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Photolytic Reactivity of Organometallic Chromium Bipyridine **Complexes**

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Supporting Information

ABSTRACT: Known stable [Cr(bpy)₂(Ph)₂](BPh₄) complexes undergo reductive elimination of biphenyl with visible-light photolysis using household incandescent or compact fluorescent light bulbs. A series of $[Cr(R-bpy)_2(Ar)_2](X)$ complexes (R = H or)CMe₃; Ar = Ph, C₆H₄-CMe₃, or C₆H₄-OMe; X = I, BPh₄, or PF₆) were prepared, and the effect of varying the bipyridine and aryl ligands on the UV-visible spectra and electrochemistry of the chromium(III) complexes was investigated. Photolysis of a mixture of two different bis(aryl) complexes gave only the homocoupled biaryl products by ¹H NMR and gas chromatography/mass spectrometry analysis. The initial product of photoinduced reductive elimination of $[Cr(bpy)_2(Ar)_2](PF_6)$ was trapped with bipyridine to generate $[Cr(bpy)_3](PF_6)$ and with benzoyl peroxide to form $[Cr(bpy)_2(O_2CPh)_2]$ - (PF_6) . The latter chromium(III) bis(benzoate) complex was also synthesized by the addition of bipyridine and PhCO₂H to Cp₂Cr, followed by air oxidation. The neutral Cr(bpy)(S₂CNMe₂)Ph₂ complex also generated biphenyl upon visible-light photolysis.



While the treatment of $Cr(Bu-bpy)(dpm)Cl_2$ [dpm = (OC'Bu)₂CH] with AgO₂CPh gave trans-Cr(Bu-bpy)(dpm)(O₂CPh)₂, reaction of the dichloro precursor with PhMgCl produced anionic $[Cr({}^{t}Bu-bpy)Ph_{3}]^{-}$ with $[Mg(dpm)(THF)_{4}]^{+}$ as the countercation, with both complexes characterized by single-crystal X-ray diffraction. Protonolysis of Cr(bpy)Ph₃(THF) with 8hydroxyquinoline produced Cr(bpy)(quin)Ph₂, which generated biphenyl under visible-light photolysis, and the initial product of reductive elimination was trapped by bipyridine or benzoyl peroxide. A related $Cr(bpy)(quin)_2$ complex was synthesized by protonolysis of $Cr(bpy)[N(SiMe_3)_2]_2$ and characterized by single-crystal X-ray diffraction.

INTRODUCTION

Open-shell organometallic complexes of first-row transition metals have experienced increasing use in catalytic C-C bondforming reactions.¹ Catalysis research involving photolysis, radicals, and redox-active ligands has been a particularly active area.² In these reactions, mechanistic studies using well-defined complexes have provided the critical insights required to design improved catalysts.³ For several first-row metals, bipyridine (bpy) ligands have been shown to be especially effective.⁴ The connection between the ancillary ligand redox activity and catalyst performance remains the focus of ongoing research.⁵

Recently, the groups of Knochel and Zeng have reported cross-coupling reactions of arylmagnesium halides and $C(sp^2)$ -X bonds (X = OMe, Cl, H) catalyzed by chromium dichloride $(CrCl_2)$.⁶ While chromium-catalyzed C–C bond-forming reactions are underdeveloped relative to iron, cobalt, or nickel, the stoichiometric reactions of chromium and aryl Grignard reagents have a long and rich history.⁸ The homocoupling of PhMgBr to biphenyl using chromium trichloride (CrCl₃) was first reported over a century ago.9 Although Hein isolated unusual organochromium complexes from these reactions, their nature remained poorly understood until Zeiss and coworkers isolated CrPh₃(THF)₃,¹⁰ and showed that tetrahy-

drofuran (THF) ligand dissociation preceded reductive elimination to form chromium(I) η^6 -arene complexes. By using bpy to prevent ligand dissociation, Zeiss and co-workers prepared unusually stable cationic chromium(III) bis(phenyl) compounds.¹¹ As shown in Scheme 1, neutral complex 1 with two unpaired electrons was initially generated from CrCl₂, with

Scheme 1. Zeiss Synthesis of Air- and Water-Stable Chromium(III) Bis(aryl) Complexes



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Scheme 2. (a) Electron Transfer from Cr^{II} to bpy and (b) Sequential Reduction of bpy Ligands in [Cr(bpy)₃]³⁺



Table 1. UV–Visible Absorbance and Electrochemical Data for $[Cr(R-bpy)_2(C_6H_4-R)_2][BPh_4]$

	complex	R-bpy	C ₆ H ₄ -R	$\lambda_{\rm max}^{a}/{\rm nm}$	$\varepsilon^a/\mathrm{M}^{-1}~\mathrm{cm}^{-1}$	$E_{1/2}^{+/0}$ /V	$E_{1/2}^{0/-b}/V$
	1(BPh ₄)	bpy	C ₆ H ₅	373	2750	-1.56	-2.07
	1a(BPh ₄)	^t Bu-bpy	C ₆ H ₅	369	2970	-1.69	-2.24
	$2(BPh_4)$	bpy	C ₆ H ₄ - ^t Bu	385	3060	-1.60	-2.14
	2a(BPh ₄)	^t Bu-bpy	C ₆ H ₄ - ^t Bu	382	3570	-1.71	-2.30
aT			[C]] ±/0] m][pp]	

^aIn acetonitrile. ^bPotentials reported versus $[Cp_2Fe]^{+/0}$. In THF at room temperature with 0.1 M $[NBu_4][PF_6]$.

subsequent air oxidation in aqueous methanol containing potassium iodide, resulting in an octahedral chromium(III) cationic complex 1(I) with three unpaired electrons.^{11d,e}

Octahedral S = 1 bpy complexes related to 1 have been shown to possess anionic bpy-ligand-based radicals antiferromagnetically coupled to $Cr^{III} d^3$ rather than the low-spin $Cr^{II} d^4$ structure they were originally assigned.¹² Such complexes can be prepared directly from well-defined chromium(II) complexes,¹³ such as Theopold and Wieghardt's recent reinvestigation of Herzog's reaction of an anhydrous chromium(II) acetate dimer and bpy (Scheme 2A).¹⁴ Wieghardt has also demonstrated that the reduction of $[Cr(bpy)_3]^{3+}$ leads to sequential occupation of the bpy π -antibonding orbitals, while the central metal remains Cr^{III} (Scheme 2B; reduction potentials referenced to $[Cp_2Fe]^{+/0}$.¹⁵ The reduced chromium(III) compounds with bpy-ligand-based radicals typically have strong absorbances in the 500-700 nm region of their UV-visible spectra.¹³ The inter-ring C(py)-C(py)bond length determined by single-crystal X-ray diffraction has been used to assign the oxidation level of bpy ligands in reduced chromium complexes.¹⁶

Studies of well-defined organochromium compounds have led to improved C–C bond-forming catalysts,¹⁷ especially for ethylene polymerization¹⁸ as well as ethylene trimerization and tetramerization.¹⁹ The unusual stability of the chromium(III) bis(aryl) complexes in Scheme 1 made them attractive as bpystabilized models for potential intermediates in CrCl₂-catalyzed reactions involving aryl Grignard reagents. In this paper, we report our investigation of known and new chromium bipyridine bis(phenyl) complexes, including their unexpected reductive elimination induced by visible light. Understanding the mechanism of the reactivity of metal complexes with ligandcentered radicals is a necessary step for the rational design of ancillary ligands for catalytic C–C bond formation.

SYNTHESIS OF CATIONIC CHROMIUM(III) BIS(ARYL) COMPLEXES

Complex 1(I) was prepared following the procedure of Sneeden and Zeiss (Scheme 1).^{11e} The use of NaBPh₄ or KPF₆ instead of KI during the air-oxidation step resulted in the corresponding 1(BPh₄) or 1(PF₆) salts, respectively. Replacing PhMgCl with the corresponding 4-^tBu-C₆H₄ or 4-OMe-C₆H₄ reagents generated [Cr(bpy)₂(C₆H₄-R)₂]⁺ (2⁺, R = ^tBu; 3⁺ R = OMe). For the C₆H₅ and C₆H₄-^tBu complexes, corresponding cationic compounds with 4,4'-di-*tert*-butylbipyridine (^tBu-bpy) were also prepared, 1a⁺ and 2a⁺, respectively.

The effects of introducing tert-butyl substituents on the electrochemistry and UV-visible spectra of the parent cationic complex 1^+ are shown in Table 1. The Cr-C₆H₄-^tBu complexes have λ_{max} values at lower energy compared to the corresponding Cr-C₆H₅ compounds. Replacing the bpy ligands with 4,4'-^tBu-bpy results in a smaller shift in λ_{max} to higher energy. In cyclic voltammetry, reversible single-electron reductions for all of the bis(aryl) compounds are observed at more negative potential than the corresponding $[Cr(bpy)_3]^{3+}$ values shown in Scheme 2B.²⁰ This is consistent with both the decreased positive total charge on the monocationic organometallic complexes and the presence of two strongly σ -donating anionic phenyl ligands. Replacing the phenyl ligands with C_6H_4 -^tBu leads to a slight shift to even more negative reduction potentials. A larger negative reduction potential change is observed when bpy is replaced with ^tBu-bpy. This larger effect is consistent with the proposed electronic structures of the reduced species, where the added electrons singly occupy the π antibonding orbitals of the ^tBu-bpy ligands.

PHOTOLYTIC REACTIVITY

The photochemistry of octahedral chromium(III) compounds has been extensively explored since the 1960s.²¹ Recent photochemical research on $[Cr(bpy)_3]^{3+}$ and related phenanthroline and terpyridine derivatives have exploited the reactivity



Figure 1. UV-visible spectra of $[Cr(bpy)_2Ph_2][BPh_4]$ (3.3 × 10⁻⁴ M in THF) before photolysis (red), after 1 h of photolysis (purple), and after air exposure of a photolyzed solution (yellow).

Scheme 3. Proposed Mechanism of the Photoinduced Reductive Elimination of Biphenyl



differences of these first-row transition-metal complexes compared to the widely used ruthenium(II) and iridium(III) catalysts.²² Although the $[Cr(bpy)_2Ar_2]^+$ complexes originally prepared by Müller and Zeiss are remarkably stable with respect to air, water, and reductive elimination,¹¹ the stabilizing bpy ligands also open up a new, previously unrecognized C-C bond-forming mechanism, via visible-light photolysis. As shown in Figure 1, a 3.3×10^{-4} M THF solution of $1(BPh_4)$ under nitrogen turns dark purple when photolyzed with a household 23 W compact fluorescent light bulb at 10 cm for 1 h. The distinctive bands in the 500-700 nm region characteristic of a bpy-based radical disappear when the photolyzed solution is exposed to air. The air-exposed solution also has a marked decrease in absorbance at ${\sim}375$ nm, the $\lambda_{\rm max}$ value of the chromium(III) bis(phenyl) starting material. Exhaustive visiblelight photolysis of 2(I) with $1,3,5-C_6H_3(OMe)_3$ as an internal standard generated 94% 4,4'-bis(tert-butyl)biphenyl by ¹H NMR.

The proposed mechanism for the photolysis process is shown in Scheme 3. The presumed initial product of the photoinduced reductive elimination of biphenyl would be $[Cr(bpy)_2]^+$, which is expected to decompose in the absence of trapping reagents. The UV–visible spectra of the photolyzed solutions matches that of $[Cr(bpy)_3]^+$ (Scheme 2b).²³ Support for this mechanism was obtained by monitoring the UV–visible spectra of $[Cr(bpy)_2Ph_2]^+$ during photolysis. The rate of growth of the strong visible absorbances was markedly increased in the presence of excess added bpy. In the absence of additional bpy, the growth was slower and showed an initial induction period, consistent with the initial decomposition of the $[Cr(bpy)_2]^+$ photoproduct being required to generate free byy in solution. Finally, no strong absorbance in the 500–700 nm region was observed during the photolysis of $[Cr-(bpy)_2Ph_2]^+$ in the presence of excess ZnCl₂, presumably because of favorable Zn(bpy)Cl₂ formation rendering bpy unavailable for chromium binding (see the Supporting Information). Note that these UV–visible monitoring results are *not* consistent with the standard mechanism for reductive elimination from octahedral chromium(III) bis(aryl) complexes, which requires the initial formation of a coordinatively unsaturated intermediate, ^{8,19a-f} e.g., by photoinduced dissociation of the bpy ligand²⁴ or by ZnCl₂-mediated removal of bpy.²⁵

Photolysis of $[Cr(bpy)_2(C_6H_4^{t}Bu)_2][BPh_4]$ was performed using various long-pass filters to establish which wavelength of light was responsible for inducing reductive elimination. As shown in Figure 2, the use of a filter with a cut-on wavelength of 475 nm, indicated by the vertical yellow line, resulted in no change in the UV–visible spectra after 85 min of photolysis. In contrast, 60 min of photolysis with 435 nm (blue) or 395 nm (red) filters resulted in the spectra of $[Cr(bpy)_3]^+$, with increased intensity observed for the 395 nm long-pass filter.

Further mechanistic information was provided by the crossover experiment shown in Scheme 4. After a 1:1 mixture of 2(I) and 3(I) was photolyzed overnight in THF with 1,3,5-tris(isopropyl)benzene as the internal standard, ¹H NMR



Figure 2. UV–visible of $[Cr(bpy)_2(C_6H_4^{+}Bu)_2][BPh_4]$ (3.3 × 10⁻⁴ M in THF) after photolysis with long-pass filters with cut-on wavelengths of 395 nm (red), 435 nm (blue), and 475 nm (yellow).

Scheme 4. Crossover Photolysis Experiment



Scheme 5. Trapping the Chromium Product of Reductive Elimination with Benzoyl Peroxide



analysis of the products after workup showed >95% yield of the two homocoupled biaryl products only. The identity of the products was confirmed by repeating the experiment and analyzing the products by gas chromatography/mass spectrometry (GC/MS). The absence of a mixed biaryl product is consistent with the concerted reductive elimination from the initial photoexcited complex.²⁶ The absence of *tert*-butylbenzene and anisole from both experiments is notably inconsistent with the generation of aryl radicals, which would be expected to rapidly abstract a H atom from the THF solvent.

As shown in Scheme 5, benzoyl peroxide was used to trap the $[Cr(bpy)_2]^+$ product of photoinduced reductive elimination. While no reaction between $[Cr(bpy)_2Ph_2](PF_6)$ and $(PhCO_2)_2$ was observed in the dark by UV–visible, photolysis of $1(PF_6)$ and benzoyl peroxide resulted in a red solution of $[Cr-(bpy)_2(O_2CPh)_2](PF_6)$. If the electronic structure of $[Cr-(bpy)_2]^+$ is presumed to be high-spin Cr^{II} antiferromagnetically coupled to a ligand-based bpy radical anion, ^{16b} oxidative addition of the weak O–O bond of benzoyl peroxide would involve single electrons from both the Cr center and ligand-based radical.²⁷ This two-electron chemistry is in contrast to the single-electron oxidative addition typically mediated by the Cr^{II}/Cr^{III} redox couple.

The chromium(III) bis(benzoate) complex $4(PF_6)$ was independently synthesized, as shown in Scheme 6. Following

Scheme 6. Independent Synthesis of Chromium(III) Bis(benzoate)



the analogous synthesis of bis(acetate) from chromium(II) shown in Scheme 2a,¹⁴ 4(PF₆) was prepared by the addition of bpy and benzoic acid at room temperature, followed by air oxidation with NH₄PF₆ in aqueous methanol. Cotton and coworkers have previously demonstrated the protonolysis of chromocene with benzoic acid and substituted derivatives.²⁸ In this case, protonolysis of the Cr $-C_5H_5$ bond may be accelerated by the initial formation of Cr(bpy)(η^5 -Cp)(η^1 -Cp).¹³

NEUTRAL BIPYRIDINE BIS(ARYL) COMPLEXES

In 1977, West reported that the neutral dithiocarbamate bipyridine complex was also anomalously stable with respect to air and water, unlike the analogous complexes with two monodentate pyridine ligands.²⁹ As shown in Scheme 7, the

Scheme 7. West Synthesis of a Neutral Chromium(III) Bis(aryl) Complex



sequential treatment of $CrCl_2$ with bpy and tetramethylthiuram disulfide produces the olive-green $CrCl_2$, which can be converted to the red bis(phenyl) complex with PhMgBr. Photolysis of the neutral dithiocarbamate bis(phenyl) complex does generate biphenyl, although the observed yield was lower than that for the cationic bis(bipyridine) complexes. On the basis of this promising initial result, alternative bidentate, monoanionic ligands were investigated to replace the dithiocarbamate ligand, which is not readily modified near the metal center and generally leads to complexes with low solubility.

In order to obtain a neutral dichloride precursor with improved solubility, the known³⁰ dipivaloylmethane (dpm) complex $Cr(dpm)Cl_2(THF)_2$ was reacted with 'Bu-bpy. As shown in Scheme 8, the dichloride was treated with AgO₂CPh to give the bis(benzoate) complex 5. In contrast, West's dithiocarbamate dichloride did not react cleanly with silver benzoate under the same conditions, possible because of competing abstraction of the soft S_2CNMe_2 ligand with the silver reagent. Single-crystal X-ray diffraction of 5 showed that the complex had trans-disposed benzoate ligands (Figure 3).

Scheme 8. Reactions of Cr(^tBu-bpy)(dpm)Cl₂



Figure 3. Thermal ellipsoid diagram (50%) of 5. All H atoms have been removed for clarity.

While the donor atoms formed a fairly regular octahedral coordination environment at chromium(III), distortion of the dpm ligand out of the coordination plane was attributed to intermolecular interactions in the unit cell. The inter-ring C(py)-C(py) distance of 1.495(3) Å in 5 is consistent with a neutral bpy ligand.¹⁶

However, the reaction of the dichloride with PhMgCl did not give the expected neutral bis(aryl) complex (Scheme 8). The Xray crystal structure of the product 6 is shown in Figure 4. The anionic chromium tris(phenyl) complex was square-pyramidal, and while it retained the ^tBu-bpy ligand, the dpm ligand was incorporated in the $Mg(dpm)(THF)_4$ countercation. Like related neutral and anionic five-coordinate chromium(III) tris(phenyl) complexes,^{19e} 6 is evidently stable with respect to the reductive elimination of biphenyl under ambient conditions despite being coordinatively unsaturated. While β diketonate substitution from Cr(acac)₃ has occasionally been used to prepare chromium(III) organometallic species,³¹ this was not the expected product. The measured magnetic moment of 2.95(9) $\mu_{\rm B}$ corresponds to two unpaired electrons, which is consistent with either a low-spin $Cr^{II} d^4$ center or $Cr^{III} d^3$ antiferromagnetically coupled to a ligand-based ^tBu-bpy radical anion. The inter-ring C(py)-C(py) distances in the ^tBu-bpy ligands of the two independent Cr anions in the unit cell are 1.427(2) and 1.428(2) Å, and the Cr-N bond lengths are relatively short [between 2.078(2) and 2.086(2) Å], consistent



Figure 4. Thermal ellipsoid diagram (50%) of one of the two crystallographically independent cation and anion pairs of 6. All H atoms have been removed for clarity.

with a bpy radical anion bound to Cr^{III} .¹⁶ Also as expected for a square-pyramidal chromium(III) complex, the Cr-C(ispo) bond lengths for the axial phenyl ligands are shorter [2.037(2) and 2.044(2) Å] than those for the phenyl ligands that are trans to the bpy N-donor atoms, which are 2.085(2), 2.089(2), 2.087(2), and 2.100(2) Å.

Gibson and co-workers used protonolysis reactions of $Cr(C_6H_4Me)Cl_2(THF)_3$ with salicylaldimines in toluene to generate chromium(III) precatalysts for screening ligand effects in ethylene polymerization reactions.³² Previously synthesized by the reactions of thermally sensitive $CrPh_3(THF)_3$ with bpy,^{11a} $Cr(bpy)Ph_3(THF)$ was an attractive potential protonolysis precursor to neutral chromium(III) bipyridine bis(aryl) complexes. As shown in Scheme 9, the reaction of known³³ $Cr(bpy)Cl_3(THF)$ with PhMgCl led to precipitation of the red $Cr(bpy)Ph_3(THF)$ product from a THF solution.^{18c} The treatment of $Cr(bpy)Ph_3(THF)$ with 8-hydroxyquinoline





(quin) gives the neutral bis(aryl) complex $Cr(bpy)(quin)Ph_2$ (7).

Photolysis of 7 produces biphenyl, as detected by ${}^{1}H$ NMR (Scheme 10). Photolysis of 7 in the presence of benzoyl

Scheme 10. Synthetic Routes to 8



peroxide results in $Cr(bpy)(quin)(O_2CPh)_2$ (8), which can be independently synthesized from $Cr(bpy)(quin)Cl_2$ and AgO₂CPh. The use of bpy to trap the initial product of biphenyl reductive elimination gives a UV-visible spectrum characteristic of a reduced bpy ligand radical complex, presumably $Cr(bpy)_2(quin)$. The spectrum is distinct from that of the related reduced product, $Cr(bpy)(quin)_2$ (9), which can be prepared by protonolysis of $Cr(bpy)[N(SiMe_3)_2]_2$ with quin (Scheme 11) and has been characterized by single-crystal X-ray diffraction (Figure 5).

Scheme 11. Independent Synthesis of 9 via $Cr-N(SiMe_3)_2$ Protonolysis



CONCLUSIONS AND OUTLOOK

In this paper, we have explored the unexpected visible-light photolytic reactivity of a class of organochromium complexes first reported almost half a century ago. The bpy ligand responsible for the remarkable air and water stability of these compounds also opens a new route for C–C bond formation. Both λ_{max} and $E_{1/2}$ can be tuned by modifying the substituents of either the bpy or aryl ligands. The reactivity of the quin complex may potentially be extended to 8-aminoquinoline derivatives, which are active substrates in catalytic C–H functionalization reactions involving cobalt(III) carboxylate intermediates.³⁴ The low-valent chromium intermediates generated by photoinduced reductive elimination from chromium(III) bipyridine bis(aryl) complexes are expected to



Figure 5. Thermal ellipsoid diagram (50%) of 9. All H atoms have been removed for clarity.

demonstrate unusual reactivity modes, potentially including activation of C–O, C–Cl, or C–H bonds⁶ and reductive coupling of unsaturated substrates.^{19,35} Through an understanding of the fundamental organometallic reactions of these paramagnetic first-row transition-metal complexes, new chromium-catalyzed $C(sp^2)-C(sp^2)$ bond-forming reactions can be explored.

EXPERIMENTAL SECTION

General Synthetic Methods. All reactions were carried out under nitrogen using standard Schlenk and glovebox techniques unless otherwise indicated. Hexanes, toluene, diethyl ether (Et₂O), tetrahydrofuran (THF), and dichloromethane (CH₂Cl₂) were purified by passage through activated alumina and deoxygenizer columns from Glass Contour Co. (Laguna Beach, CA). Celite was dried overnight at 120 °C before being evacuated and then stored under nitrogen. Chromium dichloride (CrCl₂), chromium trichloride (CrCl₃; anhydrous), acetonitrile (anhydrous), 1,4-dioxane (anhydrous), 2,2'bipyridine, 4,4'-di-tert-butyl-2,2'-bipyridine, PhMgCl (2.0 M in THF), 4-MeOC₆H₄MgBr (0.5 M in THF), 4-Me₃CC₆H₄MgBr (0.5 M in THF), anhydrous ZnCl₂ (0.5 M in THF), potassium hexafluorophosphate, potassium iodide, sodium tetraphenylborate, benzoic acid, silver benzoate, 2,2,6,6-tetramethyl-3,5-heptanedione, and 8-hydroxyquinoline (quin) were purchased from Aldrich and used as received. $CrCl_3(THF)_{3}^{36}$ Cr(bpy)[N(SiMe_3)_2]₂,¹³ and Cp₂Cr³ were prepared according to literature procedures. Authentic samples of 4,4'-di-tert-butylbiphenyl and 4,4'-dimethoxybiphenyl for a GC/MS comparison were prepared by catalytic oxidative homocoupling of the corresponding ArMgBr reagents with FeCl₃ and 1,2-dichlorobutane according to the literature procedure.³⁸ [Cr(bpy)₂(Ph)₂](I) [1(I)] was prepared by the reaction of CrCl₂ with bipyridine (bpy) and PhMgCl in THF under nitrogen, followed by air oxidation in an aqueous methanol solution of KI, according to the literature procedure.^{11e} The other $[Cr(R-bpy)_2(C_6H_4R)_2](X)$ complexes were synthesized by the same procedure using bpy or 4,4'-Bu2-bpy as a neutral ligand, C₆H₅MgCl, 4-MeO-C₆H₄MgCl, or 4-^tBu-C₆H₄MgCl as an aryl Grignard reagant, and KI, NaBPh₄, or KPF₆ as a counteranion source. Photolysis experiments were conducted using a standard household light bulb in a utility light clamp placed 10 cm from the stirring reaction. Similar results were obtained using either a 100 W incandescent bulb or a 23 W compact fluorescent bulb.

Spectroscopic and Analytical Methods. UV–visible spectroscopic data were collected on a Shimadzu UV 2550 UV–visible spectrophotometer using sealable UV–visible cells for air-sensitive samples. ¹H NMR spectra were recorded on a Varian Mercury Plus 400 spectrometer at ambient temperature. GC/MS analyses of the crossover experiment shown in Scheme 4 were conducted on an Agilent 7890B gas chromatograph with an Agilent 5977 inert chemical ionization mass detector, utilizing methane as the ionization gas. Elemental analyses were performed by the Department of Chemistry microanalytical services at the University of British Columbia's Vancouver campus. Satisfactory elemental analysis for several of the complexes could not be obtained, particularly $1(PF_6)$ and 7, which had low analyses for C. The UV–visible spectra for all compounds are provided in the Supporting Information.

Electrochemical Methods. Cyclic voltammetry was carried out under nitrogen at a 100 mV s⁻¹ standard scan rate in THF/0.1 M $[NBu_4][PF_6]$ using a three-electrode configuration (a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode) and a PARSTAT 2273 potentiostat and function generator. The ferrocene/ferrocenium couple served as an internal reference. UV–visible spectroelectrochemical measurements were performed in a 1.0-mm-path-length thin-layer quartz glass spectrochemical cell from BAS (012904 SEC-C), using a platinum mesh working electrode with a throughput transmission of 0.4, a platinum wire counter electrode, and a Ag/AgCl reference electrode.

Crystallographic Methods. Single crystals were mounted on a glass fibers, and measurements were made on a Bruker X8 APEX II diffractometer with graphite-monochromated Mo K α radiation. The data were collected at a temperature of -100 ± 1 °C in a series of φ and ω scans in 0.50° oscillations. Data were collected and integrated using the Bruker SAINT software package³⁹ and corrected for absorption effects using the multiscan technique (SADABS).40 The data were corrected for Lorentz and polarization effects, and the structure was solved by direct methods.⁴¹ Compound 6 crystallized with two independent pairs of ions in the asymmetric unit. Three of the *tert*-butyl substituents on the bpy and diketonate ligands in 6 were disordered and subsequently modeled in two orientations with the occupancies of the disorder about C37 (91:19), C74 (85:15), and C100 (76:24). The cation of Mg1 was completely disordered with O1 and O2 of the dpm ligand in constant positions. The four THF molecules bound to Mg1 and Mg1 were split into two sets and modeled separately with an approximate 66:34 occupancy of the two orientations. Bound to Mg2, one C on a THF ligand was modeled as C124 and C130 in two positions with an approximate 83:17 occupancy. Compound 9 crystallized with two independent molecules in the asymmetric unit. Additionally, two disordered molecules of toluene were also found in each asymmetric unit of 9 and each modeled in two orientations using rigid groups. All non-H atoms were refined anisotropically. All refinements were performed using the SHELXTL crystallographic software package of Bruker AXS.⁴⁷ The molecular drawings were generated by using ORTEP-343 and POV-Ray. Diffraction data are shown in Table 2.

Synthesis of [Cr(bpy)₂(Ph)₂](PF₆) [1(PF₆)]. A solution of 631 mg of bpy (4.04 mmol) in 5 mL of THF was added to a gray suspension of 254 mg of CrCl₂ (2.07 mmol) in 10 mL of THF, resulting in a darkblue suspension. The dropwise addition of 2.2 mL of PhMgCl (2.0 M in THF, 4.40 mmol) resulted in a red-purple mixture. After stirring for 17 h, the solvent was removed from the deep-violet solution in vacuo. A solution of 1.077 g of KPF₆ (5.85 mmol) in 40 mL of 2:1 methanol/ water was added to the purple residue, and air was bubbled through the stirring suspension for 30 min. The orange precipitate was isolated on a sintered glass filter and washed with 30 mL of 2:1 MeOH/H₂O in two aliquots. After drying under vacuum, 1.231 g of [Cr(bpy)₂Ph₂]-(PF₆) (92% yield) was isolated as a yellow powder. Anal. Calcd for C₃₂H₂₆CrF₆N₄P: C, 57.92; H, 3.95; N, 8.44. Found: C, 52.84; H, 4.00; N, 7.55. UV-visible [NCMe; λ_{max} nm (ε , M⁻¹ cm⁻¹)]: 373 (2300).

Synthesis of $[Cr(bpy)_2(O_2CPh)_2](PF_6)$ [4(PF_6)]. A solution of 958 mg of bpy (6.13 mmol) in 4 mL of toluene was added to a red-orange solution of 543 mg of Cp₂Cr (2.98 mmol) in 3 mL of toluene, resulting in a dark-brown solution. A solution of 749 mg of benzoic acid (6.13 mmol) in 4 mL of toluene was added, resulting in a dark-blue-black solution. An additional 10 mL of toluene was added, and the solution was stirred for 20 h. The solvent was removed in vacuo, and Cr(bpy)_2(O_2CPh)_2 was isolated as a crude purple powder of sufficient purity for subsequent reactions. A 66 mg sample of Cr(bpy)_2(O_2CPh)_2 (0.109 mmol) was dissolved in 3 mL of 2:1 methanol/water, and air was bubbled through the stirring suspension for 30 min. The reddish-pink precipitate was isolated on a sintered glass filter and washed with first 2 \times 1 mL of MeOH and then 2 \times 1

Table 2. X-ray Crystallographic Data for Complexes 5, 6, and 9

	5	6	9
formula	C43H53CrN2O6	C ₆₃ H ₉₀ CrMgN ₂ O ₆	C35H28CrN4O2
fw	745.87	1047.67	588.61
cryst color, habit	pink, irregular	black, prism	green, irregular
cryst dimens, mm	$0.02 \times 0.08 \times 0.18$	$0.33 \times 0.15 \times 0.12$	0.07 × 0.10 × 0.323
cryst syst	monoclinic	monoclinic	triclinic
space group	$P 2_1/c$	$P 2_1/c$	$P\overline{1}$
a, Å	13.2567(8)	12.0157(12)	10.7073(9)
<i>b,</i> Å	13.9631(9)	19.610(2)	12.7763(11)
<i>c,</i> Å	23.1091(15)	49.596(5)	21.3555(14)
α , deg	90.0	90.0	87.797(3)
β , deg	106.484(1)	92.328(4)	89.996(3)
γ, deg	90.0	90.0	72.059(4)
<i>V</i> , Å ³	4101.8(4)	11677(2)	2777.1(4)
Ζ	4	8	4
$D_{\rm calc}$ g cm ⁻³	1.208	1.192	1.408
F ₀₀₀	1588	4528	1224
$\mu(\operatorname{Mo}_{\operatorname{cm}^{-1}} \operatorname{Ka}),$	3.26	3.26	4.53
data images (no.; <i>t</i> , s)	999, 30	3693, 7.5	1383, 60
$2\theta_{\rm max}$	52.06°	60.058°	45.1°
reflns measd	32912	209786	45493
unique reflns, R _{int}	5737, 0.0691	34210, 0.0662	12426, 0.053
absorption, T_{\min} , T_{\max}	0.900, 0.994	0.7460, 0.6835	0.743, 0.969
obsd data [I > 2.00σ(I)]	5737	24162	9019
no. of param	469	1599	824
R1, wR2 (F ² , all data)	0.0777, 0.1185	0.0973, 0.1455	0.114, 0.232
R1, wR2 [$F, I > 2.00\sigma(I)$]	0.0465, 0.1055	0.0626, 0.1316	0.083, 0.212
GOF	1.002	1.069	1.08
max, min peak, e Å ⁻³	0.690, -0.329	0.79, -0.495	0.93, -0.43

mL of water. After drying under vacuum, 34 mg of [Cr-(bpy)₂(O₂CPh)₂](PF₆) (42% yield) was isolated as a pink powder. Anal. Calcd for C₃₄H₂₆CrF₆N₄O₄P: C, 54.34; H, 3.49; N, 7.46. Found: C, 54.72; H, 3.99; N, 6.16. UV–visible [NCMe; λ_{max} , nm (ε , M⁻¹ cm⁻¹)]: 518 (382).

Synthesis of Cr(^tBu-bpy)(dpm)Cl₂. A solution of 253 mg of dipivaloylmethane (dpm or 2,2,6,6-tetramethyl-3,5-heptanedione, 1.38 mmol) in 7 mL of THF was added to a suspension of 502 mg of $\text{CrCl}_3(\text{THF})_3$ (1.34 mmol) in 7 mL of THF at ambient temperature. After stirring for 20 h, the solvent was removed in vacuo. The deepgreen residue was extracted with 20 mL of Et₂O and filtered through Celite on a sintered glass frit. A solution of 361 mg of ^tBu-bpy (4,4'-di*tert*-butyl-2,2'-dipyridyl, 1.34 mmol) in 5 mL of Et₂O was added to the filtrate, and the solution was stirred for 20 h. The solvent was removed in vacuo, and Cr(^tBu-bpy)(dpm)Cl₂ was isolated as a green powder (740 mg, 96% yield) of sufficient purity for subsequent reactions. Anal. Calcd for C₂₉H₄₃Cl₂CrN₂O₂: C, 60.62; H, 7.54; N, 4.88. Found: C, 58.76; H, 7.26; N, 4.65. UV–visible [THF; λ_{max} , nm (ε , M⁻¹ cm⁻¹)]: 347 (5860), 498 (180), 632 (220).

Synthesis of Cr(^tBu-bpy)(dpm)(O₂CPh)₂ (5). A suspension of 60 mg of silver benzoate (0.26 mmol) in 5 mL of THF was added to a solution of 75 mg of Cr(^tBu-bpy)(dpm)Cl₂ (0.13 mmol) in 5 mL of THF. After stirring for 24 h to produce a pink solution, the solvent was removed in vacuo and the residue was extracted with 6 mL of Et₂O and filtered through Celite. Cooling the filtrate to -30 °C provided 21 mg (21% yield) of pink X-ray-quality crystals of 5 over several days in

two crops. Anal. Calcd for C₄₃H₅₃CrN₂O₆: C, 69.33; H, 7.04; N, 3.76. Found: C, 69.09; H, 7.14; N, 4.08. UV–visible [Et₂O; λ_{max} , nm (ε , M⁻¹ cm⁻¹)]: 336 (6100), 540 (390). μ (294 K) = 3.78(4) $\mu_{\rm B}$.

Synthesis of [Cr(^tBu-bpy)(Ph)₃][Mg(dpm)(THF)₄] (6). To a solution of 100 mg of Cr(^tBu-bpy)(dpm)Cl₂ (0.36 mmol) in 15 mL of THF was added PhMgCl (0.92 mL of a 2.0 M solution in THF, 2.3 mmol). The reaction mixture immediately turned color from green to dark red. After stirring for 3 days, 200 μ L of 1,4-dioxane (2.35 mmol) was added. After stirring for 1 h, the solvent was removed in vacuo and the residue was extracted with 10 mL of Et₂O and filtered through Celite. Cooling the filtrate to -30 °C provided 51 mg (13% yield) of brown X-ray-quality crystals of 6. Anal. Calcd for C₆₃H₉₀CrMgN₂O₆: C, 72.22; H, 8.66; N, 2.67. Found: C, 59.59; H, 7.69; N, not detected. UV–visible [Et₂O; λ_{max} nm (ϵ , M⁻¹ cm⁻¹)]: 338 (6900), 455 (2700), 541 (2000), 632 (1700). μ (294 K) = 2.95(9) $\mu_{\rm B}$.

Synthesis of Cr(bpy)(quin)Ph₂ (7). To a suspension of 157 mg (0.99 mmol) of CrCl₃ in 10 mL of THF was sequentially added a solution of 159 mg of bpy (1.02 mmol) in 2 mL of THF, followed by PhMgCl (1.5 mL of a 2.0 M solution in THF, 3.0 mmol). After stirring for 20 h, the suspension was filtered through a sintered glass frit. The red solid was washed with 5 mL of THF and dried under vacuum to give 392 mg of the previously reported^{11a} Cr(bpy)Ph₃(THF) as a red powder. To a suspension of this product in 5 mL of THF was added 93 mg of quin (0.64 mmol) in 3 mL of THF. After stirring for 23 h, the brown reaction mixture was filtered through a sintered glass frit. The brown solid was washed with 3 mL of THF and dried under vacuum to give 315 mg of 7 (63% yield) as a brown powder. Anal. Calcd for C₃₁H₂₄CrN₃O: C, 73.50; H, 4.78; N, 8.30. Found: C, 68.49; H, 5.34; N, 4.99. UV–visible [THF; λ_{max} , nm (ε , M⁻¹ cm⁻¹)]: 425 (2800).

Synthesis of Cr(bpy)(quin)Cl₂. A solution of 159 mg of bpy (1.02 mmol) in 2 mL of toluene was added to a suspension of 365 mg of $CrCl_3(THF)_3$ (0.97 mmol) in 10 mL of toluene at ambient temperature, resulting in a color change from a magenta suspension to a thick teal-green suspension. An additional 10 mL of toluene was added, followed by a solution of 151 mg of quin (1.04 mmol) in 2 mL of toluene, resulting in a green suspension. After stirring for 20 h, the suspension solvent was filtered through a sintered glass frit. After drying under vacuum, $Cr(bpy)(quin)Cl_2$ was isolated as a green powder (317 mg, 77% yield), which was used in subsequent reactions.

Synthesis of Cr(bpy)(quin)(O₂CPh)₂ (8). Under nitrogen, 50 mL of CH₂Cl₂ was added to 420 mg of Cr(bpy)(quin)Cl₂ (0.99 mmol) and 474 mg of silver benzoate (2.07 mmol). After stirring for 24 h, the orange suspension was filtered through Celite supported on a sintered glass frit to remove a white precipitate (presumably AgCl) and give a brown-yellow filtrate. The solvent was removed in vacuo from the filtrate, which was dissolved in 5 mL of CH₂Cl₂. The addition of 20 mL of hexanes to the solution induced the precipitation of a gold-colored product. After the solvent was removed in vacuo, 8 was isolated as a gold powder (323 mg, 55% yield). Anal. Calcd for C₃₃H₂₄CrN₃O₅: C, 66.66; H, 4.07; N, 7.07. Found: C, 64.27; H, 4.23; N, 4.56. UV-visible [NCMe; λ_{max} nm (ε , M⁻¹ cm⁻¹)]: 419 (1600).

Synthesis of Cr(bpy)(quin)₂ (9). A solution of 49 mg of quin (0.34 mmol) in 2 mL of THF was added to 87 mg of Cr(bpy)[N(SiMe₃)₂]₂ (0.16 mmol) in 2 mL of THF. After stirring for 4 h, 4 mL of hexanes was added to the dark-green suspension, and the resulting dark-green powder was isolated on a sintered glass filter and dried under vacuum, providing 72 mg of 9 (0.145 mmol, 88% yield). X-ray-quality crystals were grown from saturated solutions of the complex in toluene chilled to -30 °C. Anal. Calcd for C₂₈H₂₀CrN₄O₂: C, 67.74; H, 4.06; N, 11.28. Found: C, 65.49; H, 4.59; N, 9.88. UV-visible [toluene; λ_{max} , nm (ε , M⁻¹ cm⁻¹)]: 335 (6300), 356 (5750), 415 (3650), 443 (4100), 624 (1400), 665 (1600).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b03195.

Electrochemistry and spectroelectrochemistry of $[Cr-(bpy)_2(Ph)_2]^+$, photolysis reactions of $[Cr(R-bpy)-(C_6H_4R)_2](X)$ complexes, bpy bond lengths from X-ray structures of **5**, **6**, and **9**, and UV-visible spectra (PDF)

Accession Codes

CCDC 1812508–1812510 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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