Intramolecular Allylation of a Ru-Cp* Methyl Group

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The salts $[Ru(Cp^*)(CH_3CN)(N,N)](PF_6)$, **6** (*N,N* = bipyridine, 4,4′-dimethylbipyridine, and phenanthroline), react with allyl carbonates to afford new complexes that contain tethered ligands derived from deprotonation of one Cp* methyl group. The new Ru tetramethyl Cp complexes contain a CH_2-$CHRCH{=}CH_2$ fragment (R = H or Ph), which coordinates to the metal via the double bond. The salts **6** isomerize the branched carbonate $PhCH(OCO_2Bu^t)CH{=}CH_2$ to the linear isomer.

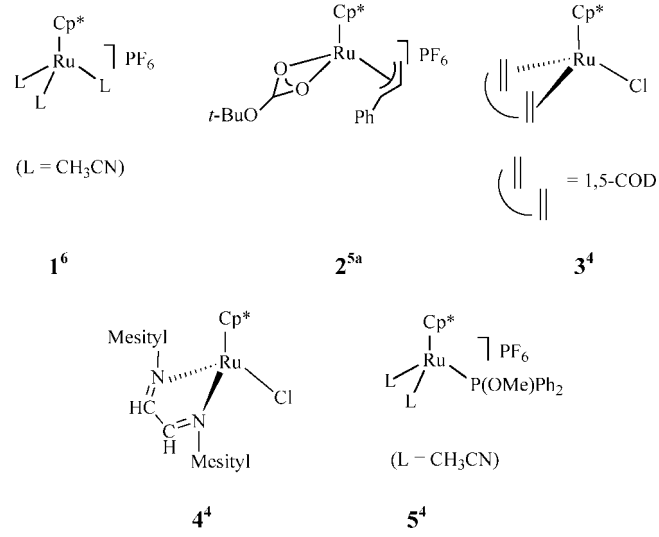
Introduction

An increasingly large number of ruthenium complexes are finding applications in homogeneous catalysis.[1–3] Among the most popular Ru derivatives are those containing Cp or Cp* ligands.[4] Although complexes of Ru(II) are still the most prevalent, there is an increasing interest in the use of Ru(IV) salts as starting materials for selected catalytic transformations.[5]

Apart from catalytic allylation with Pd and other transition metal catalysts, one finds a number of reports on Ru-catalyzed reactions[4–7] (see eq 1).

$$PhCH(X)\text{-}CH{=}CH_2 + Nu^- \xrightarrow{\text{Ru-catalyst}} Ph\text{-}CH(N)\text{-}CH{=}CH_2 \text{ and } Ph\text{-}CH{=}CH\text{-}CH_2Nu + X^- \quad (1)$$

Ruthenium allylation catalysts can be regioselective and afford high branched-to-linear ratios in the products.[4–6] A number of catalysts are known, and **1**−**5** represent typical examples. In some cases, for example, using **4** and **5**, the catalysis has been found to be relatively slow.[4] There is no immediately obvious reason for this, since oxidative addition of the branched compound $PhCH(X)CH{=}CH_2$, X = a suitable halogen or carbonate leaving group, starting from Trost's catalyst,[8] $[Ru(CH_3CN)_3(Cp^*)](PF_6)$, **1**, is complete within several minutes at room temperature and affords high yields of isolable Ru(IV) allyl complexes.[9] We show here that chelating nitrogen salts $[Ru(CH_3CN)(N,N)](PF_6)$, **6**, can (a) isomerize the branched allyl starting material and (b) produce new unexpected Ru(II) tethered complexes derived from allyl carbonates.



Results and Discussion

The chelating nitrogen complexes were prepared according to the literature.[4,7] These cationic complexes $[Ru(Cp^*)(CH_3CN)(N,N)](PF_6)$, **6**, which contain bipyridine and phenanthroline

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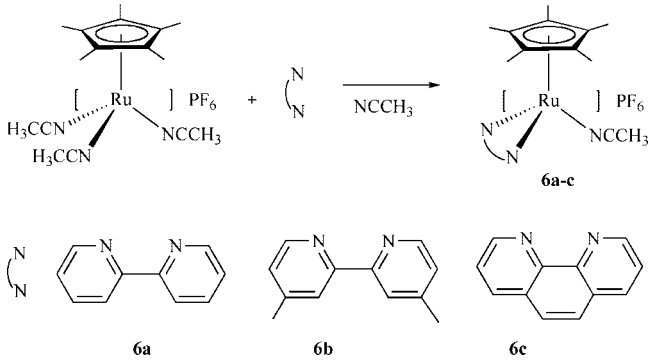
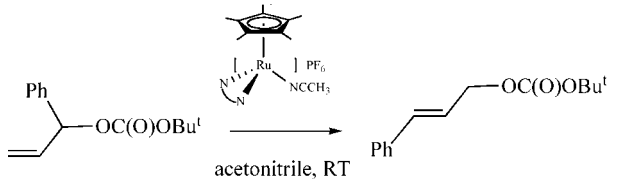
Scheme 1



ligands (see Scheme 1), were then allowed to react with 1 equiv of the branched carbonate $PhCH(OCO_2Bu^t)CH{=}CH_2$ in an NMR tube. To our surprise, we found that the branched

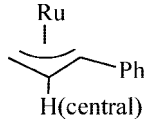


(2)

carbonate isomerizes in ca. 30 min to the linear carbonate, as indicated in eq 2.[10] Further, if one continues to monitor this solution at ambient temperature, salt **6a** requires 4 h to afford 20% of a new species (which we will show has structure **7**). Although salt **6b** manages the same 20% conversion in ca. 50 min, this is still a relatively slow reaction. If one starts from the linear carbonate, the chemistry is even slower. Using $PhCH{=}CHCH_2Cl$ as reagent, instead of the carbonate, one observes between 50% and 80% conversion to the known[7a] Ru(IV) allyl cations $[Ru(Cp^*)(N,N)(\eta^3\text{-}PhCHCHCH_2)]^+$, after ca. 20 min. While this reaction is faster, it does not go to completion, perhaps because the Cl^- set free reacts to afford a less active complex. Although not shown in Scheme 1, we have also prepared the biquinoline analogue of **6**; however, we find no reaction of this salt with either $PhCH{=}CHCH_2Cl$ or $PhCH{=}CHCH_2(OCO_2OBu^t)$ and presume that olefin complexation may be hindered.

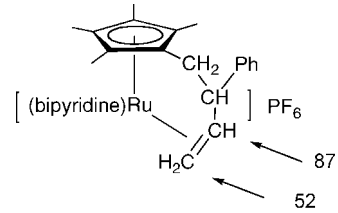
In an effort to accelerate an otherwise very slow oxidative addition step in the carbonate chemistry, 2 equiv of a carbonate were allowed to react with **6** at 333 K in acetonitrile solution. Rather than the expected Ru (IV) allyl salt, a new species, **7**, appeared; see Scheme 2.

Although the salts **7** could be prepared in good yield on a small preparative scale, the correct structures were not immediately obvious. On the basis of the absence of the relatively complicated (but typical) multiplet for the central allyl ^1H resonance (which often appears between 5 and 7 ppm[5,9,11]), it



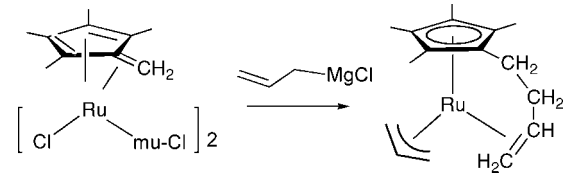
^1H(central) often appears between 5 and 7 ppm

was clear that **7** was not a routine Ru(IV) allyl salt. Both the ^1H and ^{13}C spectra revealed *four* nonequivalent Cp methyl groups, instead of the usual sharp singlet for the equivalent five methyl groups of the complexed Cp* ligand (see Figure 1). A series of two-dimensional proton and carbon correlation spectra allowed the assignment of six nonequivalent protons attached to two methine and two methylene carbons, all at relatively low frequency (in addition to the phenyl and nitrogen ligand signals). The complexed olefin ^{13}C data for **7a** are fairly typical[12–14] and reveal the CH_2 and CH-olefinic carbons at 52.0 and 87.0 ppm,



7a

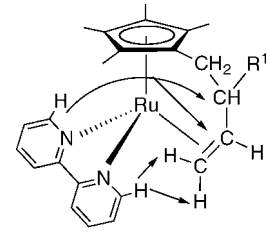
respectively. These results, combined with NOE, mass spectral, and microanalytical data, strongly support the structures indi-



(3)

cated.[15] Although Castro et al.[12] have reported a related structure using a dinuclear tetramethylfulvene as starting material (see eq 3), we believe this to be the first reported intramolecular allylation reaction of a Cp* methyl group.

The relative position of the coordinated double bond, approximately parallel to the Cp moiety, was determined via 2-D NOESY spectroscopy (see Figure 2). One finds selective cross-peaks from (a) one of the two nonequivalent *ortho* pyridine protons to the two CH_2 protons at the unsubstituted end of the



8

complexed double bond and (b) selective cross-peaks from the second *ortho* pyridine proton to the aliphatic and olefinic CH methine protons, as indicated by **8**. Further, each of the two

(10) The branched and linear carbonates have been prepared separately and their corresponding proton spectra are readily distinguishable. It is known that oxidative addition of the branched isomer can be faster than that for the linear isomer.

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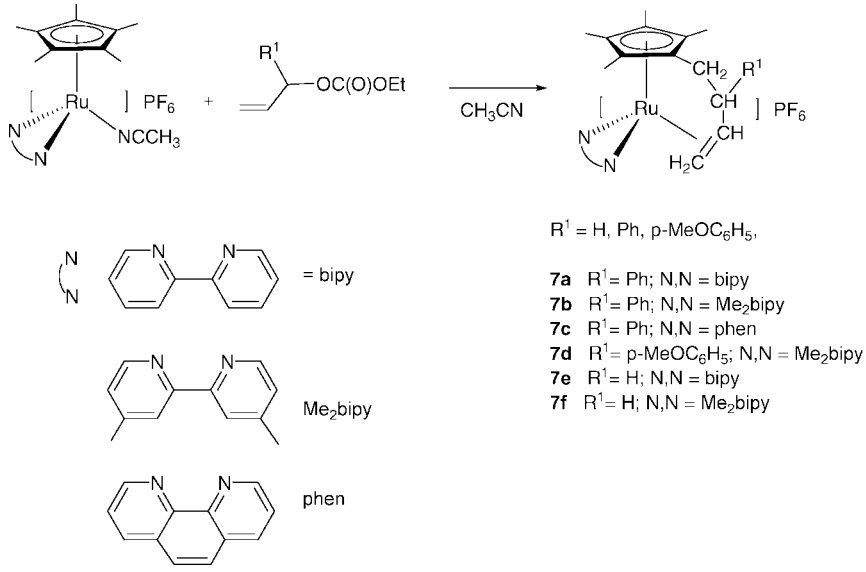
(15) We have also allowed **6b** to react with the branched naphthyl carbonate $C_{10}H_9CH(OCO_2Bu^t)CH{=}CH_2$ (substituted at the 1-naphthyl position). One observes ca 50% of the product of type **7**; however this could not be readily separated from a significant amount of side product.

Scheme 2



R^1 = H, Ph, p-$MeOC_6H_5$,

7a R^1= Ph; N,N = bipy
7b R^1= Ph; N,N = Me_2bipy
7c R^1= Ph; N,N = phen
7d R^1= p-$MeOC_6H_5$; N,N = Me_2bipy
7e R^1= H; N,N = bipy
7f R^1= H; N,N = Me_2bipy

ortho pyridine protons shows selective cross-peaks to the two proximate methyl groups of the (now) tetramethyl Cp ligand. The position of the olefin in structure **8** is in agreement with literature solid-state results for Ru(Cp-type) olefin complexes.[12–14]

A mechanistic rationalization for the appearance of the olefin complexes **7** is given in Scheme 3 On warming the sample, the oxidative addition takes place to afford a Ru(IV) allyl species. The base set free in this step (either the carbonate or the alkoxide formed when the carbonate decomposes) deprotonates one of the Cp* methyl groups, thereby generating an internal anionic carbon nucleophile. Attack of this carbon atom on the coordinated allyl moiety affords the observed Ru(II) product. One can consider this as Ru-based intramolecular allylic alkylation chemistry using allyl carbonates. The observation of the branched product is consistent with calculations[9a] that suggest an orbital-controlled product. While "tucked-in" Cp* complexes,[16–18] as well as a number of tethered Cp derivatives,[19–25] are well-known in the literature, this Ru-mediated intramolecular allylation is unprecedented.

Summarizing, at elevated temperatures the complexes **6** only transiently oxidatively add the allyl starting material as rapidly as, for example, **1**. In the absence of added nucleophile, the carbonate (or alkoxide) base, formed via the oxidative addition reaction (see Scheme 2), generates a carbon anion, which attacks the Ru(IV) allyl to form the new olefin complexes.

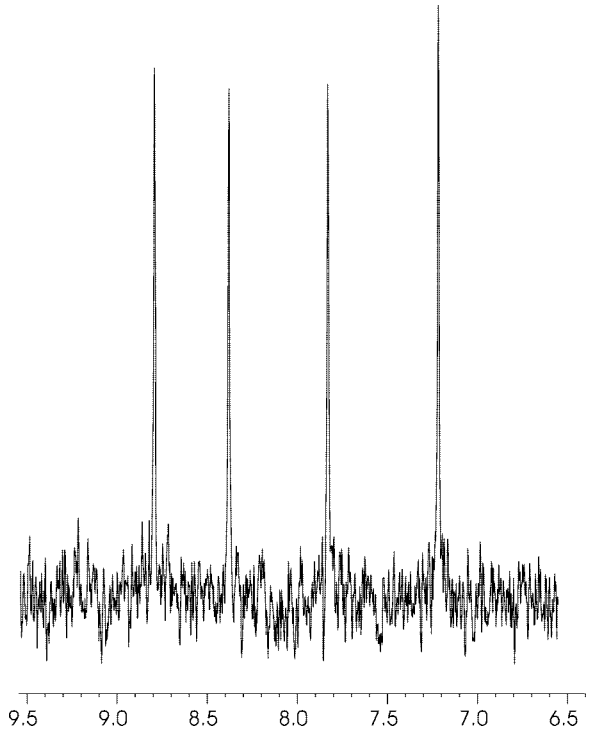


Figure 1. Section of the ^{13}C NMR spectrum of **7d** showing the four nonequivalent remaining methyl groups of the Cp moiety (500 MHz, CD_3CN).

Experimental Part

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. All solvents were distilled under nitrogen using standard drying agents. For the preparation of **7** we have used both the ethyl and *tert*-butyl carbonates. Both of these work equally well in terms of the isolated yield.

[Ru{1-(CH_2-CHPh-CH=CH_2)-2,3,4,5-tetramethylcyclopentadiene}(2,2′-dipyridyl)]PF_6, 7a. A solution of PhCH=CH-CH_2-OCO_2Et (0.0343 g, 0.166 mmol) in 2 mL of acetonitrile was added to a brown solution of **6a** (0.0481 g, 0.083 mmol) in 2 mL of acetonitrile. The reaction mixture was stirred for 16 h at 60 °C, and then the solvent was reduced under vacuum and ether was added to precipitate a brown solid. The solid was collected, washed three times with ether, and then dried under vacuum. Yield: 0.0499 g (92%). Anal. (%) Calcd for $C_{29}H_{31}N_2F_6PRu$: C 53.29, H 4.78, N 4.29. Found: C 53.44, H 4.88, N

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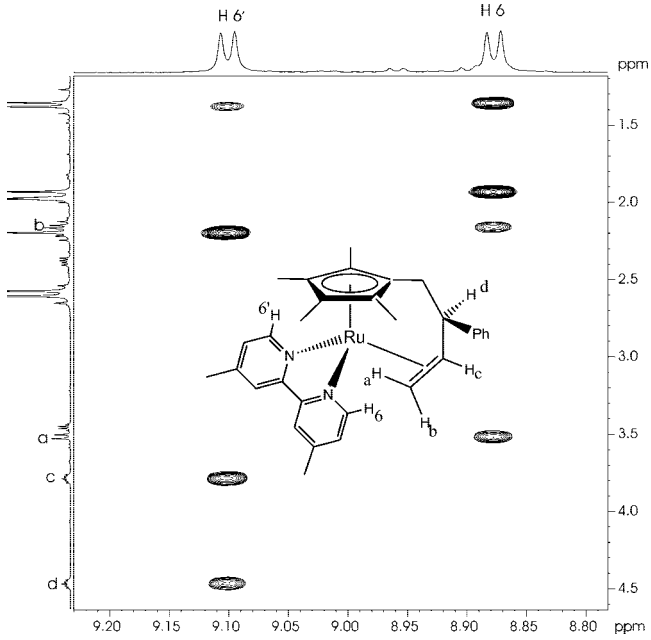
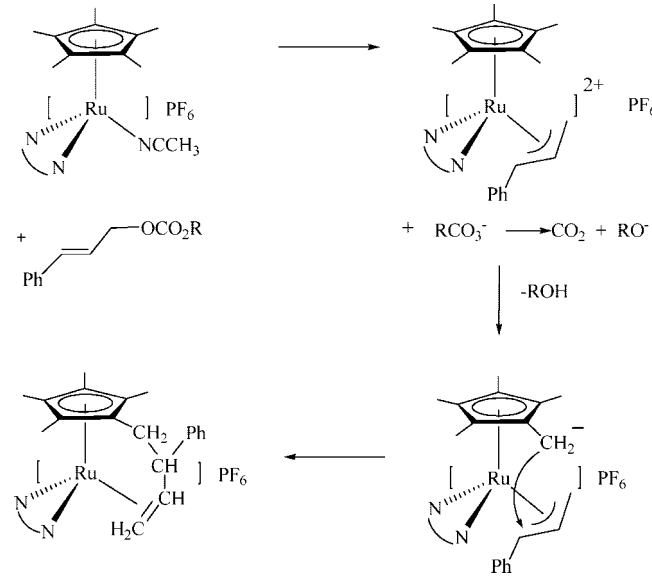


Figure 2. Section of the $^1H,^1H$ NOESY showing the correlations arising from the *ortho* 4,4′-dimethylbipyridine protons, $H_{6,6'}$. Each of these protons reveals four NOEs: two each to the proximate Cp methyl groups and (left column) two correlations from protons H_c and H_d and (right column) two from protons H_a and H_b (500 MHz, CD_3CN).

4.95. MS: *m/z* 509 [M^+]. ^1H NMR (500 MHz, CD_3CN) δ: 1.36 (s); 1.38 (s); 1.95 (s); 2.22 (s) (4 Cp* Me), 2.24; 2.40 (dd, J = 14.1 Hz, 7.7 Hz) (CH_2), 2.24; 3.56 (d, J = 3.56 Hz) (CH_2), 3.86 (m) (C*H*=CH_2), 4.49 (m) (C*H*Ph), 7.26 (Ph *para*), 7.36 (Ph *meta*), 7.52 (Ph *ortho*), 7.62; 7.69; 8.01; 8.09; 8.32; 8.35; 9.08; 9.32 (8 bipy protons). $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN) δ: 7.2; 7.8; 8.3; 8.7 (4 Cp* Me), 27.3 (CH_2), 52.0 (=CH_2), 55.8 (CHPh), 81.7 (*C*CH_3), 84.4 (*C*CH_3), 87.0 (*C*H=CH_2), 99.4 (*C*CH_3), 100.9 (*C*CH_3), 106.6 (*C*CH_3), 123.3, 123.5, 126.1, 126.4, 127.0 (Ph *para*), 127.5 (Ph *ortho*), 128.8 (Ph *meta*), 137.1, 137.9, 144.7 (Ph *ipso*), 153.8, 154.6.

[Ru{1-(CH_2-CHPh-CH=CH_2)-2,3,4,5-tetramethylcyclopentadiene}(4,4′-dimethyl-2,2′-dipyridyl)]PF_6, 7b. A solution of PhCH=CH-CH_2OCO_2Et (0.0307 g, 0.149 mmol) in 2 mL of acetonitrile was added to an orange solution of **6b** (0.0730 g, 0.120 mmol) in 2 mL of acetonitrile. The reaction mixture was stirred for 2.5 h at 60 °C, and then the solvent was reduced under vacuum and ether was added to precipitate a brown solid. The solid was collected, washed three times with ether, and then dried under vacuum. Yield: 0.0669 g. ^1H NMR of this brown solid showed that approximately 10% of the material was unreacted complex **6b**. The brown solid was dissolved in 2 mL of acetonitrile, and a further 0.0034 g (0.016 mmol) of PhCH=CH-CH_2CO_2Et in 2 mL of acetonitrile was added. The solution was stirred for 5 h at 60 °C, and then a brown solid was isolated as described above. Yield: 0.0584 g (71%). Anal. (%) Calcd for $C_{31}H_{35}N_2F_6PRu \cdot H_2O$: C 53.17, H 5.29, N 4.00. Found: C 53.22, H 5.26, N 4.65. MS: *m/z* 537 [M^+]. ^1H NMR (500 MHz, CD_3CN) δ: 1.35 (s); 1.38 (s); 1.93 (s); 2.20 (s) (4 Cp* Me), 2.22; 2.39 (dd, J = 14.4 Hz, 7.7 Hz) (CH_2), 2.14 (d, J = 8.2 Hz); 3.52 (d, J = 12.5 Hz) (=CH_2), 2.57 (s); 2.61 (s) (2 bipy Me), 3.79 (m) (C*H*=CH_2), 4.47 (m) (C*H*Ph), 7.25 (Ph *para*), 7.36 (Ph *meta*), 7.51 (Ph *ortho*), 7.45; 7.52; 8.17; 8.20; 8.88; 9.10 (6 bipy protons). $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN) δ: 7.2; 7.8; 8.4; 8.8 (4 Cp* Me), 20.4; 20.6 (2 bipy Me), 27.4 (CH_2), 51.5 (=CH_2), 55.8 (CHPh), 81.5 (*C*CH_3), 84.1 (*C*CH_3), 86.2 (*C*H=CH_2), 99.2 (*C*CH_3), 100.5 (*C*CH_3), 106.3 (*C*CH_3), 123.8, 124.0, 127.0 (Ph *para*), 127.5 (Ph *ortho*), 127.6, 128.8, 128.8 (Ph *meta*), 144.8 (Ph *ipso*), 149.6, 150.4, 153.0, 153.9 154.1, 152.2.

Scheme 3



[Ru{1-(CH_2-CHPh-CH=CH_2)-2,3,4,5-tetramethylcyclopentadiene}(1,10-phenanthroline)]PF_6, 7c. A solution of PhCH=CH-CH_2OCO_2Et (0.0396 g, 0.192 mmol) in 2 mL of acetonitrile was added to an orange solution of **6c** (0.0579 g, 0.096 mmol) in 2 mL of acetonitrile. The reaction mixture was stirred for 16 h at 60 °C, and then the solvent was reduced under vacuum and ether was added to precipitate an orange solid. The solid was collected, washed three times with ether, and then dried under vacuum. Yield: 0.0633 g (97%). Anal. (%) Calcd for $C_{31}H_{31}N_2F_6PRu$: C 54.95, H 4.61, N 4.13. Found: C 55.13, H 4.82, N 4.14. MS: *m/z* 533 [M^+]. ^1H NMR (500 MHz, CD_3CN) δ: 1.36 (s); 1.38 (s); 2.05 (s); 2.34 (s) (4 Cp* Me), 2.31 (m); 2.45 (dd, J = 14.4 Hz, 7.7 Hz) (CH_2), 2.19 (d, J = 8.1 Hz); 3.65 (d, J = 12.5 Hz) (=CH_2), 3.95 (m) (C*H*=CH_2), 4.59 (m) (C*H*Ph), 7.21 (Ph *para*), 7.34 (Ph *meta*), 7.52 (Ph *ortho*), 7.96; 8.04; 8.05; 8.12; 8.56; 8.64; 9.42; 9.63 (8 phenanthroline protons). $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN) δ: 7.4; 7.9; 8.4; 9.0 (4 Cp* Me), 27.5 (CH_2), 51.9 (=CH_2), 55.7 (CHPh), 81.2 (*C*CH_3), 83.9 (*C*CH_3), 86.9 (*C*H=CH_2), 99.8 (*C*CH_3), 100.8 (*C*CH_3), 125.3, 125.5, 127.0 (Ph *para*), 127.5 (Ph *ortho*), 127.6, 127.7, 128.8 (Ph *meta*), 130.7, 130.9, 135.8, 136.5, 146.0, 146.2, 144.7 (Ph *ipso*), 153.9, 154.9.

[Ru{1-(CH_2-CH(C_6H_4OMe)-CH=CH_2)-2,3,4,5-tetramethylcyclopentadiene}(4,4′-dimethyl-2,2′-dipyridyl)]PF_6, 7d. A solution of 4-MeO-C_6H_4-CH($OCO_2{}^tBu$)-CH=CH_2 (0.0502 g, 0.190 mmol) in 2 mL of acetonitrile was added to an orange solution of **6b** (0.0576 g, 0.095 mmol) in 2 mL of acetonitrile. The reaction mixture was stirred for 16 h at 60 °C, and then the solvent was reduced under vacuum and ether was added to precipitate an ochre solid. The solid was collected, washed three times with ether, and dried under vacuum. Yield: 0.0644 (95%). Anal. (%) Calcd for $C_{32}H_{37}N_2OF_6PRu$: C 54.01, H 5.24, N 3.94. Found: C 53.61, H 5.32, N 4.09. MS: *m/z* 567 [M^+]. ^1H NMR (500 MHz, CD_3CN) δ: 1.35 (s); 1.37 (s); 1.93 (s); 2.18 (s) (4 Cp* Me), 2.17 (d, J = 8.1 Hz); 2.35 (dd, J = 14.5 Hz, 7.7 Hz) (CH_2), 2.13; 3.50 (d, J = 12.1 Hz) (=CH_2), 2.57 (s); 2.61 (s) (2 bipy Me), 3.79 (C*H*=CH_2), 3.79 (s) (OMe), 4.41 (m) (C*H*Ph), 6.90 (Ph *ortho*), 7.42 (Ph *meta*), 7.44; 7.52; 8.17; 8.19; 8.87; 9.09; (6 bipy protons). $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN) δ: 7.2; 7.8; 8.4; 8.8 (4 Cp* Me), 20.4; 20.6 (2 bipy Me), 27.5 (CH_2), 51.4 (=CH_2), 55.1 (OMe), 55.3 (CHPh), 81.3 (*C*CH_3), 84.1 (*C*CH_3), 86.9 (*C*H=CH_2), 99.1 (*C*CH_3), 100.3 (*C*CH_3), 106.3 (*C*CH_3), 114.1 (Ph *ortho*), 123.8, 124.0, 127.0, 127.5, 128.5 (Ph *meta*), 137.0 (Ph *ipso*), 149.5, 150.3, 153.0, 153.9, 154.1, 154.2, 158.9 (Ph *para*).

[Ru{1-(CH_2-CH_2-CH═CH_2)-2,3,4,5-tetramethylcyclopentadiene}(2,2′-dipyridyl)]PF_6, 7e. A solution of CH_2═CH-CH_2O-$CO_2{}^tBu$ (0.0275 g, 0.173 mmol) in 2 mL of acetonitrile was added to a solution of **6a** (0.0503 g, 0.087 mmol) in 2 mL of acetonitrile. The reaction mixture was stirred for 16 h at 60 °C, the solvent was removed under vacuum, and the residue was washed several times with ether. The resulting red-brown solid was then dried under vacuum. Yield: 0.0427 g (85%). MS: *m*/*z* 433 [M^+]. ^{1}H NMR (500 MHz, CD_3CN) δ: 1.32 (s); 1.34 (s); 1.92 (s); 2.12 (s) (4 Cp* Me), 2.05 (d, J = 8.6 Hz); 3.43 (d, J = 12.5 Hz) (═CH_2), 2.10; 2.12 (CH_2), 2.72; 3.05 (m) (CH_2), 3.87 (m) (C*H*═CH_2), 7.60, 7.68, 8.00, 8.07, 8.31, 8.33, 9.06, 9.20 (8 bipy protons). ^{13}C{^{1}H} NMR (125 MHz, CD_3CN) δ: 7.3, 7.7, 8.2, 8.7 (4 Cp* Me), 21.2 (CH_2), 39.3 (CH_2), 54.7 (═CH_2), 80.7 (*C*CH_3), 83.0 (*C*CH_3), 85.5 (*C*H═CH_2), 98.0 (*C*CH_3), 104.4 (*C*CH_3), 109.2 (*C*CH_3), 123.2, 123.4, 126.1, 126.4, 137.0, 137.8, 153.5, 154.4, 154.5, 154.5.

[Ru{1-(CH_2-CH_2-CH═CH_2)-2,3,4,5-tetramethylcyclopentadiene}(4,4′-dimethyl-2,2′-dipyridyl)]PF_6, 7f. A solution of CH_2═CH-$CH_2OCO_2{}^tBu$ (0.0137 g, 0.087 mmol) in 2 mL of acetonitrile was added to a solution of **6b** (0.0263 g, 0.043 mmol) in 1.5 mL of acetonitrile. The reaction mixture was stirred for 16 h at 60 °C, and then the solvent was reduced under vacuum and ether was added to precipitate an ochre solid. The solid was collected, washed three times with ether, and then dried under vacuum. Yield: 0.0137 g (52%). Anal. (%) Calcd for $C_{25}H_{31}N_2F_6PRu.H_2O$: C 48.11, H 5.29, N 4.49. Found: C 48.39, H 5.43, N 5.26. MS: *m*/*z* 461 [M^+]. ^{1}H NMR (400 MHz, CD_2Cl_2,) δ: 1.35 (s); 1.37 (s); 1.90 (s); 2.11 (s) (4 Cp* Me), 2.00; 3.39 (d, J = 12.1 Hz) (CH_2), 2.08 (d, J = 8.1 Hz); 2.12 (CH_2), 2.61 (s); 2.65 (s) (2 bipy Me), 2.77 (m); 3.05 (m) (CH_2), 3.80 (m) (C*H*═CH_2), 7.40, 7.46, 8.05, 8.08, 8.82, 8.93 (6 bipy protons). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2) δ: 7.9; 8.4; 8.9, 9.4 (4 Cp* Me), 21.2; 21.3 (2 bipy Me), 21.4 (CH_2), 39.5 (CH_2), 54.8 (═CH_2), 80.4 (*C*CH_3), 82.6 (*C*CH_3), 84.9 (*C*H═CH_2), 98.1 (*C*CH_3), 104.3 (*C*CH_3), 108.7 (*C*CH_3), 123.7, 124.0, 127.2, 127.5, 149.6, 150.4, 152.1, 153.3, 153.9, 154.0.

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