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The [(η^5-C_5Me_5)(2,2′-bipyridine)Ru]$^-$ Anion and Its Use in the Synthesis of Alkyl, Gallyl, and Stannyl Complexes of Ruthenium

Benjamin V. Mork, Ashley McMillan, Holming Yuen, and T. Don Tilley*

Department of Chemistry, University of California, Berkeley, Berkeley, California 94720-1460

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Reduction of Cp*(bipy)RuCl (Cp* = η^5-C_5Me_5, bipy = 2,2′-bipyridine) with an excess of KC_8 in THF generated the dark purple-red anionic ruthenium complex K[Cp*Ru(bipy)] (**2a**). The analogous lithium salt Li[Cp*Ru(bipy)] (**2b**) was generated in situ by reaction of Cp*(bipy)RuCl with 2 equiv of lithium naphthalenide. Complex **2a** was structurally characterized as the crown adduct [K(dibenzo-18-crown-6)][Cp*Ru(bipy)] (**2a**·dibenzo-18-crown-6). Dark purple crystals of this complex were obtained from a THF/pentane solution, and its structure was determined by X-ray diffraction. The solid state structure features two ion pairs of **2a** in its asymmetric unit. In a reaction with MeI, compound **2a** was converted to the methyl complex Cp*(bipy)RuMe (**3**). Complex **2a** reacted with Me_3SnCl to produce the ruthenium stannyl complex Cp*(bipy)Ru$SnMe_3$ (**4**). Reaction of **2a** with Trip$GaCl_2$(THF) in THF gave the ruthenium gallyl derivative Cp*(bipy)Ru(GaClTrip) (**5**).

Introduction

Transition metal oxo, carbene, and imido complexes have been studied extensively, and examples of these compounds have been found to mediate transformations of organic compounds including the oxidation,[1] cyclopropanation,[2] and aziridination of olefins.[3] However, metal complexes that feature double bonds to *other* p-block elements are significantly less common. For example, compounds of the type $L_nM{=}ER$ (E = B, Al, Ga, In; R = alkyl or aryl) are rare, and very little is known about their chemical properties.[4] It is therefore of interest to investigate new complexes that possess metal−main group element double bonds of these types.

One procedure for generating a metal−element double bond involves abstraction of an anionic leaving group (such as a halide or a triflate) from a precursor that possesses a metal−element single bond (eq 1). This route has some generality, as it has been applied in syntheses of cationic silylene,[5] phosphinidine,[6] and borylene[4c] complexes.

$$L_nM{-}E(X)R_n \xrightarrow{-\,X^{\ominus}} \left[L_nM{=}ER_n\right]^{\oplus} \tag{1}$$

M = transition metal
E = Si, Ge, Sn; n = 2
E = B, Al, Ga, P; n = 1
X = Cl, Br, I, OTf
R = alkyl or aryl

To apply the method in eq 1 to new complexes with unsaturated metal−element bonds, the singly bonded precursor complexes must first be synthesized. A common strategy for the generation of metal−element single bonds employs a coordinatively unsaturated transition metal anion in reactions with main group halides (eq 2). Such reactions typically require ethereal organic solvents and proceed with the elimination of alkali metal halide salts such as LiCl or KBr. This method has been used in the formation of a variety of metal−element bonds to give (for example) alkyl,[7] boryl,[8] gallyl,[9] silyl,[10] germyl,[11] stannyl,[12] and phosphide[6] complexes.

$$M'[L_nM] + X_2ER_n \xrightarrow{-M'X} L_nM{-}E(X)R_n \tag{2}$$

M′ = Li, Na, or K
M = transition metal
E = Si, Ge, Sn; n = 2
E = B, Al, Ga, P; n = 1
X = Cl, Br, I, OTf
R = alkyl or aryl

Many of the known transition metal anions employ ancillary carbonyl ligands such as $Cp'Fe(CO)_2^-$,[7,13] $Cp'Ru(CO)_2^-$,[14] $Cp'Mo(CO)_3^-$,[15] $Cp'W(CO)_3^-$,[16] and

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[1] (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals,* 2nd ed.; Wiley-Interscience: New York, 1994. (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

[2] (a) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919. (b) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. (c) Waterman, R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2003**, *125*, 13350.

[3] (a) Li, Z.; Quan, R. W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5889. (b) Müller, P.; Fruit, C. *Chem. Rev.* **2003**, *103*, 2905. (c) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073.

[4] For examples of complexes of the type $L_nM(ER)$ (E = B, Ga, In), see: (a) Su, J.; Li, X.-W.; Crittendon, R. C.; Campana, C. F.; Robinson, G. H. *Organometallics* **1997**, *16*, 4511. (b) Braunschweig, H.; Colling, M.; Kollann, K.; Merz, K.; Radacki, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 4198. (c) Coombs, D. L.; Aldrige, S.; Jones, C.; Willock, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 6356. (d) Haubrich, S. T.; Power, P. P. *J. Am. Chem. Soc.* **1998**, *120*, 2202.

[5] Grumbine, S. K.; Mitchell, G. P.; Straus, D. A.; Tilley, T. D., Rheingold, A. L. *Organometallics* **1998**, *17*, 5607, and references therein.

[6] (a) Nakazawa, H.; Buhro, W. E.; Bertrand, G.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 3431. (b) Sterenberg, B. T.; Udachin, K. A.; Carty, A. J. *Organometallics* **2001**, *20*, 2659.

[7] See, for example: (a) Piper, T. S.; Wilkinson, G, *J. Inorg. Nucl. Chem.* **1956**, *3*, 104. (b) Green, M. L. H.; Nagy, P. L. I. *J. Organomet. Chem.* **1963** *1*, 58.

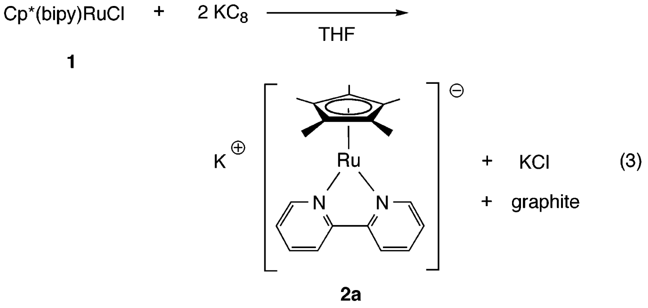
[8] Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. J. *Chem. Rev.* **1998**, *98*, 2685.

10.1021/om030695n CCC: $27.50

$Mn(CO)_5^-$ [17] ($Cp' = \eta^5$-C_5R_5, R = H or alkyl). However, such starting materials lead only to carbonyl complexes and metal centers that are not particularly electron rich. To some extent, it appears that electron-rich, donating metal fragments are effective in stabilizing ligands that are formally electron deficient (e.g., borylene[4] and silylene[5] complexes). The purpose of this study is to synthesize a new anionic transition metal complex that does not feature carbonyl ligands and to examine reactions of this anion with main group element halides. Herein we report the synthesis, structure, and main group derivatives of a new anionic ruthenium complex supported by Cp* and bipy ligands (Cp* = C_5Me_5, bipy = 2,2′-bipyridine). These complexes are related to the 4,4′,5,5′-terametyl-2,2′-biphosphinine (tmbp) complexes Cp*(tmbp)RuNa(dme)$_2$ and Cp*(tmbp)RuSnMe$_3$ recently reported by Mathey and co-workers.[18]

Results and Discussion

Generation of Cp*Ru(bipy)$^-$. The chelating ligand 2,2′-bipyridine was envisioned as a chemically robust supporting ligand and as a potential substitute for the two carbonyl ligands in the known anion Cp*Ru(CO)$_2^-$.[14] The reduction of Cp*(bipy)RuCl[19] (**1**) with an excess (3 equiv) of KC_8 in THF at −78 °C resulted in a red-purple solution of the potassium salt K[Cp*Ru(bipy)] (**2a**, eq 3). Compound **2a** is soluble in THF and slightly soluble in diethyl ether, but is insoluble in alkanes and arenes. The solution of **2a** was separated from graphite and excess KC_8 by cannula filtration; however, it was not possible to separate **2a** from the byproduct KCl. This compound is highly air- and moisture-sensitive, and it decomposed to an unidentified mixture of products when purification was attempted by crystallization from THF/toluene solvent mixtures. A ^{1}H NMR spectrum of freshly prepared **2a** in THF-d_8 was obtained, and the spectrum exhibits only resonances for the Cp*Ru(bipy)$^-$ fragment. Two of the bipyridyl proton resonances in this species are shifted upfield to δ 5.87 and 5.57. The decomposition of **2a** during simple manipulations such as crystallization attempts from arene/THF and alkane/THF mixtures prevented further characterization of bulk samples. The identity of **2a** was therefore confirmed by its reactions with electrophiles and by an X-ray crystal structure (vide infra). The potassium salt **2a** is best generated and used in situ.



The lithium analogue of **2a** was synthesized as an alternative source of the Cp*Ru(bipy)$^-$ anion. Reduction of Cp*(bipy)RuCl with 2 equiv of Li[$C_{10}H_8$] (lithium naphthalenide) in THF at −78 °C resulted in a color change from purple to red-purple. This reaction is complete in less than 1 h after warming to room temperature and produces the lithium salt Li[Cp*Ru(bipy)] (**2b**). A purple, benzene-soluble solid was obtained by removal of the volatile materials from a THF solution of **2b**. The ^{1}H NMR spectrum of this product in benzene-d_6 exhibits resonances for the Cp*(bipy)Ru fragment as well as for 2 equiv of THF. The 2 equiv of THF are likely bound to Li and could not be removed under reduced pressure. The spectrum of the crude product also revealed the presence of residual naphthalene, which could not be removed by sublimation due to the thermal decomposition of **2b**. Attempts to isolate **2b** by crystallization from benzene and toluene solutions were unsuccessful, as only complex mixtures of decomposition products were obtained. Like the potassium salt, compound **2b** is best generated and used in situ.

Structural Characterization of [K(dibenzo-18-crown-6)][Cp*Ru(bipy)]. Attempts to crystallize **2a** or **2b** from concentrated solutions were unsuccessful due to the high solubilities of the ruthenium ion pairs in THF. The thermal instability of these complexes may also complicate their isolation. Layering pentane upon THF solutions of the salts resulted in precipitation of dark purple products; however, the crystalline solids obtained were not suitable for X-ray diffraction studies. To obtain single crystals of an analogue of complex **2a**, it was crystallized in the presence of the cyclic ether dibenzo-18-crown-6. One equivalent of the crown ether was added to a THF solution of **2a**, and pentane was layered onto the red-purple solution. After 16 h the solvent layers had diffused together and X-ray quality crystals of **2a·(**dibenzo-18-crown-6) had formed.

X-ray diffraction data were collected on a dark purple crystal of **2a**·(dibenzo-18-crown-6), and an ORTEP diagram of the structure is shown in Figure 1. Details of the crystallographic experiment are included in the Supporting Information. The asymmetric unit of the crystalline structure contains two ion pairs and three molecules of THF. In addition, there is an intramolecular interaction of the π-electrons from a (crown)phenylene ring with the potassium center K1. The three K−C contacts (indicated by dashed lines in Figure 1) are longer than 3.1 Å and represent a commonly observed

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(9) (a) He, X.; Bartlett, R. A.; Power, P. P. *Organometallics* **1994**, *13*, 548. (b) Cowley, A. H.; Decken, A.; Olazábal, C. A.; Norman, N. C. *Inorg. Chem.* **1994**, *33*, 3435. (c) Yamaguchi, T.; Ueno, K.; Ogino, H. *Organometallics* **2001**, *20*, 501.

(10) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.

(11) (a) Pannell, K. H.; Sharma, S. *Organometallics* **1991**, *10*, 1655. (b) Lee, K. A.; Gladysz, J. A. *Phosphorus Sulfur Silicon Relat. Elem.* **1994**, *87*, 113. (c) Koe, J. R.; Tobita, H.; Suzuki, T.; Ogino, H. *Organometallics* **1992**, *11*, 150.

(12) (a) Holt, M. S.; Wilson, W. L.; Nelson, J. H. *Chem. Rev.* **1989**, *89*, 11. (b) Allen, J. M.; Brennessel, W. W.; Buss, C. E.; Ellis, J. E.; Minyaev, M. E.; Pink, M.; Warnock, G. F.; Winzenburg, M. L.; Young, V. G., Jr. *Inorg. Chem.* **2001**, *40*, 5279.

(13) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287.

(14) (a) Wnuk, T. A.; Angelici, R. J. *Inorg. Chem.* **1977**, *16*, 1173. (b) Waltz, K. M.; Muhoro, C. N.; Hartwig, J. F. *Organometallics* **1999**, *18*, 3393.

(15) Hayter, R. G. *Inorg. Chem.* **1963**, *2*, 1031.

(16) (a) Tripathi, S. C.; Srivastava, S. C.; Pathak, D. N. *J. Organomet. Chem.* **1976**, *107*, 315. (b) Mahmoud, K. A.; Rest, A. J.; Alt, H. G.; Eichner, M. E.; Jansen, B. M. *J. Chem. Soc., Dalton Trans.* **1984**, 175.

(17) Closson, R. D.; Kozikowski, J.; Coffield, T. H. *J. Org. Chem.* **1957**, *22*, 598.

(18) Rosa, P.; Ricard, L.; Mathey, F.; Le Floch, P. *Organometallics* **2000**, *19*, 5247.

(19) Koelle, U.; Kossakowski, J. *J. Organomet. Chem.* **1989**, *362*, 383.

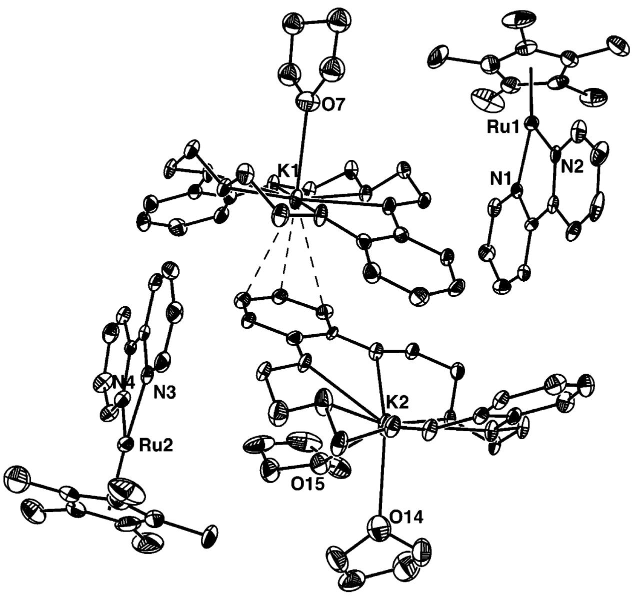
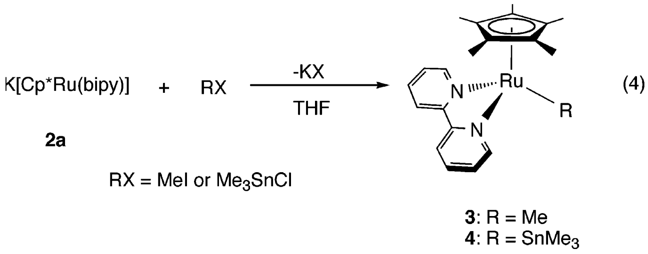


Figure 1. ORTEP diagram of [K(dibenzo-18-crown-6)]-[Cp*Ru(bipy)](THF)$_{1.5}$.

interaction between an alkali metal and an aromatic ring.[20] Most importantly, the structure contains two unsupported Cp*Ru(bipy)$^-$ anions. These anions are approximately planar at ruthenium with respect to the bipy ligand and the centroid of the Cp* ligand. This structure provides support for the identification of **2a** and **2b** as the potassium and lithium salts of the Cp*Ru(bipy)$^-$ anion, respectively.

Reactions with Main Group Element Halides. To test the utility of this anion in syntheses of compounds with ruthenium−element bonds, reactions of main group halides with potassium salt **2a** were examined. Reactions of **2a** with the silane reagents Me_3SiCl, Ph_2SiHCl, and Ph_2SiCl_2 did not lead to the formation of new ruthenium silyl complexes. These reactions were attempted at −78 °C in THF, and each one resulted in a brown-black solution from which no products could be isolated or identified. Examination of ^{1}H NMR spectra for the crude products in these reactions indicated that complex mixtures of products formed.

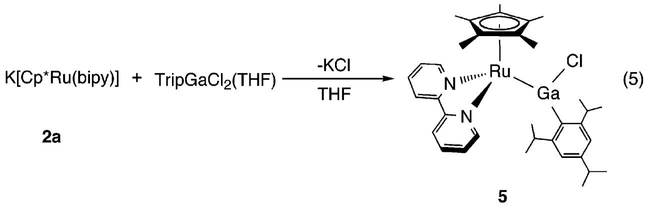
Reaction of **2a** with MeI at −78 °C resulted in a color change of the solution from red-purple to dark yellow as the methyl derivative Cp*(bipy)RuMe (**3**, eq 4) formed. The methyl complex was isolated in 24% yield after it was recrystallized twice from toluene/pentane to remove unidentified impurities. This transformation shows that compound **2a** is indeed a nucleophilic source of the Cp*Ru(bipy)$^-$ anion.



A new ruthenium stannyl complex was synthesized by reaction of **2a** with a stannyl chloride. Addition of Me_3SnCl to a THF solution of **2a** at −78 °C did not result in an immediate change in the appearance of the mixture. As the stirred mixture was allowed to warm to room temperature, the color changed to dark green and the stannyl complex Cp*(bipy)$RuSnMe_3$ (**4**, eq 4) was produced. Complex **4** was isolated in 42% yield as green crystals by recrystallization from a 3:1 pentane/toluene mixture.

It was of interest to explore the reactions of the new anionic ruthenium complex with halide reagents of the group 13 elements. Neither **2a** nor **2b** was found to react cleanly with $MesBCl_2$[21] (Mes = 2,4,6-trimethylphenyl), and isolation of ruthenium-containing product(s) by crystallization was unsuccessful. In the reaction of **2b** with $MesBCl_2$, the only product isolated (in 5% yield) and identified was the known reductive coupling product Mes(Cl)BB(Cl)Mes.[22] This result indicates that the ruthenium anion may participate in electron-transfer chemistry, with Cp*Ru(bipy)$^-$ acting as a reductant. This undesired process likely competes with the bond-forming salt metathesis reactions and apparently complicates the reactions of this anion.

Despite the redox chemistry observed in the reaction with $MesBCl_2$, a clean reaction was observed between **2a** and $TripGaCl_2$(THF) (Trip = 2,4,6-triisopropylphenyl).[23] The gallium reagent was added to a THF solution of **2a** at −78 °C, and the stirred mixture was allowed to warm to room temperature. The resulting green solution contained the product gallyl complex Cp*(bipy)-RuGaClTrip (**5**, eq 5), which was isolated as a dark green microcrystalline solid in 26% yield from a concentrated 4:1 toluene/pentane solution.



An abstraction of the chloride anion in **5** was attempted. Reaction of **5** with 1 equiv of $Li(OEt_2)_3B(C_6F_5)_4$ in fluorobenzene resulted in an immediate color change to dark brown. An attempt to crystallize any product(s) formed in this reaction by layering pentane onto the fluorobenzene solution was unsuccessful. After 18 h, a dark-colored solid had precipitated. The material was not suitable for single-crystal X-ray diffraction studies, and a ^{1}H NMR spectrum of the isolated material indicated that a complex mixture of products had formed.

Concluding Remarks

This work has shown that the anion Cp*Ru(bipy)$^-$ can be generated in situ as its lithium or potassium salt. Characterization of a dibenzo-18-crown-6 adduct of potassium salt **2b** by X-ray crystallography verified the identity of the anion and indicated that these com-

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(20) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303.

(21) Jäkle, F.; Manners, I. *Organometallics* **1999**, *18*, 2628.

(22) Hommer, H.; Nöth, H.; Knizek, J.; Ponikwar, W.; Schwenk-Kircher, H. *Eur. J. Inorg. Chem.* **1998**, 1519.

(23) Petrie, M. A.; Power, P. P.; Dias, H. V. R.; Ruhlandt-Senge, K.; Waggoner, K. M.; Wehmschulte, R. J. *Organometallics* **1993**, *12*, 1086.

pounds are stable for short periods of time in solution and in the solid state.

Reactions of **2a** and **2b** with main group halide reagents were successful in generating new examples of ruthenium alkyl, stannyl, and gallyl compounds. Failures of the attempted reactions of **2a** and **2b** with chlorosilanes and $MesBCl_2$ appear to be due to redox chemistry involving oxidation of the ruthenium anion. The ruthenium-containing products from this process have not been identified.

The Cp*Ru(bipy)$^-$ anion is a useful precursor to complexes of the type Cp*(bipy)RuER$_n$. Future work will focus on syntheses of other element derivatives of the Cp*(bipy)Ru fragment and on abstraction of leaving group anions from compounds of the type Cp*(bipy)RuE(X)R$_n$. It is of particular importance to determine the most efficient conditions and substrates for formation of new ruthenium−element bonds using **2a** and **2b**.

Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen using standard Schlenk techniques or in a drybox. Pentane was distilled from sodium/benzophenone. To remove olefin impurities, pentane was pretreated with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3M H_2SO_4, $NaHCO_3$, and then anhydrous $MgSO_4$. Benzene-d_6 was rigorously degassed, then dried over activated 4 Å molecular sieves. THF was distilled from sodium/benzophenone, and THF-d_8 was vacuum transferred from sodium/benzophenone. Other chemicals were obtained from commercial suppliers and used as received. Cp*(bipy)RuCl,[19] TripGaCl$_2$(THF),[23] and KC$_8$[24] were prepared according to published procedures. Elemental analyses were performed by the Microanalytical Laboratory in the College of Chemistry at the University of California, Berkeley. FT-infrared spectra were recorded as KBr pellets on a Mattson FTIR 3000 instrument.

NMR Measurements. Routine ^{1}H, ^{13}C{^{1}H}, and ^{119}Sn{^{1}H} NMR spectra were recorded at 298 K on a Bruker DRX-500 instrument equipped with a 5 mm broad band probe and operating at 500.13 MHz (^{1}H), 125.77 MHz (^{13}C), and 186.5 MHz (^{119}Sn). Chemical shifts are reported in ppm downfield from internal SiMe$_4$ (^{1}H, ^{13}C) and SnMe$_4$ (^{119}Sn); coupling constants are given in Hz. Bruker XWINNMR software (ver. 2.1) was used for all data processing.

X-ray Crystallography. Measurements were made on a Bruker SMART CCD area detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Data were integrated by the program SAINT and analyzed for agreement using XPREP. Empirical absorption corrections were made using SADABS. Structures were solved by direct methods and expanded using Fourier techniques. All calculations were performed using the SHELX-TL crystallographic software package. Details of data collection and refinement are in the supporting information for this paper.

Generation of K[Cp*Ru(bipy)] (2a). A Schlenk flask was charged with 0.300 g (0.701 mmol) of Cp*(bipy)RuCl, 0.284 g (2.10 mmol) of KC$_8$, and a stirbar in the drybox. The flask was cooled to −78 °C with a dry ice/acetone bath, and 30 mL of THF (cooled to −78 °C) was added via cannula. The cold bath was removed after addition of solvent, and the dark purple mixture was allowed to warm to room temperature with stirring. After 1 h, and the dark purple-red solution was separated from excess reducing agent and graphite by cannula filtration. This solution contains the product K[Cp*Ru(bipy)] (**2a**), which could not be separated from the byproduct KCl. Removal of THF under reduced pressure for 6 h resulted in 0.254 g (72% yield) of the **2a**/KCl mixture, which is insoluble in benzene. The product is extremely air and moisture sensitive; therefore it is best generated and used in situ. ^{1}H NMR (THF-d_8): δ 8.74 (m, 2 H, *bipy*), 7.07 (m, 2 H, *bipy*), 5.87 (m, 2 H, *bipy*), 5.57 (m, 2 H, *bipy*), 1.82 (s, 15 H, C$_5$*Me*$_5$).

Generation of Li[Cp*Ru(bipy)] (2b). A Schlenk tube was charged with 0.122 g (0.958 mmol) of naphthalene, 10 mg (1.4 mmol) of Li^0 wire, and 15 mL of THF. Stirring this mixture for 12 h afforded a dark green solution of lithium naphthalenide. The naphthalenide solution was then added dropwise via filter cannula to a second flask (cooled to 0 °C) containing 0.200 g (0.467 mmol) of Cp*(bipy)RuCl in 10 mL of THF. The dark red-purple mixture was stirred for 1 h and then evaporated to dryness under reduced pressure. Drying the purple solid in vacuo for 6 h resulted in isolation of crude **2b** in approximately 80% yield (0.291 g), and this product was contaminated with LiCl and 1.5 equiv of naphthalene. Attempts to remove naphthalene by sublimation at 0.005 Torr (at room temperature for 12 h or 50 °C for 2 h) resulted in the decomposition of **2b**. Compound **2b** is soluble in benzene and is pure by ^{1}H NMR spectroscopy, with the exception of residual naphthalene. All attempts to crystallize the product from benzene or toluene resulted in decomposition of **2b** to unidentified mixtures of products; therefore **2b** is best generated and used in situ. ^{1}H NMR (benzene-d_6): δ 9.04 (m, 2 H, *bipy*), 7.6 (m, naphthalene), 7.31 (m, 2 H, *bipy*), 7.24 (m, naphthalene), 6.24 (m, 2 H, *bipy*), 6.02 (m, 2 H, *bipy*), 3.14 (m br, 8 H, *THF*), 2.05 (s, 15 H, C$_5$*Me*$_5$), 1.21 (m br, 8 H, *THF*).

Cp*(bipy)RuMe (3). Potassium salt **2a** was generated in situ from 0.300 g (0.701 mmol) of Cp*(bipy)RuCl and 0.284 g of KC$_8$ as described above. The dark purple solution was filtered away from residual KC$_8$ and graphite, and then it was cooled to −78 °C in a dry ice/acetone bath. Excess MeI (62 μL, 1.5 mmol) was added to the solution via syringe, and stirring was continued at low temperature for 30 min. The cold bath was removed, and the mixture was allowed to stir for an additional 4 h at ambient temperature. The volatile materials were removed from the resultant dark yellow solution under reduced pressure to give a black solid. The solid was redissolved in 30 mL of pentane and filtered into another Schlenk flask via cannula. This solution was concentrated under reduced pressure to approximately 5 mL and placed in the freezer for 14 h at −30 °C to give 0.069 g of **3** as a black microcrystalline solid (24% yield). ^{1}H NMR (benzene-d_6): δ 8.84 (d, 2 H, *bipy*, $J_{HH} = 6$ Hz), 7.45 (d, 2 H, *bipy*, $J_{HH} = 8$ Hz), 6.81 (m, 2 H, *bipy*), 6.62 (m, 2 H, *bipy*), 1.72 (s, 15 H, C$_5$*Me*$_5$), −0.51 (s, 3 H, Ru*Me*). ^{13}C{^{1}H} NMR (benzene-d_6): δ 151.9, 150.5, 124.8, 122.1, 120.4 (s, *bipy*), 86.7 (s, *C*$_5$Me$_5$), 9.6 (s, C$_5$*Me*$_5$), 6.7 (s, Ru*Me*). IR (KBr, cm^{-1}): 2968 m, 2897 s, 2850 s, 2775 w, 1585 w, 1533 w, 1520 w, 1450 s, 1402 m, 1375 m, 1330 m, 1298 w, 1261 w, 1241 m, 1147 m, 1064 w, 1024 w, 1005 s, 979 m, 850 w, 744 s, 707 w, 627 w. Anal. Calcd for $C_{21}H_{26}N_2Ru$: C, 61.89; H, 6.43; N, 6.87. Found: C, 61.51; H, 6.51; N, 6.62.

Cp*(bipy)RuSnMe$_3$ (4). A Schlenk flask was charged with 0.150 g (0.351 mmol) of Cp*(bipy)RuCl, 0.142 g (1.05 mmol) of KC$_8$, and a stirbar. The flask was cooled to −78 °C in a dry ice/acetone bath, and 10 mL of THF was added to the solids to give a purple-red solution. A solution of Me$_3$SnCl (0.070 g, 0.351 mmol) in 5 mL of THF was added dropwise to the ruthenium anion via cannula. The cold bath was removed and the color slowly changed to dark green. The mixture was stirred for an additional 4 h at ambient temperature. Solvent was removed from the product solution under reduced pressure to give a dark green solid. This solid was dissolved in 20 mL of pentane/toluene (3:1) and filtered into another Schlenk flask. The solution was concentrated to 4 mL under reduced pressure and stored in the freezer overnight at −30 °C to give 0.082 g of dark green crystals of **3** (42% yield). ^{1}H NMR (benzene-d_6): δ 8.99 (d, 2 H, *bipy*, $J_{HH} = 6$ Hz), 7.39 (d, 2 H, *bipy*, $J_{HH} = 8$

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(24) Schwindt, M. A.; Lejon, T.; Hegedus, L. S. *Organometallics* **1990**, *9*, 2814.

Hz), 6.78 (m, 2 H, *bipy*), 6.44 (m, 2 H, *bipy*), 1.75 (s, 15 H, C_5Me_5, $J_{HSn} = 6$ Hz), −0.16 (s, 3 H, $SnMe_3$, $^2J_{HSn} = 33$ Hz). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 151.2, 151.0, 125.4, 121.7, 120.4 (*bipy*), 84.6 (s, C_5Me_5), 10.4 (s, C_5Me_5), −10.1 (s, $SnMe_3$). $^{119}Sn\{^1H\}$ NMR (benzene-d_6): δ −87.7 (s). IR (KBr, cm^{-1}) 2956 s, 2891 s, 2854 s, 2715 w, 1587 w, 1525 w, 1483 w, 1454 s, 1406 m, 1373 w, 1324 w, 1242 s, 1153 m, 1026 w, 1005 s, 943 w, 864 w, 746 s br, 656 w, 484 s, 470 m. Anal. Calcd for $C_{23}H_{32}N_2RuSn$: C, 49.66; H, 5.80; N, 4.95. Found: C, 49.52; H, 5.62; N, 5.18.

Cp*(bipy)RuGa(Cl)Trip (5). A Schlenk flask was charged with 0.150 g (0.351 mmol) of Cp*(bipy)RuCl, 0.142 g (1.05 mmol) of KC_8, and a stirbar. The flask was cooled to −78 °C in a dry ice/acetone bath, and 10 mL of THF was added to the solids to give a purple-red mixture containing **1a**. This stirred mixture was allowed to warm to room temperature for 1 h. The solution was then separated from graphite and excess KC_8 by cannula filtration. After cooling the solution of the ruthenium anion to −78 °C, TripGaCl$_2$(THF) (0.146 g, 0.351 mmol) in 5 mL of pentane was added slowly via cannula. The cold bath was removed, and the mixture was allowed to warm to room temperature with stirring. The volatile materials were removed from the product under reduced pressure, and then **5** was redissolved in 30 mL of toluene. This solution was filtered to remove insoluble materials and concentrated under reduced pressure to 4 mL. To this solution was added 1 mL of pentane. Storing the solution in a freezer at −30 °C for 14 h resulted in precipitation of 0.064 g of **5** as a black-green microcrystalline solid (26% yield). ^1H NMR (benzene-d_6): δ 8.96 (m, 2 H, *bipy*), 7.43 (m, 2 H, *bipy*), 7.06 (s, 2 H, Ar-*H*), 6.86 (m, 2 H, *bipy*), 6.47 (m, 2 H, *bipy*), 2.85 (m, 2 H, 2 ArC*H*Me$_2$), 2.84 (m, 1 H, ArC*H*Me$_2$), 1.69 (s, 15 H, C_5Me_5), 1.37 (d, 12 H, 2 ArCH*Me$_2$*, $J_{HH} = 11$ Hz), 1.26 (d, 6 H, *Ar*CH*Me$_2$*, $J_{HH} = 12$ Hz). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 154.5, 153.7, 152.9, 151.5, 148.4, 122.1, 121.7, 119.9, 119.5 (s, *Ar* and *bipy*), 85.7 (s, C_5Me_5), 36.8 (s, 2 Ar*C*HMe$_2$), 34.9 (s, Ar*C*HMe$_2$), 25.1 (s, 2 ArCH*Me$_2$*), 24.5 (s, ArCH*Me$_2$*), 10.5 (s, C_5Me_5). IR (KBr, cm^{-1}): 2955 s, 2899 s, 2864 s, 1591 w, 1551 w, 1458 s, 1412 m, 1379 m, 1359 w, 1324 w, 1251 s, 1153 w, 1027 w, 1010 s, 871 w, 754 s, 657 w. Anal. Calcd for $C_{35}H_{46}ClGaN_2Ru$: C, 59.97; H, 6.61; N, 4.00. Found: C, 59.73; H, 6.68; N, 3.90.

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Supporting Information Available: Crystallographic data and tables for the structure of **2a·**(dibenzo-18-crown-6). This material is available free of charge via the Internet at http://pubs.acs.org.

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