

## Areneruthenium(II) 4-Acyl-5-pyrazolonate Derivatives: Coordination Chemistry, Redox Properties, and Reactivity

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Areneruthenium(II) molecular complexes of the formula  $[\text{Ru}(\text{arene})(\text{Q})\text{Cl}]$ , containing diverse 4-acyl-5-pyrazolonate ligands Q with arene = cymene or benzene, have been synthesized by the interaction of HQ and  $[\text{Ru}(\text{arene})\text{Cl}(\mu\text{-Cl})_2]$  dimers in methanol in the presence of sodium methoxide. The dinuclear compound  $[\{\text{Ru}(\text{cymene})\text{Cl}\}_2\text{Q}_4\text{Q}]$  ( $\text{H}_2\text{Q}_4\text{Q}$  = bis(4-(1-phenyl-3-methyl-5-pyrazolonate)dioxohexane), existing in the  $\text{RRuSRu}$  (meso form), has been prepared similarly.  $[\text{Ru}(\text{cymene})(\text{Q})\text{Cl}]$  reacts with sodium azide in acetone, affording  $[\text{Ru}(\text{cymene})(\text{Q})\text{N}_3]$  derivatives, where  $\text{Cl}^-$  has been replaced by  $\text{N}_3^-$ . The reactivity of  $[\text{Ru}(\text{cymene})(\text{Q})\text{Cl}]$  has also been explored toward monodentate donor ligands L (L = triphenylphosphine, 1-methylimidazole, or 1-methyl-2-mercaptoimidazole) and exo-bidentate ditopic donor ligands L–L (L–L = 4,4'-bipyridine or bis(diphenylphosphino)propane) in the presence of silver salts  $\text{AgX}$  (X =  $\text{SO}_3\text{CF}_3$  or  $\text{ClO}_4$ ), new ionic mononuclear complexes of the formula  $[\text{Ru}(\text{cymene})(\text{Q})\text{L}]\text{X}$ , and ionic dinuclear complexes of the formula  $[\{\text{Ru}(\text{cymene})(\text{Q})\}_2\text{L-L}]\text{X}_2$  being obtained. The solid-state structures of a number of complexes were confirmed by X-ray crystallographic studies. Their redox properties have been investigated by cyclic voltammetry and controlled potential electrolysis, which, on the basis of their measured  $\text{Ru}^{\text{II/III}}$  reversible oxidation potentials, have allowed the ordering of the bidentate acylpyrazolonate ligands according to their electron-donor character and are indicative of a small dependence of the HOMO energy upon the change of the monodentate ligand. This is accounted for by DFT calculations, which show a relevant contribution of acylpyrazolonate ligand orbitals to the HOMOs, whereas that from the monodentate ligand is minor.

### Introduction

Half-sandwich  $\eta^6$ -arene-ruthenium compounds play an important role as catalysts and also as precursors for other Ru(0) and Ru(II) derivatives.<sup>1</sup> They can undergo a variety of substitution reactions with various ligands, yielding neutral and cationic complexes.<sup>1,2</sup> Recent interest in these complexes has arisen out of the synthesis of water-soluble arene–ruthenium complexes, which exhibit antibiotic and antiviral activities.<sup>3</sup> The reactivity of areneruthenium(II) dimers with various ligands has also been reported,<sup>4</sup> but only recently

have more detailed studies on areneruthenium(II)  $\beta$ -diketonates appeared.<sup>5</sup> Our group has been involved in the development of the coordination chemistry of a new class of  $\beta$ -diketonate ligands, namely 4-acyl-5-pyrazolonates, containing a pyrazole ring fused to the chelating fragment, which confers different and sometimes unusual physico-

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chemical properties on the corresponding metal complexes.<sup>6</sup> Here, we extend our investigation to the interaction of several acylpyrazolones with (arene)ruthenium(II) dichloride acceptors (arene = *p*-cymene or benzene) and to the exploration of the reactivity of the Ru(II) derivatives with respect to a number of mono- and bidentate donor ligands.

## Experimental Section

**Materials and Methods.** All of the reagents, 1-methylimidazole (Meim), 1-methyl-2-mercaptoimidazole (Hmimt), bis(diphenylphosphino)propane (dppp), 4,4'-bipyridyl (4,4'-bpy), and [Ru(*p*-cymene)-Cl<sub>2</sub>]<sub>2</sub>, were purchased from Alfa (Karlsruhe) and Aldrich (Milwaukee) and used as received. [Ru(benzene)Cl<sub>2</sub>]<sub>2</sub> was synthesized as previously reported.<sup>7</sup> The acylpyrazolone ligands HQ<sup>nPe</sup> (1-phenyl-3-methyl-4-*tert*-butylacetyl-5-pyrazolone), H<sub>2</sub>Q4Q (bis(4-(1-phenyl-3-methyl-5-pyrazolone))dioxohexane), HQ<sup>naph</sup> (1-phenyl-3-methyl-4-(1-naphthoyl)-5-pyrazolone), HQ<sup>CF<sub>3</sub></sup> (1-phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone), HQ<sup>pent</sup> (1-phenyl-3-methyl-4-(4-pentenoyl)-5-pyrazolone), and HQ<sup>py,CF<sub>3</sub></sup> (1-(2-pyridyl)-3-methyl-4-trifluoroacetyl-5-pyrazolone) were synthesized as previously reported.<sup>6</sup> HQ<sup>Me,mPe</sup> (1,3-dimethyl-4-*tert*-butylacetyl-5-pyrazolone) has been synthesized for the first time with a procedure similar to that used for previous reported HQ donor ligands.<sup>8</sup> The samples for microanalyses were dried in vacuo to constant weight (20 °C, ca. 0.1 Torr). Elemental analyses (C, H, N, S) were performed in-house with a Fisons Instruments 1108 CHNS–O Elemental Analyzer. IR spectra were recorded from 4000 to 100 cm<sup>-1</sup> with a PerkinElmer System 2000 FTIR instrument. <sup>1</sup>H, <sup>19</sup>F, <sup>31</sup>P, and <sup>13</sup>C NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for <sup>1</sup>H, 282.2 MHz for <sup>19</sup>F, 121.4 MHz for <sup>31</sup>P, and 75 MHz for <sup>13</sup>C). Melting points were obtained using an IA 8100 electrothermal instrument. The electrical conductances of the acetonitrile and water solutions were measured with a Crison CDTM 522 conductimeter at room temperature. The electrochemical experiments were carried out on an EG&G PAR 273A

potentiostat/galvanostat connected to a personal computer through a GPIB interface. Cyclic voltammetry (CV) studies were undertaken in a two-compartment three-electrode cell, with a platinum disc working (*d* = 0.5 mm) and counter electrodes. A Luggin capillary connected to a silver-wire pseudoreference electrode was used to control the working electrode potential. Controlled potential electrolyses (CPE) were carried out in a two-compartment three-electrode cell with a platinum-gauze working and counter electrodes in compartments separated by a glass frit; a Luggin capillary, probing the working electrode, was connected to a silver-wire pseudoreference electrode. The solutions were saturated with N<sub>2</sub> by bubbling with this gas before each run, and the oxidation potentials of the complexes were measured by CV, in the presence of ferrocene as the internal standard; the redox potential values are quoted relative to the saturated calomel electrode (SCE) by using the [Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>0/+</sup> (*E*<sub>1/2</sub><sup>ox</sup> = 0.525 V vs SCE) redox couple in the 0.2 M [Bu<sub>4</sub>N][BF<sub>4</sub>]/CH<sub>2</sub>Cl<sub>2</sub> solution.<sup>9</sup>

**Syntheses of Complexes.** A representative example is given for each type. Similarly, full details for the remainder (**4–7**, **9**, **11–14**, **16–18**) are presented in the Supporting Information (below).

**[Ru(cymene)(Q<sup>nPe</sup>)Cl] (1).** The starting complex [Ru( $\eta^6$ -cymene)Cl<sub>2</sub>]<sub>2</sub> (0.306 g, 0.5 mmol) was added to a methanol solution (30 mL) of HQ<sup>nPe</sup> (0.272 g, 1 mmol) and NaOMe (0.054 g, 1 mmol), the resulting clear solution was stirred for 4 h at room temperature, and the color changed from red to orange. The solvent was removed in vacuo, the residue was dissolved in dichloromethane (10 mL), and the solution was filtered to remove sodium chloride. The orange solution was concentrated (2 mL) and an addition of excess hexane gave the orange complex, which was separated and dried under a vacuum. Recrystallization in methanol at 4 °C slowly yielded orange-red crystals. The compound is soluble in alcohols, acetone, acetonitrile, dmso, and chlorinated solvents. Yield 86%. Mp 195–197 °C. Anal. Calcd for C<sub>26</sub>H<sub>33</sub>ClN<sub>2</sub>O<sub>2</sub>Ru: C, 57.61; H, 6.14; N, 5.17. Found: C, 57.53; H, 6.34; N, 5.22.  $\Lambda_m$  (acetonitrile, 298 K, 10<sup>-3</sup> mol/L) 6.4  $\Omega$ –1 cm<sup>2</sup> mol<sup>-1</sup>. IR (nujol, cm<sup>-1</sup>): 3061 m  $\nu$ -(C<sub>arom</sub>-H), 1608vs  $\nu$ (C=O), 471s, 387m  $\nu$ (Ru–O), 281s  $\nu$ (Ru–Cl). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K):  $\delta$ , 1.10s (9H, C(=O)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 1.34d, 1.38d (6H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.26s (3H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.36s (3H, C3-CH<sub>3</sub>), 2.60q (2H, C(=O)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 2.96m (1H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 5.42dt (4H, AA'BB' system, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 7.19t, 7.38t, 7.91d (5H, N1-C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C-{<sup>1</sup>H} (CDCl<sub>3</sub>):  $\delta$ , 18.1s (C3-CH<sub>3</sub>), 18.4s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 22.5s, 22.6s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 30.5s (C(=O)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 30.9s (C(=O)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 32.9s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 49.6s (C(=O)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 79.1s, 79.8s, 81.3s, 82.0s, 96.4s, 100.3s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 121.2s, 125.3, 128.5, 148.3s (N1-C<sub>6</sub>H<sub>5</sub>), 107.3s (C4), 138.8s (C3), 162.5s (C5), 192.9s (CO).

**[Ru(cymene)(Q<sup>nPe</sup>)N<sub>3</sub>] (2).** A mixture of compound **1** (0.542 g, 1 mmol) and sodium azide NaN<sub>3</sub> (0.065 g, 1 mmol) was stirred in dry acetone for 3 h at room temperature. The solvent was then removed in vacuo, and the residue was dissolved in dichloromethane (10 mL) and then filtered to remove sodium chloride. The solution was concentrated (2 mL) and an excess of hexane was added to assist precipitation. The orange-colored product was separated out, washed with diethyl ether, and dried under a vacuum. Recrystallization from methanol at 4 °C yielded orange crystals after 2 days. The compound is soluble in alcohols, acetone, acetonitrile, dmso, and chlorinated solvents. Yield 81%. Mp 149–151 °C. Anal. Calcd for C<sub>26</sub>H<sub>33</sub>N<sub>5</sub>O<sub>2</sub>Ru: C, 56.92; H, 6.06; N, 12.76. Found: C, 56.91; H, 6.26; N, 12.96.  $\Lambda_m$  (acetonitrile, 298 K, 10<sup>-3</sup> mol/L) 7.1  $\Omega$ –1

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cm<sup>2</sup> mol<sup>-1</sup>. IR (nujol, cm<sup>-1</sup>): 3063m  $\nu$ (C<sub>arom</sub>-H), 2019vs  $\nu$ (N<sub>3</sub>), 1605vs  $\nu$ (C=O), 469s, 398m  $\nu$ (Ru-O), 361s  $\nu$ (Ru-N). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K):  $\delta$ , 1.09s (9H, C(=O)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 1.35d, 1.39d (6H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.23s (3H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.37s (3H, C3-CH<sub>3</sub>), 2.61q (2H, C(=O)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 2.97 m (1H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 5.24dd, 5.48dd (4H, AA'BB' system, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 7.19t, 7.39t, 7.89d (5H, N1-C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C-{<sup>1</sup>H} (CDCl<sub>3</sub>):  $\delta$ , 18.1s (C3-CH<sub>3</sub>), 18.2s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 22.5s, 22.7s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 30.5s (C(=O)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 30.9s (C(=O)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 32.9s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 49.8s (C(=O)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 79.1s, 79.7s, 81.4s, 82.4s, 96.0s, 99.6s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 121.2s, 125.4, 128.6, 148.4s (N1-C<sub>6</sub>H<sub>5</sub>), 107.3s (C4), 138.7s (C3), 162.4s (C5), 193.4s (CO).

**[Ru(cymene)(Q<sup>nPe</sup>)(PPh<sub>3</sub>)SO<sub>3</sub>CF<sub>3</sub> (3).** A mixture of compound **1** (0.542 g, 1 mmol) and AgSO<sub>3</sub>CF<sub>3</sub> (0.257 g, 1 mmol) in dry acetone (30 mL) was stirred for 2 h at room temperature and then filtered to remove silver. Triphenylphosphine PPh<sub>3</sub> was added (0.262 g, 1 mmol), and the mixture was stirred for 4 h. The solvent was then removed in vacuo, the residue was dissolved in dichloromethane (5 mL), and an excess of hexane was added to assist precipitation. The yellow-colored product was separated out, washed with diethyl ether, and dried under a vacuum. Recrystallization from methanol at 4 °C slowly yielded yellow crystals. The compound is soluble in alcohols, acetone, acetonitrile, dmsO, and chlorinated solvents. Yield 64%. Mp 92–94 °C. Anal. Calcd for C<sub>45</sub>H<sub>48</sub>F<sub>3</sub>N<sub>2</sub>O<sub>5</sub>-PRuS: C, 58.88; H, 5.27; N, 3.05; S, 3.49. Found: C, 58.32; H, 5.02; N, 2.83; S, 3.32.  $\Lambda_m$  (acetonitrile, 298 K, 10<sup>-3</sup> mol/L) 137.3  $\Omega$ -1 cm<sup>2</sup> mol<sup>-1</sup>. IR (nujol, cm<sup>-1</sup>): 3058m  $\nu$ (C<sub>arom</sub>-H), 1599s  $\nu$ (C=O), 1270vs, 1149vs  $\nu$ (SO<sub>3</sub>CF<sub>3</sub>), 529s, 512s, 492m, 441m, 427m  $\nu$ (PPh<sub>3</sub>), 464m, 353m  $\nu$ (Ru-O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K):  $\delta$ , 1.05s (9H, C(=O)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 1.07d, 1.15d (6H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 1.75s (3H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.17s (3H, C3-CH<sub>3</sub>), 2.35q (2H, C(=O)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 2.51m (1H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 5.50dd, 5.71dd (4H, AA'BB' system, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 7.20–7.50m br, 7.63d (20H, N1-C<sub>6</sub>H<sub>5</sub> and P-C<sub>6</sub>H<sub>5</sub>). <sup>19</sup>F{<sup>1</sup>H} (CDCl<sub>3</sub>, 298 K):  $\delta$ , -78.4 (SO<sub>3</sub>CF<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} (CDCl<sub>3</sub>, 298 K):  $\delta$ , 32.2s (PPh<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} (CDCl<sub>3</sub>, 218 K):  $\delta$ , 32.2s (PPh<sub>3</sub>). <sup>13</sup>C-{<sup>1</sup>H} (CDCl<sub>3</sub>):  $\delta$ , 17.8s (C3-CH<sub>3</sub>), 17.9s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 21.5s, 22.4s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 30.6s (C(=O)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 31.0s (C(=O)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 32.8s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 50.2s (C(=O)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 85.3s, 86.1s, 86.7s, 89.8d (<sup>2</sup>J<sub>(C-P)</sub>: 4.5 Hz), 99.4s, 112.7d (<sup>2</sup>J<sub>(C-P)</sub>: 6.8 Hz) (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 121.0q (<sup>1</sup>J<sub>(C-F)</sub>: 218.3 Hz, SO<sub>3</sub>CF<sub>3</sub>), 134.1d (<sup>2</sup>J<sub>(C-P)</sub>: 9.9 Hz), 131.4d (<sup>1</sup>J<sub>(C-P)</sub>: 31.1 Hz), 129.3s, 129.0d (<sup>2</sup>J<sub>(C-P)</sub>: 17.6 Hz) (P-C<sub>6</sub>H<sub>5</sub>), 120.5s, 126.3, 128.8, 148.1s (N1-C<sub>6</sub>H<sub>5</sub>), 109.2s (C4), 137.7s (C3), 161.0s (C5), 195.7s (CO).

**[Ru(cymene)(Q<sup>nPe</sup>)(PPh<sub>3</sub>)ClO<sub>4</sub> (4), [Ru(cymene)(Q<sup>nPe</sup>)(Meim)]-SO<sub>3</sub>CF<sub>3</sub> (5), [Ru(cymene)(Q<sup>nPe</sup>)(Meim)]ClO<sub>4</sub> (6) and [Ru(cymene)(Q<sup>nPe</sup>)(Hmimt)]SO<sub>3</sub>CF<sub>3</sub> (7)** have been prepared following the procedure reported for compound **3**.

**[[Ru(cymene)(Q<sup>nPe</sup>)<sub>2</sub>(4,4'-bpy)](ClO<sub>4</sub>)<sub>2</sub> (8).** Compound **8** was prepared following a procedure similar to that reported for **3** by using compound **1** (0.542 g, 1 mmol), AgClO<sub>4</sub> (0.207 g, 1 mmol), and 4,4'-bpy (0.078 g, 0.5 mmol). Yield 76%. Mp 134–136 °C. Anal. Calcd for C<sub>62</sub>H<sub>74</sub>Cl<sub>2</sub>N<sub>6</sub>O<sub>12</sub>Ru<sub>2</sub>: C, 54.42; H, 5.45; N, 6.14. Found: C, 54.21; H, 5.42; N, 6.38.  $\Lambda_m$  (acetonitrile, 298 K, 10<sup>-3</sup> mol/L) 221.5  $\Omega$ -1 cm<sup>2</sup> mol<sup>-1</sup>. IR (nujol, cm<sup>-1</sup>): 3066m  $\nu$ (C<sub>arom</sub>-H), 1601s  $\nu$ (C=O), 1074vs  $\nu$ (ClO<sub>4</sub>), 465m, 381m  $\nu$ (Ru-O), 322m  $\nu$ (Ru-N). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K):  $\delta$ , 1.06s, 1.09s (18H, C(=O)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 1.20d, 1.27d, 1.31d, 1.35d (12H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.16s, 2.18s (6H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.27s, 2.29s (6H, C3-CH<sub>3</sub>), 2.62q, 2.69q (4H, C(=O)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 2.80m, 2.90m (2H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 5.60–5.80m (8H, AA'BB'

system, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 7.25m, 7.52m, 7.78d, 7.85m, 8.65m, 9.18m (10H, C<sub>arom</sub> of 4,4'-bpy and N1-C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>):  $\delta$ , 17.9s (C3-CH<sub>3</sub>), 18.02s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 22.4s, 22.6s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 30.7s (C(=O)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 31.1s (C(=O)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 33.2s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 49.9s (C(=O)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 82.2s, 82.4s, 82.9s, 83.1s, 89.2s, 98.9s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 120.9s, 126.5, 129.3, 148.5s (N1-C<sub>6</sub>H<sub>5</sub>), 120.6s, 121.7s, 124.4s, 124.9s, 150.8s, 151.1s, 153.0s, 155.4s (C<sub>arom</sub> of 4,4'-bpy), 107.4s (C4), 138.1s (C3), 161.3s (C5), 192.8s (CO).

**[[Ru(cymene)(Q<sup>nPe</sup>)<sub>2</sub>(dppp)](ClO<sub>4</sub>)<sub>2</sub> (9).** Compound **9** was prepared following the procedure reported for **3** by using compound **1**, AgClO<sub>4</sub>, and dppp.

**[[Ru(cymene)Cl]<sub>2</sub>(Q4Q)] (10).** Compound **10** was prepared following a procedure similar to that reported for **1** by using [Ru(cymene)Cl]<sub>2</sub>, H<sub>2</sub>Q4Q, and NaOMe. Yield 75%. Mp 137–140 °C. Anal. Calcd for C<sub>46</sub>H<sub>52</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>4</sub>Ru<sub>2</sub>: C, 55.36; H, 5.25; N, 5.61. Found: C, 54.94; H, 5.33; N, 5.38.  $\Lambda_m$  (acetonitrile, 298 K, 10<sup>-3</sup> mol/L) 6.3  $\Omega$ -1 cm<sup>2</sup> mol<sup>-1</sup>. IR (nujol, cm<sup>-1</sup>): 3077w  $\nu$ (C<sub>arom</sub>-H), 1605s  $\nu$ (C=O), 459m br, 394m  $\nu$ (Ru-O), 281vs  $\nu$ (Ru-Cl). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K):  $\delta$ , 1.32d, 1.35d, 1.38d, 1.41d (12H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.19s, 2.26s (6H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.32s, 2.38s (6H, C3-CH<sub>3</sub>), 2.88m, 2.95m (2H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 1.88m, 2.79m (8H, C(=O)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(=O)), 5.30m, 5.55m (8H, AA'BB' system, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 7.18t, 7.38t, 7.92dd (10H, N1-C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>):  $\delta$ , 17.3s, 17.7s, 18.1s, 18.3s (C3-CH<sub>3</sub> and CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 22.5s, 22.6s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 25.6s, 26.0s (C(=O)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(=O)), 30.9s, 31.0s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 38.2, 38.5s (C(=O)CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>C(=O)), 79.0s, 79.1s, 79.2s, 79.4s, 82.3s, 82.4s, 82.6s, 82.7s, 96.6s, 96.8s, 99.5s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 120.9s, 121.1s, 125.3, 125.4s, 128.6, 148.1s, 148.2s (N1-C<sub>6</sub>H<sub>5</sub>), 105.7s (C4), 138.8s, 138.9s (C3), 162.4s (C5), 192.8s, 192.9s (CO).

**Ru(cymene)(Q<sup>naph</sup>)Cl (11), [Ru(cymene)(Q<sup>CF3</sup>)Cl] (12), [Ru(cymene)(Q<sup>pent</sup>)Cl] (13), and [Ru(cymene)(Q<sup>Me,nPe</sup>)Cl] (14)** were prepared following the procedure reported for **1**.

**[Ru(cymene)(Q<sup>py,CF3</sup>)Cl] (15).** Compound **15** was prepared following a procedure similar to that reported for **1** by using [Ru(cymene)Cl]<sub>2</sub>, HQ<sup>py,CF3</sup> and NaOMe. Yield %. Mp 192–194 °C. Anal. Calcd for C<sub>21</sub>H<sub>21</sub>ClF<sub>3</sub>N<sub>3</sub>O<sub>2</sub>Ru: C, 46.63; H, 3.91; N, 7.77. Found: C, 46.30; H, 3.62; N, 7.83.  $\Lambda_m$  (acetonitrile, 298 K, 10<sup>-3</sup> mol/L) 4.3  $\Omega$ -1 cm<sup>2</sup> mol<sup>-1</sup>. IR (nujol, cm<sup>-1</sup>): 3061m  $\nu$ (C<sub>arom</sub>-H), 1682vs  $\nu$ (C=O), 287s  $\nu$ (Ru-Cl), 323m, 258s  $\nu$ (Ru-N). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K):  $\delta$ , 1.05d, 1.08d (6H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.33s (3H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.54 m (1H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.81s (3H, C3-CH<sub>3</sub>), 5.50dd, 5.70d (4H, AA'BB' system, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 7.11dd, 7.80dd, 8.62m (4H, N1-C<sub>5</sub>H<sub>4</sub>N). <sup>19</sup>F{<sup>1</sup>H} (CDCl<sub>3</sub>):  $\delta$ , -81.4s (CF<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>):  $\delta$ , 18.9s (C3-CH<sub>3</sub>), 19.2s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 22.2s, 22.5s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 31.2s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 81.6s, 83.2s, 84.2s, 86.0s, 100.5s, 103.8s (CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 117.2q (<sup>1</sup>J<sub>(C-F)</sub>: 287.8 Hz, CF<sub>3</sub>), 112.3, 120.7s, 140.8, 150.1s, (N1-C<sub>5</sub>H<sub>4</sub>N), 104.8s (C4), 150.2s (C3), 162.6s (C5), 172.5q (<sup>2</sup>J<sub>(C-F)</sub>: 35.9 Hz, CO).

**[Ru(cymene)(Q<sup>py,CF3</sup>)N<sub>3</sub>] (16), [Ru(cymene)(Q<sup>py,CF3</sup>)(PPh<sub>3</sub>)]-ClO<sub>4</sub> (17), and [Ru(benzene)(Q<sup>py,CF3</sup>)Cl] (18)** were prepared following a procedure similar to that reported for **1**.

**Structure Determinations.** Full spheres of CCD area-detector diffractometer data were measured at diverse temperatures ( $\omega$ -scans; monochromatic Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å) yielding  $N_{\text{(total)}}$  reflections, which merged to  $N$  unique ( $R_{\text{int}}$  cited) after an empirical/multiscan absorption correction (proprietary software), and  $N_o$  with  $I > 2\sigma(I)$  being considered observed. Full matrix least-squares refinement was on  $F^2$  on all of the data, refining anisotropic



**Table 1.** Molecular Core Geometries (ArRuXQ<sup>000</sup>)<sup>(+a)</sup>

compound	<b>1</b>	<b>2</b>	<b>6</b>	<b>10</b>	<b>12</b>	<b>14</b>	<b>15</b>	<b>17</b>	<b>18</b>
Ar, X, Y <sub>2</sub> <sup>Q</sup>	cy, Cl, O <sub>2</sub>	cy, N <sub>3</sub> , O <sub>2</sub>	cy, Meim, O <sub>2</sub>	cy, Cl, O <sub>2</sub>	cy, Cl, O <sub>2</sub>	cy, Cl, O <sub>2</sub>	cy, Cl, N <sub>2</sub>	cy, PPh <sub>3</sub> , N <sub>2</sub>	C <sub>6</sub> H <sub>6</sub> , Cl, N <sub>2</sub>
R <sub>CO</sub> <sup>Q</sup> , R <sub>N</sub> <sup>Q</sup>	nPe, Ph	nPe, Ph	nPe, Ph	(CH <sub>2</sub> ), Ph	CF <sub>3</sub> , Ph	nPe, Me	CF <sub>3</sub> , py	CF <sub>3</sub> , py	CF <sub>3</sub> , py
Distances (Å)									
Ru—C(0)	1.65 <sub>0</sub>	1.64 <sub>4</sub>	1.65 <sub>6</sub>	1.62 <sub>6</sub>	1.65 <sub>2</sub>	1.63 <sub>2</sub>	1.68 <sub>3</sub>	1.76 <sub>6</sub>	1.67 <sub>7</sub>
Ru—C <sub>ar</sub>	2.15 <sub>0</sub>	2.15 <sub>5</sub>	2.17 <sub>1</sub>	2.14 <sub>4</sub>	2.16 <sub>0</sub>	2.15 <sub>1</sub>	2.17 <sub>4</sub>	2.20 <sub>1</sub>	2.16 <sub>8</sub>
	-2.187(2)	-2.187(2)	-2.190(2)	-2.166(4)	-2.188(2)	-2.196(7)	-2.235(2)	2.294(5)	-2.200(4)
Ru—X	2.4109(5)	2.097(3)	2.119(2)	2.398(1)	2.4029(7)	2.402(2)	2.4162(6)	2.399(2)	2.401(1)
Ru—Y <sub>1</sub> <sup>Q</sup>	2.090(1)	2.094(1)	2.086(1)	2.091(3)	2.104(1)	2.107(4)	2.083(2)	2.079(4)	2.075(3)
Ru—Y <sub>2</sub> <sup>Q</sup>	2.089(1)	2.091(2)	2.090(1)	2.078(3)	2.095(1)	2.089(4)	2.103(2)	2.087(4)	2.093(3)
Angles (degrees)									
C(0)—Ru—X	130. <sub>6</sub>	127. <sub>3</sub>	131. <sub>0</sub>	129. <sub>9</sub>	129. <sub>7</sub>	129. <sub>0</sub>	128. <sub>5</sub>	131. <sub>2</sub>	128. <sub>6</sub>
C(0)—Ru—Y <sub>1</sub> <sup>Q</sup>	126. <sub>7</sub>	127. <sub>1</sub>	128. <sub>8</sub>	125. <sub>9</sub>	126. <sub>8</sub>	128. <sub>1</sub>	132. <sub>2</sub>	129. <sub>3</sub>	132. <sub>6</sub>
C(0)—Ru—Y <sub>2</sub> <sup>Q</sup>	126. <sub>9</sub>	128. <sub>2</sub>	124. <sub>9</sub>	129. <sub>2</sub>	128. <sub>5</sub>	128. <sub>1</sub>	130. <sub>9</sub>	127. <sub>3</sub>	130. <sub>9</sub>
Y <sub>1</sub> <sup>Q</sup> —Ru—X	85.23(4)	87.22(9)	83.84(6)	85.8(1)	84.27(3)	84.5(1)	84.33(5)	87.6(1)	85.19(8)
Y <sub>2</sub> <sup>Q</sup> —Ru—X	84.46(4)	85.45(8)	86.27(7)	83.4(1)	84.83(3)	84.0(1)	85.86(5)	86.7(1)	84.46(8)
Y <sub>1</sub> <sup>Q</sup> —Ru—Y <sub>2</sub> <sup>Q</sup>	88.20(5)	87.70(6)	87.12(5)	87.6(1)	87.59(5)	87.9(1)	76.77(7)	77.2(1)	76.5(1)
Ruthenium atom deviations (δÅ) from the (C <sub>3</sub> N <sub>2</sub> ) <sub>Q</sub> plane									
δRu	0.059(4)	0.227(4)	0.193(4)	0.37(1)	0.291(3)	0.14(1)	0.007(3)	0.082(9)	0.139(5)

<sup>a</sup> In **15**, **17**, and **18**, Y<sub>2</sub><sup>Q</sup> is the pyridine nitrogen atom; in **2**, Ru—N—N is 123.4(2)°; in **6**, δRu from the Meim C<sub>3</sub>N<sub>2</sub> aromatic plane is 0.057(4) Å. δRu from the (C<sub>6</sub>)<sub>py</sub> planes of **15**, **17**, and **18** are 0.053(3), 0.053(3), 0.077(5) Å, respectively; the C<sub>6</sub>/C<sub>3</sub>N<sub>2</sub> interplanar dihedral angles are 7.14(8), 1.5(2), and 15.6(1)°, respectively.

displacement parameter forms for the non-hydrogen atoms, with the hydrogen atom treatment following a riding model. Reflection weights were  $(\sigma^2(F^2) + (aP)^2 + (bP)^2)^{-1}$  ( $P = (F_o^2 + 2F_c^2)/3$ ). Neutral atom complex scattering factors were employed within the *SHELXL 97*<sup>10</sup> and *Xtal 3.7*<sup>11</sup> program systems. Pertinent results are given in the tables and figures, the latter showing non-hydrogen atoms with 50% probability amplitude envelopes, with hydrogen atoms (where shown) having arbitrary radii of 0.1 Å. Individual variations in procedure (variata) are appended as footnotes to Table 2.

**Computational Details.** The full geometry optimization of the model complexes has been carried out in Cartesian coordinates at the density functional theory (DFT) level of theory using the *Gaussian 98*<sup>12</sup> package. The calculations have been performed using Becke's three-parameter hybrid exchange functional<sup>13</sup> in combination with the gradient-corrected correlation functional of Lee, Yang, and Parr<sup>14</sup> (B3LYP). The restricted approximations for the structures with closed electron shells and the unrestricted methods for the structures with open electron shells have been employed. A quasirelativistic Stuttgart pseudopotential described 28 core electrons and the appropriate contracted basis set (8s7p6d)/[6s5p3d]<sup>15</sup> for the ruthenium atom, and the 6-31G\* basis set for other atoms

were used. Symmetry operations were not applied for all of the structures. The Hessian matrix was calculated analytically for the nonoxidized species to prove the location of correct minima (no imaginary frequencies were found). The experimental X-ray geometries of **1** and **2** were taken as a basis for the initial geometries of the optimization processes.

## Results and Discussion

**Synthesis of Ruthenium Derivatives.** The reaction of the proligand HQ<sup>nPe</sup> with the dimer [Ru( $\eta^6$ -cymene)-Cl( $\mu$ -Cl)]<sub>2</sub> in methanol, in the presence of a base such as sodium methoxide, afforded complex **1** (Scheme 1).

The compound is stable in air and in solution, very soluble in most organic solvents, and is a nonelectrolyte in acetonitrile. The IR spectrum shows the typical low-frequency shift of  $\nu$ (C=O) upon coordination<sup>16</sup> of the acylpyrazolone to the metal, and strong absorptions in the far-IR region are clearly due to  $\nu$ (Ru—O) and  $\nu$ (Ru—Cl).<sup>7</sup> The proton spectrum shows the typical set of resonances of the arene fragment and of the acylpyrazolone ligands, deshielded with respect to those of the reagents.

The chloride in **1** can be easily exchanged with the anionic azide N<sub>3</sub><sup>-</sup>, working in acetone in the presence of excess NaN<sub>3</sub>, to afford derivative **2**, or by neutral monodentate donors such as triphenylphosphine (PPh<sub>3</sub>), 1-methylimidazole (Meim), and 1-methyl-2-mercaptoimidazole (Hmimt), in acetone in the presence of the appropriate ligand and AgX (X = SO<sub>3</sub>CF<sub>3</sub> or ClO<sub>4</sub>) to afford derivatives **3–7**, as depicted in Scheme 1.

In the IR of **2**, a strong absorption at 2019 cm<sup>-1</sup> and the disappearance of the band at 280 cm<sup>-1</sup> confirm the substitution of the chloride with azide.<sup>17</sup> Apart from derivative **2**,

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Table 2. Crystal/refinement Data<sup>a</sup>

compound	1	2	6	10	12
formula	C <sub>26</sub> H <sub>33</sub> ClN <sub>2</sub> O <sub>2</sub> Ru	C <sub>26</sub> H <sub>33</sub> N <sub>5</sub> O <sub>2</sub> Ru	C <sub>30</sub> H <sub>39</sub> N <sub>4</sub> O <sub>2</sub> Ru(ClO <sub>4</sub> )	C <sub>46</sub> H <sub>52</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>2</sub> Ru <sub>2</sub>	C <sub>22</sub> H <sub>22</sub> ClF <sub>3</sub> N <sub>2</sub> O <sub>2</sub> Ru
M <sub>r</sub> (Daltons)	542.1	548.6	688.2	998.0	539.9
cryst syst	triclinic	triclinic	triclinic	monoclinic	monoclinic
space group	P1̄ (#2)	P1̄ (#2)	P1̄ (#2)	P2 <sub>1</sub> /n (#14)	P2 <sub>1</sub> /n (#14)
a (Å)	9.4109(5)	9.5495(5)	10.9624(5)	13.4826(2)	11.474(2)
b (Å)	10.2238(5)	10.1054(6)	12.4305(5)	12.44000(10)	8.592(2)
c (Å)	14.5499(7)	14.3956(8)	13.8295(6)	13.7366(6)	22.308(5)
α (deg)	100.887(1)	99.708(1)	105.087(1)		
β (deg)	98.549(1)	95.224(1)	111.831(1)	114.9620(10)	97.98(3)
γ (deg)	107.729(1)	108.935(1)	102.413(1)		
V (Å <sup>3</sup> )	1277	1279	1584	2089	2178
D <sub>c</sub> (g cm <sup>-3</sup> )	1.40 <sub>9</sub>	1.42 <sub>4</sub>	1.44 <sub>3</sub>	1.58 <sub>1</sub>	1.64 <sub>7</sub>
Z	2	2	2	2	4
μ <sub>Mo</sub> (mm <sup>-1</sup> )	0.74	0.65	0.63	7.4 (μ <sub>Cu</sub> )	0.89
specimen (mm <sup>3</sup> )	0.62 × 0.52 × 0.48	0.45 × 0.30 × 0.25	0.62 × 0.45 × 0.34	0.10 × 0.06 × 0.026	0.45 × 0.30 × 0.20
T <sub>min/max</sub>	0.91	0.87	0.90	0.80	0.87
2θ <sub>max</sub> deg	65	75	75	134	75
N <sub>i</sub>	25 074	25 417	31 511	22 437	16 337
N (R <sub>int</sub> )	9215 (0.018)	12462 (0.021)	16194 (0.016)	3710 (0.050)	10997 (0.023)
N <sub>o</sub>	8064	9651	13 188	2305	8822
R1	0.032	0.042	0.041	0.035	0.033
wR2	0.092	0.14	0.12	0.088	0.105
S	1.07	1.19	1.04	0.90	1.035
T(K)	300	150	300	100	150

compound	14	15	17	18
formula	C <sub>21</sub> H <sub>31</sub> ClN <sub>2</sub> O <sub>2</sub> Ru	C <sub>21</sub> H <sub>21</sub> ClF <sub>3</sub> N <sub>3</sub> O <sub>2</sub> Ru	C <sub>39</sub> H <sub>36</sub> F <sub>3</sub> N <sub>3</sub> O <sub>2</sub> PRu(ClO <sub>4</sub> )	C <sub>17</sub> H <sub>13</sub> ClF <sub>3</sub> N <sub>3</sub> O <sub>2</sub> Ru
M <sub>r</sub> (Daltons)	480.0	540.9	867.2	484.8
cryst syst	orthorhombic	monoclinic	triclinic	orthorhombic
space group	Pna2 <sub>1</sub> (#33)	P2 <sub>1</sub> /n (#14)	P1̄ (#2)	Pbca (#61)
a (Å)	12.536(2)	11.954(1)	10.387(4)	12.939(3)
b (Å)	9.970(2)	14.321(2)	10.633(4)	13.353(3)
c (Å)	17.205(2)	12.427(2)	19.234(7)	21.055(2)
α (deg)			89.384(6)	
β (deg)		96.510(10)	84.720(6)	
γ (deg)			62.025(5)	
V (Å <sup>3</sup> )	2150	2114	1867	3638
D <sub>c</sub> (g cm <sup>-3</sup> )	1.48 <sub>3</sub>	1.70 <sub>0</sub>	1.54 <sub>3</sub>	1.77 <sub>0</sub>
Z	4	4	2	8
μ <sub>Mo</sub> (mm <sup>-1</sup> )	0.87	0.92	0.60	1.06
specimen (mm <sup>3</sup> )	0.20 × 0.14 × 0.063	0.33 × 0.32 × 0.02	0.35 × 0.15 × 0.09	0.34 × 0.038 × 0.037
T <sub>min/max</sub>	0.82	0.86	0.73	0.86
2θ <sub>max</sub> (deg)	55	68	55	58
N <sub>i</sub>	30 189	46 994	16 337	45 247
N (R <sub>int</sub> )	4934 (0.11)	8331 (0.048)	8386 (0.034)	5302 (0.101)
N <sub>o</sub>	2637	5021	6541	3674
R1	0.045	0.034	0.065	0.058
wR2	0.080	0.082	0.17	0.075
S	0.92 (χ <sub>obs</sub> = 0.02(4))	0.95	1.09	1.09
T(K)	100	100	170	100

<sup>a</sup> Variata. **1**. The *i*-propyl group was modeled as disordered rotationally about the pendant bond, with site occupancies of the two components refining to  $x = 0.690(6)$  and the complement. **2**. The compound is isomorphous with **1** and was refined in the same cell and coordinate setting; the pendant *i*-propyl group is not disordered. **6**. The perchlorate group was modeled as disordered over two sets of sites, with the occupancies set at 0.5 after trial refinement. **10**. The material presented as only very small crystals and data were measured using monochromatic Cu K $\alpha$  radiation with  $\lambda = 1.54184$  Å. **17**. High displacement parameters were found on the anion and pendants generally, but no disorder was resolvable.

which is a neutral compound, the other compounds **3–7** are 1:1 electrolytes in acetonitrile solution.

The IR spectra of **3–7** contain the typical strong absorptions due to CF<sub>3</sub>SO<sub>3</sub> or ClO<sub>4</sub> in anionic forms,<sup>18</sup> and in all of the spectra, the substitution of chloride with the neutral donors PPh<sub>3</sub>, Meim, and Hmim has been confirmed by the disappearance of the absorption at 280 cm<sup>-1</sup> (part a of Figure 1S in the Supporting Information) and by the presence of new bands in the medium and/or low-frequency regions, for

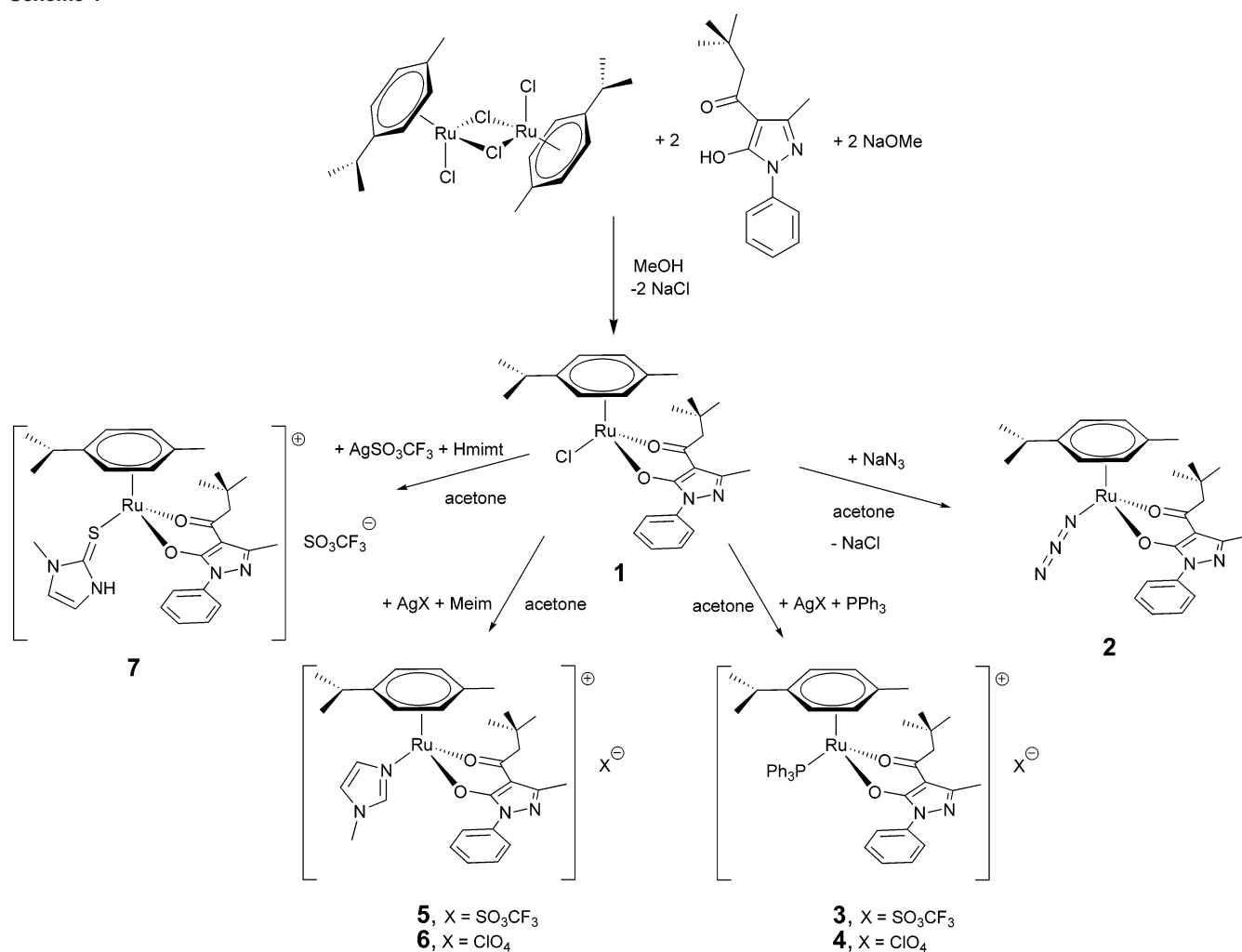
example, the absorptions in the low-frequency region due to the  $\gamma$  and  $t$  modes of vibration of triphenylphosphine (part b of Figure 1S in the Supporting Information).<sup>19</sup>

In the <sup>1</sup>H NMR spectra of **3–7**, all of the expected resonances have been observed for the arene, the acylpyrazolonate, the neutral phosphine, the 1-methylimidazole, and the 1-methyl-2-mercaptoimidazole. Compounds **1–7** are chiral-at-metal and can exist as a pair of enantiomers (Figure 1). In addition, the geminal methylene protons of the Q<sup>m</sup>Pe-

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(19) (a) Shobatake, K.; Postmus, C.; Ferraro, J. R.; Nakamoto, K. *Appl. Spectrosc.* **1969**, 23, 12. (b) Bradbury, J.; Forest, K. P.; Nuttall, R. H.; Sharp, S. W. A. *Spectrochim. Acta* **1967**, 23, 2701.

Scheme 1



acyl substituent in complexes **1**–**7** are diastereotopic and produce the expected AB quartets. In the <sup>1</sup>H and <sup>13</sup>C NMR spectra of derivatives **6** and **7**, two different sets of resonances have been observed for theazole-based neutral ligands, ascribed to their partial dissociation in solution.

The <sup>31</sup>P NMR spectra of **3** and **4** each show a single resonance above 30 ppm, cf. those of previously studied cymene ruthenium phosphino derivatives.<sup>4,5</sup>

By using potentially ditopic bidentate donor ligands, such as 4,4'-bipyridine (4,4'-bpy) and bis(diphenylphosphino)-

propane (dppp), under the same conditions (i.e., in acetone in the presence of AgClO<sub>4</sub>), the dinuclear dicationic ruthenium complexes **8** and **9** have been obtained, with the ligands 4,4'-bpy and dppp acting as bridging donors between two organometallic fragments (Scheme 2). The conductivity values in acetonitrile are in accordance with 1:2 electrolyte formulation,<sup>20</sup> and the strong IR bands at ca. 1080 cm<sup>-1</sup> indicate the presence of ionic perchlorate groups.<sup>8</sup>

We have also investigated the behavior of a different β-diketone, H<sub>2</sub>Q4Q, a bis(acylpyrazolone) that has a polymethylene chain between two pyrazolone moieties, to obtain a dinuclear derivative with different features with respect to the previous ones. Its interaction with the dimer [Ru(η<sup>6</sup>-cymene)-Cl(μ-Cl)]<sub>2</sub> in methanol, in the presence of sodium methoxide, afforded complex **10** (Scheme 3) as a neutral dinuclear compound that contains two chiral centers, as in **8** and **9**.

Complexes **8**, **9**, and **10** should exist as two diastereomers, either SRuSRu/RRuRRu or SRuRRu/RRuSRu (meso form). The single-crystal X-ray study (below) carried out on **10** shows it to exist in the RRuSRu form in the specimen studied, as also supported by the VT <sup>1</sup>H NMR studies in the temperature range of -50 to +50 °C, which show two sets

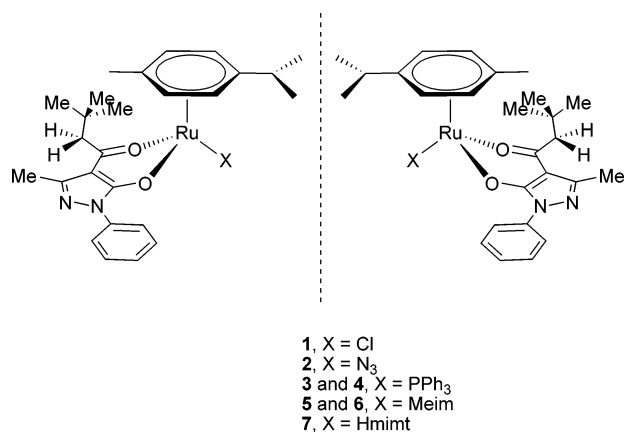
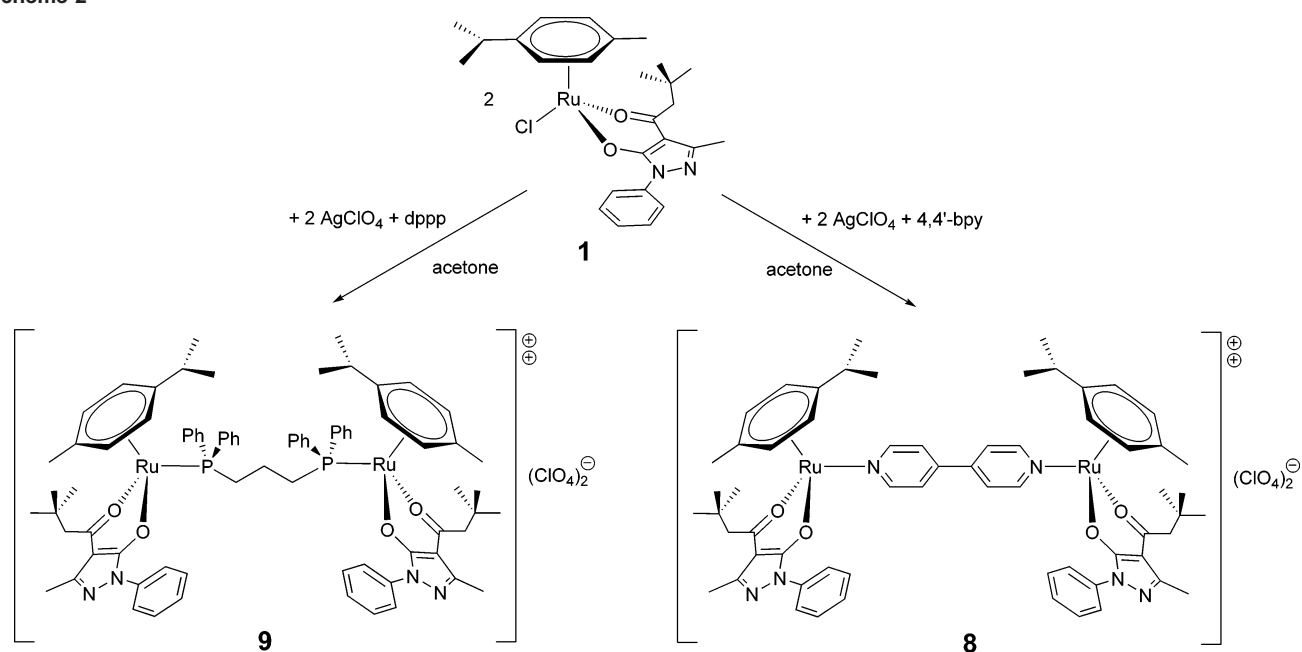


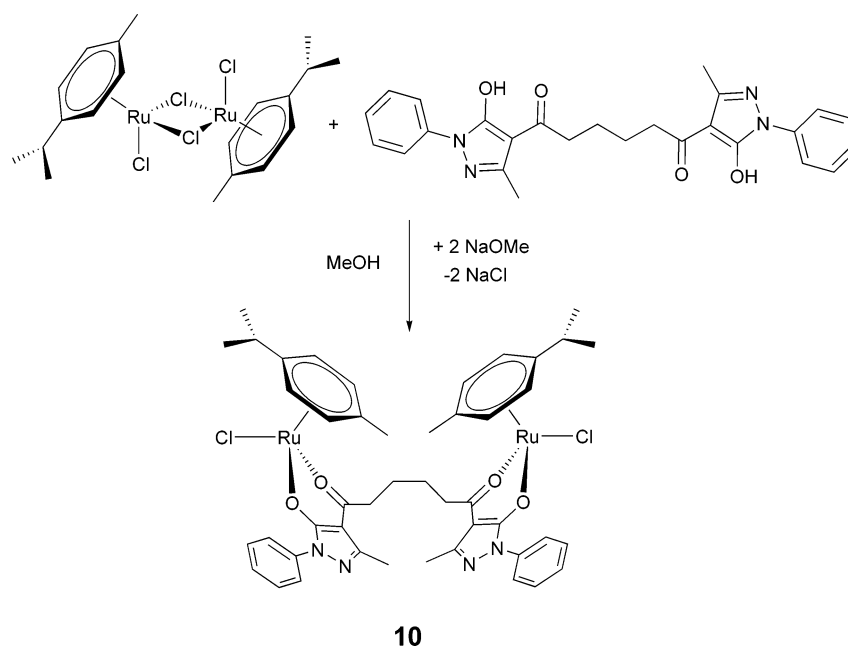
Figure 1. Enantiomers of derivatives **1**–**4** and **5**–**7**.

(20) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

Scheme 2



Scheme 3



of resonances due to the arene and pyrazolonate moieties, due to the meso form (Figure 2S in the Supporting Information). By contrast, in the VT  $^1\text{H}$  NMR spectra of derivatives **8** and **9**, more than two sets of resonances have been observed, likely indicating the presence of both diastereomers in solution, not interconverting to each other in the temperature range of  $+50$  to  $-50$   $^\circ\text{C}$  (Figures 3S and 4S, respectively, in the Supporting Information). The VT  $^{31}\text{P}$  NMR study of derivative **9** seems, however, to exclude any dppp dissociation, as two close resonances at ca. 26.5 and 25.5 ppm are always observed (Figure 5S, in the Supporting Information).

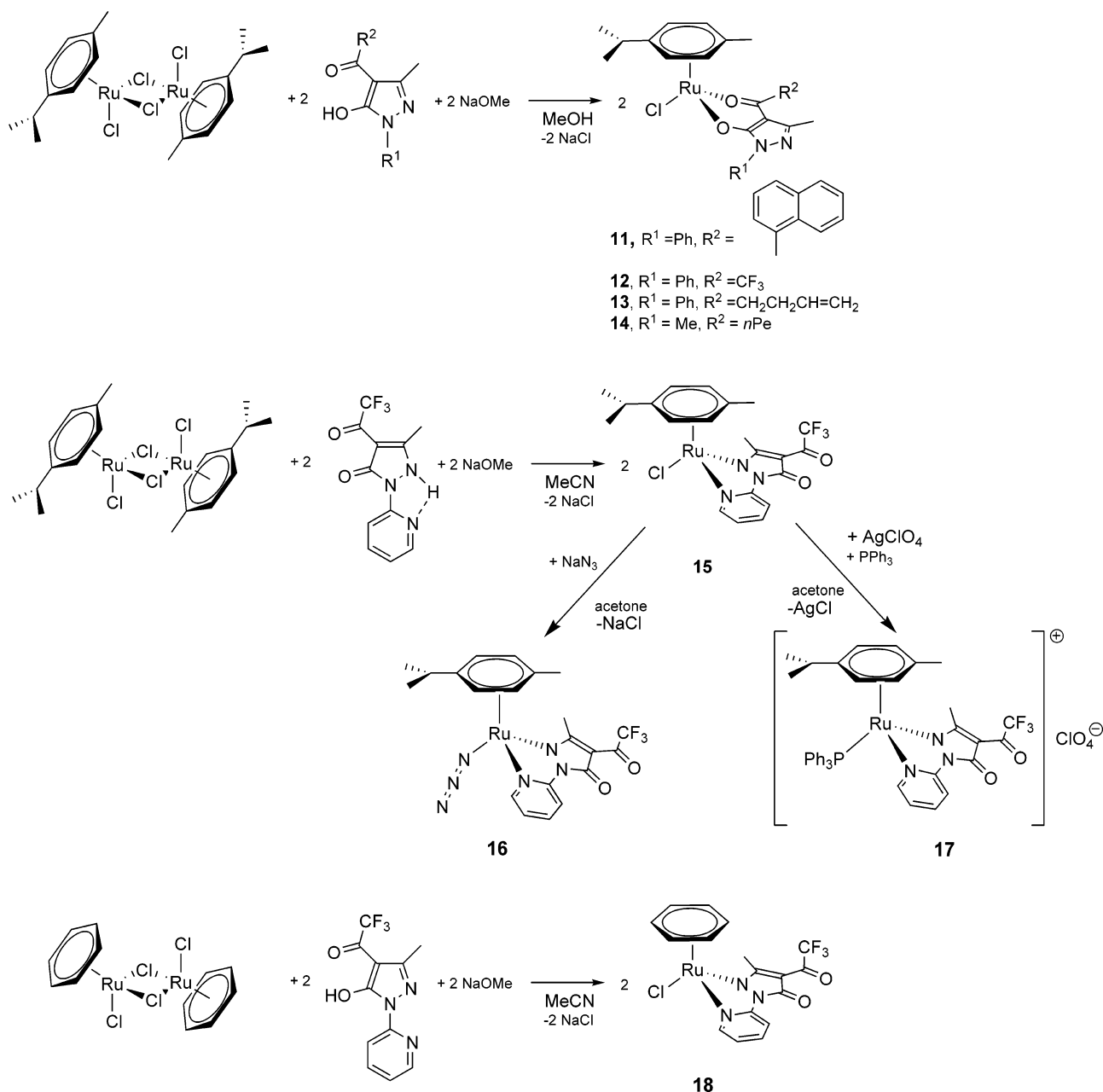
In extending our investigations, we have also synthesized new organometallic compounds using four different HQ proligands, specifically,  $\text{HQ}^{\text{maph}}$  having an extended aromatic fragment in the acyl moiety;  $\text{HQ}^{\text{CF}_3}$  with a trifluoromethyl

group in the same position;  $\text{HQ}^{\text{Me,}^i\text{Pe}}$ , which contains a methyl group bonded to N1 of the pyrazole ring; and  $\text{HQ}^{\text{py,CF}_3}$ , which differs in having a pyridine ring, in place of a phenyl, bonded to N1 of the pyrazole, thereby giving rise to two opposite chelating faces, an *O,O*-donating face and an *N,N*-donating one, as previously investigated with silver and copper acceptors.<sup>21</sup> The  $\text{HQ}^{\text{py,CF}_3}$  proligand exists in the solid state as the  $\text{N}\cdots\text{H}\cdots\text{N}$  tautomer.<sup>21</sup>

Whereas the structures of derivatives **11–14** clearly resemble that of **1**, derivative **15** contains the  $\text{Q}^{\text{py,CF}_3}$  ligand coordinated through the *N,N*-chelating face (Scheme 4), as

(21) (a) Cingolani, A.; Effendy, Marchetti, F.; Pettinari, C.; Pettinari, R.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **2004**, *43*, 4387. (b) Cingolani, A.; Marchetti, F.; Pettinari, C.; Pettinari, R.; Skelton, B. W.; Somers, N.; White, A. H. *Polyhedron* **2006**, *25*, 124.

Scheme 4

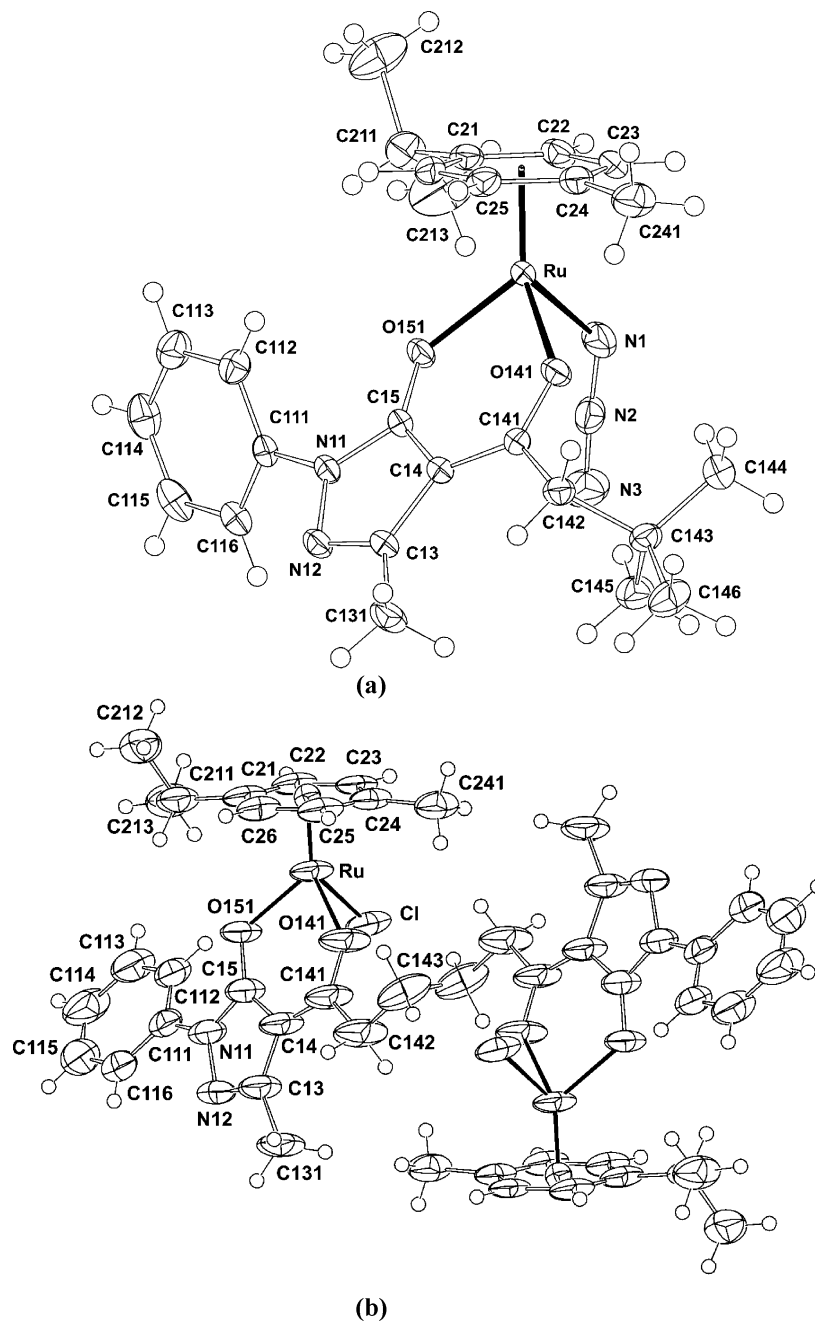


shown by the X-ray study (below). The IR spectrum of **15** shows  $\nu(\text{C}=\text{O})$  to be unchanged with respect to neutral  $\text{HQ}^{\text{py.CF}_3}$ , consistent with coordination to ruthenium through the two nitrogen atoms of the pyrazole and pyridine rings,<sup>21</sup> with the  $\text{Ru}-\text{N}$  absorption bands at 323 and 258  $\text{cm}^{-1}$ . Another difference between **11**–**15** is the high solubility of **14** in water, presumably as a consequence of the lesser steric hindrance of the methyl group in the  $R^1$  position, in place of the phenyl ring in derivatives **11**–**13**, that makes strong hydrogen interactions of water molecules with N2 of the pyrazole group possible.<sup>8</sup> Whereas in the  $^1\text{H}$  NMR recorded in  $\text{CDCl}_3$  a unique set of resonances has been detected, both for the hydrogen atoms of the cymene and the acylpyrazolonate ligand, in the  $^1\text{H}$  NMR recorded in  $\text{D}_2\text{O}$ , an additional set of resonances due to the cymene hydrogens has been found, with, moreover, a sharp singlet in place of the typical AB quartet of the geminal methylene protons of

the  $\text{Q}^{\text{Me},n\text{Pe}}$ -acyl substituent. This observation could be explained by the existence in water of a dissociative equilibrium between the neutral  $[\text{Ru}(\text{cymene})(\text{Q}^{\text{Me},n\text{Pe}})\text{Cl}]$  and the hydrate  $[\text{Ru}(\text{cymene})(\text{Q}^{\text{Me},n\text{Pe}})(\text{H}_2\text{O})]^+\text{Cl}^-$ , the latter containing a labile water molecule bonded to ruthenium and a chloride external to the metal coordination sphere. In this situation, exchange of the Q ligand site is more facile than in the neutral species, and the expected AB quartets due to diastereotopic geminal methylene protons disappear and a single resonance is produced. The conductance value further confirms the existence of a 1:1 electrolyte species, arising from **14** in a water solution.<sup>20</sup>

Derivative **15** reacts with  $\text{NaN}_3$  in acetone, affording the neutral azide compound **16**, whereas, in the presence of  $\text{AgClO}_4$  and an equiv of triphenylphosphine, the 1:1 ionic derivative **17** has been obtained, containing the phosphine bonded to the metal atom (Scheme 4). Accordingly, the IR





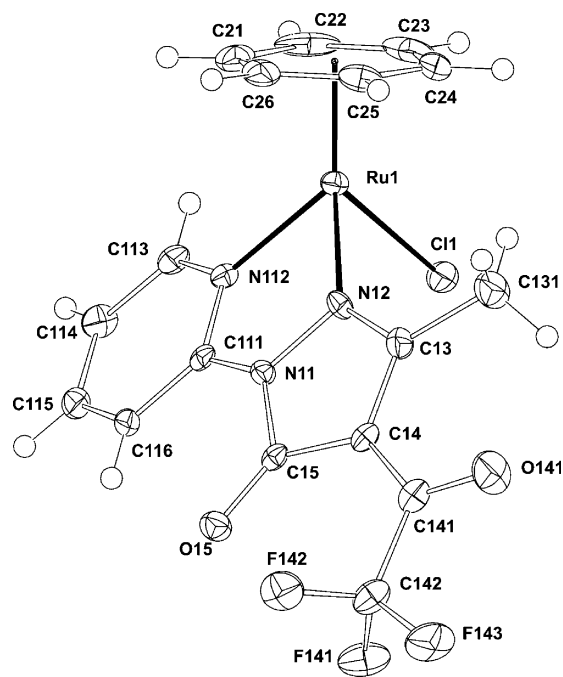
**Figure 2.** (a,b) Projections of the molecules of **2** and (centrosymmetric) **10**.

spectrum of **16** shows a strong band at  $2032\text{ cm}^{-1}$  due to azide,<sup>17</sup> and the IR of **17** shows a strong band at  $1080\text{ cm}^{-1}$  due to ionic perchlorate,<sup>18</sup> and typical  $\gamma$ - and  $t$ -mode frequency bands in the region of  $400\text{--}550\text{ cm}^{-1}$  due to the phosphine.<sup>19</sup>

By using  $\text{HQ}^{\text{py.CF}_3}$  and a different arene ruthenium precursor, the dimer  $[\text{Ru}(\eta^6\text{-benzene})\text{-Cl}(\mu\text{-Cl})_2]$  in acetonitrile, in the presence of sodium methoxide, compound **18** has been synthesized, again containing  $\text{Q}^{\text{py.CF}_3}$   $N,N$ -bonded to ruthenium (Scheme 4).

**Structural Studies.** Single-crystal X-ray studies have been executed on (a) **1**, **2**, **6**, **12**, **14** and (b) **15**, **17**, **18**, all of the compounds having a single formula unit, devoid of crystallographic symmetry as the asymmetric unit of the structure; all of the crystalline forms studied are racemates. The

structure of the neutral binuclear molecule **10** is also recorded; the molecule is disposed with a crystallographic inversion center lying at the midpoint of the central C–C bond, so that it is  $RS$  in form; one-half of the molecule comprises the asymmetric unit of the structure, with a conformation and geometry closely resembling those found in the other cymene/ $\text{Cl}/O,O'$ - $Q$  systems (Figure 3 and Table 1). In all of the cases, the ruthenium atom is coordinated  $\eta^6$  by the cymene or benzene group, considered to occupy three coordination sites of a quasi-octahedral array, the other three sites being occupied (i) by a unidentate group, which may be anionic ( $\text{Cl}$ ,  $\text{N}_3$ ) (in which case the complex is a neutral molecule) or neutral ( $\text{Meim}$ ,  $\text{PPh}_3$ ) (within a cation, with perchlorate or trifluoromethanesulfonate – triflate – counterion) and (ii) the bidentate  $Q$  ligand. The latter coordinates



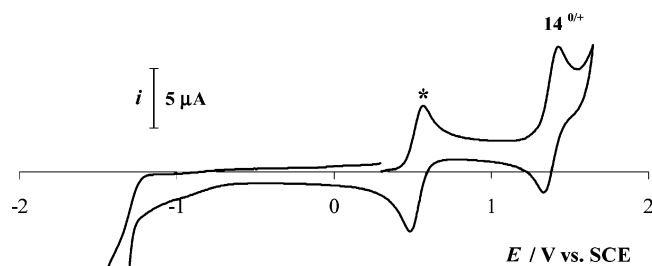
**Figure 3.** Projection of the molecule of **18**.

as a quasi- $\beta$ -diketonate  $O,O$ -donor in the group (a) complexes, with a six-membered chelate ring or as a quasi- $N,N$ -aromatic bidentate for group (b) with a five-membered ring; a representative selection is depicted in Figures 2 and 3.

Ru–Q–donor distances vary little (Table 1), the range across the whole array spanning only 2.075(3)–2.107(4) Å, regardless of  $O,O$  or  $N,N$ -donor type, but there is a change of ca.  $10^\circ$  in the bite between the  $O,O$ - (range: 87.12(5)–88.20(5) $^\circ$ ) and  $N,N$ - (76.5(1)–77.2(1) $^\circ$ ) forms, the difference being absorbed in quite minor changes in the other C(0)–Ru–X,  $Y_n^O$  and X–Ru– $Y_n^O$  angles, the latter ranging in totality from 84.0(1)–87.22(9) $^\circ$ , C(0)–Ru–X from 127.3 to 131.2 $^\circ$  and C(0)–Ru– $Y_n^O$  from 124.9–132.6 $^\circ$ . Whereas changes in ligand donor types have little impact on these angles and the Ru– $Y_n^O$  distances, with similar ineffectual changes in the  $\eta^6$ -Ar donor, the same cannot be said of the effect of the change in the X donor, where, with the change in X from Cl to  $N_3$  to Meim having a minimal impact, the introduction of  $PPh_3$  as a donor influences the Ru–Ar interaction considerably (while not at all affecting the Ru–Q<sup>X</sup> interaction), with the Ru–Ar centroid distance increasing by ca. 0.1 Å.

Substituent dispositions, as represented in Figures 2 and 3 are essentially representative of the whole array. The *i*-propyl substituents of the cymene ligands lie away from the X donor, whereas the phenyl or pyridyl substituents on the pyrazole ring are quasi-coplanar with it; in the  $Q^{nPe}$  ligands, the *nPe* substituent is directed away from the pyrazolyl methyl group but not so as to lie coplanar with the adjacent oxygen donor. In  $CF_3$ /py ligands, the acyl oxygen atom lies adjacent to the pyrazolyl methyl group.

**Electrochemical Studies.** The redox properties of our compounds have been investigated by cyclic voltammetry (CV), using a platinum electrode, in a 0.2 M [ $^nBu_4N$ ][ $BF_4$ ]/ $CH_2Cl_2$  solution, at 25  $^\circ C$ . Those that are stable in solution



**Figure 4.** Cyclic voltammogram of a 3.0 mM solution of [Ru(cymene)-(Q<sup>py,CF<sub>3</sub></sup>)Cl] **14**, in  $CH_2Cl_2$  with 0.2 M [ $Bu_4N$ ][ $BF_4$ ], with a platinum-disc electrode ( $d = 0.5$  mm). (\*) Redox wave of [ $Fe(\eta^5-C_5H_5)_2$ ]<sup>0/+</sup>, internal standard.

**Table 3.** Cyclic Voltammetric Data for Cymeneruthenium(II)-4-Acyl-5-pyrazolonate Compounds<sup>a</sup>

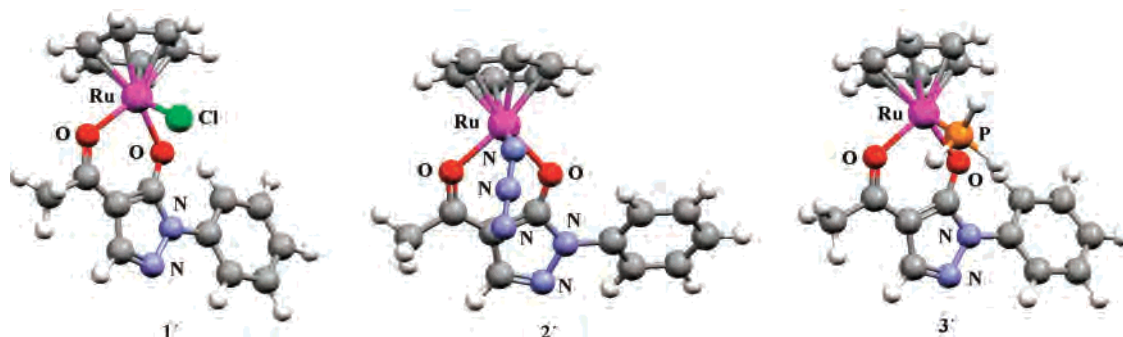
compound	$E_{1/2}^{ox}/V$ versus SCE <sup>b</sup>
<b>1</b> [Ru(cymene)(Q <sup>nPe</sup> )Cl]	+1.30
<b>2</b> [Ru(cymene)(Q <sup>nPe</sup> )N <sub>3</sub> ]	+1.26
<b>3</b> [Ru(cymene)(Q <sup>nPe</sup> )(PPh <sub>3</sub> )]SO <sub>3</sub> CF <sub>3</sub> <sup>c</sup>	(+1.63)
<b>4</b> [Ru(cymene)(Q <sup>nPe</sup> )(PPh <sub>3</sub> )]ClO <sub>4</sub> <sup>d</sup>	+1.55
<b>10</b> {[Ru(cymene)]Cl <sub>2</sub> (Q <sub>4</sub> Q)}	+1.33
<b>11</b> [Ru(cymene)(Q <sup>naph</sup> )Cl]	+1.38
<b>12</b> [Ru(cymene)(Q <sup>CF<sub>3</sub></sup> )Cl] <sup>e</sup>	+1.57
<b>13</b> [Ru(cymene)(Q <sup>Me,nPe</sup> )Cl]	+1.25
<b>14</b> [Ru(cymene)(Q <sup>py,CF<sub>3</sub></sup> )Cl] <sup>f</sup>	+1.38
<b>15</b> [Ru(cymene)(Q <sup>py,CF<sub>3</sub></sup> )N <sub>3</sub> ] <sup>g</sup>	+1.38
<b>16</b> [Ru(cymene)(Q <sup>py,CF<sub>3</sub></sup> )(PPh <sub>3</sub> )]ClO <sub>4</sub> <sup>h</sup>	+1.60

<sup>a</sup> Values in  $V \pm 0.02$  versus SCE ( $CH_2Cl_2$ /[ $^nBu_4N$ ][ $BF_4$ ],  $\nu = 0.1$  V s<sup>-1</sup>, for further details see the Experimental section). <sup>b</sup> Half-wave oxidation potential of a reversible or quasi-reversible wave; for the irreversible wave of **3**, the peak potential ( $E_p$ ) is given in brackets. <sup>c</sup> An irreversible reduction wave is observed at  $E_p^{red} = -1.08$  V. <sup>d</sup> An irreversible reduction wave is observed at  $E_p^{red} = -1.04$  V. <sup>e</sup> Irreversible reduction waves are observed at  $E_p^{red} = -0.75$  and  $-1.60$  V. <sup>f</sup> An irreversible reduction wave is observed at  $E_p^{red} = -1.35$  V. <sup>g</sup> An irreversible reduction wave is observed at  $E_p^{red} = -1.27$  V. <sup>h</sup> Irreversible reduction waves are observed at  $E_p^{red} = -0.99$  and  $-1.23$  V.

exhibit (Figure 4 for complex **14**) a single-electron (per metal atom) reversible oxidation (irreversible only for the trifluoromethanesulfonate compound **3**), assigned to the Ru<sup>II</sup> → Ru<sup>III</sup> oxidation,<sup>22–25</sup> at the half-wave oxidation potential values ( $E_{1/2}^{ox}$  in V vs the saturated calomel electrode (SCE)) given in Table 3 (in the ranges of 1.25–1.57 and 1.55–1.63 V vs SCE for the neutral and cationic species, respectively).

The occurrence of a single-electron oxidation per Ru<sup>II</sup> atom has been confirmed by exhaustive controlled potential electrolysis (CPE), for both mono- and dinuclear compounds, at a potential slightly anodic to that of the peak potential. The oxidized Ru<sup>III</sup> compounds are not stable in the solvent/

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**Figure 5.** Equilibrium structures of **1**<sup>+</sup>–**3**<sup>+</sup>. Carbon and hydrogen atoms are not labelled.

electrolyte medium along the CPE, because the Ru<sup>III/II</sup> reduction wave corresponding to the Ru<sup>III</sup> analogue of the starting Ru<sup>II</sup> complex is not observed at the end of the electrolysis.

The oxidized compound **3**<sup>+</sup> with the SO<sub>3</sub>CF<sub>3</sub><sup>-</sup> counterion is particularly unstable and decomposes even on the time scale of the CV (above), which suggests the involvement of this counterion in the chemical reaction of the Ru<sup>III</sup> species that follows the electron-transfer step.

The observation of only a single reversible oxidation wave (at  $E_{1/2}^{\text{ox}} = 1.33$  V) for dinuclear compound **10** shows that there is no detection of electronic communication between the two ruthenium atoms via the bridging ligand, in accordance with the long and saturated tetramethylene chain between the two ligated carbonyl groups of the bridge. In contrast, long distance metal–metal interactions could be expected via unsaturated and conjugated bridges.<sup>26–29</sup>

The solutions of compounds that undergo partial ligand dissociation (**5**–**9**) exhibit more complex cyclic voltammograms, on account of the presence of decomposition species. Hence, for example, the cyclic voltammogram of a solution of the dinuclear compound [Ru(cymene)(Q<sup>nPe</sup>)]<sub>2</sub>(dppp)]-(SO<sub>3</sub>CF<sub>3</sub>)<sub>2</sub> (the analogue of **9** but with the triflate counterion instead of ClO<sub>4</sub><sup>-</sup>) shows, apart from an irreversible oxidation wave due to this cationic complex, at  $E_p^{\text{ox}} = 1.55$  V, another oxidation wave, with a much lower peak-current intensity, at a potential of ca. 1.30 V. This value falls within the range of those of the related neutral mononuclear complexes (**1** and **2**) and can tentatively be assigned to the oxidation of [Ru(cymene)(Q<sup>nPe</sup>)(SO<sub>3</sub>CF<sub>3</sub>)] formed in solution upon partial replacement of the phosphine ligand by SO<sub>3</sub>CF<sub>3</sub><sup>-</sup>.

Some of the compounds also show irreversible reduction waves in the –0.8 to –1.4 V range (Figure 5 for complex **14**), which can involve the acyl-pyrazolonate ligands (when uncoordinated, they undergo irreversible reductions in that range of potentials, e.g., at –1.12 and –1.17 V for HQ<sup>nPe</sup> and HQ<sup>naph</sup>, respectively) and were not investigated further. In contrast to the common reversibility of the oxidation wave of our complexes, the free ligands only undergo irreversible

oxidations at higher potentials (e.g., complexes **1**, **2**, and **11** are reversibly oxidized at 1.30, 1.26, and 1.38 V, respectively, whereas the free HQ<sup>nPe</sup> and HQ<sup>naph</sup> show a first irreversible oxidation correspondingly at  $E_p^{\text{ox}}$  of 1.64 and 1.65 V).

The values of the Ru<sup>II/III</sup> oxidation potentials of our complexes reflect the electron-donor character of their ligands as follows:

Replacement of the chloride ligand in [Ru(cymene)(Q<sup>nPe</sup>)-Cl] **1** by azide to form **2** results in a measurable (although rather small) cathodic shift of the potential (from +1.30 to +1.26 V), in accordance with the slightly better electron-donor character of the latter ligand, on account of the marginally lower value of the Lever  $E_L$  electrochemical ligand parameter (–0.30 for N<sub>3</sub><sup>-</sup>, whereas for Cl<sup>-</sup> the  $E_L$  value is –0.24 V).<sup>22</sup> However, there is a negligible potential drift upon Cl<sup>-</sup> displacement in **14** by N<sub>3</sub><sup>-</sup> to afford **15**.

In contrast, displacement of Cl<sup>-</sup> in **1** or in **14** by PPh<sub>3</sub> (a much weaker electron-donor ligand, with  $E_L = +0.39$  V)<sup>22</sup> to form **4** or **16**, respectively, is concomitant with a significant anodic shift of the oxidation potential,  $\Delta E_{1/2}^{\text{ox}} = 0.25$  or 0.22 V, respectively. Nevertheless, this shift is smaller than that expected for a Ru<sup>II/III</sup> redox pair in hexa-coordinate octahedral-type ruthenium complexes, on the basis of the Lever<sup>22</sup> linear relationship (1), valid for such complexes, that relates to the redox potential (V vs NHE) with the sum of the  $E_L$  values for all of the ligands ( $\sum E_L$ ). The slope ( $S_M$ ) and intercept ( $I_M$ ) are dependent upon the metal, redox couple, spin state, and stereochemistry, being 0.97 and 0.04 V vs NHE, respectively, for the octahedral Ru<sup>II/III</sup> couple.<sup>22</sup>

$$E = S_M (\sum E_L) + I_M \quad (1)$$

Application of this equation to an octahedral complex with a chloride ligand and to the analogue with PPh<sub>3</sub> instead of chloride, what corresponds to a  $\sum E_L$  variation of 0.39 (PPh<sub>3</sub>) – (–0.24) (Cl<sup>-</sup>) = 0.63 V, would lead to an expected oxidation potential drift  $\Delta E$  of 0.61 V (i.e., 0.63 V × 0.97), a value considerably higher than those we have observed in our cases (0.25 or 0.22 V, above).

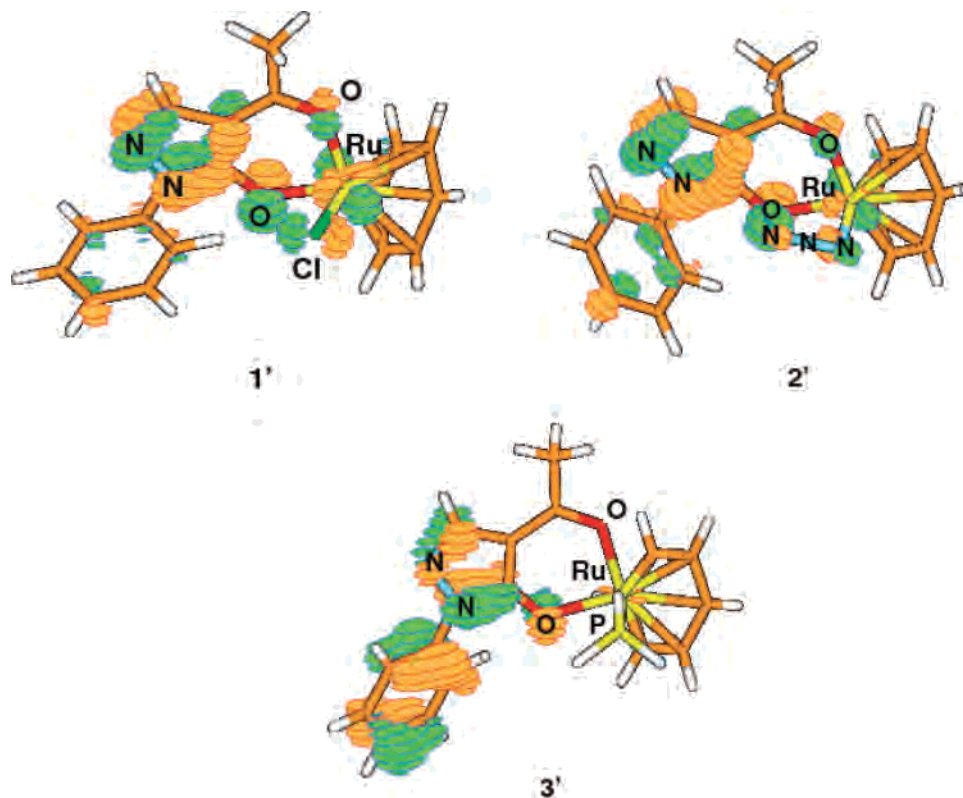
These observations on the low sensitivity of the oxidation potential of our complexes upon change of a ligand L (Cl<sup>-</sup>, N<sub>3</sub><sup>-</sup>, or PPh<sub>3</sub>), although being based on a rather limited number of examples, suggest that the highest occupied molecular orbitals (HOMOs) of the complexes should involve a small contribution from the ligand L, thus providing only small changes in the HOMO energy upon ligand L

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**Figure 6.** Plots of the first HOMO (**1'** and **3'**) and the second HOMO (**2'**).

replacement. Hence, a relatively low  $S_M$  value in eq 1 is expected for the  $\text{Ru}^{\text{II/III}}$  redox pair in such a type of complex.

To check this hypothesis, quantum-chemical calculations of the model complexes  $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{Q}')\text{L}]^{+/2+}$  ( $\text{L} = \text{Cl}^-$  (**1'**/**1'+**),  $\text{N}_3^-$  (**2'**/**2'+**),  $\text{PH}_3$  (**3'**/**3'+**), and  $\text{Q}' = 1\text{-phenyl-4-acetyl-5-pyrazolonate}$ , Figure 6) have been performed at the DFT level of theory. The calculated structural parameters of **1'** and **2'** are in good agreement with the experimental data for complexes **1** and **2** (Tables 1 and 1S in the Supporting Information). The maximum deviation was found for the  $\text{Ru}-\text{C}_{\text{benzene}}$  bonds (0.04–0.05 Å) and does not exceed 0.023 Å for the other bonds, often lying within the  $3\sigma$  interval of the experimental data. The analysis of the composition of frontier MOs of **1'**–**3'** and the oxidized species with unrelaxed geometry  $\{\mathbf{1}'^+\}-\{\mathbf{3}'^+\}$  indicates that, upon oxidation, the electron is removed from the first HOMO of **1'** and **3'**. In the case of azide complex **2'**, the energies of the first and second HOMOs are similar (differing only by 0.36 eV), and the electron leaves mainly from the second HOMO.

The main contribution to the HOMOs affected by the oxidation comes from  $p_z$  orbitals of the pyrazolonate ligand and, for **1'** and **2'**, also from the  $d_z^2$  orbital of the metal, whereas the involvement of the orbitals of ligand L is not significant (8.5% for **1'**, 5.3% for **2'**, and 3.7% for **3'**), thus confirming our initial hypothesis (Figure 6). As a result, the HOMO energies and the calculated vertical ionization potentials<sup>30</sup> ( $I_v$ ) of **1'** and **2'** are very similar ( $I_v = 6.89$  and 6.78 eV, respectively), in agreement with the experimental data. On the basis of the model, the higher oxidation potential of **3** in comparison with **1** and **2** would be mainly accounted

for by the positive overall charge of the complex moiety rather than by  $\pi$  acceptance of the phosphine group (very small contribution of the  $\text{PH}_3$  orbitals to the HOMO), but in the real  $\text{PPh}_3$  complex, the  $\pi$ -accepting ability of the aromatic phosphine can also play a role.

An electrochemical behavior related to that of our complexes, that is, lower-than-expected changes in the oxidation potential upon ligand variation, is known<sup>31–33</sup> to be exhibited by octahedral-type complexes that bear binding metal centers with strong  $\pi$  acceptors such as carbynes, CO, and  $\text{NO}^+$  and has been rationalized<sup>32</sup> by MO calculations on some W-carbyne/carbonyl complexes, on account of the delocalisation of the HOMO toward such  $\pi$  acceptors. Replacement of another ligand, with the preservation of those strong  $\pi$  acceptors, has thus only a small effect on the redox potential. However, in our case, no involvement of the  $\pi^*$  orbitals of the ligands L was found in the several HOMOs of complexes **1'**–**3'**. Hence, the  $\pi$ -back-donation effect is not responsible for the observed electrochemical properties.

Nevertheless, the oxidation potentials of our complexes show a noticeable dependence on the type of the bidentate acyl-pyrazolonate ligand, in accordance with the major contribution of its orbitals to the HOMOs. The potential increases are in the following order within the series of

(30) Vertical ionization potentials are calculated as a difference of the total energies  $E_{\text{ox}} - E_{\text{nox}}$ , where the index nox corresponds to the nonoxidized complex, and the index ox corresponds to the oxidized complex with an unrelaxed geometry.

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analogous chloro-compounds: [Ru(cymene)(Q<sup>Me,nPe</sup>) Cl] **13** (1.25 V) < [Ru(cymene)(Q<sup>nPe</sup>) Cl] **1** (1.30 V) < [Ru(cymene)(Q<sup>naph</sup>) Cl] **11** (1.38 V), [Ru(cymene)(Q<sup>py,CF<sub>3</sub></sup>) Cl] **14** (1.38 V) < [Ru(cymene)(Q<sup>CF<sub>3</sub></sup>) Cl] **12** (1.57 V). Similarly, for the available azide complexes, [Ru(cymene)(Q<sup>nPe</sup>) N<sub>3</sub>] **2** (1.26 V) < [Ru(cymene)(Q<sup>py,CF<sub>3</sub></sup>) N<sub>3</sub>] **15** (1.38 V), and for the PPh<sub>3</sub> complexes, [Ru(cymene)(Q<sup>nPe</sup>)(PPh<sub>3</sub>)]ClO<sub>4</sub> **4** (1.55 V) < [Ru(cymene)(Q<sup>py,CF<sub>3</sub></sup>)(PPh<sub>3</sub>)]ClO<sub>4</sub> **16** (1.60 V).

This is indicative of the following order of the electron-donor abilities of the acyl-pyrazolonate ligands: Q<sup>Me,nPe</sup> (*O,O*-type, with electron-donor alkyl substituents at both the pyrazolyl and the acyl groups) > Q<sup>nPe</sup> (*O,O*-type, with an electron-acceptor aromatic substituent at the pyrazolyl group and an alkyl group at the acyl group) > Q<sup>naph</sup> (*O,O*-type, with two electron-acceptor aromatic substituents), Q<sup>py,CF<sub>3</sub></sup> (*N,N*-type, with a pyridyl group and an electron-acceptor CF<sub>3</sub> substituent) > Q<sup>CF<sub>3</sub></sup> (*O,O*-type, with both electron-acceptor substituents, a phenyl group at the pyrazolyl group, and a CF<sub>3</sub> at the acyl group). This should correspond to the increasing order of the corresponding  $E_L$  values, which, however, cannot be estimated (eq 1) once  $S_M$  and  $I_M$  are unknown for ruthenium half-sandwich complexes. The

weakest electron-donor acyl-pyrazolonate ligands are those with the CF<sub>3</sub> substituent, that is, Q<sup>CF<sub>3</sub></sup> and Q<sup>py,CF<sub>3</sub></sup>, the latter (of the *N,N*-type) being a more effective donor than the former (of the *O,O*-type).

Within the family of complexes with *O,O*-type ligands, the above trend follows the opposite order of the electron withdrawing ability of the substituents, as expected.

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**Supporting Information Available:** Complete analytical and spectroscopic data for derivatives **4–7**, **9**, **11–14**, and **16–18**; Figures 1S, 2S, 3S, 4S, and 5S; full crystallographic data in CIF format for the structure determinations of **1**, **2**, **6**, **10**, **12**, **14**, **15**, **17**, and **18**; and a table with the main calculated bond lengths of **1'–3'**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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