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JOURNAL OF THE CHINESE CHEMICAL SOCIETY

# Ruthenium Complexes with an Anthyridine-based Ligand. Synthesis, Characterization and Catalytic Activity

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(Received: Feb. 5, 2013; Accepted: Mar. 12, 2013; Published Online: Apr. 15, 2013; DOI: 10.1002/jccs.201300084)

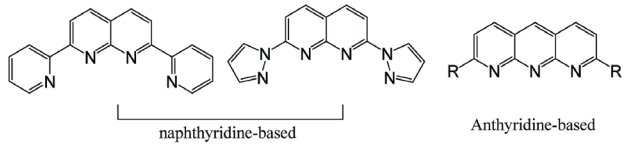
Complexation of 2,7-bis(2-pyridinyl)-9-phenylanthyridine (**4**) with $[RuCl_2(CO)_3(THF)]$ and $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ provided the mono-nuclear complex $[(\mathbf{4})Ru(CO)_3Cl][RuCl_3(CO)_3]$ (**5**) and the dinuclear complex $[(\mathbf{4})Ru_2(p\text{-cymene})_2Cl_2]$ (**6**), respectively. Both complexes have been characterized by spectroscopic, elemental and crystallographic analyses. Complex **6** is an efficient catalyst for the oxidative cyanation of various tertiary arylamines.

**Keywords:** Ruthenium; Anthyridine; Cyanation.

## INTRODUCTION

Bimetallic complexes with the metal centers in close proximity have received much attention due to the possible synergistic effect between the metal ions.[1-4] In this context, the ligand design for the accommodation of two metal ions in close proximity play a key role for the study. Among various ligand systems, we have been working on the development of naphthyridine-based ligands (Scheme I), which are suitable for building the corresponding dimetallic systems.[4] Unlike naphthyridine, anthyridine-based ligands are less explored,[5] which are also a good bridging donors for the construction of polymetallic species. Here we describe the coordination chemistry of 2,7-bis(2-pyridinyl)-9-phenylanthyridine toward ruthenium ions and the catalytic activity of the resulting complexes on cyanation of tertiary amine compounds.

**Scheme I** Naphthyridine and anthyridine-based ligands

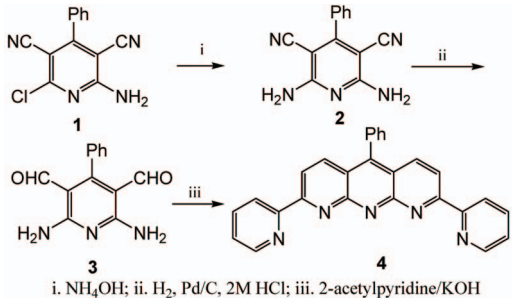



## RESULTS AND DISCUSSION

### Preparation and Characterization of Complexes

Ligand **4** was prepared by a double Friedländer reaction according to the literature procedure (Scheme II).[6] Starting with **1**, aminolysis followed by the conversion of the cyano group into the carbaldehyde gave 2,6-diamino-3,5-pyridinedicarboxaldehyde **3**, which then underwent the condensation reaction with 2-acetylpyridine to give the desired anthyridine ligand **4**. Compound **4** was characterized by NMR spectroscopy.

**Scheme II** Preparation of the anthyridine ligand **4**




Complexation of **4** with $[RuCl_2(CO)_3(THF)]$ and $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ was investigated (Shceme III). Reaction of **4** with $[RuCl_2(CO)_3(THF)]$ in a molar ratio of 1:2 provided the mono-nuclear complex **5** in 80% yield. We did not observe the formation of dinuclear species in this reaction, even with excess of ruthenium precursor or at a higher reaction temperature. On the other hand, treatment of **4** with equal molar amount of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ yielded a di-ruthenium complex **6** in 89% yield.

Both complexes **5** and $\mathbf{6}\cdot(CH_2Cl_2)_2$ were isolated as crystalline solids and were thoroughly characterized by NMR spectroscopic and x-ray crystallographic analyses. The presence of CO bands (2126, 2086, and 2068 $cm^{-1}$) in the IR spectrum of **5** are quite similar to those of $[\{(bpy)Ru(CO)_3Cl\}\{Ru(CO)_3Cl_3\}]$, suggesting that

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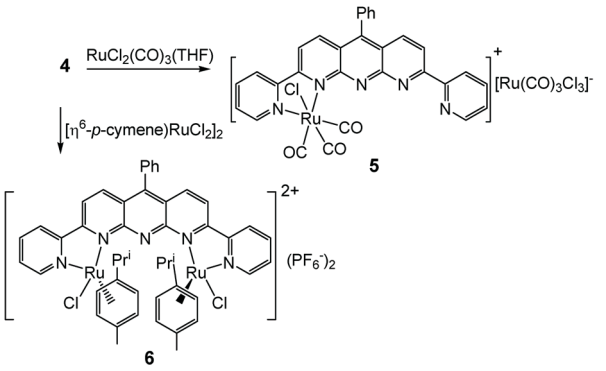
**Scheme III** Coordination of **4** with ruthenium complexes

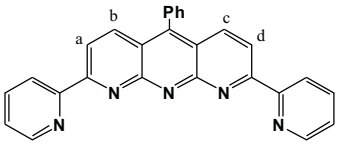



$RuCl_2(CO)_3(THF)$ undergoes not only the coordination toward ligand **4** also the disproportion reaction to yield the anion of $[Ru(CO)_3Cl_3]$. $^{13}C$ NMR spectrum of **5** shows four peaks for the carbonyl carbon atoms. Accordingly, the CO carbon atoms of the anion part $[Ru(CO)_3Cl_3]^-$ is chemically equivalent and appear at δ 185.3 as a single shift. Three other CO-carbon signals are assigned to the CO-carbon of "$Ru(CO)_3Cl$" coordinating to the ligand. The carbonyl carbon atoms in *trans* position of the ligand and chloride are chemically non-equivalent; each CO ligand has its own resonance and three carbonyl carbon shifts are observed at δ 187.7, 184.7 and 182.8 ppm.

$^1H$ NMR shifts of the anthyridine ligand in the complex **5** also provide useful structural information. These chemical shifts are summarized in Table 1. In contrast to the free ligand, the $^1H$ NMR spectrum of **5** exhibits 10 signals for the anthyridinyl and pyridinyl groups (resonances of three protons are overlapped), which clearly indicates the unsymmetric nature of the complex.

For complex **6**, the $^1H$ NMR spectrum reveals that the anthyridine protons of the ligand **4** are split into two set of doublets (Table 1). In addition, four sets of resonances corresponding to the pyridinyl protons of **6** appear in its $^1H$ NMR spectrum. These observations clearly suggest the symmetrical nature of the complex, which is consistent with the proposed structure. However, the signals for the *p*-cymene ring protons show to be broad at 298 K (Figure 1a). By lowering the temperature, the splitting pattern of these protons becomes clear and appears to two sets of doublet as expected (Figure 1d). This observation is in agreement with other related $\eta^6$-*p*-cymene ruthenium complexes, which is due to the different conformers obtained by the rotation of the *p*-cymene ring about the ruthenium-arene (centroid) bond axis.[7] In addition to the spectroscopic analysis, the detailed coordination configurations of complexes **5** and **6**·$(CH_2Cl_2)_2$ were confirmed by X-ray diffraction analysis on their single crystals.

Table 1. Selected $^1H$ NMR shifts of anthyridine ligand in complexes **5** and **6**




| Complex | **5** | **6** |
|---|---|---|
| H-a | 8.85 (m)[a] | 8.77 (d) |
| H-b | 9.02 (d) | 8.85 (d) |
| H-c | 8.78 (m)[a] | 8.85 (d) |
| H-d | 8.36 (d) | 8.77 (d) |

[a] Overlapped with other protons

**Crystallography**

Both complexes **5** and **6**·$(CH_2Cl_2)_2$ were obtained in single crystalline form by re-crystallization from dichloromethane/hexane solutions. The crystal structure of **6** has been solved and refined, despite the crystal exhibiting as a twin crystal with disorder phenomena. The ORTEP plots of **5** and **6** are depicted in Figures 2 and 3, respectively. Selected bond distances and bond angles are collected in Tables 2 and 3, respectively.

The molecular structure of **5** displays an octahedral geometry with a chelating bound anthyridine, a chloride and three carbonyl ligands completing the coordination sphere at the metal center. The bipyridine fragment of **4** and the chloride ligand around the metal center in complex **5** are arranged in a *facial* configuration due to the *trans*-influ-

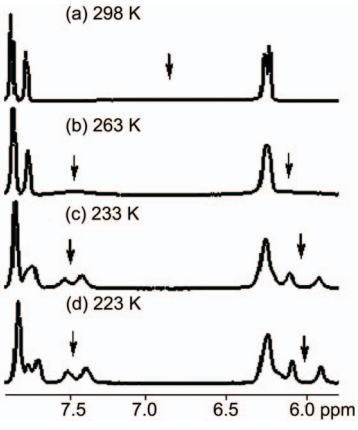



Fig. 1. NMR spectra of *p*-cymene ring protons in **6**.

ence. This coordination mode is very similar to that of [{(bpy)Ru(CO)$_3$Cl}{Ru(CO)$_3$Cl$_3$}].[8] The ligands around the ruthenium center of the anion part are also seated in the *facial* arrangement. The angle P(1)-Ru(1)-N(1) [77.21(9)°] is not 90°, showing a small bite angle attributable to the bipyridine fragment. The bond lengths Ru(1)-N(1), Ru(1)-N(2) and Ru(1)-Cl(1) are 2.102(2), 2.112(2) and 2.3831(8) Å, respectively. These compare well to those observed in related Ru(II) complexes.[8]

As shown in Fig. 3, complex **6** consists of two [(*p*-cymene)RuCl] groups linked by the anthyridine ligand **4** through the chelation of two bipyridine fragments. Both ruthenium atoms in **6** are surrounded by the $\eta^6$-bonded *p*-cymene ring, a chelating bipyridine fragment, and the chloride and attains a pseudo octahedral "three legged piano stool" geometry.[7] A notable feature of the structure **6** is that two cymene rings are opposite along the anthyridine rings presumably due to the steric interaction. All Ru-N bond lengths are quite similar, at 2.06 ~ 2.12 Å, which are in agreement with those of other reported ruthenium *p*-cymene complexes.[7] Both bite angles N(1)-Ru(1)-N(2) [77.7(3)°] and N(4)-Ru(2)-N(5) [77.1(3)°] are similar to that of **5** and comparable to those of [(bipyridine)RuCl(L)]. The distance of Ru(1)···Ru(2) is 5.443 Å, indicating that two metal centers are far away from each other.

**Catalysis**

According to the above investigation on Ru(II) complexes, it would be interesting to test the catalytic activity of these species particularly the di-ruthenium complex **6**. In recent works, Murahashi and co-workers have successfully demonstrated the use of ruthenium complexes on the oxidative cyanation of tertiary amines with NaCN.[9] Few other reports concerning this catalysis also appeared.[10] Here, we investigate the catalytic activity of complexes **5** and **6** on the oxidative α-cyanation of tertiary amines.

To obtain information on the catalytic systems, we explored the α-cyanation of *N,N*-dimethylaniline with NaCN as a model system (Eq. 1). In a typical experiment for the reaction, a mixture of *N,N*-dimethylaniline, NaCN and Ru(II) complex (mole ratio = 1: 1.2 : 0.01) in a solution

Table 2. Selected bond distances (Å) and bond angles (deg) for **5**

| | | | |
|---|---|---|---|
| Ru(1)-Cl(1) | 2.3831(8) | Ru(1)-C(1) | 1.910(4) |
| Ru(1)-C(2) | 1.947(3) | Ru(1)-C(3) | 1.914(4) |
| Ru(1)-N(1) | 2.102(2) | Ru(1)-N(2) | 2.112(2) |
| C(1)-O(1) | 1.089(4) | C(2)-O(2) | 1.119(4) |
| C(3)-O(3) | 1.125(4) | Ru(2)-C(31) | 1.882(4) |
| N(1)-Ru(1)-N(2) | 77.21(9) | N(1)-Ru(1)-C(2) | 174.24(11) |
| N(2)-Ru(1)-C(3) | 171.41(12) | Cl(1)-Ru(1)-C(1) | 178.40(10) |
| Cl(2)-Ru(2)-C(31) | 177.68(11) | Cl(2)-Ru(2)-C(32) | 86.87(11) |

Table 3. Selected bond distances (Å) and bond angles (deg) for **6**

| | | | |
|---|---|---|---|
| Ru(1)-N(1) | 2.068(6) | Ru(2)-N(4) | 2.119(7) |
| Ru(1)-N(2) | 2.111(7) | Ru(2)-N(5) | 2.062(6) |
| Ru(1)-Cl(2) | 2.387(2) | Ru(2)-Cl(1) | 2.375(2) |
| N(1)-Ru(1)-N(2) | 77.7(3) | N(4)-Ru(2)-N(5) | 77.1(3) |
| N(1)-Ru(1)-Cl(2) | 81.75(18) | N(4)-Ru(2)-Cl(1) | 86.49(18) |
| N(2)-Ru(1)-Cl(2) | 88.05(17) | N(5)-Ru(2)-Cl(1) | 82.31(18) |

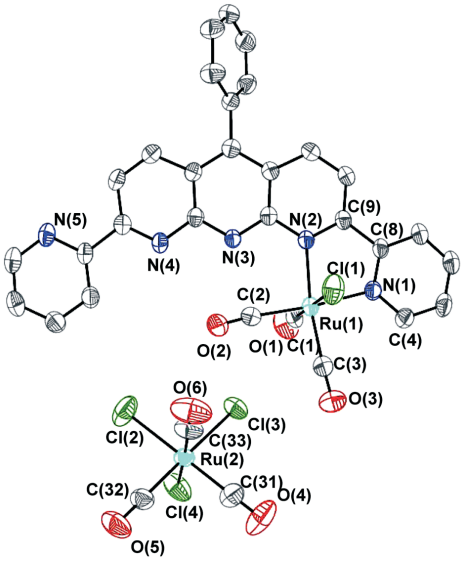



Fig. 2. ORTEP plot of **5** (Drawn with 30% probability ellipsoids).

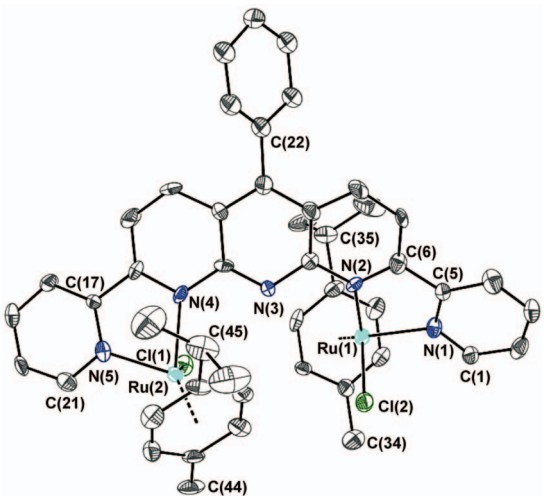
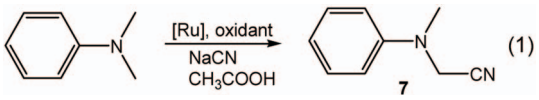



Fig. 3. ORTEP plot of **6** (Drawn with 30% probability ellipsoids).

(selected solvent/acetic acid = 3:1, 0.4 mL) was heated to 60 °C in the presence of oxidant for a certain period. The desired product 7 was extracted and then analyzed by $^1$H NMR spectroscopy. Results are summarized in Table 4.




From entries 1~2 and 13~15 (Table 4), these results clearly reveal that the di-ruthenium complex **6** is the best catalyst for this transformation, whereas the mono-nuclear complexes show less activity. This catalytic conversion was also influenced by the oxidants. The yield of cyanation product could not reach to 100% by using dioxygen as the oxidant. By using excess amount of hydrogen peroxide as the oxidant increases the conversion dramatically (Table 4, entry 6). Notably, by a slow addition of $H_2O_2$ to the reaction mixture, the amount of reagent could be reduced (Table 4, entry 13). Among the solvents tested, methanol gave the cyanation product **7** in the highest yield.

To further validate the activity of the complex **6**, a series of arylamines were also subjected to the in situ oxidation-imine formation conditions (Table 5). Under the optimal catalytic conditions, various *para*-substituted dimethyl-anilines provided the corresponding cyanation product quantitatively, except the amino-substituted one (Table 5, entry 6). For diethylarylamine, the cyanation took place at α-position, as expected, to give *N*-ethyl-*N*-(1-cyanoethyl)-aniline in 73% yield. However, we did not obtain any di-cyanation product even with the prolong heating or excess of reagents. For the selectivity, the cyanation prefers to take place at the methyl group over the ethyl as illustrated in entry 8. Thus, the catalytic reaction of *N*-ethyl-*N*-methyl-aniline with NaCN yielded *N*-ethyl-*N*-(cyanomethyl)aniline as the exclusive product.

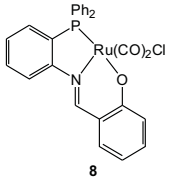
## CONCLUSIONS

In summary, we have prepared and characterized ruthenium complexes containing a 2,7-dipyridinylanthyridine ligand. Further utilization of these complexes for α-cyanation of tertiary arylamines with NaCN was investigated. It appears that di-ruthenium complex **6** is an excellent catalyst for the α-cyanation of *N,N*-dialkylanilines, presumably due to the cooperative effect between the two ruthenium centers in the complex. Further studies concerning the cooperative effect between metal centers in **6** are currently in progress.

Table 4. Results of α-cyanation of $C_6H_5N(CH_3)_2$ with NaCN[a]

| Entry | Catalyst | Oxidant | Solvent[b] | Temp. | Time(h) | Yield[c] |
|---|---|---|---|---|---|---|
| 1 | **5** | $O_2$ | MeOH | 60 °C | 24 h | 0% |
| 2 | **6** | $O_2$ | MeOH | 60 °C | 2 h | < 10% |
| 3 | **6**[d] | $O_2$ | MeOH | 60 °C | 2 h | 20% |
| 4 | **6** | $O_2$ | MeOH | 60 °C | 24 h | 37% |
| 5 | **6** | - | MeOH | 60 °C | 24 h | 0% |
| 6 | **6** | $O_2$ | $Me_2CHOH$ | 80 °C | 24 h | 68% |
| 7 | **6** | $O_2$ | i-AmOH | 100 °C | 24 h | 67% |
| 8 | **6** | $O_2$ | toluene | 100 °C | 24 h | 6% |
| 9[e] | **6** | $H_2O_2$[e] | MeOH | 25 °C | 24 h | 28% |
| 10 | **6** | $H_2O_2$[e] | MeOH | 60 °C | 24 h | 100% |
| 11[e] | **6** | $H_2O_2$[e] | MeOH | 60 °C | 24 h | 0% |
| 12 | **6** | $H_2O_2$[e] | $CH_3CN$ | 60 °C | 24 h | 28% |
| 13 | **6** | $H_2O_2$[f] | MeOH | 60 °C | 8 h | 100% |
| 14 | **5**[g] | $H_2O_2$[f] | MeOH | 60 °C | 24 h | 16% |
| 15 | **8**[g] | $H_2O_2$[f] | MeOH | 60 °C | 24 h | 38% |

[a] *N,N*-dimethylaniline (0.25 mmol), Ru(II) complex (1 mol%), NaCN (0.3 mmol) in a solution. [b] A mixed solvent (organic solvent/acetic acid: 0.3 mL/0.1 mL). [c] NMR yields. [d] 5 mol%. [e] 0.6 mmol. [e] No acetic acid. [f] 0.25 mmol, but was added gradually over 40 min. [g] 2 mol%.



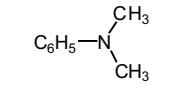
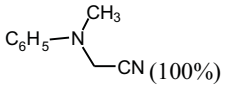
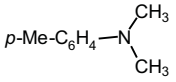
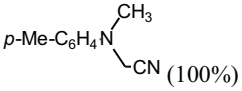
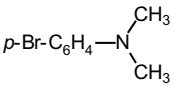
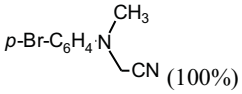
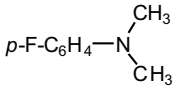
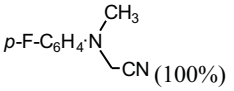
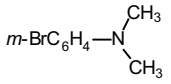
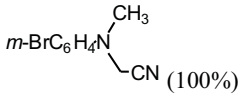
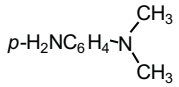
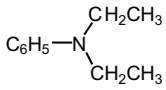
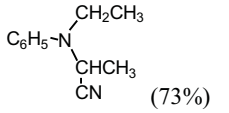
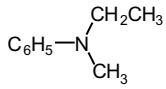
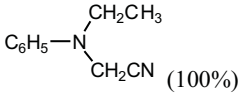

## EXPERIMENTAL

**General information.** All reactions and manipulations steps were performed under a nitrogen atmosphere. Dichloromethane and acetonitrile were dried over $CaH_2$ and distilled under nitrogen. Other chemicals and solvents were of analytical grade and were used after degassed process. Nuclear magnetic resonance spectra were recorded on a Bruker AVANCE 400 spectrometer. Chemical shifts are given in parts per million relative to $Me_4Si$ for $^1$H and $^{13}$C NMR. Infrared spectra were measured on a Nicolet Magna-IR 550 spectrometer (Series-II). UV-Vis spectra were recorded on a Hitachi U-2900 spectrometer. Compound **3** was prepared according to the reported method.[6]

**Ligand 4**. A mixture of di-aldehyde **3** (0.10 g, 0.42 mmol) and 2-acetylpyridine (0.1 g, 0.85 mmol) in ethanol (4 mL) was heated at 60 °C for 2 h. A solution of 10% KOH in ethanol (0.1 mL) was added to the above reaction mixture. The resulting mixture was heated to reflux for another 12 h. After cooling, the mixture was extracted with $CH_2Cl_2$/water and the organic extracts were concentrated to give yellow brown solids. The crude product

Table 5. α-Cyanation of various tertiary amines[a]

| Entry | Substrate | Time | Product (yield) |
|---|---|---|---|
| 1 |  | 8 h |  (100%) |
| 2 |  | 10 h |  (100%) |
| 3 |  | 10 h |  (100%) |
| 4 |  | 8 h |  (100%) |
| 5 |  | 24 h |  (100%) |
| 6 |  | 24 h | No reaction |
| 7 |  | 24 h |  (73%) |
| 8 |  | 24 h |  (100%) |

[a] Amine (0.25 mmol), complex **6**, and NaCN (0.3 mmol) in a solution of MeOH/acetic acid: 0.3 mL/0.1 mL was heated at 60 °C with a slow addition of $H_2O_2$ (0.25 mmol).

was crystallized from $CH_2Cl_2$/hexane to give **4** as yellow solids (0.13 g, 73%): $^1$H NMR (400 MHz, $CDCl_3$): δ 9.07 (d, *J* = 8.0 Hz, 2H, Py-*H*), 8.75 (d, *J* = 8.0 Hz, 2H, An-*H*), 8.68 (d, *J* = 8.0 Hz, 2H, Py-*H*), 8.23 (d, *J* = 8.0 Hz, 2H, An-*H*), 7.92 (t, *J* = 8.0 Hz, 2H, Py-*H*), 7.65 (m, 3H, Ph-*H*), 7.49 (m, 2H, Ph-*H*), 7.40 (m, 2H, Py-*H*). $^{13}$C NMR (100 MHz): δ 161.8, 156.0, 155.2, 151.0, 149.1, 137.1, 136.6, 134.1, 130.7, 129.2, 128.9, 125.1, 123.3, 120.6, 119.7.

**Complex 5**. A mixture of **4** and $[RuCl_2(CO)_3(THF)]$ (80 mg, 0.25 mmol) in $CHCl_3$ (5 mL) was heated at 40 °C for 12 h. After removal of solvents, the residue was re-precipitated in $CH_2Cl_2$/hexane. The desired complex **5** was obtained as brownish solids after filtration (89 mg, 80%). $^1$H NMR (400 MHz, $CDCl_3$): δ 9.31 (d, *J* = 8 Hz, 1H, Py-*H*), 9.13 (d, *J* = 8 Hz, 1H, Py-*H*), 9.02 (d, *J* = 8 Hz, 1H), 8.91 (d, *J* = 8 Hz, 1H, An-*H*), 8.89 (d, *J* = 8 Hz, 1H, An-*H*), 8.80 (d, *J* = 8 Hz, 1H, An-*H*), 8.85 (m, 1H, Py-*H*), 8.61 (t, *J* = 8 Hz, 1H, Py-*H*), 8.36 (d, *J* = 8 Hz, 1H, An-*H*), 7.96 (t, *J* = 8 Hz, 1H, Py-*H*), 7.87 (t, *J* = 8 Hz, 1H, Py-*H*),7.70 (m, 3H, Ph-*H*), 7.60 (m, 1H, Ph-*H*), 7.49 (m, 1H, Ph-*H*), 7.40(m, 1H, Py-*H*). $^{13}$C NMR (100 MHz): δ 187.7, 185.3, 184.7, 182.8, 164.5, 162.2, 156.7, 155.5, 155.0, 154.8, 154.2, 150.7, 149.6, 144.0, 142.8, 137.4, 137.2, 132.0, 130.7, 130.5, 129.5, 129.3, 126.0, 123.4, 122.7, 121.9, 121.5; ESI-MS: *m/z* calcd. for 604.01 $C_{29}H_{17}ClN_5O_2Ru$ ([**M**-Ru(CO)$_3$Cl$_3$-CO]$^+$), found 604.08; IR (KBr): 2126, 2057, 1995 cm$^{-1}$ ($\upsilon_{CO}$); UV-Vis (acetone): λmax (ε[M$^{-1}$cm$^{-1}$]) = 331 (10000), 410 (29000).

**Complex 6.** A mixture of **4** (60 mg, 0.15 mmol), [($\eta^6$-*p*-cymene)$RuCl_2$]$_2$ (95 mg, 0.16 mmol) and $KPF_6$ (45 mg, 0.24 mmol) in a round-bottom flask was flashed with nitrogen and then added acetonitrile (5 mL). The resulting mixture was heated to reflux for 12 h. After removal of solvent, the residue was washed with $CH_2Cl_2$, methanol and water. Complex **4** was obtained (146 mg, 89%). Recrystallization from $CH_2Cl_2$ at -20 °C gave **6** as golden yellow crystalline solids suitable for X-ray structural analysis. $^1$H NMR (400 MHz, $d_6$-acetone, at 223 K): δ 9.74 (d, *J* = 7 Hz, 2H, Py-*H*), 9.15 (d, *J* = 7 Hz, 2H, Py-*H*), 8.85 (d, *J* = 7 Hz, 2H, An-*H*), 8.77 (d, *J* = 7 Hz, 2H, An-*H*), 8.56 (t, *J* = 7 Hz, 2H, Py-*H*), 8.12 (t, *J* = 7 Hz, 2H, Py-*H*), 7.93 (m, 3H, Ph-*H*), 7.76 (m, 2H, Ph-*H*), 7.35 (d, *J* = 7 Hz, 2H, Ar-*H*), 6.51 (br, 4H, Ar-*H*), 6.23 (d, *J* = 7 Hz, 2H, Ar-*H*), 3.21 (m, 1 H, -C*H*), 2.61 (s, 3H,-C$H_3$), 1.61 (br, 6H, -C$H_3$), 1.42 (m, 1 H, -C*H*), 0.93 (s, 3 H, -C$H_3$), 0.50 (m, 3H, -C$H_3$), 0.25 (br, 3H, -C$H_3$). $^{13}$C NMR (100 MHz, $d_3$-$CD_3CN$): δ 165.3, 158.5, 157.5, 157.2, 155.4, 142.2, 141.2, 133.3, 132.3, 131.8, 130.6, 130.4, 128.5, 124.1, 121.9, 107.5, 102.6, 88.3, 86.0, 84.9, 31.9, 22.5, 21.5, 18.6; ESI-MS: *m/z* calcd. for 1098.08 [$C_{47}H_{45}Cl_2F_6N_5PRu_2$ ([**M**-Cl]$^+$)], found 1098.17; UV-Vis (acetone): λmax (ε[M$^{-1}$cm$^{-1}$]) = 337 (19000), 377 (22000), 396 (26000), 417 (28000), 512 (5100).

**General Procedure for Catalysis.** A mixture of amine (0.25 mmol), complex **6**, and NaCN (0.3 mmol) in a solution of MeOH/acetic acid: 0.3 mL/0.1 mL) was heated at 60 °C. $H_2O_2$ (0.25 mmol) was added slowly (over a period of 40 min). The mixture was stirred at 60 °C for a certain period. After the reaction, water and ethyl acetate were added. The organic extract was separated, dried and concentrated. The desired product was purified by chromatography with $CH_2Cl_2$/EtOAc as eluent. All products were characterized by $^1$H and $^{13}$C NMR spectroscopy.

## Spectroscopic Data for the Cyanation Products

***N*-(Cyanomethyl)-*N*-methylaniline**. $^1$H NMR (400 MHz, $CDCl_3$): δ 3.00 (s, 3 H, -$CH_3$), 4.17 (s, 2 H, -C$H_2$), 6.90 (br, 3 H, Ar-*H*), 7.30 (t, *J* = 6 Hz, 2 H, Ar-*H*). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 147.6, 129.3, 120.1, 115.3, 114.8, 42.4, 39.3. ***N*-(Cyanomethyl)-*N*-methyl-*p*-methylaniline.** $^1$H NMR (400 MHz, $CDCl_3$): δ 2.28 (s, 3 H, -C$H_3$), 2.95 (s, 3 H, -C$H_3$), 4.11 (s, 2H, -C$H_2$), 6.79 (d, *J* = 8 Hz, 2 H, Ar-*H*), 7.11 (d, *J* = 8 Hz, 2 H, Ar-*H*). $^{13}$C NMR

Table 6. Crystal data for **5** and **6**·$(CH_2Cl_2)_2$

| Complex | **5** | **6**·$(CH_2Cl_2)_2$ |
|---|---|---|
| Formula | $C_{33}H_{17}Cl_4N_5O_6Ru_2$ | $C_{48}H_{47}Cl_4F_{12}N_5P_2Ru_2$ |
| Fw | 923.46 | 1327.79 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | P2(1)/n | P2(1)/n |
| *a*, Å | 11.0852(3) Å | 19.168(2) |
| *b*, Å | 21.4350(5) Å | 11.0351(5) |
| *c*, Å | 14.6507(4) Å | 27.4941(14) |
| α, deg | 90 | 90 |
| β, deg | 95.887(3) | 105.048(8)° |
| γ, deg | 90 | 90 |
| V, Å$^3$; Z | 3462.81(16), 4 | 5616.3(7), 4 |
| d (calc.), Mg/m$^3$ | 1.771 | 1.570 |
| F(0,0,0) | 1816 | 2656 |
| Crystal size, mm$^3$ | 0.20 × 0.15 × 0.10 | 0.15 × 0.10 × 0.10 |
| Rflns collected | 24984 | 16711 |
| Independent rflns | 7941 [R(int) = 0.0357] | 16716 [R(int) = 0.0000] |
| θ range, deg | 2.91 to 27.50° | 2.98 to 27.50° |
| Refined method | Full-matrix least-squares on F2 | |
| Goodness of fit on F$^2$ | 1.031 | 1.376 |
| R indices [I > 2σ(I)] | R1 = 0.0354, wR2 = 0.0634 | R1 = 0.0794, wR2 = 0.2027 |
| R indices (all data) | R1 = 0.0616, wR2 = 0.0721 | R1 = 0.1201, wR2 = 0.2199 |

(100 MHz): δ 145.6, 129.9, 129.8, 115.4, 115.3, 42.7, 39.4, 20.3. ***N*-(Cyanomethyl)-*N*-methyl-*p*-bromoaniline.** $^1$H NMR (400 MHz, $CDCl_3$): δ 2.98 (s, 3 H, -C*H*$_3$), 4.13 (s, 2H, -C*H*$_2$), 6.71 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 7.38 (d, *J* = 8.8 Hz, 2 H, Ar-*H*). $^{13}$C NMR (100 MHz): δ 146.8, 132.3, 116.5, 115.1, 112.6, 42.2, 39.4. ***N*-(Cyanomethyl)-*N*-methyl-*p*-fluoroaniline.**$^1$H NMR (400 MHz, $CDCl_3$): δ 2.92 (s, 3 H, -$CH_3$), 4.10 (s, 2 H, -C*H*$_2$), 6.83 (m, 2 H, Ar-*H*), 7.00 (t, *J* = 8 Hz, 2 H, Ar-*H*). $^{13}$C NMR (100 MHz): δ 157.6 (*J* = 238 Hz), 144.2, 116.9 (*J* = 8 Hz), 115.8 (*J* = 22 Hz), 115.1, 43.3, 39.9. ***N*-(Cyanomethyl)-*N*-methyl-*m*-bromoaniline.** $^1$H NMR (400 MHz, $CDCl_3$): δ 2.99 (s, 3 H, -$CH_3$), 4.15 (s, 2 H, -C*H*$_2$), 6.74 (d, *J* = 8 Hz, 1 H, Ar-*H*), 6.96 (s, 1 H, Ar-*H*), 7.01 (d, *J* = 8 Hz, 1 H, Ar-*H*), 7.14 (t, *J* = 8.0 Hz, 1 H, Ar-*H*). $^{13}$C NMR (100 MHz): δ 148.9, 130.7, 123.6, 123.0, 117.6, 115.1, 113.1, 41.9, 39.2. ***N*-(1-Cyanoethyl)-*N*-ethylaniline**. $^1$H NMR (400 MHz, $CDCl_3$): δ 1.19 (t, *J* = 7.0 Hz, 3H, -C*H*$_3$), 1.56 (d, *J* = 7.0 Hz, 3 H, -C*H*$_3$), 3.35 (m, 2 H, -C*H*$_2$-), 4.46 (q, *J* = 7 Hz, 1 H, -C*H*-), 6.95 (m, 3 H, Ar-*H*), 7.29 (t, *J* = 8 Hz, 2H, Ar-H). $^{13}$C NMR (100 MHz): δ 146.7, 129.2, 121.7, 119.3, 118.9, 48.3, 43.7, 18.6, 14.0. ***N*-(Cyanomethyl)-*N*-ethylaniline**. $^1$H NMR (400 MHz, $CDCl_3$): δ 1.25 (t, *J* = 7.0 Hz, 3H, -$CH_3$), 3.43 (q, *J* = 7.0 Hz, 2H, -C*H*$_2$), 4.14 (s, 2 H, -C*H*$_2$), 6.88 (m, 3 H, Ar-*H*), 7.29 (t, *J* = 8.2 Hz, 2 H, Ar-H). $^{13}$C NMR (100 MHz): δ 146.5, 129.3, 121.7, 119.5, 116.2, 114.6, 46.2, 39.4, 12.2.

**Crystallography**. Crystals suitable for X-ray determination were obtained for **5** and **6**·$(CH_2Cl_2)_2$ by recrystallization at room temperature. Cell parameters were determined either by a Siemens SMART CCD diffractometer. The structure was solved using the SHELXS-97 program[11a] and refined using the SHELXL-97 program[11b] by full-matrix least-squares on *F*2. It should be noted that **6** were in twin crystals and refined SHELXL HKLF 5 (two sets) programs. CCDC-921735 (**5**) & 921736 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## ACKNOWLEDGEMENTS

We thank the National Science Council for financial support (NSC-100-2113-M002-001-MY3).

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