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Electron-Rich CpIr(biphenyl-2,2'-diyl) Complexes with π -Accepting Carbon Donor Ligands

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Abstract

Cp*Ir^{III} and CpIr^{III} complexes have attracted interest as catalysts for oxidative transformations, and highly oxidizing iridium species are postulated as key intermediates in both catalytic water and C–H bond oxidation. Strongly electron-donating ligand sets have been shown to stabilize Ir^{IV} complexes. We describe the synthesis and reactivity of complexes containing the CpIr(biphenyl-2,2'-diyl) moiety stabilized by a series of strong donor carbon-based ligands. The oxidation chemistry of these complexes has been characterized electrochemically, and a singly oxidized Ir^{IV} species has been observed by X-band EPR for the complex CpIr(biph)(*p*-CNCH₂SO₂C₆H₄CH₃).

INTRODUCTION

Cp*Ir^{III} complexes are common in organometallic chemistry but only recently have been found to be precatalysts for a number of oxidative transformations.^{1–7} Several half-sandwich Ir^{III} species catalyze water oxidation,^{8–11} and our group has recently developed a wide variety of complexes of this type that are also active precatalysts for C–H bond

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Notes

The authors declare no competing financial interest.

Supporting Information

Figures, tables, and CIF files giving NMR spectra, the IR spectrum of **3**, a representative spectrum and raw data from the synthesis of **3** at varied [I], and crystallographic details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

oxidation.^{12–16} These precatalysts give relatively high turnover frequencies for water oxidation in comparison to ruthenium-based systems,^{17–25} but oxidative degradation of the molecular complexes is a concern.^{26–29} Recently, we investigated this degradation by dynamic light scattering, identifying the conditions under which the precatalysts remain molecular during turnover.³⁰

Despite increased effort in the area, relatively little mechanistic data are available regarding these iridium-catalyzed oxidative transformations. A catalytic cycle involving a series of proton-coupled single-electron oxidations to generate an active Ir^V oxo species has been proposed on the basis of kinetic, electrochemical, and computational¹³ results, but experimental data on the key high-valent intermediate(s) remain elusive. A recent study from our group demonstrated that Cp*IrCl(κ^2 C²,C^{2'}-1,3-diphenylimidazol-2-ylidene) (**T1**) (Figure 1), a precatalyst for water oxidation that contains a highly donating ligand set, undergoes one-electron oxidation with [Ru(bpy)₃]³⁺ to generate an Ir^{IV} species that was observed by EPR spectroscopy.¹² The transient Ir^{IV} complex decomposes within minutes at room temperature under an inert atmosphere. Furthermore, this Ir^{IV} species contains an inner-sphere chloride ligand and, thus, is unlikely to be involved directly in a catalytic cycle for water or C–H bond oxidation where water is expected to have replaced chloride. Nevertheless, the observation of an Ir^{IV} species suggests that a mechanism involving sequential single-electron-oxidation steps is plausible. We postulated that a more strongly donating ligand set would further stabilize half-sandwich Ir^{IV} species and allow us to study the reactivity in more detail.

Specifically, we anticipated that moving to an X₂ chelate from the previously studied L–X chelate in **T1** would increase σ donation to the metal center. In spite of its analogy with 2,2'-dipyridyl and 2-phenylpyridine, biphenyl-2,2'-diyl (biph) has rarely been used as a ligand for iridium systems.^{31–33} CpIr(biph)CO has been prepared by Rausch and co-workers by the addition of fluorenone to CpIr(CO)I₂, but this synthetic route gives low yields.³² Subsequently, Wakatsuki and coworkers prepared the Cp* analogue in a significantly higher yield by addition of a sodium fluorenone complex to [Cp*IrCl₂]₂.³³ To date, these are the only reported half-sandwich Ir(biph) complexes. A variety of biph-containing transition-metal complexes have been prepared by oxidative addition of the strained C–C bond in biphenylene,^{34–37} and in 1995, we reported that biphenylene can oxidatively add to [Ir(cod)Cl]₂ (where cod = 1,4-cyclooctadiene) to form [(cod)Ir(biph)Cl]₂ in high yields.³¹ This complex has subsequently been used as a precursor for other Ir(biph) species,^{38,39} as the cod ligand in [(cod)Ir(biph)Cl]₂ is labile and can be displaced by reaction with phosphine ligands. Several Ir^{IV} derivatives were generated and examined by EPR spectroscopy, including a unique Ir^{IV} boryl species that was isolated and characterized by X-ray crystallography.

Here we describe the synthesis of CpIr(biph)(η^2 -cod) and find that the ligand set is so donating that only strong π acceptor ligands can displace cod. The previously reported CO complex has been obtained in moderate yield, and the new monomeric species CpIr(biph)(C $\equiv$ NCH₂SO₂PhMe) and a dimeric species, [(CpIr(biph))₂(μ - η^2 : η^2 -cod)], with a bridging cod ligand, have been isolated and characterized. The new complexes have been investigated electrochemically, and for the isonitrile complex a one-electron-oxidized Ir^{IV} species has been observed and characterized by EPR spectroscopy.

RESULTS AND DISCUSSION

Synthesis of CpIr(biph)L Complexes

The addition of sodium cyclopentadienide to a suspension of [Ir(cod)(biph)-Cl]₂ in dichloromethane generated CpIr(biph)(cod) (**1**) in moderate yield. Interestingly, cod was

found to bind the resulting complex in the η^2 mode rather than in the η^4 chelate or bridging modes more commonly observed (Scheme 1). Due to the loss of the nonchelated olefin moiety, the resultant complex $\text{CpIr}(\text{biph})(\text{cod})$ (**1**) slowly dimerizes upon heating or standing in solution. This dimerization, resulting in the formation of complex **2**, is slow at room temperature, presumably due to the strength of the iridium–olefin bond. Dimer **2** was never obtained in high purity, as it is not easily separated from **1** and the dimerization does not proceed to completion. However, it was possible to characterize both the monomeric and dimeric forms by X-ray crystallography (Figure 2). The structure of **1** represents only the second crystallographically characterized iridium complex in which cod binds in an η^2 fashion⁴⁰ and the first example of an Ir^{III} species. Similarly, there exists only one previous example of an iridium dimer containing a μ - η^2 : η^2 -cod moiety,⁴¹ and there are no prior examples of Ir^{III} species. In all other crystallographically characterized complexes, cod is found to chelate one iridium in an η^4 manner.

1 crystallizes with minor disorder in the cyclooctadiene moiety arising from the presence of two partially occupied conformations. **2** crystallizes from dichloromethane/pentane as a dichloromethane solvate in the high-symmetry $P4_2bc$ space group with two halves of two different dimers in the asymmetric unit. The cod C=C bond lengths in **1** of 1.399(15) and 1.314(14) Å for the coordinated and uncoordinated olefins, respectively, are consistent with a significant amount of π back-bonding from iridium, as would be expected from an electron-rich metal.⁴² In **2**, the olefinic C=C bond length is 1.42(2) Å, indicative of similar Dewar–Chatt/metallopropene character in the dimer.

At elevated temperatures cod can be exchanged, but only for other π -accepting ligands (Scheme 1). Placing **1** under 1 atm of CO in 5 mL of 1,2-dichloroethane at 50 °C affords a mixture of the dimerized product **2** and the monomeric carbonyl complex **3**. When the reaction is performed at a lower iridium concentration (vide infra), the formation of **3** is favored. Full conversion to **3** was obtained by carbonylation of **1** in a Parr reactor under 68 atm of CO. Complex **3**, which was previously reported but not characterized,³² has now been isolated in 47% yield and characterized by NMR and IR spectroscopy and elemental analysis. The CO stretching band at 1994 cm^{-1} is at the low end of the range seen with other previously reported $\text{Cp}^*\text{Ir}^{\text{III}}$ and CpIr^{III} carbonyl complexes and highlights the strongly donating nature of the ligand set.^{43–48} Additionally, treatment of complex **1** with a slight excess of $\text{C}\equiv\text{NCH}_2\text{SO}_2\text{PhMe}$ in dichloromethane at reflux yielded the isonitrile complex **4** (Scheme 1).

Attempts to substitute the cod ligand in **1** with other types of ligands were unsuccessful. Reactions with ligands such as acetate, 2,4,6-trimethylaniline, and pyridine all returned mixtures of starting material and dimerized product **2**. Surprisingly, even PPh_3 , $\text{P}(\text{tBu})_3$, and PMe_3 were found to be incapable of displacing cod from **1**, suggesting that only strong π -acceptor ligands can bind competitively. Furthermore, neither treatment with iodine nor use of a high pressure of hydrogen generated any new products. A full list of attempted ligand substitution reactions is provided in the Supporting Information.

Also unsuccessful were attempts to synthesize the Cp^* analogue of **1**. Reaction of lithium pentamethylcyclopentadienide with $[\text{Ir}(\text{cod})(\text{biph})\text{Cl}]_2$ yielded only starting material and decomposition products. This is a rare case in which the $\text{Cp}^*\text{Ir}^{\text{III}}$ complex is more difficult to access than the corresponding CpIr^{III} complex.¹³

Product Distribution in Synthesis of $\text{CpIr}(\text{biph})\text{CO}$

As mentioned above, exposing the cod complex **1** to 1 atm of CO in 1,2-dichloroethane yielded a mixture of both the carbonyl species **3** and dimerized product **2**. At reduced

concentrations of starting material **1**, dimerized product **2** was observed in smaller quantities. Therefore, the dependence of the product distribution was investigated as a function of iridium concentration.

All reactions were carried out at 50 °C in 1,2-dichloroethane under 1 atm of CO. In order to determine concentration dependence, the reaction was run to completion in different solvent volumes with a constant molar quantity of starting material **1**. Only carbonyl complex **3** and dimer **2** were observed as products by ^1H NMR spectroscopy. The product distribution was determined as an average of two runs using the relative integrations of the Cp signals (see the Supporting Information). The results are shown in Figure 3.

Formation of the carbonyl species **3** is favored under more dilute conditions, whereas dimer formation is favored when using higher concentrations of the reacting complex **1**. The highest concentration tested, 3.87 mM **1**, shows a product distribution of about 3:1 of carbonyl complex **3** to dimer **2**. A distribution of 96:4 of carbonyl complex **3** to dimer **2** is obtained when the reaction is run using 0.48 mM **1**.

Unfortunately, further attempts to describe the kinetics of this reaction were unsuccessful. Observing the formation of the dimer **2** from monomer **1** was complicated by limited solubility of **2** at the necessary concentrations for continuous observation by ^1H NMR spectroscopy.

Electrochemical Oxidation

With these complexes in hand, we next turned our attention to the cyclic voltammetry (CV) of **1**, **3**, and **4** to characterize their potentials for oxidation. Since the ligand set is strongly σ donating, we expected readily accessible metal-centered oxidations from Ir^{III} to Ir^{IV} , in analogy to previously reported complexes.^{12,13,27} The cyclic voltammetry results are summarized in Figure 4.

Each of the compounds undergoes a quasi-reversible redox event above 1.2 V vs NHE. These redox processes become more reversible at higher scan rates, consistent with the limited stability of the oxidized species formed at the electrode. Specifically, at a scan rate of 100 mV/s, **1** has a midpoint potential ($E_{1/2}$) of 1320 mV with a peak separation of 157 mV. The ratio of peak currents for the process ($i_{\text{p,c}}/i_{\text{p,a}}$) is 0.70, suggesting that a majority of the species resulting from the electrochemical oxidation survives to be reduced back to the Ir^{III} state. Isonitrile derivative **4** is slightly more reversible, with a peak separation of only 100 mV and a ratio of peak currents of 0.75. Interestingly, the net electronic contribution from the cod ligand must be similar to that of the isonitrile, since the $E_{1/2}$ value for isonitrile **4** is 1330 mV, nearly identical with that of **1**.

The midpoint potential for the CO complex **3** is 1550 mV and the couple is less reversible, having a peak separation of 220 mV. Moreover, very little of the oxidized species survives to be reduced, with a ratio of peak currents of only 0.35. Thus, iridium is more electron deficient when bound to CO as compared to the other ligands surveyed here, resulting in higher potentials for oxidation and more unstable oxidized iridium species as a result.

The observed reduction potentials of **1**, **3**, and **4** are all higher than those of other half-sandwich iridium complexes studied in our laboratory.^{12,13,16,27} This is noteworthy, as the donor power of biph is greater than that of the chelate ligand present in any of our other complexes. However, the presence of the strongly π -accepting ligand in the sixth coordination site reduces the electron density around iridium enough to overcome the additional donor power gained by using biph. The lowest observed potential for oxidation of any of our complexes is from **T1** and centered at 0.9 V vs NHE.¹² The L-type ligand in this

complex is the N-heterocyclic carbene, which is an exceptionally poor π acceptor. **T1** also contains Cp*, which is a stronger electron donor than Cp. Thus, it appears electrochemically that the net donor power of all ligands present is optimal in complexes such as **T1**. If the ligand L in the CpIr(biph)L framework could be replaced with a weaker π acceptor, the reduction potential of the complexes could perhaps be pushed below that of **T1**. Unfortunately, as described above, this is not possible with our synthetic route.

EPR Spectroscopy

A relatively small number of stable Ir^{IV} species have been previously reported,^{31,49–52} and few examples of EPR spectra of Cp*Ir^{IV} species have been observed.^{12,53–55} Recently our laboratory designed a method for observing unstable Cp*Ir^{IV} species by mixing solutions of Cp*Ir^{III} precursor and a stoichiometric oxidant, [Ru(bpy)₃]³⁺, at cold temperatures in a glovebox and then rapidly freezing the mixture to trap oxidized iridium species. This procedure yielded the EPR spectrum of the previously mentioned complex [**T1**]⁺.¹² In the case of this compound, quasi-reversible electrochemical oxidation of the Ir^{III} starting material gave a strong indication that the oxidation product was stable, at least transiently, and suitable for EPR work aimed at detecting oxidized intermediate(s).

On the basis of these results, we applied the same method to this family of CpIr(biph)L complexes. Analogous to previous experiments,¹² test complexes were first dissolved in a glassing solvent mixture, 1/1 dichloromethane/toluene, in a glovebox. These solutions were then mixed with 0.75 equiv of [Ru(bpy)₃]³⁺ in 1/1 dichloromethane/toluene and rapidly frozen for EPR analysis.

Oxidation of the isocyanide complex **4** gives a weak rhombic spectrum (Figure 5). This complex gave fairly reversible electrochemistry (the ratio of peak currents was 0.75) (Figure 4), which is consistent with the ability to observe a metastable oxidation product. The spectrum itself is unremarkable, with *g* values at 2.44, ca. 2.08, and 1.91. Also present is a background signal (in Figure 5, visible as the sloping baseline at lower fields) attributable to unreduced [Ru(bpy)₃]³⁺, as previously reported.^{12,56} The midpoint potential obtained from the CV for **4** is at about 1.3 V vs NHE, while the standard reduction potential for [Ru(bpy)₃]³⁺/[Ru(bpy)₃]²⁺ is 1.26 V vs NHE. Thus, Ru^{III} has enough oxidizing potential to oxidize complex **4**. The Ir^{IV} species generated from **4** shows limited thermal stability. Warming the sample to room temperature for 20 min results in the disappearance of the Ir^{IV} EPR signal. No EPR signal was observed by mixing complex **1** or complex **3** with [Ru(bpy)₃]³⁺ under the same conditions used for **4**. In the case of **3**, this is likely due to Ru^{III} lacking sufficient driving force to oxidize the CO-bound iridium center.

CONCLUSIONS

We have described a new synthetic route for CpIr^{III} complexes of the strongly electron donating ligand biph and have explored the reactivity of these complexes both synthetically and electrochemically. This ligand framework is so electron donating that the complex seems to require strong π acceptor ligands in the sixth coordination site of iridium. Accordingly, we find a low $\nu_{\text{C=O}}$ in the infrared spectrum of CpIr(biph)CO of 1994 cm⁻¹ in comparison with other literature CpIrCO complexes. The isonitrile-bound compound CpIr(biph)(*p*-CNCH₂SO₂C₆H₄CH₃) shows a quasi-reversible iridium-centered oxidation by cyclic voltammetry, and the resulting iridium(IV) species generated on oxidation has been observed by EPR spectroscopy.

EXPERIMENTAL SECTION

[Ir(cod)Cl]₂, [Ir(cod)(biph)Cl]₂, and [Ru(bpy)₃](PF₆)₃ were pre-pared according to literature procedures.^{31,56,57} Dichloromethane was dried on a Grubbs-type solvent purification system.⁵⁸ Anhydrous 1,2-dichloroethane was purchased from Aldrich in a Sure/Seal bottle to ensure purity. All other reagents and materials were commercially available and were used without further purification. ¹H NMR spectra were recorded at room temperature on a 400 MHz Bruker spectrometer and referenced to the residual solvent peak (δ in ppm, *J* in Hz). ¹³C{¹H} NMR spectra were recorded on a 500 MHz Varian spectrometer and referenced to the residual solvent peak. EPR spectra were recorded on an X-band Bruker ELEXSYS E500 spectrometer equipped with an Oxford ESR-900 cryostat. The nominal temperature for experiments was 7 K. The modulation amplitude was set to 2 G and the microwave frequency set to 9.398 673 GHz. Experiments were recorded with a time constant of 41 ms. Elemental analysis was performed by Robertson Microlit Laboratories (Ledgewood, NJ).

Electrochemical Studies

Electrochemical measurements were made on a Princeton Applied Research Versastat 4–400 or Model 273 potentiostat/galvanostat using a standard three-electrode configuration. A basal plane graphite electrode (surface area 0.09 cm²) was used as the working electrode to minimize background oxidative current. The electrode was constructed and prepared for experiments as described previously.¹³ A platinum wire was used as the counter electrode, and Ag/0.1 M AgNO₃ in acetonitrile was used as the reference electrode. Ferrocene was used as an external standard to calibrate the reference electrode versus NHE (Fc/Fc⁺: +0.690 V vs NHE).⁵⁹ Experiments were carried out in dry dichloromethane solution containing 0.1 M tetrabutylammonium hexafluorophosphate (Sigma-Aldrich) as the supporting electrolyte.

CpIr(biph)(cod) (1)—A flame-dried 100 mL Schlenk flask containing 638 mg of [Ir(cod)(biph)Cl]₂ (1.31 mmol, 1 equiv) was placed under nitrogen, and 10 mL of dry, degassed dichloromethane was added via syringe, followed by 1.25 mL of sodium cyclopentadienide (2.0 M in tetrahydrofuran) (2.50 mmol, 1.9 equiv). The mixture was stirred under nitrogen for 3 h. The resulting solution was filtered through Celite in air. Ten milliliters of diethyl ether was added, and the solution was cooled overnight, forming a precipitate. The precipitate was collected by vacuum filtration in air, washed with 10 mL of diethyl ether, and dried in vacuo to give the product as a dark brown solid. Yield: 230 mg (33.9%). Crystals suitable for X-ray diffraction were grown by layering diethyl ether on a saturated dichloromethane solution. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.57 (dd, *J* = 7.5, 0.8 Hz, 2H), 7.34 (dd, *J* = 7.6, 1.3 Hz, 2H), 6.88 (td, *J* = 7.5, 1.2 Hz, 2H), 6.73 (td, *J* = 7.4, 1.5 Hz, 2H), 5.55 (m, 2H), 5.34 (s, 5H), 2.68 (m, 2H), 2.40 (m, 2H), 2.30 (m, 2H), 1.98 (dd, *J* = 19.9, 10.4 Hz, 2H), 1.85 (m, 2H). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 32.01, 35.37, 64.27, 90.93, 121.00, 123.30, 125.54, 130.77, 140.50, 142.88, 154.09. Anal. Calcd for C₂₅H₂₅Ir: C, 58.00; H, 4.87. Found: C, 57.63; H, 4.76.

CpIr(biph)(CO) (3)—In a Parr reactor 48.2 mg of CpIr(biph)(cod) (0.093 mmol) was dissolved in 21 mL of dry 1,2-dichloroethane. The mixture was placed under 68 atm of CO gas and heated to 70 °C for 24 h with stirring. The resulting mixture was cooled to room temperature, and the pressure was reduced to 1 atm. The solvent was removed using a rotary evaporator, and the resulting light brown solid was washed with hexane and dried in vacuo to yield pure product. Yield: 22.5 mg (47.1%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.55 (m, 4H), 7.08 (t, *J* = 7.4 Hz, 2H), 6.83 (t, *J* = 7.4 Hz, 2H), 5.70 (s, 5H). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 89.76, 121.76, 124.85, 126.34, 131.58, 141.77, 155.63, 166.85. Anal. Calcd for C₁₈H₁₃IrO: C, 49.41; H, 2.99. Found: C, 49.17; H, 3.10.

CpIr(biph)(*p*-CNCH₂SO₂C₆H₄CH₃) (4)—A flame-dried 100 mL Schlenk flask with an attached reflux condenser containing 42.0 mg of CpIr(biph)(cod) (0.082 mmol, 1 equiv) and 25.5 mg of tosylmethyl isocyanide (0.131 mmol, 1.6 equiv) was placed under nitrogen, and 10 mL of dry, degassed dichloromethane was added. The mixture was heated to reflux for 24 h and then cooled to room temperature. Solvent was removed by rotary evaporation, and the resulting solid was dissolved in 5 mL of dichloromethane, filtered, and washed with excess hexane. The product precipitated out in the filtrate and was filtered and dried in vacuo to give a light brown solid. Yield: 22.5 mg (49.5%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.49 (dd, *J* = 7.5, 1.1 Hz, 2H), 7.40 (dd, *J* = 7.6, 1.4 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.94 (td, *J* = 7.4, 1.2 Hz, 2H), 6.69 (td, *J* = 7.4, 1.5 Hz, 2H), 5.48 (s, 5H), 4.55 (s, 2H), 2.35 (s, 3H). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 21.92, 63.53, 87.92, 90.76, 121.12, 123.72, 125.74, 129.22, 130.57, 133.25, 136.37, 141.71, 146.62, 155.76. Anal. Calc. for C₂₆H₂₂IrNO₂S: C, 51.64; H, 3.67; N, 2.32. Found: C, 51.98; H, 3.83; N, 2.02.

Procedure for Product Distribution Experiment

A small round-bottom flask containing 5 mg of CpIr(cod)(biph) (**1**) was placed under nitrogen and 2.5, 5, 10, 15, or 20 mL of 1,2-dichloroethane was added. The reaction was sparged with CO and stirred at 50 °C for 24 h under 1 atm of CO. The solution was then cooled rapidly to room temperature and the solvent removed using a rotary evaporator. The resulting light brown solid was washed with hexane and dried in vacuo. The product distribution was determined by relative integration of the ¹H NMR signals from the Cp protons of each compound (**2** or **3**).

Procedure for EPR Experiment

The method for preparation of the EPR samples is a slight modification of our previously published procedure.¹² In a glovebox, 2 μmol of iridium complex was dissolved in 1 mL of 1/1 dichloromethane/toluene and transferred to an EPR tube placed in a cold well. Separately, 0.75 equiv of [Ru(bpy)₃](PF₆)₃ was dissolved in 1 mL of dichloromethane/toluene. The [Ru(bpy)₃](PF₆)₃ solution was then layered onto the frozen solution of iridium complex and chilled. EPR samples were then removed from the glovebox while cold and immediately stored in a liquid nitrogen bath. Just prior to recording the spectra, the samples were briefly warmed above the freezing point of the solvent mixture, rapidly mixed, and refrozen, and spectra were recorded. Samples containing CpIr(biph)-(*p*-CNCH₂SO₂C₆H₄CH₃) (**4**) were then allowed to stand at room temperature for 20 min prior to refreezing to examine the thermal stability of the observed iridium(IV) species.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

T1, a water oxidation precatalyst with a highly donating ligand set.¹²

Figure 2. ORTEP drawings of **1** (left) and **2** (right) shown at the 50% probability level. Solvent molecules and disorder modeling have been omitted for clarity.

Figure 3.

Dependence of mole fraction of **2** and **3** on [1]. Reactions were run at 50 °C in 1,2-dichloroethane under 1 atm of CO. Diamonds correspond to the mole fraction of **3** after reaction. Squares correspond to the mole fraction of **2**.

Figure 4.

Cyclic voltammetry of **1** (top panel, a), **3** (middle panel, b), and **4** (lower panel, c). Conditions: $[\text{Ir}] = 10^{-3} \text{ M}$; dichloromethane solution with 0.1 M NBu_4PF_6 as supporting electrolyte; basal-plane graphite working electrode. Further details can be found in the Experimental Section.

Figure 5. X-band EPR spectrum of **4** upon mixing with 0.75 equiv of $[\text{Ru}(\text{bpy})_3]^{3+}$ in a 1/1 dichloromethane/toluene mixture. Conditions: $[\text{Ir}] = 10^{-3} \text{ M}$; microwave frequency 9.398 673 GHz; 7 K. For details, see the Experimental Section.

Scheme 1.
Synthesis of CpIr(biph)L Complexes³¹