <sup>3</sup>J<sub>P–H</sub> = 5.2 Hz) due to the CH<sub>3</sub>–Ru group and one set of signals due to the phosphine and C<sub>60</sub>Me<sub>5</sub> ligand. The <sup>13</sup>C NMR spectrum exhibited a doublet of quartets signal (δ –28.03, <sup>1</sup>J<sub>C–H</sub> = 131.0 Hz, <sup>2</sup>J<sub>P–C</sub> = 12.9 Hz) due to the methyl carbon.

X-ray crystallographic analysis (Figure 4) was performed for the methyl complex **9** recrystallized from chlorobenzene/ethanol as a 1:1 mixture of **9** and chlorobenzene. The selected bond distances and angles of **9** are shown in Table 4. The methyl group on the ruthenium center is located above one of the five methyl groups on the fullerene sphere, despite apparent steric problems. Coordination of the MeFCp ligand is therefore slightly disturbed (Ru–C(Cp) = 2.272(4)–2.331(4) Å). The Ru–CH<sub>3</sub> distance (2.168(5) Å) is comparable to that of a cyclopentadienyl methyl complex such as Ru[C<sub>5</sub>Me<sub>4</sub>(neomenthyl)](CH<sub>3</sub>)(CO)(PPh<sub>3</sub>) (Ru–CH<sub>3</sub> = 2.166 Å).<sup>31</sup>

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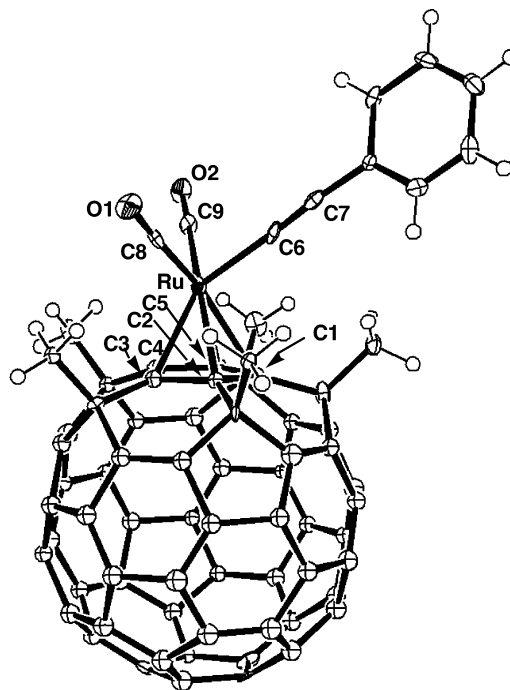
**Table 4. Selected Bond Distances and Angles for 9**

Bond Distances (Å)			
Ru–C1	2.331(4)	Ru–C6	2.168(5)
Ru–C2	2.287(4)	Ru–C7	1.867(5)
Ru–C	2.272(4)	Ru–C8	1.878(5)
Ru–C4	2.286(4)	O1–C7	1.149(6)
Ru–C5	2.302(4)	O2–C8	1.136(6)
Ru–C(Cp) (av)	2.296		
Ru–(centroid of Cp)	1.947		
C(Cp)–C(Cp) (av)	1.429		
C(Cp)–C(α) (av)	1.512		
C(α)–C(β) (av)	1.542		
C(β)–C(β) (av)	1.374		
Bond Angles (deg)			
C6–Ru–C7	83.1(2)	C7–Ru–C8	90.5(2)
C6–Ru–C8	84.6(2)		
hold-back angle			17.63
sum of three angles around C(Cp) (av) <sup>a</sup>			356.14
sum of three angles around C(α) (av) <sup>a</sup>			312.86
sum of three angles around C(β) (av)			353.66

<sup>a</sup> Within the fullerene core.

Alkynylation of **1** also took place smoothly by treatment with an alkynyl Grignard reagent or an alkynyl-lithium reagent; the reaction of **1** with 1.2 equiv of (phenylethynyl)magnesium bromide in toluene at 0 °C afforded a ruthenium alkynyl dicarbonyl complex, Ru( $\eta^5$ -C<sub>60</sub>Me<sub>5</sub>)(C≡CPh)(CO)<sub>2</sub> (**12**) (Scheme 1). Similarly, the reactions using 1-hexynylmagnesium bromide, ((trimethylsilyl)ethynyl)magnesium bromide, and ethynylmagnesium bromide afforded Ru( $\eta^5$ -C<sub>60</sub>Me<sub>5</sub>)(C≡C<sup>n</sup>Bu)(CO)<sub>2</sub> (**13**), Ru( $\eta^5$ -C<sub>60</sub>Me<sub>5</sub>)(C≡CSiMe<sub>3</sub>)(CO)<sub>2</sub> (**14**), and Ru( $\eta^5$ -C<sub>60</sub>Me<sub>5</sub>)(C≡CH)(CO)<sub>2</sub> (**15**), respectively, as orange microcrystals, all in good yield (87–93%).<sup>32</sup> These alkynyl complexes were characterized by <sup>1</sup>H and <sup>13</sup>C NMR and APCI-mass spectroscopic analyses as well as by combustion analysis. The NMR spectroscopic analyses of these complexes are straightforward; their <sup>1</sup>H NMR spectra exhibited one set of signals due to both the  $\eta^5$ -C<sub>60</sub>Me<sub>5</sub> ligand and the substituted or unsubstituted alkynyl ligand in a 1:1 integral ratio. The <sup>13</sup>C NMR spectra show the alkyne carbons at  $\delta$  113.05 (Ru–C≡CPh), 100.89 (Ru–C≡CPh), 110.86 (Ru–C≡C<sup>n</sup>Bu), 99.51 (Ru–C≡C<sup>n</sup>Bu), 120.00 (Ru–C≡CSiMe<sub>3</sub>), 99.60 (Ru–C≡CSiMe<sub>3</sub>), 113.23 (Ru–C≡CH), and 99.37 (Ru–C≡CH, <sup>1</sup>J<sub>C–H</sub> = 231.4 Hz). The IR spectra of the alkynyl complexes showed the expected stretching absorptions C≡C ( $\nu$ /cm<sup>-1</sup>: 2132 for **12**, 2163 for **13**, and 2163 for **14**) and CO absorptions ( $\nu$ /cm<sup>-1</sup>: 2038 and 1991 for **12**, 2041 and 1989 for **13**, 2036 and 1995 for **14**, and 2046 and 1994 for **15**).

The molecular structure of the phenylalkynyl complex **12** was determined by X-ray analysis. Single crystals of **12** suitable for X-ray crystallographic analysis were obtained from a mixture of chlorobenzene and methanol. The molecular structure of **12** is shown in Figure 5, and selected bond lengths and angles are listed in Table 5. A longer Ru–C(alkyne) bond length (2.05(1) Å) and a shorter C≡C triple bond (1.165(12) Å) compared to those of reported phenylethynyl complexes (Ru–C = 2.00–2.03 Å; C≡C = 1.20–1.22 Å)<sup>33</sup> are best interpreted in terms of a great deal of inefficient  $\pi$  electron back-

**Figure 5.** Molecular structure of **12** with 30% probability level ellipsoids. The chlorobenzene molecule found in the unit cell is omitted for clarity.**Table 5. Selected Bond Distances and Angles for 12**

Bond Distances (Å)			
Ru–C1	2.314(9)	Ru–C6	2.05(1)
Ru–C2	2.258(9)	Ru–C8	1.875(9)
Ru–C3	2.265(9)	Ru–C9	1.913(9)
Ru–C4	2.282(9)	O1–C8	1.15(1)
Ru–C5	2.293(8)	O2–C9	1.107(9)
C6–C7	1.17(1)		
Ru–C(Cp) (av)	2.282		
Ru–(centroid of Cp)	1.929		
C(Cp)–C(Cp) (av)	1.432		
C(Cp)–C(α) (av)	1.502		
C(α)–C(β) (av)	1.544		
C(β)–C(β) (av)	1.368		
Bond Angles (deg)			
C6–Ru–C8	82.0(3)	C8–Ru–C9	92.6(4)
C6–Ru–C9	85.7(4)		
hold-back angle			17.28
sum of three angles around C(Cp) (av) <sup>a</sup>			356.22
sum of three angles around C(α) (av) <sup>a</sup>			312.72
sum of three angles around C(β) (av)			353.16

<sup>a</sup> Within the fullerene core.

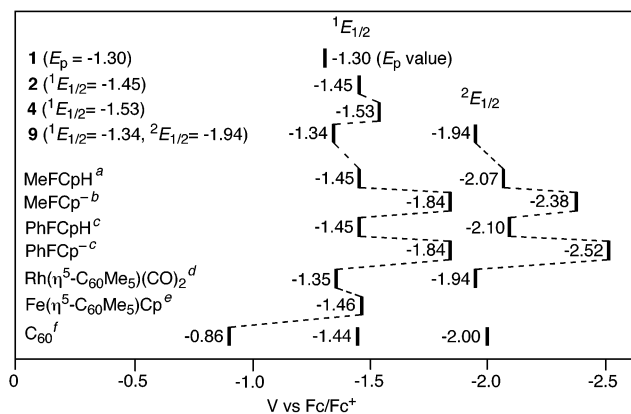
donation from the d orbital of the metal fragment to the sp-hybridized orbital of the C≡CPh fragment. The metal center thus can be regarded as being electron deficient, owing to an electron-withdrawing effect of the C<sub>60</sub>Me<sub>5</sub> ligands.

**Electrochemical Studies of the Ru–MeFCp Complexes and Related Compounds.** The redox behavior of the Ru–MeFCp complexes was examined. The cyclic voltammogram of **1** in THF or in dichloromethane

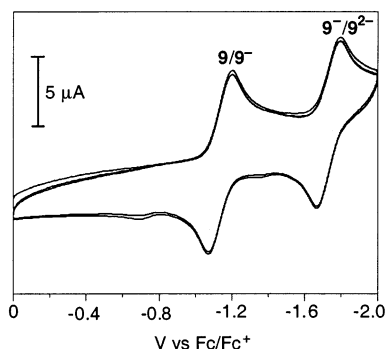
(32) For the corresponding Cp analogue of **15**, RuCp(CCH)(CO)<sub>2</sub>, see: Viola, E.; Lo Sterzo, C.; Crescenzi, R.; Frachey, G. *J. Organomet. Chem.* **1995**, *493*, 55.

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**Figure 6.** Reduction potentials of **1**, **2**, **4**, **9** and related compounds in THF. Legend: (a) ref 13; (b) ref 34; (c) ref 16; (d) ref 13; (e) ref 14; (f) ref 36.



**Figure 7.** Cyclic voltammograms of **9** in THF at 25 °C showing successive reversible reductions to  $9^{2-}$ .

showed an irreversible reduction behavior with an  $E_p$  value of  $-1.30$  V (vs  $Fc/Fc^+$ , in THF), while no oxidation wave was observed for the window of THF. However, the phosphine complex **2** and the isonitrile complex **4** exhibited reversible one-electron reduction, the values of which are  $E_{1/2} = -1.45$  and  $-1.53$  V, respectively. Note that, usually, ruthenium(II) cyclopentadienyl complexes are not reduced under the same conditions. These reduction potentials are comparable to those of the Ru–MeFCp complex  $Rh(\eta^5-C_{60}Me_5)(CO)_2$  ( $E_{1/2} = -1.35$  V),<sup>13</sup> the Fe–MeFCp complex  $Fe(\eta^5-C_{60}Me_5)(\eta^5-Cp)$  ( $E_{1/2} = -1.46$  V),<sup>14</sup> and the parent molecule  $C_{60}Me_5H$  ( $E_{1/2} = -1.45$  V), indicating the one-electron reductions found in **2** and **4** are due to reductions of the fullerene moieties (Figure 6). This observation of the metal-dependent change of the reduction potential allows us to consider that the redox behavior in the fullerene moiety can be controlled by the changing the ligands on the metal center.<sup>16</sup> We can rationalize the irreversible reduction of **1** by assuming irreversible loss of chloride anion or carbonyl ligand from the metal center, which is triggered by initial reduction of the fullerene moiety followed by electron transfer to the metal center. The lack of a reduction wave due to the  $MeFCp^-$  anion ( $-1.84$  and  $-2.38$  V)<sup>34</sup> indicates that the metal–MeFCp bond is not cleaved in this process.

The methyl complex **9** showed reversible two-electron reductions ( $-1.34$  and  $-1.94$  V; Figure 7), whereas the alkynyl complexes **12**–**15** do not show reversible redox behavior. The second reduction potential of **9** is com-

parable to those of  $Rh(\eta^5-C_{60}Me_5)(CO)_2$  ( $E_{1/2} = -1.94$  V),<sup>13</sup>  $C_{60}Me_5H$  ( $E_{1/2} = -2.07$  V), and the third reduction potential of the parent [60]fullerene ( $-2.00$  V in THF and  $-1.87$  V in toluene/MeCN vs  $Fc/Fc^+$ ).<sup>6b,35,36</sup> Since the Ru–MeFCp complexes bearing suitable ligands retain the inherent reduction property of fullerene, as indicated by the above data, we therefore expect that the present Ru–MeFCp complexes can be applied to catalytic reactions both under neutral and under reductive conditions.

## Conclusion

We have demonstrated that the ruthenium chloro dicarbonyl complex **1**, bearing the MeFCp ligand, can be synthesized in high yield on a large scale and be derivatized with retention of metal–FCp bonding. While the ligand exchange reaction of the carbonyl ligand in the previous mononuclear transition-metal fullerene complex was not successful, owing to loss of the fullerene ligand,<sup>8,12</sup> the carbonyl ligands in the present complexes can be cleanly replaced to obtain the phosphine and isonitrile complexes without cleavage of the fullerene–metal bond. Moreover, the metal–halogen bonds in the present complexes can be exploited for further reaction: alkylation and alkynylation reactions of **1** take place smoothly to afford various alkyl and alkynyl complexes. In light of the high stability of the metal–fullerene bond under redox conditions, we expect that the present Ru–MeFCp complexes as well as their congeners will serve as key compounds in catalysis<sup>18</sup> and in materials science.<sup>37–40</sup>

## Experimental Section

**General Procedures.** All manipulations involving air- and moisture-sensitive compounds were carried out using standard Schlenk techniques under nitrogen or argon. Hexane, toluene, THF, benzene- $d_6$ , and THF- $d_8$  were distilled from Na/K alloy and thoroughly degassed by trap-to-trap distillation before use. Pentamethyl-hydro-[60]fullerene,  $C_{60}Me_5H$ , was prepared according to the literature.<sup>15c</sup>  $t$ -BuOK in THF was purchased from Sigma-Aldrich and used as received.

The  $^1H$  (500, 400 MHz),  $^{13}C$  (125, 100 MHz), and  $^{31}P$  (200, 160 MHz) NMR spectra were measured on a Bruker DRX500 or JEOL EX 400 spectrometer. When benzene- $d_6$ , toluene- $d_8$ , and THF- $d_8$  were used as solvents, the spectra were referenced to residual solvent protons in the  $^1H$  NMR spectra and to the solvent signal in the  $^{13}C$  NMR spectra. Other spectra were recorded on the following instruments: IR spectra, JASCO IR-420 and Applied Systems Inc. ReactIR 1000; UV/vis spectra, HITACHI U3500; mass spectra, Shimadzu LCMS-QP8000, Waters ZQ2000, and JEOL JMS T100LC. Elemental analyses were performed at the organic elemental analysis laboratory in this department.

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(34) Determined for  $K(MeFCp)$ .

**Preparation of Ru( $\eta^5$ -C<sub>60</sub>Me<sub>5</sub>)Cl(CO)<sub>2</sub> (1).** To a solution of C<sub>60</sub>Me<sub>5</sub>H (1.00 g, 1.25 mmol) in THF (200 mL) was added a solution of *t*-BuOK (2.50 mmol) in THF (2.50 mL) at 25 °C. After the mixture was stirred for 15 min, [RuCl<sub>2</sub>(CO)<sub>3</sub>]<sub>2</sub> (1.28 g, 2.50 mmol) was added to the resulting dark brown solution at 25 °C, and this reaction mixture was stirred for 30 min at 25 °C. Insoluble products were separated through a pad of silica gel, and purification of the soluble products through HPLC (Nacalai Tesque, Buckyprep, 250 mm, 7/3 toluene/2-propanol) afforded orange microcrystals of **1** (990 mg, 1.00 mmol, 80% yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  2.18 (s, 15H, C<sub>60</sub>Me<sub>5</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  30.82 (5C, C<sub>60</sub>Me<sub>5</sub>), 51.19 (5C, C<sub>60</sub>(C <sub>$\alpha$</sub> )), 111.69 (5C, C<sub>60</sub>(C <sub>$\beta$</sub> )), 143.83 (10C, C<sub>60</sub>), 144.17 (10C, C<sub>60</sub>), 147.42 (5C, C<sub>60</sub>), 148.60 (10C, C<sub>60</sub>), 148.98 (5C, C<sub>60</sub>), 152.28 (10C, C<sub>60</sub>(C <sub>$\beta$</sub> )), 196.93 (2C, CO). UV-vis (7/3 toluene/*i*-PrOH):  $\lambda_{\text{max}}$  370 (sh), 395 nm. IR (diamond probe):  $\nu(\text{CO})/\text{cm}^{-1}$  2052 (s), 2006 (s). APCI-MS (+): *m/z* 988 (M<sup>+</sup>). The cyclic voltammogram of **1** in THF or in dichloromethane showed irreversible reduction behavior with an E<sub>p</sub> value of -1.30 V (vs Fc/Fc<sup>+</sup> in THF), while no oxidation wave was observed. Anal. Calcd for C<sub>74</sub>H<sub>23</sub>ClO<sub>2</sub>Ru·C<sub>7</sub>H<sub>8</sub>: C, 82.25; H, 2.15. Found: C, 81.78; H, 2.52.

**Preparation of Ru( $\eta^5$ -C<sub>60</sub>Me<sub>5</sub>)Cl(PET<sub>3</sub>)(CO) (2).** To a solution of **1** (100 mg, 0.101 mmol) in toluene (20 mL) was added a solution of PET<sub>3</sub> (0.152 mmol) in toluene (0.15 mL). The mixture was stirred and heated at 70 °C for 12 h, and the progress of the reaction was monitored by HPLC. Insoluble products were separated through a pad of silica gel, and purification by HPLC afforded orange microcrystals of **2** (105 mg, 0.0971 mmol, 96% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.19 (qd, <sup>3</sup>J<sub>H-H</sub> = 7.7 Hz, <sup>2</sup>J<sub>P-H</sub> = 23.8 Hz, 6H, CH<sub>2</sub>CH<sub>3</sub>), 1.42 (td, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz, <sup>3</sup>J<sub>P-H</sub> = 15.1 Hz, 9H, CH<sub>2</sub>CH<sub>3</sub>), 2.47 (s, 15H, C<sub>60</sub>Me<sub>5</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  8.71 (qd, <sup>1</sup>J<sub>C-H</sub> = 128.0 Hz, <sup>2</sup>J<sub>P-C</sub> = 4.8 Hz, CH<sub>2</sub>CH<sub>3</sub>), 21.84 (td, <sup>1</sup>J<sub>C-H</sub> = 127.7 Hz, <sup>1</sup>J<sub>P-C</sub> = 28.4 Hz, CH<sub>2</sub>CH<sub>3</sub>), 29.19 (q, <sup>1</sup>J<sub>C-H</sub> = 130.7 Hz, 5C, C<sub>60</sub>Me<sub>5</sub>), 51.44 (s, 5C, C<sub>60</sub>(C <sub>$\alpha$</sub> )), 109.98 (s, 5C, C<sub>60</sub>(C <sub>$\beta$</sub> )), 143.66 (s, 10C, C<sub>60</sub>), 143.68 (s, 10C, C<sub>60</sub>), 147.08 (s, 5C, C<sub>60</sub>), 148.21 (s, 10C, C<sub>60</sub>), 148.41 (s, 5C, C<sub>60</sub>), 152.72 (s, 10C, C<sub>60</sub>(C <sub>$\beta$</sub> )), 204.84 (d, <sup>2</sup>J<sub>P-C</sub> = 24.7 Hz, 2C, CO). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  32.28 (PET<sub>3</sub>). IR (diamond probe):  $\nu(\text{CO})/\text{cm}^{-1}$  1937 (s). APCI-MS (+): *m/z* 1079 (M<sup>+</sup>). Complex **2** exhibited reversible one-electron reduction at -1.45 V (vs Fc/Fc<sup>+</sup>) in THF. Anal. Calcd for C<sub>72</sub>H<sub>30</sub>ClOPRu·C<sub>7</sub>H<sub>8</sub>: C, 81.05; H, 3.27. Found: C, 80.54; H, 3.50.

**Preparation of Ru( $\eta^5$ -C<sub>60</sub>Me<sub>5</sub>)Cl(PPh<sub>3</sub>)(CO) (3).** To a solution of **1** (40 mg, 0.041 mmol) in toluene (10 mL) was added a solution of PPh<sub>3</sub> (0.41 mmol) in toluene (0.41 mL). The mixture was stirred and heated at 70 °C for 12 h, and the progress of the reaction was monitored by HPLC. Insoluble products were separated through a pad of silica gel, and purification by HPLC afforded orange microcrystals of **3** (26 mg, 0.021 mmol, 51% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  2.22 (s, 15H, C<sub>60</sub>Me<sub>5</sub>), 7.10 (t, 1H, *p*-Ph), 7.24 (s, 2H, *m*-Ph), 7.76 (s, 2H, *o*-Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  28.27 (5C, C<sub>60</sub>Me<sub>5</sub>), 51.75 (5C, C<sub>60</sub>(C <sub>$\alpha$</sub> )), 109.75 (5C, C<sub>60</sub>(C <sub>$\beta$</sub> )), 128–135 (Ph), 143.50 (10C, C<sub>60</sub>), 143.66 (10C, C<sub>60</sub>), 147.10 (5C, C<sub>60</sub>), 148.23 (10C, C<sub>60</sub>), 148.23 (5C, C<sub>60</sub>), 152.43 (10C, C<sub>60</sub>(C <sub>$\beta$</sub> )), 201.93 (d, <sup>2</sup>J<sub>P-C</sub> = 24.2 Hz, 2C, CO). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  37.23 (PPh<sub>3</sub>). IR (diamond probe):  $\nu(\text{CO})/\text{cm}^{-1}$  1950 (s). APCI-MS (+): *m/z* 1223 (M<sup>+</sup>). Anal. Calcd for C<sub>84</sub>H<sub>30</sub>ClOPRu: C, 82.51; H, 2.47. Found: C, 82.24; H, 2.50.

**Preparation of Ru( $\eta^5$ -C<sub>60</sub>Me<sub>5</sub>)Cl(*t*-BuNC)(CO) (4).** To a solution of **1** (50 mg, 0.050 mmol) in toluene (10 mL) was added a solution of *tert*-butyl isocyanide (0.075 mmol) in toluene (0.75 mL). The mixture was stirred and heated at 70 °C for 12 h, and the progress of the reaction was monitored by HPLC. Insoluble products were separated through a pad of silica gel, and purification by HPLC afforded orange microcrystals of **4** (50 mg, 0.048 mmol, 94% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  1.74 (s, 9H, Me<sub>3</sub>C), 2.44 (s, 15H, C<sub>60</sub>Me<sub>5</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  29.42 (q, <sup>1</sup>J<sub>C-H</sub> = 130.8 Hz, 5C, C<sub>60</sub>Me<sub>5</sub>), 30.84 (q, <sup>1</sup>J<sub>C-H</sub> = 129.1 Hz, 1C, Me<sub>3</sub>C), 51.12 (s, 5C, C<sub>60</sub>(C <sub>$\alpha$</sub> )), 59.20 (s, 1C,

Me<sub>3</sub>C), 108.01 (s, 5C, C<sub>60</sub>(C <sub>$\beta$</sub> )), 143.69 (s, 10C, C<sub>60</sub>), 143.81 (s, 10C, C<sub>60</sub>), 147.06 (s, 5C, C<sub>60</sub>), 148.19 (s, 10C, C<sub>60</sub>), 148.49 (s, 5C, C<sub>60</sub>), 152.79 (s, 10C, C<sub>60</sub>(C <sub>$\beta$</sub> )), 200.38 (s, 1C, CO), 211.65 (s, 1C, NC). IR (diamond probe):  $\nu(\text{NC})/\text{cm}^{-1}$  2159 (s),  $\nu(\text{CO})/\text{cm}^{-1}$  1976 (s). APCI-MS (+): *m/z* 1044 (M<sup>+</sup>). Complex **4** exhibited reversible one-electron reduction at -1.53 V (vs Fc/Fc<sup>+</sup>) in THF. Anal. Calcd for C<sub>71</sub>H<sub>24</sub>ClNORu: C, 81.72; H, 2.32; N, 1.34. Found: C, 81.50; H, 2.30; N, 1.27.

**Preparation of Ru( $\eta^5$ -C<sub>60</sub>Me<sub>5</sub>)Cl(MeNC)(CO) (5).** The procedure described for **4** was performed to obtain **5**. Complex **5** was prepared from **1** (20 mg, 0.020 mmol) and methyl isocyanide (0.050 mmol) in toluene (0.5 mL). Yield: 18 mg (0.019 mmol, 93%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  2.43 (s, 15H, C<sub>60</sub>Me<sub>5</sub>), 2.45 (s, 3H, MeNC). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  29.47 (5C, C<sub>60</sub>Me<sub>5</sub>), 29.73 (1C, MeNC), 51.09 (5C, C<sub>60</sub>(C <sub>$\alpha$</sub> )), 108.06 (5C, C<sub>60</sub>(C <sub>$\beta$</sub> )), 143.62 (10C, C<sub>60</sub>), 143.69 (10C, C<sub>60</sub>), 146.98 (5C, C<sub>60</sub>), 148.10 (10C, C<sub>60</sub>), 148.42 (5C, C<sub>60</sub>), 152.59 (10C, C<sub>60</sub>(C <sub>$\beta$</sub> )), 199.99 (2C, CO), 220.78 (1C, MeNC). IR (diamond probe):  $\nu(\text{NC})/\text{cm}^{-1}$  2188 (s),  $\nu(\text{CO})/\text{cm}^{-1}$  1976 (s). APCI-MS (+): *m/z* 1002 (M<sup>+</sup>). Anal. Calcd for C<sub>68</sub>H<sub>18</sub>ClNORu: C, 81.55; H, 1.81; N, 1.40. Found: C, 81.22; H, 2.02; N, 1.35.

**Preparation of Ru( $\eta^5$ -C<sub>60</sub>Me<sub>5</sub>)Cl(XylNC)(CO) (6).** The procedure described for **4** was performed to obtain **6**. Complex **6** was prepared from **1** (70 mg, 0.071 mmol) and 2,6-dimethylphenyl isocyanide (20 mg, 0.15 mmol) in toluene (0.5 mL). Yield: 70 mg (0.064 mmol, 90%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  2.35 (s, 15H, C<sub>60</sub>Me<sub>5</sub>), 2.44 (s, 6H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 6.74 (d, 2H, *m*-C<sub>6</sub>H<sub>3</sub>), 6.84 (t, 1H, *p*-C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  29.63 (2C, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 29.74 (5C, C<sub>60</sub>Me<sub>5</sub>), 51.41 (5C, C<sub>60</sub>(C <sub>$\alpha$</sub> )), 109.32 (5C, C<sub>60</sub>(C <sub>$\beta$</sub> )), 125.64 (1C, *p*-C<sub>6</sub>H<sub>3</sub>), 128.88 (2C, *m*-C<sub>6</sub>H<sub>3</sub>), 135.71 (2C, *o*-C<sub>6</sub>H<sub>3</sub>), 144.14 (10C, C<sub>60</sub>), 144.21 (10C, C<sub>60</sub>), 147.50 (5C, C<sub>60</sub>), 148.63 (10C, C<sub>60</sub>), 148.98 (5C, C<sub>60</sub>), 152.25 (*ipso*-C<sub>6</sub>H<sub>3</sub>), 153.08 (10C, C<sub>60</sub>(C <sub>$\beta$</sub> )), 201.13 (1C, CO), 203.98 (1C, NC). IR (diamond probe):  $\nu(\text{NC})/\text{cm}^{-1}$  2140 (s),  $\nu(\text{CO})/\text{cm}^{-1}$  1978 (s). APCI-MS (+): *m/z* 1092 (M<sup>+</sup>). Anal. Calcd for C<sub>75</sub>H<sub>24</sub>ClNORu: C, 82.52; H, 2.22; N, 1.28. Found: C, 82.21; H, 2.34; N, 1.26.

**Preparation of Ru( $\eta^5$ -C<sub>60</sub>Me<sub>5</sub>)Cl(*t*-BuNC)<sub>2</sub> (7).** To a solution of **1** (50 mg, 0.050 mmol) in toluene (10 mL) was added a solution of *tert*-butyl isocyanide (0.50 mmol) in toluene (5.0 mL). The mixture was stirred and heated at 100 °C for 24 h, and the progress of the reaction was monitored by HPLC. Insoluble products were separated through a pad of silica gel, and purification by HPLC afforded orange microcrystals of **7** (30 mg, 0.027 mmol, 54% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  1.70 (s, 18H, Me<sub>3</sub>C), 2.43 (s, 15H, C<sub>60</sub>Me<sub>5</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  29.29 (q, <sup>1</sup>J<sub>C-H</sub> = 130.7 Hz, 5C, C<sub>60</sub>Me<sub>5</sub>), 31.26 (q, <sup>1</sup>J<sub>C-H</sub> = 129.0 Hz, 1C, Me<sub>3</sub>C), 51.25 (s, 5C, C<sub>60</sub>(C <sub>$\alpha$</sub> )), 64.62 (s, 1C, Me<sub>3</sub>C), 103.79 (s, 5C, C<sub>60</sub>(C <sub>$\beta$</sub> )), 143.50 (s, 10C, C<sub>60</sub>), 144.11 (s, 10C, C<sub>60</sub>), 147.07 (s, 5C, C<sub>60</sub>), 148.11 (s, 10C, C<sub>60</sub>), 148.37 (s, 5C, C<sub>60</sub>), 153.69 (s, 10C, C<sub>60</sub>(C <sub>$\beta$</sub> )), 206.09 (s, 2C, NC). APCI-MS (+): *m/z* 1099 (M<sup>+</sup>).

**Preparation of Ru( $\eta^5$ -C<sub>60</sub>Me<sub>5</sub>)Cl(XylNC)<sub>2</sub> (8).** The procedure described for **7** was performed to obtain **8**. Complex **8** (18 mg, 0.015 mmol, 51% yield) was synthesized from **1** (30 mg, 0.030 mmol) and 2,6-dimethylphenyl isocyanide (39 mg, 0.30 mmol). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  2.50 (s, 15H, C<sub>60</sub>Me<sub>5</sub>), 2.67 (s, 12H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 7.18 (s, 6H, *m*- and *p*-C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  19.33 (4C, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 29.68 (5C, C<sub>60</sub>Me<sub>5</sub>), 51.29 (5C, C<sub>60</sub>(C <sub>$\alpha$</sub> )), 106.03 (5C, C<sub>60</sub>(C <sub>$\beta$</sub> )), 128.04 (6C, *m*- and *p*-C<sub>6</sub>H<sub>3</sub>), 135.16 (4C, *o*-C<sub>6</sub>H<sub>3</sub>), 143.60 (10C, C<sub>60</sub>), 144.00 (10C, C<sub>60</sub>), 147.07 (5C, C<sub>60</sub>), 148.17 (10C, C<sub>60</sub>), 148.43 (5C, C<sub>60</sub>), 152.32 (*ipso*-C<sub>6</sub>H<sub>3</sub>), 153.33 (10C, C<sub>60</sub>(C <sub>$\beta$</sub> )), 180.33 (2C, NC). APCI-MS (+): *m/z* 1195 (M<sup>+</sup>).

**Preparation of Ru( $\eta^5$ -C<sub>60</sub>Me<sub>5</sub>)(CH<sub>3</sub>)(CO)<sub>2</sub> (9).** To a solution of **1** (33 mg, 0.033 mmol) in THF (8.0 mL) was added a solution of MeMgBr (1.5 equiv, 0.050 mmol) in THF (0.050 mL) at 25 °C. The reaction mixture was stirred for 10 min at 25 °C. After removal of the solvent, the resulting solid was extracted with toluene (30 mL). Purification by HPLC afforded orange microcrystals of **9** (29 mg, 0.030 mmol, 90% yield). <sup>1</sup>H



**Table 6. Crystal Data and Data Collection Parameters for 1, 2, 4, 9, and 12**

	1·C <sub>7</sub> H <sub>8</sub>	2·C <sub>7</sub> H <sub>8</sub>	4·C <sub>7</sub> H <sub>8</sub>	9·C <sub>6</sub> H <sub>5</sub> Cl	12·C <sub>6</sub> H <sub>5</sub> Cl
formula	C <sub>77</sub> H <sub>23</sub> ClO <sub>2</sub> Ru	C <sub>79</sub> H <sub>38</sub> ClOPRu	C <sub>78</sub> H <sub>24</sub> ClNORu	C <sub>74</sub> H <sub>25</sub> ClO <sub>2</sub> Ru	C <sub>81</sub> H <sub>25</sub> ClO <sub>2</sub> Ru
fw	1080.618	1170.58	1127.50	1080.44	1166.61
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)	<i>P</i> 1 (No. 2)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)
<i>a</i> , Å	11.7640(6)	9.989(2)	15.967(2)	11.6440(4)	9.910(3)
<i>b</i> , Å	16.9730(9)	15.136(4)	9.9800(16)	17.0040(9)	17.204(5)
<i>c</i> , Å	21.9850(12)	17.686(5)	30.543(4)	21.7500(10)	27.875(9)
α, deg	90	70.886(12)	90	90	90
β, deg	97.444(3)	75.406(17)	105.269(9)	96.644(3)	99.98(2)
γ, deg	90	85.650(17)	90	90	90
<i>V</i> , Å <sup>3</sup>	4352.8(4)	2445.0(11)	4695.2(11)	4277.5(3)	4680.6(2)
<i>Z</i>	4	2	4	4	4
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.649	1.590	1.649	1.678	1.655
<i>T</i> , K	193(2)	120(2)	120(2)	153(2)	93(2)
cryst size, mm	0.50 × 0.22 × 0.12	0.45 × 0.22 × 0.18	0.40 × 0.22 × 0.05	0.25 × 0.10 × 0.05	0.25 × 0.10 × 0.05
2θ <sub>min</sub> , 2θ <sub>max</sub> , deg	4.44, 51.16	4.22, 51.66	4.30, 51.52	4.82, 51.74	6.00, 60.20
no. of rflns measd (unique)	7506	6501	8469	8131	13 588
no. of rflns measd ( <i>I</i> > 2.0σ( <i>I</i> ))	6148	5202	6032	6814	5523
no. of params	721	749	767	704	521
R1, wR2 (all data)	0.155, 0.471	0.099, 0.253	0.106, 0.245	0.074, 0.195	–, 0.243
<i>R</i> , <i>R</i> <sub>w</sub> ( <i>I</i> > 2.0σ( <i>I</i> ))	0.144, 0.464	0.084, 0.224	0.080, 0.215	0.062, 0.171	0.148, –
GOF on <i>F</i> <sup>2</sup>	2.22	1.9	1.07	1.07	1.027
Δ, e Å <sup>-3</sup>	2.79, –1.37	1.64, –1.31	1.34, –1.13	2.35, –1.88	0.171, –0.105

NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 1.17 (s, 3H, Ru–CH<sub>3</sub>), 2.01 (s, 15H, C<sub>60</sub>Me<sub>5</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ –28.23 (1C, Ru–CH<sub>3</sub>), 30.197 (5C, C<sub>60</sub>Me<sub>5</sub>), 51.18 (5C, C<sub>60</sub>(C<sub>α</sub>)), 112.18 (5C, C<sub>60</sub>(C<sub>β</sub>)), 144.08 (10C, C<sub>60</sub>), 144.39 (10C, C<sub>60</sub>), 147.34 (5C, C<sub>60</sub>), 148.48 (10C, C<sub>60</sub>), 148.99 (5C, C<sub>60</sub>), 153.09 (10C, C<sub>60</sub>(C<sub>β</sub>)), 195.26 (2C, CO). IR (diamond probe): ν(CO)/cm<sup>-1</sup> 2014 (s), 1955 (s). APCI-MS (+): *m/z* 968 (M<sup>+</sup>). Complex **9** showed reversible two-electron reductions (–1.34 and –1.94 V vs Fc/Fc<sup>+</sup>) in THF. Anal. Calcd for C<sub>68</sub>H<sub>18</sub>O<sub>2</sub>Ru·C<sub>7</sub>H<sub>8</sub>: C, 84.97; H, 2.47. Found: C, 84.88; H, 2.71.

**Preparation of Ru(η<sup>5</sup>-C<sub>60</sub>Me<sub>5</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>)(CO)<sub>2</sub> (10).** The procedure described for **9** was performed to obtain **10**. Complex **10** (6.2 mg, 0.0060 mmol, 78% yield) was derived from **1** (8.0 mg, 0.0081 mmol) and Me<sub>3</sub>SiCH<sub>2</sub>MgCl (0.0122 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 0.55 (s, 9H, Si–CH<sub>3</sub>), 1.03 (s, 2H, Ru–CH<sub>2</sub>), 2.15 (s, 15H, C<sub>60</sub>Me<sub>5</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ –28.50 (2C, Ru–CH<sub>2</sub>), 2.16 (3C, SiMe<sub>3</sub>), 30.00 (5C, C<sub>60</sub>Me<sub>5</sub>), 51.32 (5C, C<sub>60</sub>(C<sub>α</sub>)), 112.66 (5C, C<sub>60</sub>(C<sub>β</sub>)), 144.09 (10C, C<sub>60</sub>), 144.27 (10C, C<sub>60</sub>), 147.35 (5C, C<sub>60</sub>), 148.50 (10C, C<sub>60</sub>), 149.00 (5C, C<sub>60</sub>), 152.94 (10C, C<sub>60</sub>(C<sub>β</sub>)), 202.96 (2C, CO). IR (diamond probe): ν(CO)/cm<sup>-1</sup> 2013 (s), 1954 (s). APCI-MS (+): *m/z* 1040 (M<sup>+</sup>). Anal. Calcd for C<sub>70</sub>H<sub>24</sub>O<sub>2</sub>RuSi: C, 81.93; H, 2.36. Found: C, 81.79; H, 2.42.

**Preparation of Ru(η<sup>5</sup>-C<sub>60</sub>Me<sub>5</sub>)Me(PEt<sub>3</sub>)(CO) (11).** To a solution of **2** (15 mg, 0.014 mmol) in THF (4.0 mL) was added a solution of MeMgBr (1.5 equiv, 0.021 mmol) in THF (0.021 mL) at 25 °C. The reaction mixture was stirred for 30 min at 25 °C. After removal of the solvent, the resulting solid was extracted with toluene (20 mL). Purification by HPLC afforded orange microcrystals of **11** (13.8 mg, 0.013 mmol, 93% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.77 (d, <sup>3</sup>J<sub>P–H</sub> = 5.2 Hz, 3H, Ru–CH<sub>3</sub>), 1.33 (td, <sup>3</sup>J<sub>H–H</sub> = 7.6 Hz, <sup>3</sup>J<sub>P–H</sub> = 14.8 Hz, 9H, CH<sub>2</sub>CH<sub>3</sub>), 2.15 (qd, <sup>3</sup>J<sub>H–H</sub> = 7.5 Hz, <sup>2</sup>J<sub>P–H</sub> = 22.2 Hz, 6H, CH<sub>2</sub>CH<sub>3</sub>), 2.41 (s, 15H, C<sub>60</sub>Me<sub>5</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ –28.03 (qd, <sup>1</sup>J<sub>C–H</sub> = 131.0 Hz, <sup>2</sup>J<sub>P–C</sub> = 12.9 Hz, Ru–CH<sub>3</sub>), 8.43 (qd, <sup>1</sup>J<sub>C–H</sub> = 127.7 Hz, <sup>2</sup>J<sub>P–C</sub> = 3.2 Hz, CH<sub>2</sub>CH<sub>3</sub>), 21.95 (td, <sup>1</sup>J<sub>C–H</sub> = 128.8 Hz, <sup>1</sup>J<sub>P–C</sub> = 27.4 Hz, CH<sub>2</sub>CH<sub>3</sub>), 30.11 (q, <sup>1</sup>J<sub>C–H</sub> = 130.0 Hz, 5C, C<sub>60</sub>Me<sub>5</sub>), 51.45 (s, 5C, C<sub>60</sub>(C<sub>α</sub>)), 110.32 (d, 5C, <sup>2</sup>J<sub>P–C</sub> = 1.9 Hz, C<sub>60</sub>(C<sub>β</sub>)), 143.48 (s, 10C, C<sub>60</sub>), 144.18 (s, 10C, C<sub>60</sub>), 146.95 (s, 5C, C<sub>60</sub>), 148.01 (s, 10C, C<sub>60</sub>), 148.35 (s, 5C, C<sub>60</sub>), 153.61 (s, 10C, C<sub>60</sub>(C<sub>β</sub>)), 208.33 (d, <sup>2</sup>J<sub>P–C</sub> = 23.4 Hz, 2C, CO). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 37.82 (PEt<sub>3</sub>). APCI-MS (–): *m/z* 1058 (M<sup>+</sup>). Anal. Calcd for C<sub>73</sub>H<sub>33</sub>OPRu: C, 82.86; H, 3.14. Found: C, 82.54; H, 3.40.

**Preparation of Ru(η<sup>5</sup>-C<sub>60</sub>Me<sub>5</sub>)(CPh)(CO)<sub>2</sub> (12).** To a solution of **1** (50 mg, 0.051 mmol) in THF (8.0 mL) was added a solution of PhCCMgBr (1.5 equiv, 0.075 mmol) in THF (0.075

mL) at 25 °C. The reaction mixture was stirred for 10 min at 25 °C. After removal of the solvent, the resulting solid was extracted with toluene (40 mL). Purification by HPLC (Nacalai Tesque, Buckyprep, 250 mm, 7/3 toluene/2-propanol) afforded orange microcrystals of **12** (50 mg, 0.047 mmol, 93% yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 2.22 (s, 15H, C<sub>60</sub>Me<sub>5</sub>), 7.10 (t, 1H, *p*-Ph), 7.24 (s, 2H, *m*-Ph), 7.76 (s, 2H, *o*-Ph). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 30.67 (5C, C<sub>60</sub>Me<sub>5</sub>), 50.97 (5C, C<sub>60</sub>(C<sub>α</sub>)), 100.89 (1C, CPh), 112.61 (5C, C<sub>60</sub>(C<sub>β</sub>)), 113.05 (1C, Ru–CPh), 144.15 (10C, C<sub>60</sub>), 144.15 (10C, C<sub>60</sub>), 147.35 (5C, C<sub>60</sub>), 148.53 (10C, C<sub>60</sub>), 149.00 (5C, C<sub>60</sub>), 152.60 (10C, C<sub>60</sub>(C<sub>β</sub>)), 197.42 (2C, CO). IR (diamond probe): ν(CC)/cm<sup>-1</sup> 2132 (s), ν(CO)/cm<sup>-1</sup> 2038 (s), 1989 (s). APCI-MS (+): *m/z* 1054 (M<sup>+</sup>). Anal. Calcd for C<sub>75</sub>H<sub>20</sub>O<sub>2</sub>Ru: C, 85.45; H, 1.91. Found: C, 85.31; H, 2.20.

**Preparation of Ru(η<sup>5</sup>-C<sub>60</sub>Me<sub>5</sub>)(CC<sup>n</sup>Bu)(CO)<sub>2</sub> (13).** The procedure described for **12** was performed to obtain **13**. Complex **13** (19 mg, 0.018 mmol, 91% yield) was derived from **1** (20 mg, 0.020 mmol) and <sup>n</sup>BuCCMgBr (0.030 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 1.05 (t, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.67 (qt, 2H, CH<sub>2</sub>CH<sub>3</sub>), 1.75 (tt, 2H, CCCH<sub>2</sub>CH<sub>2</sub>), 2.23 (s, 15H, C<sub>60</sub>Me<sub>5</sub>), 2.66 (t, 2H, CCCH<sub>2</sub>), <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 14.05 (3C, CH<sub>2</sub>CH<sub>3</sub>), 22.10 (2C, CH<sub>2</sub>CH<sub>3</sub>), 22.57 (2C, CCCH<sub>2</sub>), 30.67 (5C, C<sub>60</sub>Me<sub>5</sub>), 33.00 (2C, CCCH<sub>2</sub>CH<sub>2</sub>), 50.97 (5C, C<sub>60</sub>(C<sub>α</sub>)), 99.51 (1C, C<sup>n</sup>Bu), 110.86 (1C, Ru–CC<sup>n</sup>Bu), 112.28 (5C, C<sub>60</sub>(C<sub>β</sub>)), 144.14 (10C, C<sub>60</sub>), 144.24 (10C, C<sub>60</sub>), 147.35 (5C, C<sub>60</sub>), 148.52 (10C, C<sub>60</sub>), 149.00 (5C, C<sub>60</sub>), 152.78 (10C, C<sub>60</sub>(C<sub>β</sub>)), 197.93 (2C, CO). IR (diamond probe): ν(CC)/cm<sup>-1</sup> 2163 (s), ν(CO)/cm<sup>-1</sup> 2041 (s), 1991 (s). APCI-MS (+): *m/z* 1034 (M<sup>+</sup>). Anal. Calcd for C<sub>73</sub>H<sub>24</sub>O<sub>2</sub>Ru: C, 84.78; H, 2.34. Found: C, 84.52; H, 2.60.

**Preparation of Ru(η<sup>5</sup>-C<sub>60</sub>Me<sub>5</sub>)(CCSiMe<sub>3</sub>)(CO)<sub>2</sub> (14).** The procedure described for **12** was performed to obtain **14**. Complex **14** (29 mg, 0.027 mmol, 92% yield) was derived from **1** (30 mg, 0.030 mmol) and Me<sub>3</sub>SiCCMgBr (0.045 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 0.47 (s, 9H, SiCH<sub>3</sub>), 2.20 (s, 15H, C<sub>60</sub>Me<sub>5</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 1.47 (q, <sup>1</sup>J<sub>C–H</sub> = 117.5 Hz, 3C, SiCH<sub>3</sub>), 30.71 (q, <sup>1</sup>J<sub>C–H</sub> = 131.0 Hz, 5C, C<sub>60</sub>Me<sub>5</sub>), 50.95 (5C, C<sub>60</sub>(C<sub>α</sub>)), 99.60 (s, 1C, CCSi), 112.53 (s, 5C, C<sub>60</sub>(C<sub>β</sub>)), 120.00 (s, 1C, Ru–CC), 144.14 (10C, C<sub>60</sub>), 144.16 (10C, C<sub>60</sub>), 147.34 (5C, C<sub>60</sub>), 148.52 (10C, C<sub>60</sub>), 149.00 (5C, C<sub>60</sub>), 152.61 (10C, C<sub>60</sub>(C<sub>β</sub>)), 197.35 (2C, CO). IR (diamond probe): ν(CC)/cm<sup>-1</sup> 2163 (s), ν(CO)/cm<sup>-1</sup> 2036 (s), 1999 (s). APCI-MS (+): *m/z* 1050 (M<sup>+</sup>). Anal. Calcd for C<sub>72</sub>H<sub>24</sub>O<sub>2</sub>RuSi: C, 82.34; H, 2.30. Found: C, 82.45; H, 2.51.

**Preparation of Ru(η<sup>5</sup>-C<sub>60</sub>Me<sub>5</sub>)(CCH)(CO)<sub>2</sub> (15).** The procedure described for **12** was performed to obtain **15**. Complex **15** (21 mg, 0.022 mmol, 87% yield) was derived from **1** (25 mg, 0.025 mmol) and HCCMgBr (0.038 mmol). <sup>1</sup>H NMR

(C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  1.42 (s, 1H, CCH), 2.20 (s, 15H, C<sub>60</sub>Me<sub>5</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  30.70 (q, <sup>1</sup>J<sub>C-H</sub> = 131.1 Hz, 5C, C<sub>60</sub>Me<sub>5</sub>), 50.94 (s, 5C, C<sub>60</sub>(C<sub>o</sub>)), 99.37 (d, <sup>1</sup>J<sub>C-H</sub> = 231.4 Hz, CCH), 112.38 (s, 5C, C<sub>60</sub>(C<sub>cp</sub>)), 113.23 (s, Ru-CCH), 144.13 (s, 10C, C<sub>60</sub>), 144.14 (s, 10C, C<sub>60</sub>), 147.34 (s, 5C, C<sub>60</sub>), 148.53 (s, 10C, C<sub>60</sub>), 148.98 (s, 5C, C<sub>60</sub>), 152.61 (s, 10C, C<sub>60</sub>(C<sub>β</sub>)), 197.42 (s, 2C, CO). IR (diamond probe):  $\nu$ (CO)/cm<sup>-1</sup> 2047 (s), 2003 (s). APCI-MS (-): *m/z* 978 (M<sup>-</sup>). Anal. Calcd for C<sub>69</sub>H<sub>16</sub>O<sub>2</sub>Ru: C, 84.74; H, 1.65. Found: C, 84.53; H, 1.69.

**Crystallographic Data Collection and Structure Determination of 1, 2, 4, 9, and 12.** Crystals of **1**, **2**, **4**, and **9** suitable for X-ray diffraction study were mounted on a MacScience DIP2030 imaging plate diffractometer for data collection using Mo K $\alpha$  (graphite monochromated,  $\lambda$  = 0.710 69 Å) radiation. Crystal structural analysis of **12** was performed by using a Rigaku RAXIS-RAPID imaging plate diffractometer for data collection using Mo K $\alpha$  (graphite monochromated,  $\lambda$  = 0.710 69 Å, fine focused) radiation. Crystal data and data statistics are summarized in Table 6.

The structure of the complexes **1**, **2**, **4**, **9**, and **12** were solved by direct methods (SHELXS-97)<sup>41</sup> and expanded using Fourier techniques (DIRDIF-94).<sup>42</sup> The positional parameters and thermal parameters of non-hydrogen atoms of **1**, **2**, **4**, **9**, and **12** were refined using a full-matrix least-squares method. Hydrogen atoms were placed at calculated positions (C-H = 0.95 Å) and kept fixed. All non-hydrogen atoms of **1**, **2**, **4**, and

**9** were anisotropically refined. The ruthenium atom, oxygen atoms, and carbon atoms of the phenylethynyl group and carbonyl group of **12** were anisotropically refined, while the carbon atoms in the C<sub>60</sub> skeleton of **12** were refined isotropically. 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  $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$  and  $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^4)]^{1/2}$ . Due to the Cl/CO disorder in **1**, the Ru-Cl, Ru-C(O), and C-O distances have less certainty than those of **2**, **4**, **9**, and **12**.

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

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**Supporting Information Available:** Lists of positional parameters, thermal displacement parameters, bond lengths, and bond angles for **1**, **2**, **4**, **9**, and **12**; these data are also available as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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