Chapter 6. Group VIII Coordination Chemistry Supported by the Bis(quinolinyl)amido Ligand

Portions of the following work were completed by a former postdoc in the Peters Group, Dr. Baixin X. Qian.

Abstract

Entry into the group VIII chemistry of the bis(8-quinolinyl)amine (BQA, **6.1**) ligand was effected by both protolytic and metathetical strategies. The bis-ligated Fe(III) complex $[Fe(BQA)_2][BPh_4]$ (**6.2**) was prepared via amine addition to $FeCl_3$ in the presence of base and $NaBPh_4$. The cation **6.2** is low-spin (S = ½) and exhibits a rhombic EPR signal (4 K, X-band). Complexes featuring a single BQA ligand were prepared for Ru and Os. Reaction of the polymeric $[RuCl_2(cod)]_n$ species with one equivalent of LiBQA afforded the divalent complex (BQA)RuCl(cod) (**6.3**), while two equivalents of LiBQA afforded the neutral congener of **6.2** $Ru(BQA)_2$ (**6.4**) (cod = 1,4-cycloocatdiene). Reaction of LiBQA with the phosphine containing precursors $(PPh_3)_3MCl_2$ exclusively afforded the *trans*-$(BQA)MCl(PPh_3)_2$ complexes (M = Ru **6.5**, Os **6.6**). Reaction of HBQA with $(PPh_3)_3MCl_2$ and external base (NEt_3) afforded **6.5** for M = Ru, but afforded the isomer of **6.6** *cis*-$(BQA)OsCl(PPh_3)_2$ (**6.7**) for M = Os. Complexes **6.3**, **6.5**, and **6.6** were crystallographically characterized in the solid-state by X-ray diffraction. Complexes **6.2**, **6.5**, and **6.6** were examined for the electrochemical behavior and displayed well-defined reversible $M^{II/III}$ redox events. All three species exhibit a second reversible redox event that may be attributable to a reversible oxidation of the BQA ligand. Complex **6.4** was compared electrochemically against the dication $[(tpy)_2Ru]^{2+}$ and the monocation $[(tpy)Ru(BQA)]^{+}$ (**6.9**). The $Ru^{II/III}$ redox couple shifts -0.6 V from the dication to the monocation **6.9** and an additional -0.5 V from **6.9** to the neutral complex **6.4**. Phosphine exchange from **6.5** provided $(BQA)RuCl(PEt_3)_2$ (**6.10**) and $(BQA)RuCl(PMe_3)_2$ (**6.11**), preserving the *trans* arrangement of the phosphine ligands. Halide substitution of **6.11** was effected by refluxing in THF with KX salts to yield $(BQA)RuBr(PMe_3)_2$ (**6.12**) and

(BQA)RuI(PMe_3)$_2$ (**6.13**). Metathesis reactions with **6.11** also yielded the hydride (BQA)RuH(PMe_3)$_2$ (**6.14**), methyl (BQA)RuMe(PMe_3)$_2$ (**6.15**), and azide (BQA)RuBr(PMe_3)$_2$ (**6.16**) complexes. The bidentate, monoanionic ligand 3,5-(CF_3)$_2$Ph-QA was installed onto the (BQA)Ru platform from its sodium precursor to yield (BQA)Ru(3,5-(CF_3)$_2$Ph-QA)(PPh_3) (**6.19**) and its carbonyl complex (BQA)Ru(3,5-(CF_3)$_2$Ph-QA)(CO) (**6.19**). Addition of a bis(phosphino)borate ligand to **6.5** yielded the anionic complex [($Ph_2B(CH_2PPh_2)_2$RuCl(BQA)][NEt_4] (**6.21**). Treatment of **6.21** with alcohol precipitated the stable five-coordinate complex ($Ph_2B(CH_2PPh_2)_2$Ru(BQA) **6.22**. The addition of CO gas to **6.21** or **6.22** formed the carbonyl complex [(Ph_2BP_2)Ru(CO)(BQA)] (**6.21**). Halide abstraction from **6.5** in the presence of a coordinating ligand yielded the cationic complexes [(BQA)Ru(CH_3CN)(PPh_3)$_2$][BPh_4] (**6.24**), [(BQA)Ru(CO)(PPh_3)$_2$][BPh_4] (**6.25**), and [(BQA)Os(CO)(PPh_3)$_2$][PF_6] (**6.26**). While reaction of **6.5** with AgOTf resulted in the oxidized product [(BQA)RuCl(PPh_3)$_2$][OTf] (**6.27**), Tl halide abstraction from **6.5** provided the dinitrogen complexes [(BQA)Ru(N_2)(PPh_3)$_2$][PF_6] (**6.30**), [(BQA)Ru(N_2)(PPh_3)$_2$][PF_6] (**6.31**), and [(BQA)Os(N_2)(PPh_3)$_2$][PF_6] (**6.32**). The latter complex was crystallographically characterized.

6.1. Introduction

With the discovery of the first N_2 complex of a transition metal complex in 1965 came the hope that many N_2 complexes would be shortly forthcoming.[1] Since that original discovery, hundreds of N_2 complexes have been prepared for almost every transition metal as well as some lanthanides and actinides.[2] As a consequence of these efforts, the field of dinitrogen coordination chemistry is now a relatively mature one in which many modes of N_2 coordination have been identified,[3] complete rupture of the N—N triple bond has been observed,[4] and functionalization and even catalytic N_2 reduction has been achieved.[5] However, catalytic functionalization or reduction of N_2 to amine products under mild conditions has yet to be reported.

A wealth of interesting work surrounding N_2 coordination chemistry has been achieved with early and mid-transition metals, particularly group VI. These metal complexes are often mid- to high-valent species and feature a wide range of ancillary ligands. Anilide, and more generally, amide ligands have been particularly well explored in this context, a few examples of which are shown in Figure 6.1. Fryzuk's lab has used a diamide-bisphosphine ligand framework to demonstrate hydrogenation,[6] hydroboration,[7] and hydrosilylation[8] of bound N_2 on Zr and Ta. On the molybdenum front, the laboratories of Cummins and Schrock have used hard anilide ligands to effect N—N bond cleavage and catalytic dinitrogen reduction, respectively.[4,5d] These examples, as well as earlier work from the labs of Chatt[9] and Hidai[10], all feature metal products in their highest oxidation states. Thus, either strong reductants are required to return the metal

center to a state where dinitrogen can be bound, or the metal-N species represents a thermodynamic sink which precludes further reactivity.

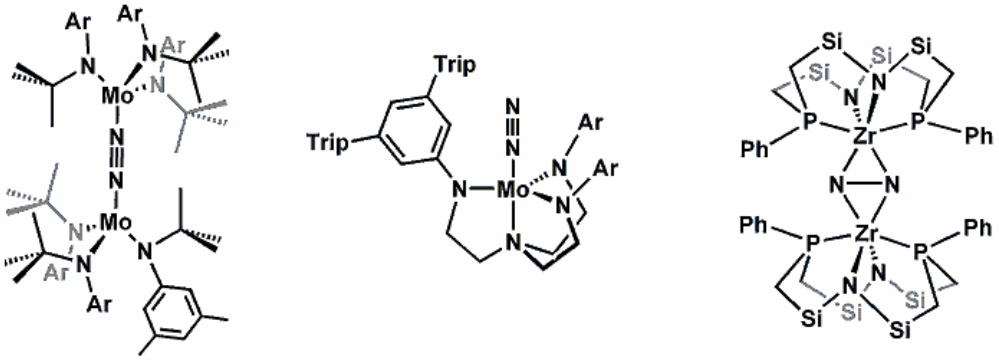


Figure 6.1. Examples of early and mid transition metal complexes employing amide ligands. Representative complexes from the labs of Cummins (left), Schrock (middle), and Fryzuk (right).

For this reason, late transition metals — group VIII in particular — have become an attractive alternative to these early and mid-transition metal systems. Late transition metals have the ability to achieve higher oxidation states (e.g., M(IV-VI)), but are commonly most stable in lower oxidation states (e.g., M(II-III)) which is evidenced in their reaction chemistry. Collman's group focused on synthesizing cofacial metallodiporphyrins for the purpose of electro-catalyzed reduction of dinitrogen utilizing late transition metals.[11] Although they did not succeed in reducing dinitrogen, they were able to demonstrate the complete microscopic reverse by oxidizing ammonia stepwise back to dinitrogen (Figure 6.2). In an effort to demonstrate the disproportionation of a bimetallic N_2 complex (M(N≡N)M→2 M≡N), Taube observed that two osmium nitrides couple to form a half equivalent of dinitrogen upon the oxidation of $[Os(NH_3)_5(CO)]^{2+}$.[12a] In later reports,[12b,c] Taube's group showed that the propensity for the nitride coupling is enhanced upon substitution of the parent amine ligands for pyridine derivatives (pyridine,

2, 2'-bipyridine (bpy), and 2,2':6,2"-terpyridine (tpy)) (Figure 6.3). Meyer's group showed the reversible interconversion between the Os^{VI} nitride, *trans*-$[Os(N)(tpy)(Cl)_2]^+$, and the Os^{II} amine complex, *trans*-$[Os(NH_3)(tpy)(Cl)_2]^{2+}$ (Figure 6.3).[13] The collective importance of this work is that ruthenium and osmium do form well-defined, characterizable intermediates along the dinitrogen reduction pathway, as well as exhibiting the desired conversion of metal nitrides to the corresponding metal amines.

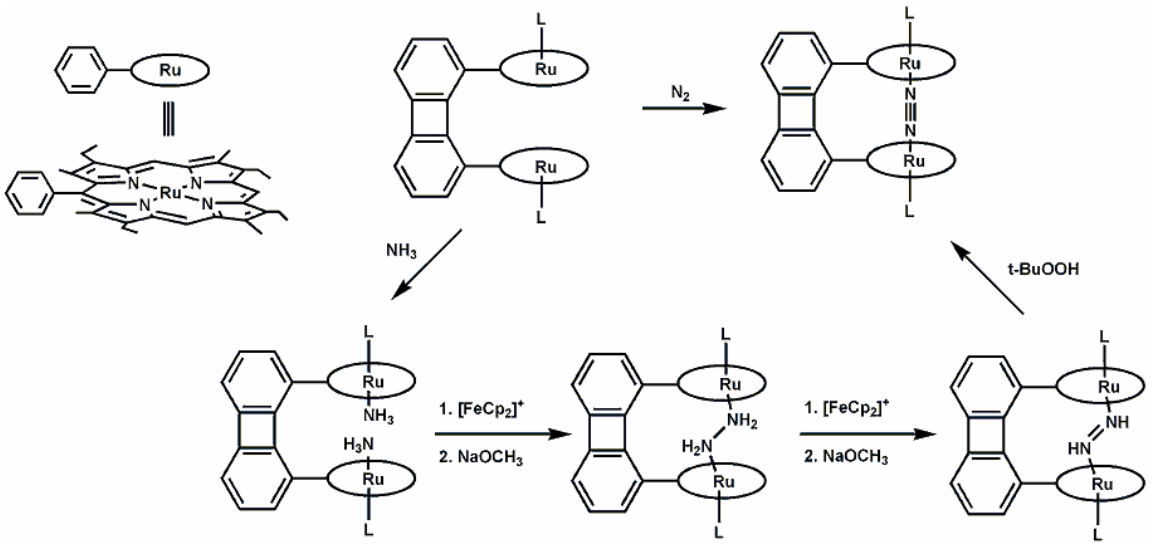


Figure 6.2. Stepwise oxidation of bound ammonia molecules in a diruthenium, cofacial porphyrin complex from Collman's laboratories.

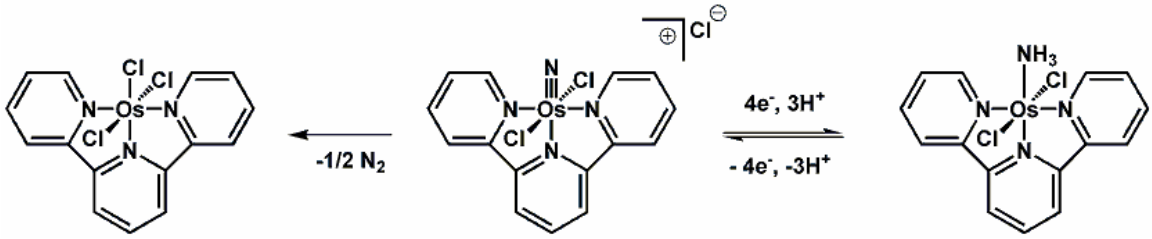
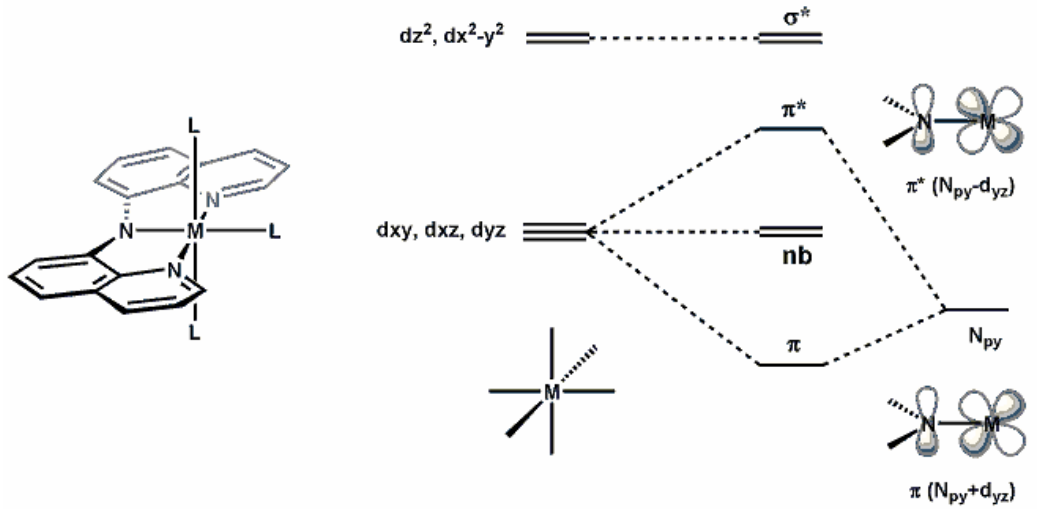


Figure 6.3. Chemistry observed from a $[(tpy)Os(N)Cl_2]Cl$ complex: oxidative nitride coupling (left, Taube) and nitride reduction to amine (right, Meyer).

The chemistry of late transition metal complexes with hard amido ligands has not been thoroughly examined, presumably due to a hard-soft mismatch between the ligand and metal. Interactions between the lone pair of electrons on the nitrogen and a filled d-orbital of appropriate symmetry on the metal center destabilizes the N—M bond, rendering the linkage quite reactive. This incompatibility can be circumvented by using pincer ligand scaffolds where the *hard* functionality (e.g., R_2N^-, R_2C^-) is attached to one or more *soft* functionalities (e.g., R_3N, R_3P), providing a strong chelate-effect and thereby stabilizing the hard-soft, ligand-metal mismatch.[14]

With this in mind, we set out to synthesize group VIII transition metal complexes supported by the rigorously planar bis(8-quinolinyl)amide ligand (BQA) as a monoanionic analog to terpyridine.[15] The filled amido p orbital is adjacent to a filled metal d orbital in d^6 metal complexes (Scheme 6.1). If significant mixing of the amido p orbital and metal d orbital occurs, the highest occupied molecular orbital (HOMO) will be raised in energy. This HOMO-raising may manifest itself at the metal complex by an increased affinity for π-acidic ligands. Herein, we report our progress concerning the coordination chemistry we have observed with this ligand scaffold on group VIII metals, including the coordination of N_2.

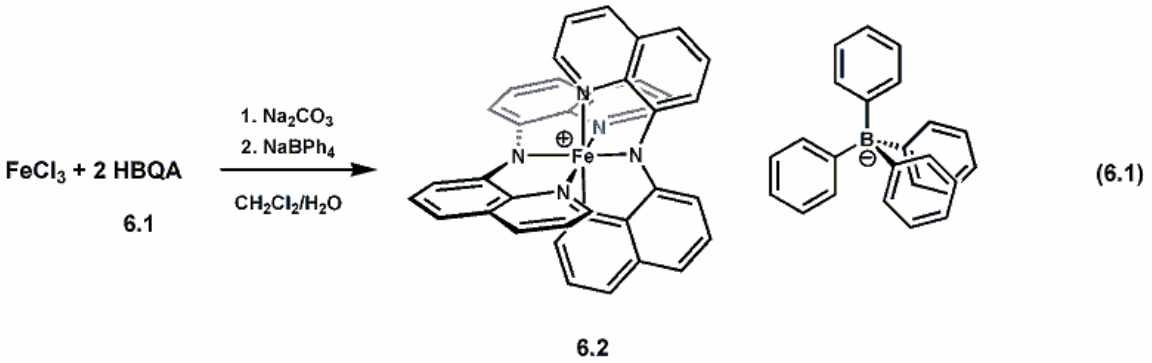
Scheme 6.1



6.2. Results and Discussion

6.2.1. Preparation of BQA complexes of Fe. Delivery of the bis(quinolinyl)amine (HBQA, **6.1**) ligand to group 10 metals has been achieved via two routes: reaction of a metal halide with **6.1**[Li] or reaction of the free amine **6.1** with metal precursor in the presence of excess base.[15] Attempts to generate mono-BQA substituted Fe complexes were unsuccessful, as the bis-substituted species $Fe(BQA)_2$ formed extensively in the reaction mixture despite careful control of reactant stoichiometry. The limited solubility of $Fe(BQA)_2$ prevented its thorough characterization, either in solution, or in the solid state. To circumvent this, metalation of the BQA ligand was carried out with $FeCl_3$ (anhydrous) via an *in situ* salt metathesis reaction (Eq. 6.1). Reacting two equivalents of the amine **6.1** with $FeCl_3$ in dichloromethane with the addition of Na_2CO_3 in water resulted in rapid formation of the desired complex $[Fe(BQA)_2][Cl]$. Addition of an aqueous solution of $NaBPh_4$ to the reaction afforded $[Fe(BQA)_2][BPh_4]$ (**6.2**). The resulting brick red cationic Fe^{III} species is air stable and is readily soluble in polar solvents (CH_2Cl_2, DMSO), unlike the insoluble neutral $Fe(BQA)_2$ species. Complex **6.2**

exhibits paramagnetically shifted ^{1}H NMR resonances and features a doublet ground state (μ_{eff} = 2.1 BM) as determined by the Evans method,[16] indicating the Fe nucleus is low-spin.



A dichloromethane solution of **6.2** exhibits multiple intense transitions in the UV-visible region, [λ_{max}/nm (ε/M^{-1}cm^{-1})]: 1030(11000), 680(2700), 514(33000), 418(49000), 306(90000) (Fig. 1). The high extinction coefficients for the intense transitions at 514, 418, and 306 nm are most likely ligand based π-π* transitions, which is in agreement with the spectrum published for [Co(BQA)$_2$][ClO$_4$] by Lahiri.[17] However, the presence of a weak transition at 680 nm may be the d-d transition ($^3A_1 \rightarrow {}^2T_g$) for the d^5 system. The large extinction coefficient for the band at 1030 nm suggests it is a charge transfer band, quite possibly a LMCT event where a ligand based electron is excited into the singly-occupied d orbital.

The EPR of a solid sample of **6.2** was also collected at 4 K, shown in Figure 6.2. The spin S = ½ state of **6.2** gives rise to a rhombic signal where the three g tensors are resolved: g_z = 2.39, g_y = 2.14, g_x = 1.98. No hyperfine coupling to nitrogen is observed.

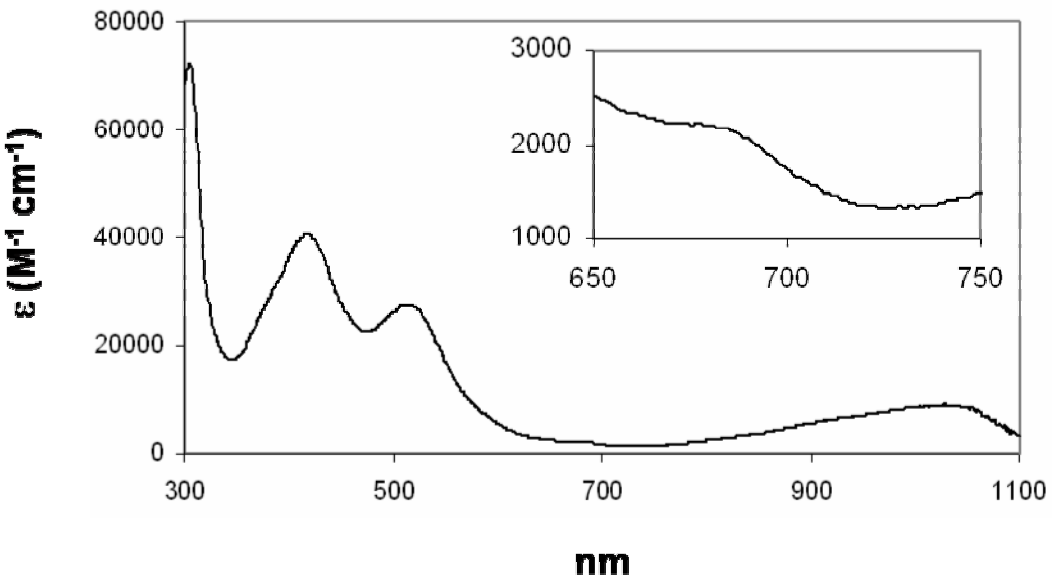


Figure 6.4. Electronic spectrum of $[Fe(BQA)_2][BPh_4]$ (**6.2)**, inset highlights spectrum from 650-750 nm.

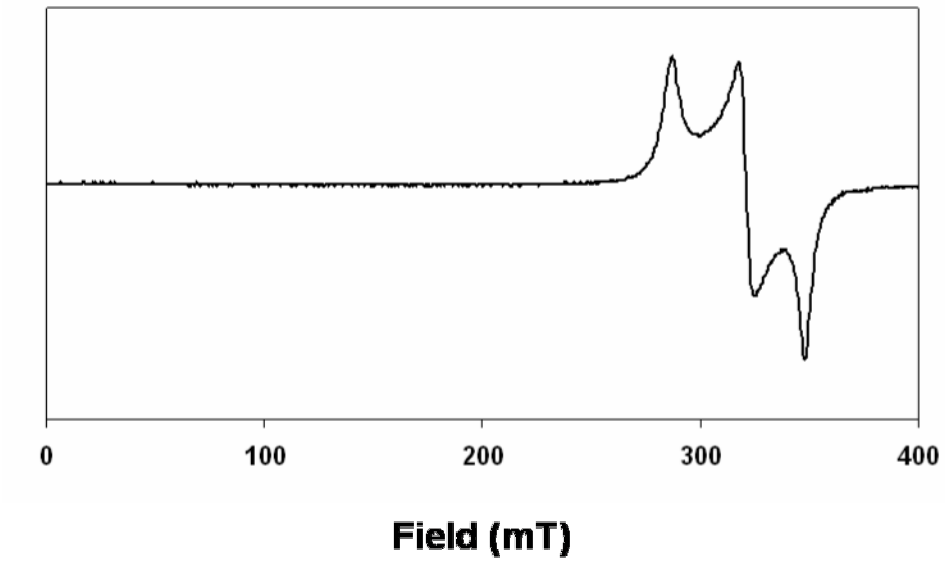


Figure 6.5. EPR spectrum of solid **6.2** (4K, X-band, 9.62 GHz).

6.2.2. Preparation of BQA complexes of Ru and Os. In contrast to metalation with Fe, a single BQA ligand can be installed onto divalent Ru or Os from a variety of precursors.

For example, reaction of the polymeric $[RuCl_2(cod)]_n$ with one equivalent of **6.1**[Li] yielded (BQA)RuCl(COD) (**6.3**) and variable amounts of the di-substituted species $Ru(BQA)_2$ (Eq. 6.2) (cod = cyclooctadiene). Flash chromatography effectively separated the products. Complex **6.3** has been characterized in the solid-state by X-ray crystallography and its solid-state structure is shown in Figure **6.3**. Quantitative conversion to the di-substituted species $Ru(BQA)_2$ (**6.4**) was achieved by refluxing $[RuCl_2(COD)]_n$ with two equivalents of **6.1**[Li] in toluene. An electrospray mass spectrum (ES·MS) of the product mixture reveals only the parent ion peak for the disubstituted species **6.4** at m/z = 642, without **6.3** or any ligand fragmentation apparent in the spectrum.

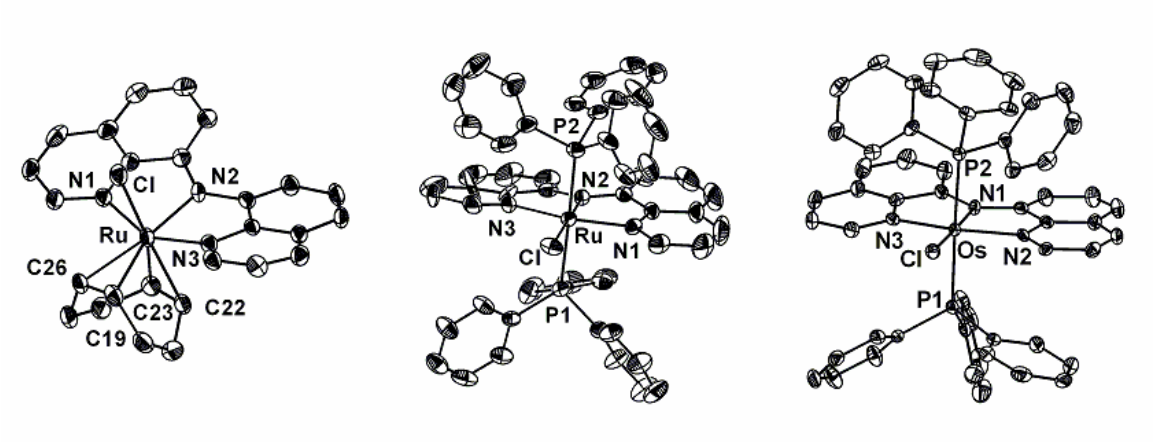
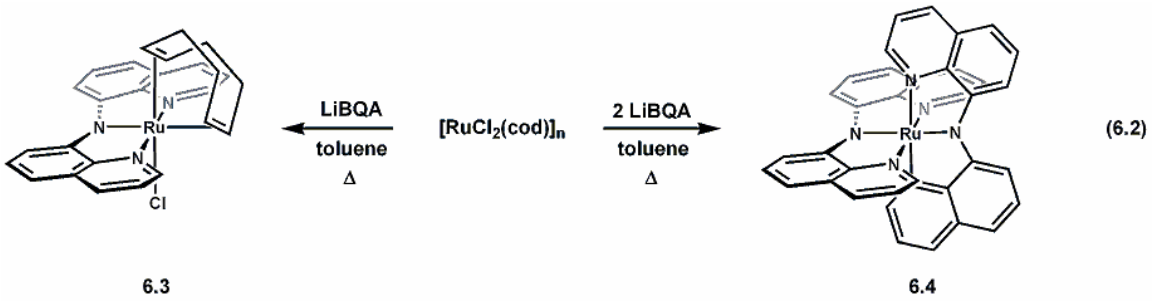
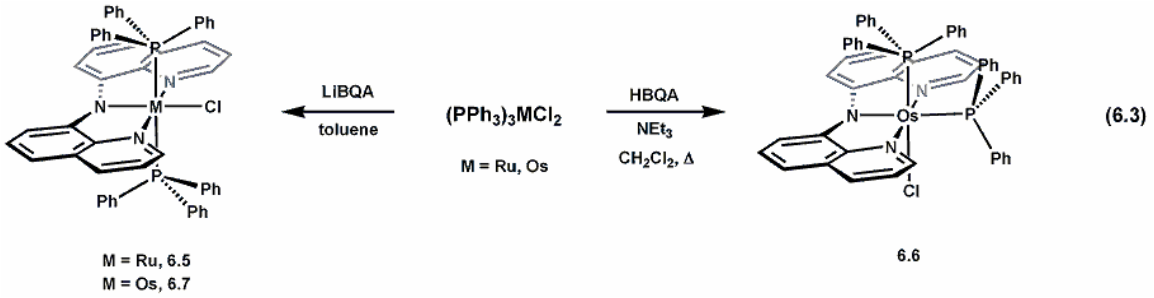


Figure 6.6. Displacement ellipsoid representation (50%) of (left) (BQA)RuCl(cod) (**6.3**), (center) (BQA)RuCl(PPh_3)$_2$ (**6.5**), and (right) (BQA)OsCl(PPh_3)$_2$ (**6.6**). Hydrogen atoms have been removed for clarity. Selected bond distances (Å) and angles (º), for **6.3**: Ru-N1 2.128(3), Ru-N2 2.048(2), Ru-N3 2.126(3), Ru-Cl 2.426(1), avg. Ru-C 2.215(3), N1-Ru-N2 76.9(1), N2-Ru-N3 77.9(1), N1-Ru-N3 151.5(1); for **6.5**: Ru-N1 2.066(3), Ru-N2 2.005(2), Ru-N3 2.061(3), Ru-Cl 2.482(1), Ru-P1 2.397(1), Ru-P2 379(1), N1-Ru-N2 80.4(1), N2-Ru-N3 80.3(1), N1-Ru-N3 160.7(1), P1-Ru-P2 178.9(1); for **6.6**: Os-N1 2.063(3), Os-N2 2.023(3), Os-N3 2.064(3), Os-Cl 2.488(1), Os-P1 2.368(1), Os-P2 381(1), N1-Os-N2 81.5(1), N2-Os-N3 80.1(1), N1-Os-N3 161.5(1), P1-Os-P2 174.8(1).



Refluxing $RuCl_2(PPh_3)_3$ in dichloromethane with the free amine of BQA in the presence of excess base (NEt_3) resulted in the formation of $(BQA)RuCl(PPh_3)_2$ (**6.5**) which can be isolated in crystalline yields exceeding 85% (Eq. 6.3). The ^{31}P NMR spectrum of **6.5** shows a single chemical shift at δ = 29 ppm in benzene, suggesting the phosphorus nuclei are *trans*-disposed with the BQA ligand bound in a *mer* fashion. Product **6.5** can also be obtained via reaction of **6.1**[Li] and $RuCl_2(PPh_3)_3$ in toluene at room temperature. Similarly, the Os congener $(BQA)OsCl(PPh_3)_2$ (**6.6**) can be formed via reaction of **6.1**[Li] and $OsCl_2(PPh_3)_3$ in toluene at room temperature. However, in reacting $OsCl_2(PPh_3)_3$ with the free amine **6.1** in the presence of excess triethylamine base, the *cis*-product of **6.6**, *cis*-$(PPh_3)_2OsCl(BQA)$ (**6.7**), is obtained exclusively as indicated by the ^{31}P NMR spectrum (δ 2.2, -0.9, $^2J_{P\text{-}P}$ = 10.7 Hz) (Eq. 6.3). While **6.7** can be isolated as a brown solid, attempts to crystallize this species exclusively yielded crystals of the green *trans*-disposed product **6.6**. Solid-state crystal structures for complexes **6.5** and **6.6** are shown in Figure 6.6**.** The solid-state structures for **6.3**, **6.5** and **6.6** all demonstrate that the BQA ligand binds in a mer-fashion. The amido N-M bond distances are consistently shorter (Δ = 0.06 Å) than the quinolinyl N-M bond distances. The proclivity for the BQA ligand to pinch back is also apparent by the N1-M-N3 bond angles which range from 150-160º.



6.2.3. Electrochemical Analysis of $(BQA)_nM$ Complexes. It is interesting to compare the $Fe^{III/II}$ redox potentials of **6.2** to other examples of homoleptic Fe complexes. Figure 6.7 shows the cyclic voltammogram of **6.2** in 0.1M $^nBu_4NPF_6$ in dichloromethane and referenced against an internal Fc/Fc^+ standard. The $Fe^{III/II}$ couple for **6.2** ($E_{½}$ = -0.79 V, Δ_p = 65 mV) is 0.79 V more reducing than the $Fe^{III/II}$ couple for Fc, suggesting **6.2** could be used as a mild oxidizing agent.[18] The electron-releasing amides are more reducing than even Cp^*_2Fe, which exhibits an $Fe^{III/II}$ couple at -0.48 V.[18] In addition to the $Fe^{III/II}$ couple, complex **6.2** exhibits a second, quasi-reversible redox event at $E_{½}$ = +0.14 V. The shape of the secondary oxidation event was independent of scan rate (0.05-0.5 V/s) and did not change noticeably when THF or dichloromethane was the solvent. This second redox event could signify a quasi-reversible $Fe^{IV/III}$ redox event, or it could represent some redox process taking place on the BQA ligand itself. The BQA ligand, which exhibits an irreversible oxidation event at +0.56 V (vs. Fc/Fc^+),[17] is most likely the candidate for oxidation in this case. If this second redox event is, in fact, ligand based, the radical can easily be delocalized over the quinoline rings of BQA. The contributing resonance structures are presented in Scheme 6.2.

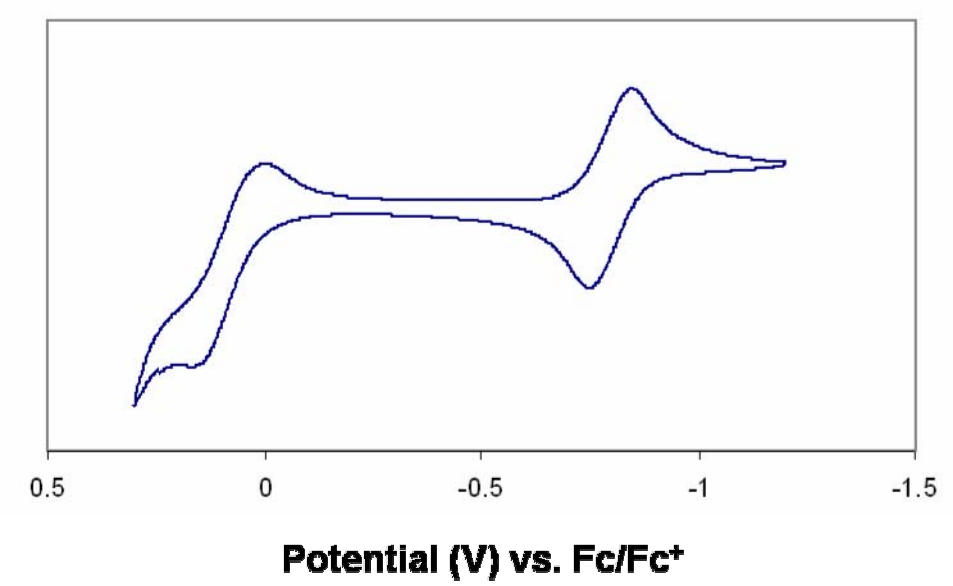
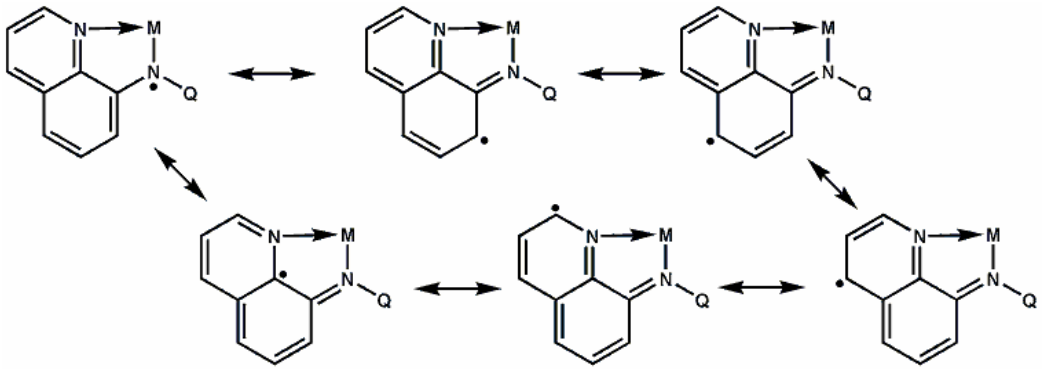


Figure 6.7. Cyclic voltammetry of **6.2** in 0.4 M $^{n}Bu_4NPF_6$/THF, scan rate = 75 mV/s.

Scheme 6.2



In addition to the iron complexes, a series of ruthenium complexes bearing the BQA ligand and 2,2',2"-terpyridine (tpy) ligands were synthesized to further assess the BQA ligand's electron releasing character: $[Ru(tpy)_2]^{2+}$ (**6.8**),[19] $[(terpy)Ru(BQA)][BPh_4]$ (**6.9**), and $Ru(BQA)_2$ (**6.4**). Terpyridine was chosen as a coligand to maintain a nitrogenous donor sphere and because of its structural resemblance to BQA. Complex **6.9** was synthesized by refluxing a dichloromethane solution of $(tpy)RuCl_2(PPh_3)$[20] with one

equivalent of $NaBPh_4$ and **6.1** in the presence of three equivalents of triethylamine. The cyclic voltammograms for **6.8**, **6.9**, and **6.4** are presented in Figure 6.8. The measurements were taken in 0.1M $^{n}Bu_4NPF_6$ in dichloromethane and referenced against an internal Fc/Fc^{+} standard. Complexes **6.8**, **6.9**, and **6.4** all exhibit reversible $Ru^{III/II}$ couples, labeled (A), (B), and (C) in Fig. 6.8, respectively. The $Ru^{III/II}$ couple shifts -0.62 V going from the dication **6.8** ($E_{½}$ = 0.92 V)[19] to the monocation **6.9** ($E_{½}$ = 0.31 V, Δ_p = 89 mV); and the $Ru^{III/II}$ couple shifts an additional -0.52 V going from **6.9** to neutral **6.4** ($E_{½}$ = -0.21 V, Δ_p = 99 mV). Like complex **6.2**, neutral **6.4** exhibits a second reversible wave centered at $E_{½}$ = +0.60 V (Δ_p = 97 mV). This event may be attributable to a reversible $Ru^{IV/III}$ redox event or may represent a reversible oxidation of the BQA ligand like that observed for **6.2**. The latter scenario is the more likely.

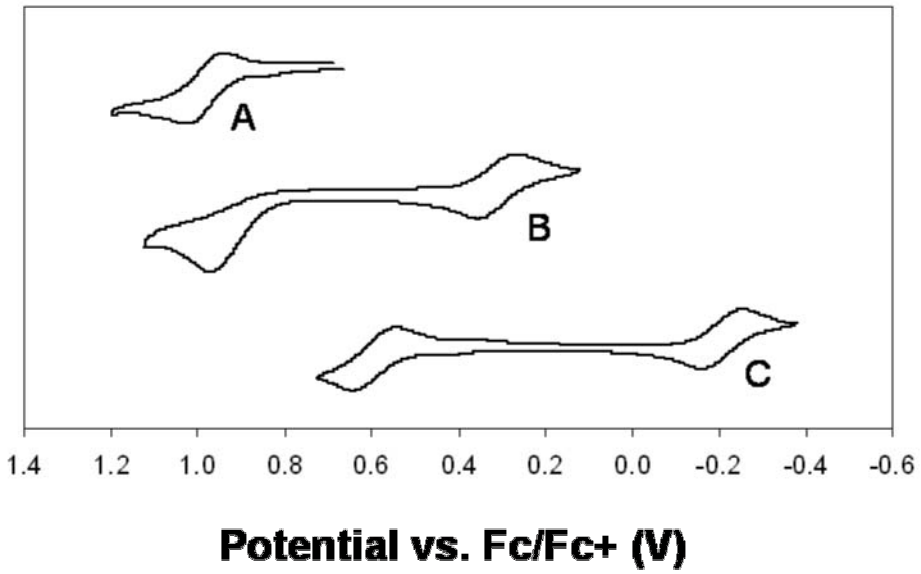


Figure 6.8. Cyclic voltammetry of (top) $[(tpy)_2Ru]^{2+}$ (**6.8**), (middle) $[(tpy)Ru(BQA)]^{+}$ (**6.9**), (bottom) $Ru(BQA)_2$ (**6.4**); in 0.4 M $^{n}Bu_4NPF_6/CH_2Cl_2$, scan rate = 75 mV/s.

The potential $M^{III/IV}$ redox couples observed for **6.2** and **6.4** prompted us to examine whether this feature was limited to complexes of the composition $M(BQA)_2$. Interestingly, both the ruthenium and osmium complexes, **6.5** and **6.6**, exhibit two reversible redox processes as shown in Figure 6.9 (0.4 M $^{n}Bu_4NPF_6$ in dichloromethane, referenced to internal Fc/Fc^{+}). Complex **6.5** exhibits a reversible redox wave at $E_{½}$ = -0.55 V (Δ_p = 78 mV) assigned as the $Ru^{II/III}$ couple. The second reversible redox wave comes at $E_{½}$ = +0.45 V (Δ_p = 76 mV) and is assigned as a reversible BQA oxidation event. This second redox couple is close to the second redox couple observed for complex **6.4** ($E_{½}$ = +0.60 V). The Os complex **6.6** similarly displays two reversible redox processes centered at $E_{½}$ = -0.72 V ($Os^{II/III}$, Δ_p = 85 mV) and $E_{½}$ = +0.23 V (BQA/BQA^{+}, Δ_p = 83 mV). The reversible nature of the second redox couple observed for **6.4**, **6.5**, and **6.6**, suggests that they are metal based redox events, whereas the irreversible nature of the second redox event for **6.2** indicates a ligand-centered oxidation mechanism is more likely.

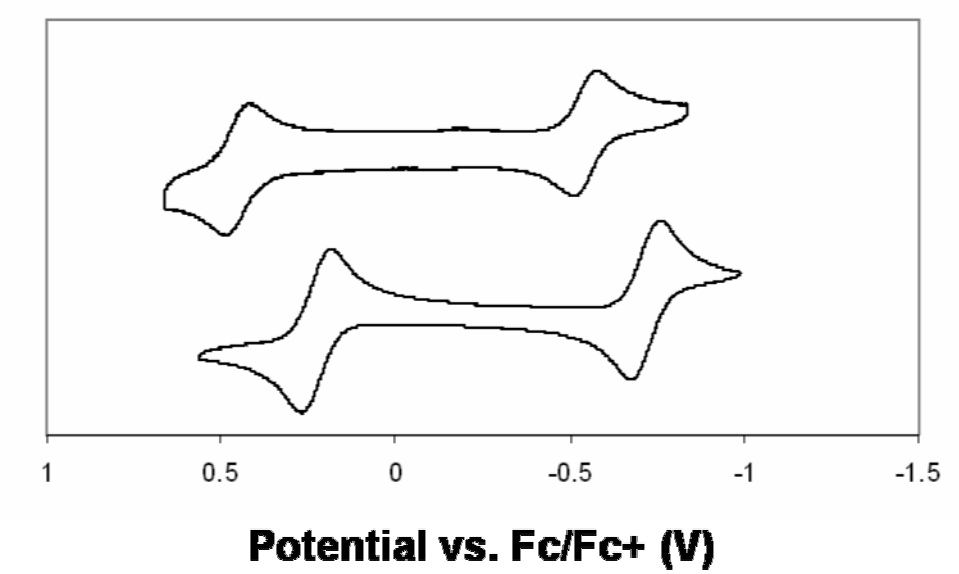
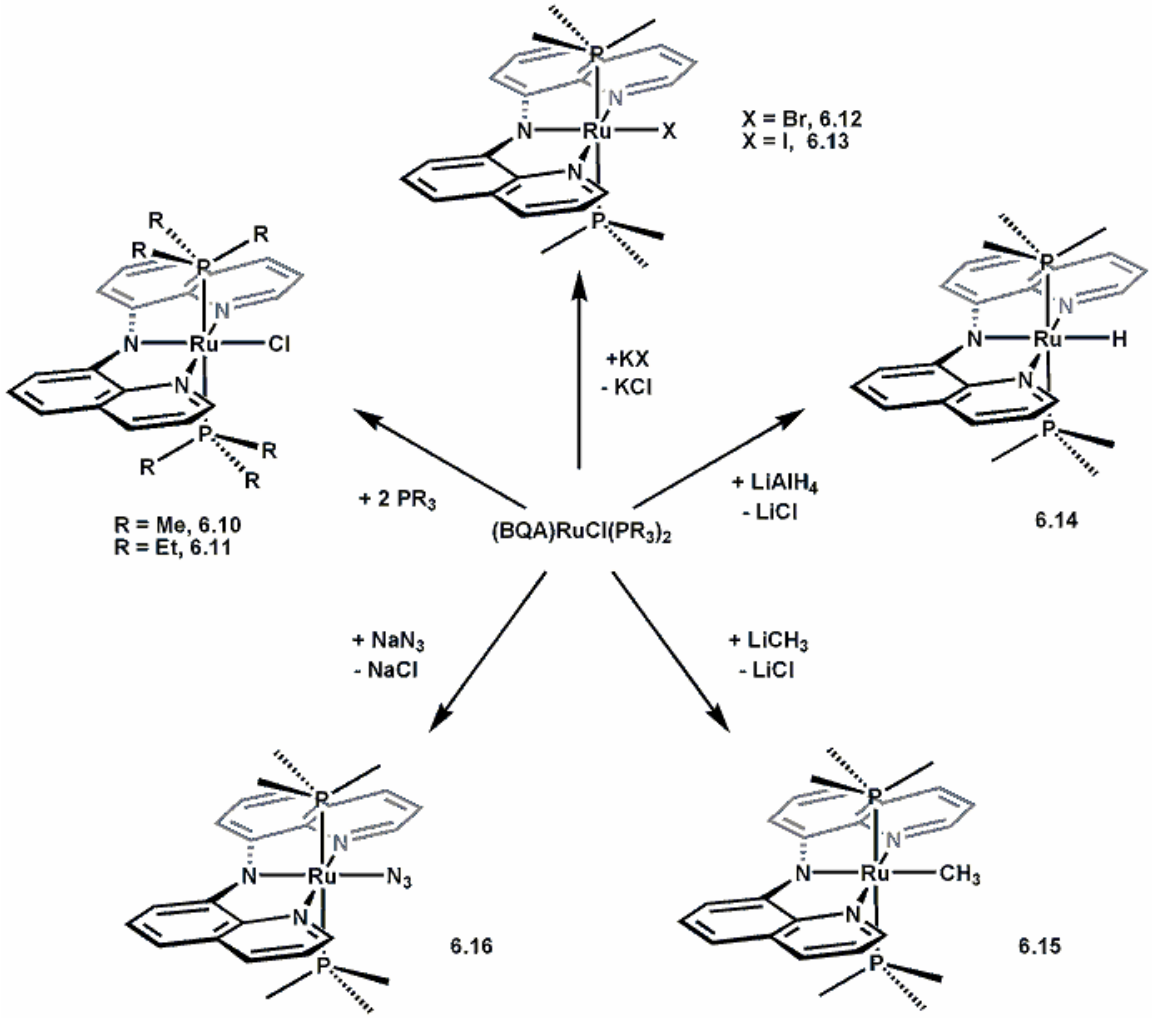


Figure 6.9. Cyclic voltammetry of (top) (BQA)RuCl(PPh_3)$_2$ (**6.5**) and (bottom) (BQA)OsCl(PPh_3)$_2$ (**6.6**); in 0.1 M ^{n}Bu$_4$NPF$_6$/CH_2Cl_2, scan rate = 50 mV/s.

6.2.4. Ligand Exchange Reactions. To survey the general reactivity of the (BQA)MX(PPh_3)$_2$ complexes, we probed the exchange reactions of the phosphine and halide ligands (Scheme 6.3). Substitution of the PPh_3 units on **6.5** for smaller, stronger σ-donor phosphine ligands occurs under relatively mild conditions. Triethylphosphine substitutes twice at 40 ºC to form *trans*-(BQA)RuCl(PEt_3)$_2$ (**6.10**), while trimethylphosphine substitutes at room temperature to form *trans*-(BQA)RuCl(PMe_3)$_2$ (**6.11**) (Scheme **6.3**). The *trans* geometry is preserved from **6.5**, as evidenced by the ^{31}P NMR which shows a single chemical shift for both **6.10** and **6.11** at 11.8 and 0.5 ppm, respectively. Refluxing **6.5** in excess pyridine resulted in incomplete phosphine substitution as ascertained by ^{31}P NMR, while acetonitrile does not affect any phosphine displacement under refluxing conditions. Likewise, refluxing precursor **6.5** with larger

ligand types like PCy_3 or N-heterocyclic carbenes did not result in any phosphine displacement.

Scheme 6.3

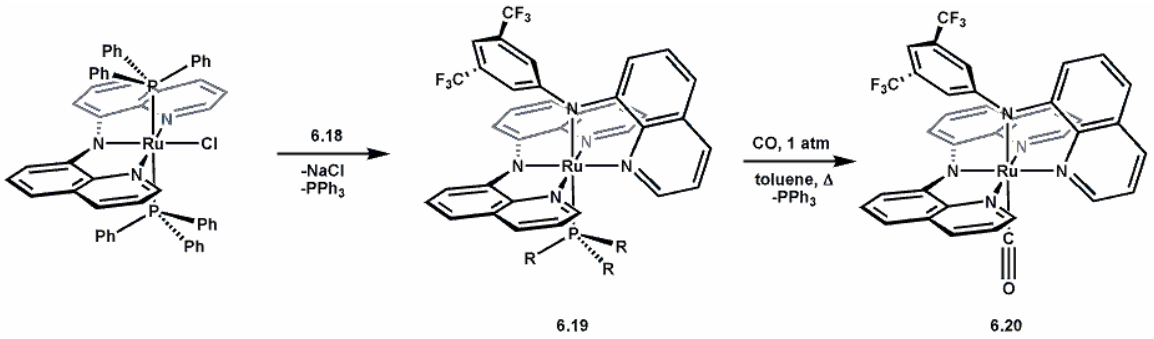


One of the questions concerning the BQA ligand moiety was whether the amido nitrogen would display any *trans*-influence in octahedral complexes. Thus, we probed replacing the halide ligand in **6.11** with a range of anionic ligands to determine the effect of having the amido nitrogen *trans* to the X-type ligand. Refluxing **6.11** in THF with 4 equivalents of the appropriate potassium salt achieved substitution of the halide ligand to produce the bromide and iodide complexes *trans*-(BQA)RuBr$(PMe_3)_2$ (**6.12**) and *trans*-

(BQA)RuI(PMe_3)$_2$ (**6.13**) (Scheme 6.3). Reacting **6.11** with $LiAlH_4$ in toluene at room temperature provided the hydride *trans*-(BQA)RuH(PMe_3)$_2$ (**6.14**) in moderate yield, while synthesis of the methyl complex *trans*-(BQA)RuMe(PMe_3)$_2$ (**6.15**) required excess MeLi in refluxing toluene. The azide complex *trans*-(BQA)Ru(N_3)(PMe_3)$_2$ (**6.16**) was prepared by refluxing NaN_3 and **6.11** in a mixture of THF and dichloromethane for several hours. Complexes **6.12**-**6.16** all maintain the coordination environment of the parent species **6.11**, showing no propensity to redistribute the X-type ligands as a result of the *trans*-influence from the BQA amido nitrogen to leave the strong *trans*-influencing ligands *cis*-disposed.[21]

Contrary to this trend observed above, reaction of **6.5** with the sodium salt of the monoquinolinyl-amide [3,5-(CF_3)$_2$Ph-QA][Na(Et_2O)] (**6.18**) resulted in formation of the deep purple complex (BQA)Ru(3,5-(CF_3)$_2$Ph-QA)(PPh_3) (**6.19**) (Scheme 6.4). For **6.19**, the amide from the mono-quinoline ligand is *trans* to the phosphine ligand, orienting the bulky *bis*-3,5-triflouromethyl phenyl amide substituent on the opposite side of the BQA plane from the phosphine ligand. This orientation was verified via crystallographic characterization of **6.19** whose solid-state structure is shown in Figure 6.10. Phosphine ligand substitution only occurred when **6.19** was refluxed in toluene. For example, the carbonyl adduct (BQA)Ru(3,5-(CF_3)$_2$Ph-QA)(CO) (**6.20**) could only be formed by refluxing **6.19** in toluene under an atmosphere of CO gas for 20 hours. Formation of **6.20** from **6.19** was accompanied by a color change from deep purple to an intense red.

Scheme 6.4



Reaction of **6.5** with the anionic bis-phosphine $[Ph_2B(CH_2PPh_2)_2][NEt_4]$ (hereafter referred as $[Ph_2BP_2]$)[22] in THF generated the product $[(Ph_2BP_2)RuCl(BQA)][NEt_4]$ (**6.21**) as a midnight blue solid. The ^{31}P NMR for complex **6.21** displays a doublet of doublets (δ 54, 28.3 ppm, $^2J_{P\text{-}P}$ = 36 Hz), indicating the phosphorous inequivalent environments as confirmed by a solid state X-ray diffraction study (Figure 6.10). Installation of the $[Ph_2BP_2]^-$ ligand affected complete displacement of the phosphine ligands from **6.5**, though the chloride remains bound to the metal *cis* to the amido nitrogen. Washing **6.21** with ethanol abstracted an equivalent of NEt_4Cl and precipitated the 16 e^-, neutral complex $(Ph_2BP_2)Ru(BQA)$ (**6.22**) as a wine red solid (Scheme 6.5). Complex **6.22** displayed a singlet in the ^{31}P NMR at 69 ppm, indicating the equivalent phosphine positions with **6.22** adopting trigonal-bipyramidal geometry. Complex **6.22** is stable as a coordinatively-unsaturated complex and does not pick up an equivalent of dinitrogen to fill the vacant coordination site, even under elevated pressures (60-80 psi). However, the carbonyl complex $(Ph_2BP_2)Ru(CO)(BQA)$ (**6.23**) was readily prepared by addition of CO gas to a solution of **6.22** in dichloromethane, or alternatively, by chloride displacement in **6.21** in THF.

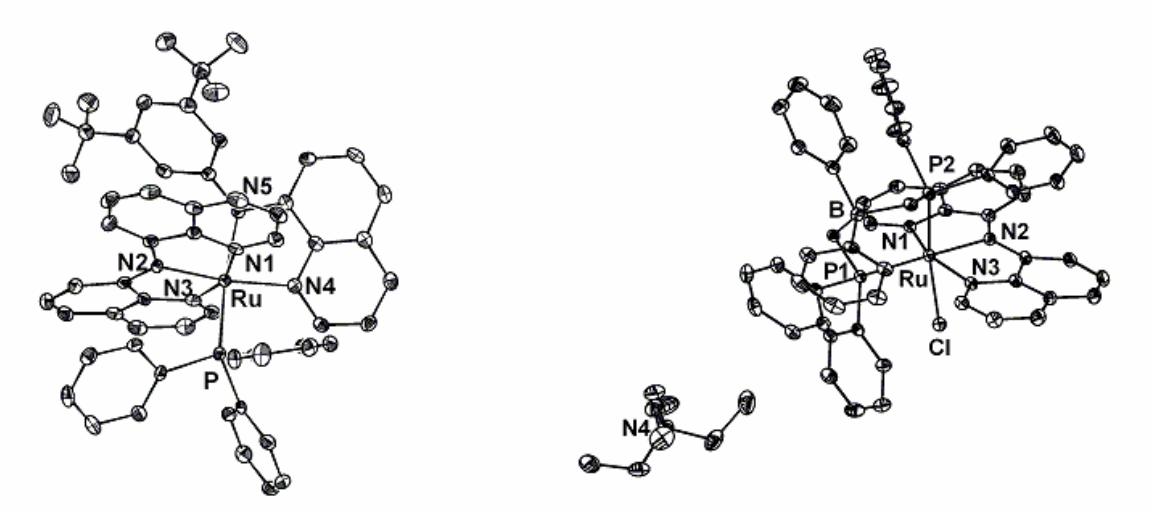
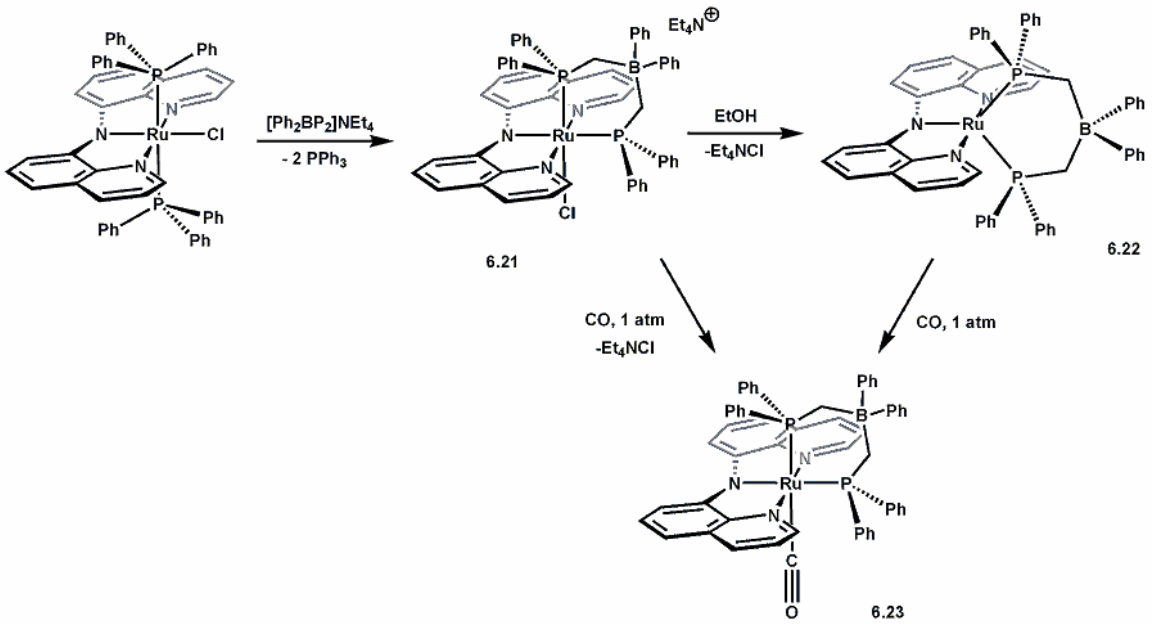


Figure 6.10. Displacement ellipsoid representation (50%) of (left) (BQA)Ru(3,5-$(CF_3)_2$Ph-QA)(PPh_3) (**6.19**) and (right) [(Ph_2BP_2)RuCl(BQA)][NEt_4] (**6.21**). Hydrogen atoms and solvent molecules have been removed for clarity. Selected bond distances (Å) and angles (º), for **6.19**: Ru-N1 2.066(3), Ru-N2 2.021(3), Ru-N3 2.045(3), Ru-N4 2.094(3), Ru-N5 2.144(3), Ru-P1 2.319(1), N1-Ru-N2 81.02(1), N2-Ru-N3 80.88(1), N1-Ru-N3 160.82(1), N4-Ru-N5 77.48(1), N5-Ru-P1 170.99(1); for **6.21**: Ru-N1 2.095(4), Ru-N2 2.050(4), Ru-N3 2.078(4), Ru-Cl 2.515(1), Ru-P1 2.353(1), Ru-P2 2.291(1), N1-Ru-N2 78.9(1), N2-Ru-N3 79.8(1), N1-Ru-N3 158.1(1), P1-Ru-P2 90.33(5).

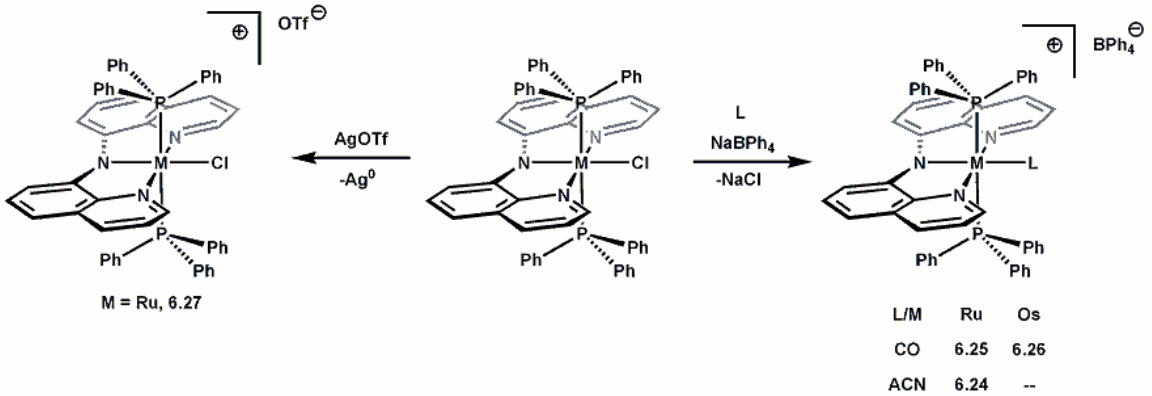
Scheme 6.5



6.2.5. Formation of Cationic Species. An alternative route to opening the coordination sphere of the Ru and Os complexes was to remove the halide ligands from complexes **6.5** and **6.6**. Salt metathesis on **6.5** or **6.6** with simple sodium or potassium reagents (e.g., $NaBPh_4$ or KPF_6) was not observed in the absence of a strongly binding ligand. Reaction of **6.5** with $NaBPh_4$ in a mixture of THF/acetonitrile immediately produced the purple solvento species $[(BQA)Ru(NCCH_3)(PPh_3)_2][BPh_4]$ (**6.24**) with concomitant production of NaCl (Scheme 6.6). However, complex **6.5** was unreactive with an excess of $NaBPh_4$ under a dinitrogen atmosphere over a period of several days. The observed reactivity did not change even under elevated pressures (14-80 psi) of N_2, nor did it change using a variety of solvents (THF, THF/EtOH, CH_2Cl_2). In contrast, reaction of **6.5** and $NaBPh_4$ under an atmosphere of carbon monoxide in THF produces the cherry red complex $[(BQA)Ru(CO)(PPh_3)_2][BPh_4]$ (**6.25**) within minutes (Scheme 6.6). The Os congener $[(BQA)Os(CO)(PPh_3)_2][BPh_4]$ (**6.26**) was similarly synthesized from **6.6** and $NaBPh_4$.

For both **6.25** and **6.26**, the phosphines remain *trans*-disposed as indicated by their ^{31}P NMR which show single peaks for both species (δ = 30.1 ppm for **6.25**, 0.31 ppm for **6.26**). The infrared stretching frequency of the carbonyl ligand for cationic **6.25** (ν_{CO} = 1946 cm^{-1}) is lower than that of the neutral terpyridine complex (trpy)$RuCl_2(CO)$ (ν_{CO} = 1953 cm^{-1}).[20] The Os complex **6.26** features a reduced carbonyl stretching frequency (ν_{CO} = 1921 cm^{-1}) from **6.25**.

Scheme 6.6



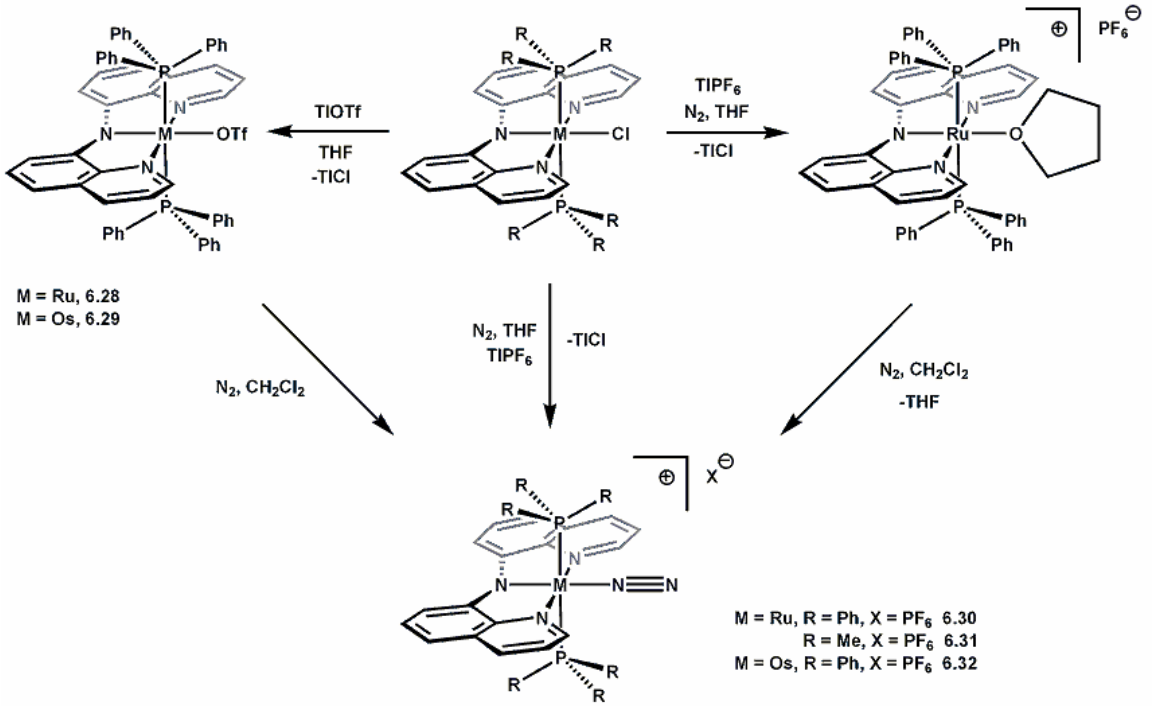
In an effort to synthesize a dinitrogen complex of Ru or Os, more aggressive halide scavenging reagents were tried. Puenta et al. successfully employed AgOTf as a halide scavenger to form a cationic dinitrogen complex en route to $[TpRu(N_2)(PEt_3)_2][BPh_4]$ (Tp = hydrotris(pyrazolyl)borate).[23] Van Koten successfully produced the pincer complex $[Ru^{II}(OTf)\{C_6H_2(CH_2PPh_2)_2\}(PPh_3)]$ using AgOTf with the corresponding chloride precursor.[24] In an attempt to facilitate a similar transformation from **6.5**, a solution of **6.5** in THF was reacted with an equimolar amount of AgOTf in the dark. The initial aqua-blue hue of **6.5** immediately faded as a dark brown precipitate formed with concomitant formation of Ag^0. The isolated brown solid was identified as

the oxidized product $[(BQA)Ru^{III}Cl(PPh_3)_2][OTf]$ (**6.27**) (Scheme 6.6). Oxidation of the Ru center is kinetically favored over halide-abstraction.

To circumvent this undesirable oxidation event, Tl reagents were then investigated to facilitate the halide abstraction. The M^{II} triflate complexes $(BQA)Ru(OTf)(PPh_3)_2$ (**6.28**) and $(BQA)Os(OTf)(PPh_3)_2$ (**6.29**) were readily afforded by reaction of the corresponding chloride complexes **6.5** and **6.6** with TlOTf in THF (Scheme 6.7). These complexes could not be isolated as single complexes because the triflate ligand showed a propensity to dissociate. Upon reacting **6.5** with $TlPF_6$ in a THF solution, the color of the solution darkened within minutes to produce a midnight blue solution with concomitant formation of a white precipitate. The ^{31}P NMR of this solution taken *in situ* shows a very modest shift from **6.5** (δ = 29 ppm) to 28 ppm, whereas the solution IR did not reveal any different vibrational intensities from the parent species **6.5**. Removal of the volatiles *in vacuo* yielded a purple solid that had limited solubility in THF and was completely insoluble in hydrocarbon solvents. The purple solids readily dissolved in dichloromethane to give an intense cherry-red solution (λ_{max} = 542 nm). The solution IR of the red solution displayed an intense vibration at 2130 cm^{-1} which was attributed to a dinitrogen molecule binding *trans* to the BQA amido nitrogen in the complex $[(BQA)Ru(N_2)(PPh_3)_2][PF_6]$ (**6.30**). Complex **6.30** shows a single ^{31}P NMR resonance at 25 ppm shifted upfield from the parent species **6.5**. The purple intermediate that preceded formation of **6.30** has been postulated as a solvento species where THF binds in place of the Cl. The THF complex has not been completely characterized due to its propensity to form **6.30** upon storage under N_2 atmospheres. Thallium halide abstraction from the PMe_3 complex **6.11** with $TlPF_6$ proceeded directly to a dinitrogen

adduct complex $[(BQA)Ru(N_2)(PMe_3)_2][PF_6]$ (**6.31**), even in THF solutions (KBr/THF; ν_{NN} = 2129 cm^{-1}) without an observable solvento intermediate. Reaction of the Os complex **6.6** with $TlPF_6$ likewise produced the dinitrogen adduct $[(BQA)Os(N_2)(PPh_3)_2][PF_6]$ (**6.32**) with no observable THF-solvent adduct intermediate (Scheme 6.7). The Os congener **6.32** is remarkably stable and even identifiable as the Os—N_2 cation via electrospray mass-spectrometry. We obtained a solid state structure via X-ray crystallography which confirms the N_2 molecule is *trans* to the amido nitrogen (Figure 6.11). The N_2 ligand does not exhibit any elongation from free N_2,[25] indicative that the N_2 is not being activated by Os^{2+} which is also evident from the high stretching frequency (υ_{NN} = 2071 cm^{-1}) observed for **6.32**.

Scheme 6.7



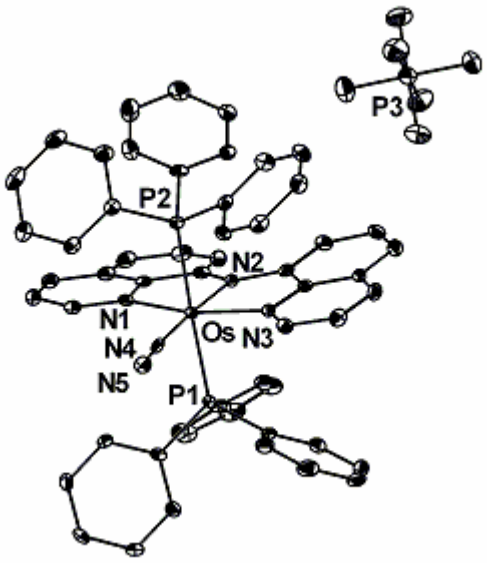


Figure 6.11. Displacement ellipsoid representation (50%) of $[(BQA)Os(N_2)(PPh_3)_2][PF_6]$ (**6.32**). Hydrogen atoms have been removed for clarity. Selected bond distances (Å) and angles (º), for **6.32**: Os-N1 2.096(2), Os-N2 2.032(3), Os-N3 2.062(2), Os-N4 1.954(3), N4-N5 1.080(4), Os-P1 2.403(1), Os-P2 2.403(1), N1-Os-N2 79.97(1), N2-Os-N3 80.80(1), N1-Os-N3 160.6(1), P1-Os-P2 177.4(1).

6.3. Conclusions.

The coordination chemistry of group VIII complexes supported by the bis(quinolinyl)amide (BQA) ligand has been explored. While only a bis-ligated complex of Fe could be isolated, both Ru and Os BQA complexes show a large degree of ligand substitution chemistry. Electrochemical analyses of these complexes indicate that the high-energy amido lone pair may be exhibiting reversible oxidation chemistry. The (BQA)Ru core undergoes facile phosphine substitution as well as halide exchange reactions. Methathetic routes yielded (BQA)Ru complexes featuring hydrides, azides, and even methyl ligands. Formation of Ru and Os cationic species by halide abstraction

provided convenient entry routes to carbonyl and dinitrogen complexes. While the π-acidic ligands prefer a trans-disposition to the BQA amido nitrogen, the stretching frequencies for the CO and N_2 ligands measured by IR do not indicate a substantial degree of π back-donation from the metal center. Thus, our original hypothesis that having the amido lone pair adjacent to a filled metal d orbital (of appropriate symmetry) would raise the complex HOMO to facilitate interactions with π-acidic ligands may not be occurring to a large extent. Because the (BQA)Ru and (BQA)Os complexes are excellent synthons for ligand-exchange reactions, these may be candidates to facilitate group transfer chemistry, such as epoxidation, cyclopropanation, or aziridination chemistry from azide precursors.

Table 6.1. X-ray diffraction experimental details for (BQA)RuCl(cod) (**6.3**), (BQA)RuCl(PPh_3)$_2$ (**6.5**), (BQA)OsCl(PPh_3)$_2$ (**6.6**), (BQA)Ru(3,5-(CF_3)$_2$Ph-QA)(PPh_3) (**6.19**), [($Ph_2B(CH_2PPh_2)_2$)RuCl(BQA)][NEt_4] (**6.21**), and [(BQA)Os(N_2)(PPh_3)$_2$][PF_6] (**6.32**).

	6.3	**6.5**	**6.6**·C_6H_6	**6.19**	**6.21**·2 CH_2Cl_2· THF	**6.32**
Chemical Formula	$C_{32}H_{30}ClN_3Ru$	$C_{54}H_{41}ClN_3P_2Ru$	$C_{60}H_{48}ClN_3OsP_2$	$C_{53}H_{36}F_6N_5PRu$	$C_{70}H_{78}BCl_5N_4O_2P_2Ru$	$C_{54}H_{42}F_6N_5OsP_3$
Formula Weight	593.11	930.36	1098.60	988.91	1342.43	1158.04
T (ºC)	177	177	177	177	177	177
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
a (Å)	11.570(3)	10.5631(9)	15.009(5)	18.610(5)	11.9746(11)	11.7356(9)
b (Å)	20.291(6)	18.5043(16)	21.087(7)	12.525(3)	12.7722(12)	13.4605(10)
c (Å)	21.838(6)	21.8173(18)	15.205(5)	17.854(5)	22.031(2)	16.7482(13)
α (º)	90	90	90	90	102.928(2)	85.072(1)
β (º)	90	90.775(2)	101.351(5)	93.307(4)	97.964(2)	72.800(1)
γ (º)	90	90	90	90	94.613(2)	64.240(1)
V (Å^3)	5127(2)	4264.1(6)	4718(3)	4178(2)	3230.7(5)	2273.4(3)
Space Group	Pbca	P2(1)/n	P2(1)/n	Cc	P-1	P-1
Z	8	4	4	4	2	4
D_{calcd} (g/cm^3)	1.537	1.449	1.547	1.572	1.380	1.692
μ (cm^{-1})	7.43	5.48	28.72	4.87	5.46	29.81
R1, wR2 (I>2σ(I))	0.0299, 0.0631	0.0502, 0.0849	0.0244, 0.0582	0.0256, 0.0487	0.0696, 0.1359	0.0288, 0.0642

$R1 = \Sigma ||F_o|-|F_c|| / \Sigma |F_o|$, w$R2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

6.4 Experimental Section

6.4.1 General Considerations. All manipulations were carried out using standard Schlenk or glove-box techniques under a dinitrogen atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thorough sparging with N_2 gas followed by passage through an activated alumina column. Non-halogenated solvents were typically tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective oxygen and moisture removal. The reagents $NaBPh_4$, $TlPF_6$, $FeCl_2$, and $FeCl_3$(anhydrous) were purchased from commercial vendors and used without further purification. HBQA (**6.1**, HBQA = bis(quinolinyl)amide),[15] $RuCl_2(PPh_3)_3$,[26] $[RuCl_2(cod)]_n$,[27] $OsCl_2(PPh_3)_3$,[28] and $[Ph_2B(CH_2PPh_2)_2][NEt_4]$[22] were synthesized as described previously. Deuterated solvents were degassed and stored over activated 3-Å molecular sieves prior to use. Elemental analyses were carried out at Desert Analytics, Tucson, Arizona. NMR spectra were recorded at ambient temperature on Varian Mercury 300 MHz, Joel 400 MHz, and an Anova 500 MHz spectrometers, unless otherwise noted. ^{1}H and ^{13}C NMR chemical shifts were referenced to residual solvent. ^{31}P NMR, ^{11}B NMR, and ^{19}F NMR chemical shifts are reported relative to an external standard of 85% H_3PO_4, neat $BF_3{\cdot}Et_2O$, and neat $CFCl_3$ respectively. IR spectra were recorded on a Bio-Rad Excalibur FTS 3000 spectrometer controlled by Win-IR Pro software. MS data for samples were obtained by injection of a hydrocarbon solution into a Hewlett Packard 1100MSD Mass Spectrometer (ES^+) or an Agilent 5973 Mass Selective Detector (EI). UV-vis measurements were taken on a Hewlett Packard 8452A diode array spectrometer using a quartz crystal cell with a Teflon cap. X-ray diffraction studies were carried out in

the Beckman Institute Crystallographic Facility on a Bruker Smart 1000 CCD diffractometer.

6.4.2. X-ray Crystallography Procedures. X-ray quality crystals were grown as indicated in the experimental procedures for each complex. The crystals were mounted on a glass fiber with Paratone-N oil. Structures were determined using direct methods with standard Fourier techniques using the Bruker AXS software package. In some cases, Patterson maps were used in place of the direct methods procedure.

6.4.3. EPR Measurements. X-band EPR spectra were obtained on a Bruker EMX spectrometer equipped with a rectangular cavity working in the TE_{102} mode. Variable temperature measurements were conducted with an Oxford continuous-flow helium cryostat (temperature range 3.6-300 K). Accurate frequency values were provided by a frequency counter built in the microwave bridge. Solution spectra were acquired in toluene for all of the complexes. Sample preparation was performed under a nitrogen atmosphere.

6.4.4. Syntheses of Compounds.

Synthesis of $[Fe(BQA)_2][BPh_4]$ (6.2). HBQA (0.82 g, 3.02 mmol) and $FeCl_3$ (anhydrous) (245 mg, 1.5 mmol) were added to a vigorously stirring solution of CH_2Cl_2. A solution of Na_2CO_3 (320 mg, 3.05 mmol) and $NaBPh_4$ (517 mg, 1.5 mmol) in H_2O (30 mL) was added to the CH_2Cl_2 solution. The reaction solution was stirred for 20 h at room temperature. The product was extracted into CH_2Cl_2 and washed with H_2O (3 x 25 mL). The organic phase was evaporated to dryness to yield a red powder (0.98 g, 71%). ^1H NMR (DMSO-d_6, 300 MHz, 25°C): δ 29.1, 19.8, 7.17, 6.91 (t, J = 6.6 Hz), 6.77 (t, J = 6.6 Hz), -8.3, -29.0, -61.7, -65.3. UV-Vis region, [λ_{max}/nm ($\varepsilon/M^{-1}cm^{-1}$)]: 1030(11000),

680(2700), 514(33000), 418(49000), 306(90000). ES-MS (Electrospray): positive mode $[(BQA)_2Fe]^+$ m/z 596, found $(M)^+$ m/z 596; $[Ph_4B]^-$ m/z 319, found $(M)^-$ m/z 319. Anal. Calcd for $C_{60}H_{44}BFeN_6$: C, 75.45; H, 4.58; N, 11.12; found: C, 75.22; H, 4.68; N, 11.00.

Synthesis of (BQA)RuCl(COD) (6.3). A suspension of $Ru(COD)Cl_2$ (0.36 g, 1.3 mmol) in toluene (10 mL) was treated with a solution of [BQA][Li] (0.35 g, 1.3 mmol) in toluene (10mL) at room temperature. After the mixture was stirred for 48 h the solvent was removed *in vacuo*. The residue was extracted with dichloromethane and filtered through Celite on a sintered glass frit to yield a purple filtrate. Layering the filtrate with petroleum ether precipitated a purple solid. The product was collected via filtration, washed with copious amounts of petroleum ether and dried *in vacuo* (0.41 g, 62%). ^1H NMR ($CDCl_3$, 300 MHz) δ 9.12–9.11 (m, 2H), 8.12–8.09 (m, 2H), 7.90–7.87 (m, 2H), 7.48–7.37 (m, 2H), 7.01–6.98 (m, 2H), 4.52–4.50 (m, 2H), 3.19–3.17 (m, 2H), 2.67–2.60 (m 2H), 2.29 –2.20 (m, 2H), 1.96 –1.92 (m, 2H), 1.80 –1.74 (m, 2H). ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 149.94, 137.14, 131.68, 128.83, 128.42, 122.60, 122.03, 113.52, 112.85, 94.75, 89.92, 30.39, 28.68. UV-Vis region, $[\lambda_{max}/nm$ $(\varepsilon/M^{-1}cm^{-1})]$: 324 (9900), 302 (7000), 590 (6200). Anal. Calcd for $C_{26}H_{24}ClN_3Ru$: C, 60.64; H, 4.70; N, 8.16; found: C, 60.73; H, 4.82; N, 7.89.

Synthesis of $Ru(BQA)_2$ (6.4). A suspension of $Ru(COD)Cl_2$ (0.36 g, 1.3 mmol) in toluene (10 mL) was added to a solution of [BQA][Li] (0.72 g, 1.32 mmol) in toluene (10mL) in a bomb reactor with a Teflon stopcock. The mixture was heated at reflux for 48 h. The volatiles were removed *in vacuo* and the residue was extracted with dichloromethane and filtered through Celite on a sintered glass frit to yield a red-purple filtrate. Layering the filtrate with petroleum ether precipitated a burgundy solid. The

product was collected via filtration, washed with copious amounts of petroleum ether and dried *in vacuo* (1.52 g, 89%). ^{1}H NMR (CD_2Cl_2, 300 MHz, 25°C): δ 9.10 (dd, *J* = 4.8 Hz, 1.5 Hz, 4H), 7.16 (d, *J* = 7.8 Hz, 4H), 7.05 (t, *J* = 8.1 Hz, 4H), 6.65 (d, *J* = 7.8 Hz, 8H), 6.35 (dd, *J* = 4.8 Hz, 1.5 Hz, 4H). ^{13}C {^{1}H} NMR (CD_2Cl_2, 75 MHz) δ 150, 138, 132, 129, 128.4, 122.8, 122. Anal. Calcd for $C_{36}H_{24}N_6Ru$: C, 67.38; H, 3.77; N, 13.10; found: C, 67.63; H, 3.66; N, 13.12.

Synthesis of *trans*-(BQA)RuCl(PPh$_3$)$_2$ (6.5). A solution of HBQA (500 mg, 1.84 mmol) and NEt_3 (373 mg, 3.69 mmol) in CH_2Cl_2 (5 mL) was added to a stirring solution of $RuCl_2(PPh_3)_4$ (2.25 g, 1.84 mmol) in CH_2Cl_2 (8 mL). The reaction solution was heated to 65ºC for 5h. The reaction was then cooled to room temperature and the solvent removed *in vacuo*. The green solid was washed with ethanol (2 x 15 mL), Et_2O (2 x 15 mL), and petroleum ether (2 x 15 mL). The remaining solid was dried *in vacuo* yielding 1.21 g of **6.5** (70.2%). Crystals of (BQA)RuCl(PPh_3)$_2$ were grown by vapor diffusion of petroleum ether into benzene. ^{1}H NMR (C_6D_6, 300 MHz, 25°C): δ 9.036 (dd, *J* = 4.8 Hz, 1.5 Hz, 2H), 7.49 (m, 12H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.96 (t, *J* = 8.1 Hz, 2H), 6.75-6.87 (m, 20 H), 6.53 (d, *J* = 7.8 Hz, 4H), 6.40 (dd, *J* = 4.8 Hz, 1.5 Hz, 4H). ^{31}P {^{1}H} NMR (C_6D_6, 121.4 MHz, 25°C): δ 29.2. ES-MS (Electrospray): calcd for $C_{54}H_{42}ClN_3P_2Ru$ $(M)^-$ m/z 931, found (M+H) m/z 931, 669 (M-PPh_3). Anal. Calcd for $C_{54}H_{42}ClN_3P_2Ru$: C, 69.63; H, 4.55; N, 4.51; found: C, 68.93; H, 4.69; N, 4.49.

Synthesis of *trans*-(BQA)OsCl(PPh$_3$)$_2$ (6.6). A solution of [BQA][Li] (300 mg, 1.11 mmol) in toluene (5 mL) was added to a stirring solution of $OsCl_2(PPh_3)_4$ (1.156 g, 1.11 mmol) in toluene (8 mL) at room temperature. The reaction solution was heated to 65 ºC for 5h. The reaction was then cooled to room temperature and the volatiles were

removed *in vacuo*. The green solid was washed with ethanol (2 x 15 mL), Et_2O (2 x 15 mL), and petroleum ether (2 x 15 mL). The remaining solid was dried *in vacuo* yielding 1.04 g of analytically pure material (92%). Crystals of **6.6** were grown by vapor diffusion of petroleum ether into benzene. ^{1}H NMR (CD_2Cl_2, 300 MHz, 25°C): δ 8.44 (dd, *J* = 4.8 Hz, 1.5 Hz, 2H), 7.62 (m, 12H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.94 (t, *J* = 8.2 Hz, 2H), 6.75-6.87 (m, 20 H), 6.48 (d, *J* = 7.8 Hz, 4H), 6.38 (dd, *J* = 4.8 Hz, 1.5 Hz, 4H). ^{31}P {^{1}H} NMR (C_6D_6, 121.4 MHz, 25°C): δ -8. ES-MS (Electrospray): calcd for $C_{54}H_{42}ClN_3P_2Os$ (M) m/z 1020, found (M+H) m/z 1021, 986 (M-Cl). Anal. Calcd for $C_{54}H_{42}ClN_3P_2Os$: C, 63.55; H, 4.15; Cl, 3.47; N, 4.12; found: C, 63.46; H, 4.02; N, 4.10.

Synthesis of *cis*-(BQA)OsCl(PPh$_3$)$_2$ (6.7). A solution of HBQA (500 mg, 1.84 mmol) and NEt_3 (373 mg, 3.69 mmol) in CH_2Cl_2 (5 mL) was added to a stirring solution of $OsCl_2(PPh_3)_3$ (1.93 g, 1.84 mmol) in CH_2Cl_2 (8 mL). The reaction solution was heated to 65ºC for 5h. The reaction was then cooled to room temperature and the volatiles were removed *in vacuo*. The brown solid was washed with ethanol (2 x 15 mL), Et_2O (2 x 15 mL), and petroleum ether (2 x 15 mL). The remaining solid was dried *in vacuo* yielding 1.26 g of **6.7** (67%). Vapor diffusion of petroleum ether into a solution of **6.7** in benzene yielded crystals of the *trans*-product **6.6**. ^{1}H NMR (C_6D_6, 300 MHz, 25°C): δ 8.8 (dd, *J* = 4.8 Hz, 1.5 Hz, 2H), 7.6-6.5 (m, 36 H), 6.40 (dd, *J* = 4.8 Hz, 1.5 Hz, 4H). ^{31}P {^{1}H} NMR (C_6D_6, 121.4 MHz, 25°C): δ 2.2 (d, *J* = 10.7 Hz), -0.92 (d, *J* = 10.7 Hz). ES-MS (Electrospray): calcd for $C_{54}H_{42}ClN_3P_2Os$ $(M)^+$ m/z 1020, found (M+H) m/z 1021, 986 (M-Cl).

Synthesis of [(tpy)Ru(BQA)][BPh$_4$] (6.9). A solution of HBQA (32.6 mg, 0.12 mmol) and NEt_3 (30 mg, 0.37 mmol) in CH_2Cl_2 (5 mL) was added to a stirring solution

of (tpy)$RuCl_2(PPh_3)$ (50 mg, 0.075 mmol) and $NaBPh_4$ (15 mg, 0.075 mmol) in ethanol (5 mL) at room temperature. The reaction solution was then heated at 65 ºC for 15h. The reaction mixture was then cooled to room temperature and the volatiles were removed *in vacuo*. The red solid was washed with Et_2O (2 x 15 mL) and petroleum ether (2 x 15 mL). The remaining solid was dried *in vacuo* yielding 59.6 mg of analytically pure material (86%). ES-MS (Electrospray): calcd for $C_{33}H_{23}N_6Ru$ $(M)^+$ m/z 605, found (M^+) m/z 605. Anal. Calcd for $C_{57}H_{43}BN_6Ru$: C, 74.10; H, 4.69; N, 9.10; found: C, 74.35; H, 4.75; N, 9.06.

Synthesis of *trans*-(BQA)RuCl(PEt_3)$_2$ (6.10). A blue solution of **6.5** (0.15 g, 0.47 mmol) in toluene (10 mL) was treated with neat triethylphosphine (0.20 mL, 2.0 mmol) at room temperature. The mixture was heated to reflux for 18 h. The reaction mixture was cooled down and all volatile materials were removed *in vacuo*. The green solids were washed with Et_2O (3 x 15 mL) and petroleum ether (3 x 15 mL). The remaining green solid was dried *in vacuo* to yield analytically pure material (0.073 g, 70%) ^{1}H NMR (C_6D_6, 300 MHz) δ 9.06 (dd, J = 4.8 Hz, 1.5 Hz, 4H), 7.18 (d, J = 7.8 Hz, 4H), 7.04 (t, J = 8.2 Hz, 4H), 6.72 (d, J = 7.8 Hz, 8H), 6.40 (dd, J = 4.8 Hz, 1.5 Hz, 4H), 1.82 (m, 12 H), 0.70 (d, 18H) . $^{31}P\{^1H\}$ NMR (C_6D_6, 121 MHz) δ 11.8. Anal. Calcd for $C_{30}H_{42}ClN_3P_2Ru$: C, 56.02; H, 6.58; N, 6.53. Found C, 55.88; H, 6.48; N, 6.51.

Synthesis of *trans*-(BQA)RuCl(PMe_3)$_2$ (6.11). A blue solution of **6.5** (0.44 g, 0.47 mmol) in THF (10 mL) was treated with neat trimethylphosphine (0.19 mL, 1.9 mmol) at –30 °C. The mixture was allowed to warm to room temperature during which time the solution turned green. After the mixture was stirred at room temperature for 1 h, all volatile materials were removed *in vacuo*. Flash column chromatography with 4:1

toluene:ethyl acetate yielded black purple analytically pure solid (0.18 g, 69%) (R_f = 0.21). ^{1}H NMR (C_6D_6, 300 MHz) δ 9.06–9.03 (m, 2H), 7.70–7.67 (m, 2H), 7.34–7.22 (m, 4H), 6.74–6.72 (m, 2H), 6.58–6.53 (m, 2H), 0.68 (t, *J* = 3.0 Hz, 18H). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz) δ 152.56, 151.74, 148.27 (t, *J* = 2.4 Hz), 132.32 (t, *J* = 1.7 Hz), 131.78, 128.14, 121.94, (t, *J* = 1.6 Hz), 113.69, 113.36, 11.03 (t, *J* = 11.3 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz) δ 0.47. ES-MS (Electrospray): calcd for $C_{24}H_{30}ClN_3P_2Ru$ $(M)^+$ m/z 559, found (M^+) m/z 559. Anal. Calcd for $C_{24}H_{30}ClN_3P_2Ru$ C, 51.57; H, 5.41; N, 7.52. Found C, 51.66; H, 5.35; N, 7.43.

Synthesis of *trans*-(BQA)RuBr(PMe$_3$)$_2$ (6.12). A green solution of **6.11** (0.13 g, 0.23 mmol) in 4 mL THF/MeOH (1:1) was mixed with potassium bromide (90 mg, 0.76 mmol) at room temperature. The mixture was heated to 50 °C for 4 h, cooled, and filtered over a pad of Celite. The filtrate was dried *in vacuo* then redissolved in toluene and flashed through silica gel. The volatiles were removed *in vacuo* to yield a purple solid. The purple product was washed with petroleum ether (2 x 15 mL) and dried *in vacuo* (0.11 g, 77%). ^{1}H NMR (C_6D_6, 300 MHz) δ 9.19–9.17 (m, 2H), 7.70–7.67 (m, 2H), 7.30–7.22 (m, 4H), 6.73–6.70 (m, 2H), 6.53–6.48 (m, 2H), 0.72 (t, *J* = 3.0 Hz, 18H). ^{13}C{^{1}H } NMR (C_6D_6, 75 MHz) δ 152.02, 151.52, 149.72 (t, *J* = 2.3 Hz), 132.42, 131.68, 128.12, 122.02, 113.66, 113.41, 11.54 (t, *J* = 11.5 Hz). ^{31}P{^{1}H } NMR (C_6D_6, 121 MHz) δ –0.94. Anal. Calcd for $C_{24}H_{30}BrN_3P_2Ru$ C, 47.77; H, 5.01; N, 6.96. Found C; 50.72; H, 5.30; N, 6.50.

Synthesis of *trans*-(BQA)RuI(PMe$_3$)$_2$ (6.13). A green solution of **6.11** (89 mg, 0.16 mmol) in 4 mL THF/MeOH (1:1) was mixed with potassium iodide (90 mg. 0.54 mmol) at room temperature. The mixture was heated at 50 °C for 4 h, filtered over a pad

of Celite, and the volatiles removed *in vacuo* to yield a purple solid. The filtrate was dried *in vacuo* then redissolved in toluene and flashed through silica gel. Removal of the volatiles *in vacuo* afforded analytically pure material (87 mg, 84%). ^{1}H NMR (C_6D_6, 300 MHz) δ 9.38–9.35 (m, 2H), 7.71–7.68 (m, 2H), 7.28–7.22 (m, 4H), 6.70–6.68 (m, 2H), 6.46–6.41 (m, 2H), 0.79 (t, *J* = 3.0 Hz, 18H). ^{13}C{^{1}H } NMR (C_6D_6, 75 MHz) δ 152.59 (m), 151.50, 150.73, 132.75, 131.79, 128.30, 122.32, 113.82, 113.65, 12.83 (t, *J* = 11.9 Hz). ^{31}P{^{1}H } NMR (C_6D_6, 121 MHz) δ –2.96. Anal. Calcd. For $C_{24}H_{30}IN_3P_2Ru$: C, 44.32; H, 4.65; N, 6.46. Found, C, 44.32; H, 4.70; N, 6.48.

Synthesis of *trans*-(BQA)RuH(PMe$_3$)$_2$ (6.14). To a green solution of **6.11** (37 mg, 0.066 mmol) in toluene (5 mL) was added 68 μL of a 0.25 M solution of $LiAlH_4$ in THF at room temperature. The mixture was stirred at room temperature for 5 h, after which the volatiles were removed *in vacuo*. The residue was extracted into toluene and filtered through a Celite pad. The volatiles were removed *in vacuo* and the solid obtained was triturated with petroleum ether to give an analytically pure, black green solid (26 mg, 75%). Scaling the reaction up resulted in drastically diminished yields. ^{1}H NMR (C_6D_6, 300 MHz) δ 8.44 (br, s, 2H), 7.87–7.84 (m, 2H), 7.39–7.28 (m, 4H), 6.75–6.72 (m, 2H), 6.37–6.33 (m, 2H), 0.80 (br, s, 18H), –11.75 (t, $^{2}J_{P\text{-}H}$ = 27.4 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz) δ 1.47. IR (Nujol mull/KBr) $\upsilon_{Ru\text{-}H}$ 1743.0 cm^{-1}. Anal. Calcd. For $C_{24}H_{31}N_3P_2Ru$: C, 54.95; H, 5.96; N, 8.01. Found C, 54.99; H, 5.88; N, 7.96.

Synthesis of *trans*-(BQA)RuMe(PMe$_3$)$_2$ (6.15). A green solution of **6.11** (0.10 g, 0.19 mmol) in toluene (5 mL) was treated with 3.5 equivalents of MeLi (1.0 M) in diethyl ether at – 30 ºC. The mixture was then heated at 60 ºC for 12 h. The reaction mixture was cooled to room temperature and the excess MeLi was quenched with ethanol. The

volatiles were then removed *in vacuo*. The resulting residue was extracted with benzene and filtered through a pad of Celite. The filtrate was concentrated *in vacuo*, triturated with petroleum ether, and dried *in vacuo* to yield a green solid (51 mg, 50%). ^{1}H NMR (C_6D_6, 300 MHz) δ 8.28–8.26 (m, 2H), 7.84–7.81 (m, 2H), 7.37–7.30 (m, 4H), 6.75–6.72 (m, 2H), 6.47–6.42 (m, 2H), 0.57 (t, *J* = 2.7 Hz, 18H, P(C*H*$_3$)$_3$), 0.01 (t, *J* = 9.8 Hz, 3H, RuC*H*$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz) δ 3.18. Anal. Calcd $C_{25}H_{33}N_3P_2Ru$ C, 55.75; H, 6.18; N, 7.80. Found C, 55.36; H, 6.00; N, 7.78.

Synthesis of *trans*-(BQA)RuN$_3$(PMe$_3$)$_2$ (6.16). A green solution of **6.11** (0.10 g, 0.19 mmol) in CH_2Cl_2 was treated with solid sodium azide (48 mg, 0.70 mmol). The mixture was stirred at 50 ºC for 4h. The volatiles were then removed *in vacuo*. The resulting residue was extracted with benzene and filtered through a pad of Celite. The filtrate was concentrated *in vacuo*, triturated with petroleum ether, and dried *in vacuo* to yield a green solid (64 mg, 64%). ^{1}H NMR (C_6D_6, 300 MHz) δ 8.78–8.75 (m, 2H), 7.66–7.63 (m, 2H), 7.31–7.20 (m, 4H), 6.72–6.69 (m, 2H), 6.59–6.54 (m, 2H), 0.56 (t, *J* = 3.0 Hz, 18H). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz) δ 1.66. IR (Nujol/KBr) υ_{N3} = 2028.1 cm^{-1}. Anal. Calcd. For $C_{24}H_{30}N_6P_2Ru$: C, 50.97; H, 5.35; N, 14.86. Found C, 51.14; H, 5.23; N, 14.40.

Synthesis of Synthesis of 3,5-(CF$_3$)$_2$Ph-QAH (6.17). A 200 mL reaction vessel equipped with a Teflon stopcock and stir bar was charged with $Pd_2(dba)_3$ (0.218 g, 0.238 mmol), 1,1′-bis(diphenylphosphino)ferrocene (DPPF) (0.264 g, 0.476 mmol) and toluene (30 mL) under a dinitrogen atmosphere. The resulting solution was allowed to stir for five minutes, after which time 3,5-bis(triflouromethyl)bromobenzene (3.49 g, 11.9 mmol), 8-aminoquinoline (2.48 g, 11.9 mmol), and additional toluene (70 mL) were

added. The subsequent addition of sodium *tert*-butoxide (1.60 g, 16.66 mmol) resulted in a brown solution that was stirred vigorously for three days at 110°C under vacuum. The solution was then allowed to cool and filtered through a silica plug that was then extracted with dichloromethane to ensure complete removal of the desired product. Concentration of the collected extracts and removal of solvent yielded a crude red solid (3.98 g, 94%). Purification by flash chromatography on silica gel (4:1 toluene:ethyl acetate) yielded a burgundy red liquid as a spectroscopically pure and synthetically useful compound (3.7 g, 87.3%). ^{1}H NMR (C_6D_6, 300 MHz, 25°C): δ 8.50 (dd, *J* = 1.8, 4.2 Hz, 1H), 8.40 (s, *1*H), 7.53 (dd, *J* = 1.8, 8.4 Hz, 1H), 7.36 (m, *J* = 0.9 Hz, 1H), 7.28 (s, 2H), 7.23 (dd, *J* = 1.5, 7.2 Hz, 1H), 6.95-7.04 (m, 2H), 6.82 (dd, *J* = 4.2, 4.2 Hz, 1H) . ^{13}C NMR (C_6D_6, 75.409 MHz, 25°C): δ 148.1, 144.2, 139.6, 138.7, 136.5, 133.3, 132.9, 129.5, 127.6, 126.1, 122.4, 119.4, 118.2, 114.5 (m), 110.1. ^{19}F NMR (C_6D_6, 282.127 MHz, 25°C): δ -63.4. ES-MS (Electrospray): calcd for $C_{17}H_{10}F_6N_2$ $(M)^+$ m/z 356, found $(M+H)^+$ m/z 357.

Synthesis of 3,5-$(CF_3)_2$Ph-QA[Na]·(Et_2O) (6.18). A suspension of NaH (60% by weight) (57 mg, 1.4 mmol) in Et_2O (2 mL) was added to a solution of 3,5-$(CF_3)_2$Ph-QAH (500 mg, 1.4 mmol) in Et_2O (4 mL). Upon heating to 65°C, a red-orange salt precipitated. After 10 hours of heating, the reaction was cooled to room temperature and the solvent decanted away. The salt was washed with petroleum ether (4 x 5 mL) and dried in vacuum to afford an orange powder (544 mg, 86%). Hydrolysis of the salt with water cleanly affords the parent amine. ^{1}H NMR (C_6D_6, 300 MHz, 25°C): δ 7.58 (dd, *J* = 1.8, 4.2 Hz, 1H), 7.49 (dd, *J* = 1.8, 8.4 Hz, 1H), 7.38 (dd, *J* = 1.2, 7.8 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.12 (s, 1H), 7.08 (s, 2H), 6.84 (dd, *J* = 1.2, 7.8 Hz, 1H), 6.65 (dd, *J* = 4.2,

8.4 Hz, 1H), 3.01 (q, $(CH_3CH_2)_2O$ J = 7.2 Hz, 4H), 0.86 (t, $(CH_3CH_2)_2O$ J = 7.2 Hz, 6H). ^{19}F NMR (C_6D_6, 282.127 MHz, 25°C): δ -65.

Synthesis of (BQA)Ru(3,5-$(CF_3)_2$Ph-QA)(PPh_3) (6.19). A solution of **6.18** (245.1 mg, 0.54 mmol) in THF (2 mL) was added dropwise to a stirring solution of **6.5** (500mg, 0.54 mmol) in THF (4 mL). The reaction solution was heated to 80 ºC for 3h. The reaction was then cooled to room temperature and the volatiles removed *in vacuo*. The purple solid was washed with a 3:1 petroleum ether and ethanol mix (3 x 5 mL). The remaining solid was dried *in vacuo* yielding 476 mg of analytically pure material (90%). Crystals were grown by cooling a solution of **6.19** in benzene layered with petroleum ether. ^1H NMR (C_6D_6, 300 MHz, 25°C): δ 8.99 (dd, J = 1.2, 4.8 Hz, 1H), 7.57 (dd, J = 1.2, 4.8 Hz, 2H), 7.49 (dd, J = 1.2, 8.2 Hz, 1H), 7.19 (d, J = 1.2 Hz, 1H), 6.77-7.08 (m, 14H), 6.75 (m, 6H), 6.58-6.64 (m, 5H), 6.53 (dd, J = 5.4, 7.2 Hz, 1H), 6.44 (s, 2H), 6.08 (dd, J = 4.8, 8.2 Hz, 2H). ^{31}P $\{^1H\}$ NMR (C_6D_6, 121.4 MHz, 25°C): δ 50.5. ^{19}F NMR (C_6D_6, 282.127 MHz, 25°C): δ -64. ES-MS (Electrospray): calcd for $C_{53}H_{36}F_6N_5PRu$ $(M)^+$ m/z 988, found $(M+H)^+$ m/z 989. Anal. Calcd. For $C_{53}H_{36}F_6N_5PRu$: C, 64.37; H, 3.67; N, 7.08. Found C, 64.38; H, 3.64; N, 7.08.

Synthesis of (BQA)Ru(3,5-$(CF_3)_2$Ph-QA)(CO) (6.20). A 100 mL reaction vessel equipped with a Teflon stopcock and stir bar was charged with a solution of **6.19** (50 mg, 0.05 mmol) in toluene (15 mL). The reaction vessel was evacuated and then exposed to 1 atm of CO gas. The reaction mixture was heated at reflux with vigorous stirring for 8 h. The reaction was then cooled to room temperature and the volatiles removed *in vacuo*. The red solid was washed with a 3:1 petroleum ether and ethanol mix (3 x 5 mL). The remaining solid was dried *in vacuo* yielding 36 mg of analytically pure

material (95%). ^{1}H NMR (C_6D_6, 300 MHz, 25°C): δ 9.01 (dd, *J* = 1.2, 4.8 Hz, 1H), 7.50 (dd, *J* = 1.2, 4.8 Hz, 2H), 7.48 (dd, *J* = 1.2, 8.2 Hz, 1H), 7.20 (d, *J* = 1.2 Hz, 1H), 6.77-7.08 (m, 14H), 6.70 (m, 6H), 6.58-6.64 (m, 5H), 6.52 (dd, *J* = 5.4, 7.2 Hz, 1H), 6.44 (s, 2H), 6.08 (dd, *J* = 4.8, 8.2 Hz, 2H). ^{19}F NMR (C_6D_6, 282.127 MHz, 25°C): δ -64. Anal. Calcd. For $C_{36}H_{21}F_6N_5ORu$: C, 57.30; H, 2.80; N, 9.28. Found C, 57.02; H, 2.78; N, 9.18.

Synthesis of [(BQA)RuCl(PhBP$_2$)][NEt$_4$] (6.21). A solution of [$Ph_2B(CH_2PPh_2)_2$][NEt_4] (354 mg, 0.51 mmol) in THF (2 mL) was added dropwise to a stirring solution of **6.5** (471mg, 0.51 mmol) in THF (4 mL). The reaction solution was heated to 80 ºC for 3h. The reaction was then cooled to room temperature and the solvent removed *in vacuo*. The dark purple solid was washed with Et_2O (2 x 15 mL) and petroleum ether (2 x 15 mL). The remaining solid was dried *in vacuo* yielding 497 mg of analytically pure material (89%). Crystals of **6.21** were grown by vapor diffusion of petroleum ether into THF. ^{1}H NMR (C_6D_6, 300 MHz, 25°C): δ 8.46 (bs, 4H), 7.93 (bs, 2H), 7.75 (bs, 2H), 7.49 (d, *J* = 6.3 Hz, 2H), 6.95-7.39 (m, 18H), 6.79 (t, *J* = 7.2 Hz, 5H), 6.67 (t, *J* = 7.2 Hz, 4H), 6.36-6.47 (m, 9H), 3.29 (q, *J* = 7.5 Hz, 8H), 2.35 (bs, 2H), 1.81 (bs, 2H), 1.23 (tt, *J* = 1.5, 7.2 Hz, 12 H). ^{31}P {^{1}H} NMR (C_6D_6, 121.4 MHz, 25°C): δ 54 (d, *J* = 36 Hz), 28.3 (d, *J* = 36 Hz). ^{11}B {^{1}H} NMR (C_6D_6, 128.3 MHz, 25°C): δ -11.8. Anal. Calcd. For $C_{64}H_{66}BClN_4P_2Ru$: C, 69.85; H, 6.04; N, 5.09. Found C, 69.78; H, 6.05; N, 5.08.

Synthesis of (BQA)Ru(PhBP$_2$) (6.22). Solid **6.21** (100.6 mg, 0.09 mmol) was stirred vigorously in ethanol (6 mL) for 30 minutes. A red solid precipitated from solution and was isolated by decanting the liquor away. The solids were dissolved in CH_2Cl_2 and filtered through a pad of Celite. The solvent was removed *in vacuo* and the

remaining wine red solid was washed with petroleum ether (2 x 3 mL) and dried *in vacuo* yielding 72 mg of analytically pure material (84%). ^{1}H NMR (C_6D_6, 300 MHz, 25°C): δ 8.17 (s, 5 H), 7.72 (d, *J* = 4.8 Hz, 2H), 7.54 (m, 10 H), 7.30 (d, *J* = 6 Hz, 4H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.851 (d, *J* = 7.8 Hz, 2H), 6.50 (m, 10 H), 6.2 (m, 2 H), 5.81 (m, 2 H), 2.69 (s, 4 H). ^{31}P {^{1}H} NMR (C_6D_6, 121.4 MHz, 25°C): δ 69.45. ^{11}B {^{1}H} NMR (C_6D_6, 128.3 MHz, 25°C): δ -12.1. Anal. Calcd. For $C_{56}H_{46}BN_3P_2Ru$: C, 71.95; H, 4.96; N, 4.50. Found C, 71.78; H, 5.05; N, 4.44.

Synthesis of (BQA)Ru(CO)(PhBP$_2$) (6.23). A 20 mL vial containing **6.21** (60 mg, 0.054 mmol) in CH_2Cl_2 (2 mL) was sparged with CO gas. The solution instantly reddened upon contact with the gas. The solvent was removed *in vacuo* and the remaining red solid was washed with ethanol (2 x 2 mL). The resulting powder was washed with petroleum ether (2 x 3 mL) and dried *in vacuo* yielding 45 mg of analytically pure material (86%). ^{1}H NMR (C_6D_6, 300 MHz, 25°C): δ 7.90 (m, 4 H), 7.75 (d, *J* = 4.5 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 2 H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.11-7.22 (m, 8H), 7.04 (t, *J* = 7.5 Hz, 4H), 6.92 (s, 6 H), 6.67 (t, *J* = 6.6 Hz, 2 H), 6.53 (d, *J* = 7.5 Hz, 2 H), 6.27-6.44 (m, 10 H), 2.78 (d, J = 12 Hz, 2 H), 2.02 (d, J = 13.8 Hz, 2 H). ^{13}C NMR (C_6D_6, 75.409 MHz, 25°C): δ 155, 151, 149, 137, 135, 133.2, 133.1, 132.6, 132.5, 131, 129, 128.5, 128.4, 128, 127, 126.8, 126.7, 123, 120, 114. ^{31}P {^{1}H} NMR (C_6D_6, 121.4 MHz, 25°C): δ 35.17 (d, *J* = 35 Hz), 18.81 (d, *J* = 35 Hz). ^{11}B {^{1}H} NMR (C_6D_6, 128.3 MHz, 25°C): δ -11.9. IR: (CH_2Cl_2) υ_{CO} = 1970 cm^{-1}. Anal. Calcd. For $C_{57}H_{46}BN_3OP_2Ru$ C, 71.10; H, 4.82; N, 4.36 Found C, 71.06; H, 4.70; N, 4.28.

Synthesis of [*trans*-(BQA)Ru(CO)(PPh$_3$)$_2$][BPh$_4$] (6.25). $NaBPh_4$ (18.2mg, 0.05 mmol) in ethanol (1 mL) was added to a solution of **6.5** (45mg, 0.05 mmol) in THF (2

mL) in a 10 mL Sclenk flask equipped with a stir bar and septum. The flask was evacuated then exposed to 1 atm of CO gas. The green solution reddens instantly upon exposure to CO. The reaction was allowed to stir for 30 minutes before the volatiles were removed *in vacuo*. The red solid was washed with ethanol (2 x 3 mL) and Et_2O (2 x 3 mL). The remaining solid was dried *in vacuo* yielding 49 mg of analytically pure material (82%). ^{1}H NMR not diagnostic. ^{31}P $\{^1H\}$ NMR (C_6D_6, 121.4 MHz, 25°C): δ 30.1. IR: (CH_2Cl_2/KBr) υ_{CO} = 1970 cm^{-1}. ES-MS (Electrospray): calcd for $C_{55}H_{42}N_3OP_2Ru$ $(M)^+$ m/z 924, found $(M)^+$ m/z 924, 662 (M-PPh_3). Anal. Calcd. For $C_{79}H_{62}BN_3OP_2Ru$: C, 76.32; H, 5.03; N, 3.38. Found C, 76.15; H, 4.87; N, 3.36.

Synthesis of [*trans*-(BQA)Ru(CH_3CN)(PPh_3)$_2$][BPh_4] (6.24). A solution of **6.5** (88 mg, 0.094 mmol) in a mixture of acetonitrile and methanol (2 mL/4 mL) was added to a solution of $NaBPh_4$ (51 mg, 0.15 mmol) in methanol (2 mL) at room temperature. The resulting mixture was stirred at room temperature for 4 h then the volatiles were removed *in vacuo*. The solid residue was extracted with dichloromethane (5 mL) and filtered through a Celite pad. The volatiles were removed *in vacuo* and the purple solid was triturated with petroleum ether. The solids were dried *in vacuo* to afford 78 mg of analytically pure material (67%). ^{1}H NMR not diagnostic.. ^{31}P$\{^1H\}$ NMR ($CDCl_3$, 121 MHz) δ 28.7 (bs). Anal. Calcd. For $C_{78}H_{62}BN_3P_2Ru$: C, 77.09; H, 5.14; N, 3.46. Found C, 77.48; H, 5.69; N, 3.69.

Synthesis of [*trans*-(BQA)Os(CO)(PPh_3)$_2$][PF_6] (6.26). A solution of $TlPF_6$ (13.6 mg, 0.02 mmol) in THF (1 mL) was added to a solution of **6.6** (40 mg, 0.02 mmol) in THF (2 mL) in a 10 mL Sclenk flask equipped with a stir bar and septum. The flask was evacuated then exposed to 1 atm of CO gas. The green solution reddens after stirring

vigorously over the period of 1 h. The reaction was allowed to stir for 5 h and then the volatiles were removed *in vacuo*. The red solid was washed with ethanol (2 x 3 mL) and Et_2O (2 x 3 mL). The remaining solid was dried *in vacuo* yielding 48 mg of analytically pure material (90%). ^1H NMR not diagnostic. ^{31}P $\{^1H\}$ NMR (C_6D_6, 121.4 MHz, 25°C): δ 0.31. IR: (CH_2Cl_2/KBr) υ_{CO} = 1921 cm^{-1}. ES-MS (Electrospray): calcd for $C_{55}H_{42}N_3OOsP_2$ $(M)^+$ m/z 1013, found $(M)^+$ m/z 1014. Anal. Calcd. For $C_{55}H_{42}F_6N_3OOsP_3$ C, 57.04; H, 3.66; N, 3.63. Found C, 56.64; H, 3.51; N, 3.60.

Synthesis of [*trans*-(BQA)RuCl(PPh$_3$)$_2$][OTf] (6.27). To a vigorously stirring solution of **6.5** (0.11 g, 0.12 mmol) in toluene (5 mL) was added solid AgOTf (30 mg, 0.12 mmol) at room temperature. The reaction mixture turned brown instantly while a black precipitate formed. After the mixture was stirred for 1 h, the solution was filtered through a Celite pad to remove the precipitate. The volatiles were removed *in vacuo*. The solids were then extracted into CH_2Cl_2 (5 mL) and filtered again through a Celite pad. The volume of the filtrate was reduced to 1 mL, layered with diethyl ether, and allowed to stand. A yellow precipitate formed and was isolated by decanting the liquor. The solids were dried *in vacuo* to afford analytically pure material (0.12 g, 93%). ES-MS (Electrospray): calcd for $C_{54}H_{42}ClN_3P_2Ru$ $(M)^+$ m/z 931, found $(M+H)^+$ m/z 931. Anal. Calcd. For $C_{55}H_{42}ClF_3N_3O_3P_2RuS$: C, 61.14; H, 3.92; N, 3.89. Found: C, 60.81; H, 3.70; N, 3.76.

Synthesis of [*trans*-(BQA)Ru(N$_2$)(PPh$_3$)$_2$][PF$_6$] (6.30). $TlPF_6$ (18.8 mg, 0.054 mmol) in THF (1 mL) was added to a solution of **6.5** (50 mg, 0.054 mmol) in THF (2 mL) at room temperature. The green solution darkens to a midnight blue after stirring for several hours and the evolution of a white precipitate is noticeable. The reaction mixture

was allowed to stir for 24 h, filtered through a Celite pad, and then the volatiles were removed *in vacuo*. Dissolution the blue solids in CH_2Cl_2 caused the color to change to an intense red. The solution was filtered through a Celite pad and the volatiles were removed *in vacuo*. The red solid was washed with Et_2O (2 x 3 mL). The remaining solid was dried *in vacuo* yielding 56 mg of analytically pure material (83%). ^{1}H NMR (CD_2Cl_2, 300 MHz, 25°C): δ 8.64-7.04 (m, 42H). ^{31}P {^{1}H} NMR (CD_2Cl_2, 121.4 MHz, 25°C): δ 25, -143 (sept, J = 711 Hz). ES-MS (Electrospray): calcd for $C_{54}H_{42}ClN_5P_2Ru$ $(M)^+$ m/z 924, found $(M+H)^+$ m/z 896 $(M-N_2)^+$. IR: (CH_2Cl_2/KBr) υ_{NN} = 2130 cm^{-1}. Anal. Calcd. For $C_{54}H_{42}F_6N_5P_3Ru$: C, 60.68; H, 3.96; N, 6.55. Found C, 60.55; H, 3.90; N, 6.48.

Synthesis of [*trans*-(BQA)Ru(N_2)(PMe_3)$_2$][PF_6] (6.31). $TlPF_6$ (18.8 mg, 0.054 mmol) in THF (1 mL) was added to a solution of **6.5** (30 mg, 0.054 mmol) in THF (2 mL) at room temperature. The green solution reddens after stirring for several hours and the evolution of a white precipitate is noticeable. The reaction mixture was allowed to stir for 36 h, filtered through a Celite pad, and then the volatiles were removed *in vacuo*. The solids were dissolved in CH_2Cl_2, filtered through a Celite pad, and the volatiles were removed *in vacuo*. The red solid was washed with Et_2O (2 x 3 mL). The remaining solid was dried *in vacuo* yielding 36 mg of analytically pure material (78%). ^{1}H NMR (CD_2Cl_2, 300 MHz, 25°C): δ 8.35 (d, J = 5.1Hz, 2H), 8.04 (d, J = 7.8 Hz, 2H), 7.91 (d, J = 7.8 Hz, 2H), 7.54 (t, J = 7.8 Hz, 2H), 7.25 (dd, J = 7.8, 7.8 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 0.72 (t, J = 2.7Hz, 9H). ^{31}P {^{1}H} NMR (CD_2Cl_2, 121.4 MHz, 25°C): δ 0.42, -143 (sept, J = 711 Hz). ES-MS (Electrospray): calcd for $C_{24}H_{30}N_5P_2Ru$ $(M)^+$ m/z 552, found $(M+H)^+$ m/z 524 $(M-N_2)^+$. IR: (CH_2Cl_2/KBr) υ_{NN} = 2129 cm^{-1}. Anal. Calcd. For $C_{24}H_{30}F_6N_5P_3Ru$: C, 41.39; H, 4.34; N, 10.05. Found: C, 41.29; H, 4.15; N, 9.89.

Synthesis of [*trans*-(BQA)Os(N_2)(PPh_3)$_2$][PF_6] (6.32) A solution of $TlPF_6$ (13.6 mg, 0.02 mmol) in THF (1 mL) was added to a solution of **6.6** (40 mg, 0.02 mmol) in THF (2 mL) at room temperature. The green solution reddens after stirring vigorously over the period of several hours. The reaction was allowed to stir for 24 h, filtered through a Celite pad, and then the volatiles were removed *in vacuo*. The red solid was extracted into CH_2Cl_2 and filtered through a Celite pad. The volatiles were removed *in vacuo* and the resultant solids were washed with Et_2O (2 x 3 mL). The remaining solid was dried *in vacuo* yielding 48 mg of analytically pure material (89%). ^1H NMR not diagnostic. ^{31}P $\{^1H\}$ NMR (C_6D_6, 121.4 MHz, 25°C): δ -3.7. IR: (CH_2Cl_2/KBr) υ_{NN} = 2073 cm^{-1}. ES-MS (Electrospray): calcd for $C_{54}H_{42}N_5OsP_2$ $(M)^+$ m/z 1013, found $(M)^+$ m/z 1014, 986 $(M-N_2)^+$. Anal. Calcd. For $C_{54}H_{42}F_6N_5OsP_3$ C, 56.00; H, 3.66; N, 6.05. Found C, 55.92; H, 3.61; N, 5.99.

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